BRITISH CHEMICAL ABSTRACTS

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1933

A—PURE CHEMISTRY

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BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1933.

General, Physical, and Inorganic Chemistry.

Light excitation and emission in hydrogen sparks under increased pressure. W. FINKELNBURG (Physikal. Z., 1932, **33**, 888—889). A. J. M.

Bands due to the hydrogen molecule: $2p^3\Pi$ bands of hydrogen. I. SANDEMAN (Proc. Roy. Soc., 1932, **A**, **138**, 395—411).—The proposed arrangement of the new H_2 bands described by Richardson and Davidson (A., 1931, 887) is criticised, and a simpler scheme is suggested. L. L. B.

Optical investigations of the accommodation coefficient and distribution function for molecular translation at low pressures. L. S. ORNSTEIN and W. R. VAN WIJK (Z. Physik, 1932, **78**, 734—743).—A Fabry–Perot etalon was used to measure the distribution of intensity in a spectral line of He, and calculations are given relating this distribution to the distribution of velocities in the gas; the calculations give an accommodation coeff. of 0·3 for He colliding with a glass wall at 650°. A. B. D. C.

Optical investigation of the collisions of gas molecules with a wall. L. S. ORNSTEIN and W. R. VAN WIJK (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 722—726).—The problem of the collision of gas mols. with a wall has been investigated by spectroscopic observation of an electrical discharge in He at 0·01 cm. pressure, contained in an annular space between two walls, the inner cooled, and the outer heated to 320°. J. W. S.

Quantum defect for highly excited S states of para- and ortho-helium. L. P. SMITH (Physical Rev., 1932, [ii], **42**, 176—181).—Calc. vals. of the quantum defects for the o- and p-systems are 0·289 and 0·160, respectively, compared with 0·230 and 0·122 obtained by Hylleraas (cf. A., 1930, 1487) uncorrected for polarisation of the atom core, and 0·298 and 0·140 needed to yield the experimental term vals. N. M. B.

Photometric investigation of the most intense emission bands of fluorine. J. AARS (Z. Physik, 1932, **79**, 122—138).—A discussion of the intensities of F_2 lines in bands at 17,439, 16,379, and 18,548 cm.$^{-1}$ A. B. D. C.

Spectrum of doubly-ionised neon (Ne III). T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 819—826).—Ne III spectrum has been photographed to 2000 Å., and new lines have been measured and classified. J. W. S.

Lifetime of the metastable $^3P_2$ neon atom. E. MATUYAMA (Physical Rev., 1932, [ii], **42**, 373—378).—Measurements of the rate of decrease of absorption of the 6402 Å. line of Ne excited by a high-frequency oscillatory current gave the val. 0·005 sec. at 5·2 mm. pressure. N. M. B.

Duration of metastable states: neon. J. M. ANDERSON (Canad. J. Res., 1932, **7**, 434—443; cf. A., 1931, 781).—Decay curves for the absorption lines λλ 6402, 6334, 6266, 6163, 6143, and 5945 at room and liquid air temp. are shown for a series of pressures, and half life–pressure curves are recorded. At the same pressure and temp. the rate of decay varies for different lines. N. M. B.

Energy balance of a positive column of sodium vapour. M. J. DRUYVESTEYN (Physikal. Z., 1932, **33**, 822—823).—The distribution of radiation between the D lines and the infra-red bands of Na vapour has been measured for a column of Na vapour. W. R. A.

Continuous spectrum of sodium. H. HAMADA (Nature, 1932, **130**, 811—812). L. S. T.

Vibrational and rotational structure of yellow-red emission band spectrum of sodium molecule. Y. UCHIDA (Japan. J. Physics, 1932, **8**, 25—50; cf. A., 1932, 667).—Full data for rotational lines of the first five order groups are given, and lines are identified with the wave nos. calc., with the mol. consts. obtained from absorption data, and their quantum transitions are fixed. The mol. consts. of Na_2 were B_0'' 0·15399, α_1 0·0007, and α_0 0·00003 cm.$^{-1}$ N. M. B.

Spectral lines of Cl V and Cl IV. S. C. DEB (Bull. Acad. Sci. Agra and Oudh, 1932, **2**, 43—50).—The spectral lines of Cl IV and Cl V are classified. The ionisation potentials are, respectively, 55·17 and 69·36 volts, which are larger than Bowen's vals. (A., 1928, 210). M. S. B.

Continuous spectrum of pure argon. S. P. MCCALLUM, L. KLATZOW, and J. E. KEYSTON (Nature, 1932, **130**, 810—811).—The special characteristics which appear in the spectrum of highly-purified A are described. L. S. T.

Spectrum of potassium hydride. G. M. ALMY and C. D. HAUSE (Physical Rev., 1932, [ii], **42**, 242—266).—Full data and analyses for the lines of 29 bands in the range 4100—6600 Å. are tabulated. Absorption bands were masked by alkali bands except in the region 4600—4800 Å. Heats of dissociation are 1·25 and 2·06 volts for the excited and ground states, respectively. A Franck–Condon

intensity diagram is in good agreement with observed intensities. N. M. B.

Change of wave-length and intensity in iron, nickel, and titanium lines by disruptive discharge. H. NAGAOKA, T. FUTAGAMI, and I. MACHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **19**, 169—184).—Line shifts are characteristic of different spectral series, and are classified into several types. Relation with stellar spectra is discussed. N. M. B.

Interferometer measurements in the extreme ultra-violet region of copper. J. C. MCLENNAN and (MISS) F. M. QUINLAN (Phil. Mag., 1932, [vii], **14**, 823—829).—Cu arc lines between λ 2276 and 1980 Å. were measured. H. J. E.

Hyperfine structure of arc lines and the nuclear moment of copper. R. RITSCHL (Z. Physik, 1932, **79**, 1—25).—Both Cu isotopes have nuclear moment 3/2. A. B. D. C.

Spark spectra of copper, silver, and gold between 1300 and 300 A. L. BLOCH, E. BLOCH, and J. FARINEAU (J. Phys. Radium, 1932, [vii], **3**, 437—451).—Wave-lengths and intensities are tabulated for approx. 400 lines of Cu, 640 lines of Ag, and 540 lines of Au, in the ranges 1377·48—385·94, 1321·02—260·17, and 1341·58—296·13 Å., respectively. N. M. B.

Spark spectrum of rubidium in the ultra-violet. J. JANIN (Compt. rend., 1932, **195**, 1010—1012).—Using the electrodeless dischargo and Rb prepared from RbN_3, 96 lines between λ 2400 and 2150 Å. have been measured, of which 20 are assigned to Rb II, 29 to Rb III, and 5 to Rb IV. C. A. S.

First spark spectrum of antimony. R. J. LANG and E. H. VESTINE (Physical Rev., 1932, [ii], **42**, 233—241).—Full data and analyses for about 200 lines in the range 7000—600 Å. are tabulated. N. M. B.

Hyperfine structure in the antimony spark spectrum and the nuclear moment of antimony isotopes. J. S. BADAMI (Z. Physik, 1932, **79**, 206—223).—Hyperfine structure of a series of Sb II lines indicates the moment 3/2 for Sb^{121} and 7/2 for Sb^{123}. A. B. D. C.

Hyperfine structure in the antimony arc spectrum, Sb I. J. S. BADAMI (Z. Physik, 1932, **79**, 224—230). A. B. D. C.

Spectrum of iodine in adsorbed state. D. CHILTON and E. RABINOWITSCH (Z. physikal. Chem., 1932, **B**, **19**, 107—112).—The absorption spectrum of I sorbed on a chabasite crystal is similar to that of I dissolved in C_6H_6 or that of I vapour, except that it exhibits two, or possibly three, max. It is concluded that sorption is mol., and that the sorbate consists of several layers differing in the firmness with which they are attached to the surface. The spectrum is widened somewhat towards the ultra-violet, compared with the other two; this is ascribed to sorptive forces. R. C.

Extinction of iodine fluorescence by magnetic fields and foreign gases. W. BERG (Z. Physik, 1932, **79**, 89—107).—An investigation of extinction by magnetic fields and foreign gases shows that the magnetic field not only itself extinguishes the fluorescence, but also increases the effective cross-section of the mols. for collision with I, N_2, O_2, and A. A. B. D. C.

Absorption of the fluorescent light of iodine by its vapour. I. I. AGARBICEANU (Compt. rend., 1932, **195**, 947—949; cf. A., 1932, 891).—The temp.–absorption curves of six lines of the fluorescence spectrum of I by I vapour in air at temp. 23—270° show that increase of absorption with rise of temp. is due both to the gases of the air and also to increase in collisions bringing I_2 mols. into various states. C. A. S.

Lanthanum spectra (La I, La II, La III). H. N. RUSSELL and W. F. MEGGERS (Bur. Stand. J. Res., 1932, **9**, 625—668).—The available data on the La spectrum have been analysed and the lines classified as belonging to the La I, La II, and La III series. The ionisation potentials are 5·59 volts for La, 11·38 volts for La^+, and 19·1 volts for La^{++}. D. R. D.

Collision phenomena on optical excitation of various mercury isotopes. S. MROZOWSKI (Z. Physik, 1932, **78**, 826—843).—Improved apparatus confirms the result that a non-extinguishing inert gas exerts a selective effect on the intensities of hyperfine lines of the Hg isotopes. A. B. D. C.

Emission life of the mercury resonance line at 2537 A. S. MROZOWSKI (Z. Physik, 1932, **78**, 844—846).—Measurements of the emission life of the Hg resonance line 2537 Å. do not agree with observations on absorption. A. B. D. C.

Spectra of high-frequency discharges. I. Comparison of damped with undamped electrodeless excitation. J. K. ROBERTSON (Phil. Mag., 1932, [vii], **14**, 795—806).—The spectra of the discharges in Hg and Cd vapours are compared. H. J. E.

Isotope displacement in hyperfine structure. G. BREIT (Physical Rev., 1932, [ii], **42**, 348—354).—The order of magnitude of isotope displacements can be explained as due to small changes in nuclear radii. Data for Hg, Tl, and Pb arc and spark spectra are in agreement with this theory. N. M. B.

Mercury vapour discharge. E. LÜBCKE (Physikal. Z., 1932, **32**, 890—895).—The probability of ionisation in the Hg discharge is calc. In the Hg arc at low pressures the concn. of electrons is smaller than that of positive ions. There must be heavier negative carriers present. A. J. M.

Spectrum of trebly-ionised lead. J. KISHEN (Nature, 1932, **130**, 739).—A necessary modification of this spectrum gives $6s^2S$ a val. of 340,180, yielding an ionisation potential of 41·9 volts. L. S. T.

Hyperfine structure of arc lines in vacuum of bismuth in the visible and the ultra-violet regions. W. MOHAMMAD and P. N. SHARMA (Phil. Mag., 1932, [vii], **14**, 977—990).—The hyperfine structure of 13 Bi lines in the violet and ultra-violet regions has been examined, using two Lummer plates. J. W. S.

Cold cathode vacuum arc. F. H. NEWMAN (Phil. Mag., 1932, [vii], 14, 788—794).—The mechanism of starting and maintaining the arcs is discussed. H. J. E.

Structures in the K absorption spectra of Cu and Zn in brass. S. KAWATA (Japan. J. Physics, 1932, 8, 51—56).—The structures for the pure elements and in some kinds of brass were largely influenced by the phases of the absorbing atoms, and showed no satisfactory agreement with Kronig's theory (cf. A., 1931, 993). N. M. B.

N-Series for the elements 73 Ta to 81 Tl. I. T. MAGNUSSON (Z. Physik, 1932, **79**, 161—169).—The lines $N_{IV}N_{VI}$ and $N_{V}N_{VI, VII}$ were measured for Ta, W, Os, Ir, Pt, Au, and Tl, and the K-absorption edge was determined for C. A. B. D. C.

Measurements of the absorption coefficient for X-rays in the neighbourhood of the L-edges of the elements Pt and Au. M. WOLF (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 547—550).—The results are used to calculate the no. of dispersion electrons connected with each of the 3 L-levels. H. J. E.

X-Ray study of the density distribution in the discharge tube. Y. ISHIDA and T. SUETSUGU (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **19**, 185—188).—Qual. investigations of pressure variations in the positive column of various Hg discharge tubes were made by means of X-ray photographs. N. M. B.

Origin of the spectral selective photo-electric effect in thin alkali metal films. R. SUHRMANN and A. SCHALLAMACH (Z. Physik, 1932, **79**, 153—160).—An investigation of the spectral selective photo-effect for K films on Ag surfaces with films greater and less than the monoat. layer shows that the layer of K atoms can reduce the energy required to extract electrons from the Ag. No barrier layer photo-effect need be postulated. A. B. D. C.

Long-wave limit of the photo-electric effect determined from atomic volume of the elements. G. SCHWEIKERT (Z. Physik, 1932, **79**, 248—253).—Theoretical. The long-wave photo-electric limit is shown to be proportional to the 2/3 power of the at. vol. A. B. D. C.

Diffraction of fast protons by gold foil. E. RUPP (Z. Physik, 1932, **78**, 722—727).—Protons traversing gold foil gave X-ray interference patterns for the wave-length $6{\cdot}4 \times 10^{-12}$ cm. corresponding with the accelerating potential of 200 kv. Atom factors for protons were determined. A. B. D. C.

Emission of positive ions from cold surfaces under the influence of strong electric fields. W. R. HARPER (Nature, 1932, **130**, 775). L. S. T.

Reflexion of atomic beams from sodium chloride crystals. R. M. ZABEL (Physical Rev., 1932, [ii], **42**, 218—228).—The wave nature of He, Ne, and A was investigated by the reflexion of beams of these gases from natural NaCl, and laboratory-grown NaCl crystals cleaved under various conditions; evidence of diffraction was obtained in all cases. N. M. B.

Diffusion of positive ions of salts through copper at high temperature. Mass spectrograph analysis of the emitted ions. J. CICHOCKI (J. Phys. Radium, 1932, [vii], **3**, 478—485).—When the chlorides of Li, Na, K, Mg, Cu, Sr, and Ba enclosed in a Cu film are heated to a high temp., the positive ions of the salt diffuse through the film and become a source of complex ions consisting of combinations of the metal of the salt with the Cu or the Pt forming the supporting electrode. N. M. B.

Magnetic spectra of secondary electrons from silver. S. CHYLINSKI (Physical Rev., 1932, [ii], **42**, 393—399).—Kinetic energy distribution curves are given for Ag bombarded with cathode rays in the energy range 2·1—30 equiv. kv. Peak locations vary somewhat with the primary voltage; the curve forms are similar to those of the continuous X-ray spectrum. N. M. B.

Kinematographic electron microscopy of oxide cathodes. E. BRÜCHE and H. JOHANNSON (Ann. Physik, 1932, [v], **15**, 145—166).—Film exposures of emitting oxide cathodes are examined by an electric electron microscope and results are discussed. W. R. A.

New cathode investigations with the electrical electron microscope. E. BRÜCHE and H. JOHANNSON (Physikal. Z., 1932, **33**, 898—899).—The electron microscope (cf. A., 1932, 209) has been used to study cathodes of pure W, and of Th and W. The former differs considerably from an oxide cathode in its behaviour, whilst the latter occupies a position between the two types. A. J. M.

Polarisation of electrons. E. RUPP (Physikal. Z., 1932, **33**, 937—940).—The earlier experiments (A., 1932, 317) have been extended and a new one is described for double scattering at 90°. Polarisation brought about by this method must be due to a different cause from that in the earlier experiments. It may result from polarisation of the nucleus. A. J. M.

Large-angle scattering of electrons in gases. II. C. B. O. MOHR and F. H. NICOLL (Proc. Roy. Soc., 1932, **A**, **138**, 469—478; cf. A., 1932, 1185).—Angular distributions of scattered electrons in H_2, CO_2, CH_4, N_2, Ne, PH_3, and H_2S have been measured to 160° for 30—150 volt electrons. The elastic and inelastic scattering curves are found to be closely similar. The elastic scattering curves show a gradual change in form for successive elements in the periodic table. L. L. B.

Motion of an electron in a crystalline lattice. G. C. WICK (Atti R. Accad. Lincei, 1932, [vi], **16**, 142—149).—Theoretical. Taking into account the resonance forces between a conducting electron and the bound electrons of the lattice, the energy levels of the former are calc. approx. There is an energy max. for zero velocity of the electron. O. J. W.

Velocity distribution of electrons in the positive column. M. J. DRUYVESTEYN (Physikal. Z., 1932, **33**, 856—863).—The diffusion of electrons in the positive column is investigated for small c.d. The gradient of the column is calc., and the formulæ are applied to the positive column in Ne. A. J. M.

Quantum theory of diffusion of electrons. L. GOLDSTEIN (Compt. rend., 1932, **195**, 864—866).

Quantum mechanics [applied to] the formation of negative ions. Y. ROCARD (Compt. rend., 1932, **195**, 945—947).—Calculation of the nature of the spectrum emitted on the fixation of an electron by H_2 or He shows that this process may be the origin of some of the light of the night sky. C. A. S.

Revision of at. wt. of silicon. Ratio $SiCl_4 : SiO_2$. P. F. WEATHERILL and P. S. BRUNDAGE (J. Amer. Chem. Soc., 1932, **54**, 3932—3938).—This ratio, determined by hydrolysis of $SiCl_4$ in dil. HCl, gives $28{\cdot}103 \pm 0{\cdot}003$ for the at. wt. of Si. L. P. H. (*c*)

Method of separation of isotope mixtures and its application to the isotopes of neon. G. HERTZ (Z. Physik, 1932, **79**, 108—121).—Diffusion through porous walls in vac. gave partial separation of the Ne isotopes. A. B. D. C.

New isotopes of mercury. F. W. ASTON (Nature, 1932, **130**, 846).—Definite traces of new lines 197 and 203 have been obtained in the mass spectrum of Hg. The former is due to a new isotope, but the latter may be due to the hydride of 202, although this is considered improbable. The proportions of Hg^{197} and Hg^{203} are 0·01 and 0·006%, respectively, and their effect on the mean at. wt. is therefore negligible. L. S. T.

Atomic disruption by means of hydrogen canal rays. F. KIRCHNER (Physikal. Z., 1932, **33**, 777).—The at. disruption of Li has been studied by an apparatus essentially simpler than the apparatus of Cockroft and Walton (cf. A., 1932, 893), whose results are confirmed. W. R. A.

Period of radium. E. GLEDITSCH and E. FOYN (Amer. J. Sci., 1932, [v], **24**, 387—393).—Boltwood's method on a Norwegian broeggenite gives 1691 years. C. W. G.

Passage of neutrons through matter. H. S. W. MASSEY (Proc. Roy. Soc., 1932, **A**, **138**, 460—469; cf. A., 1932, 443).—Mathematical. Born's quantum theory of collisions is applied to the elastic collisions of neutrons with material particles. A neutron model consisting of a H atom in a nearly zero quantum state is considered. The experimental evidence indicates that the radius of such an atom must be $< 2{\cdot}0 \times 10^{-13}$ cm. L. L. B.

Radioactivity of samarium. G. VON HEVESY and M. PAHL (Nature, 1932, **130**, 846—847).—Sm is radioactive, emitting a radiation of the α-ray type, the intensity of which is reduced to half its val. by 1·3 μ of Al. L. S. T.

Ionising effect of α-rays in solid dielectrics. H. FOLMER (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 636—642).—An improved technique has shown that α-radiation influences the conduction of paraffin exposed to Po radiation and suggests the probability of ionisation in solid dielectrics. W. R. A.

Temperature variation of the total current-carrying elements in air. A. BECKER and I. SCHAPER (Z. Physik, 1932, **79**, 186—193).—Saturation current due to complete absorption of Po α-rays by a vol. of air increased as the temp. of the air rose from −80° to 250°; the increase must be due to variation of the energy required for formation of the current-carrying elements. A. B. D. C.

β-Rays of active deposit of actinium. S. Y. SZE (Compt. rend., 1932, **195**, 773—775; cf. A., 1932, 790).—$H\rho$ and the energies and origins of the groups in the β-ray spectrum of this deposit, relative to the Th-*B* line $H\rho$ 1398, have been redetermined with substantially different results (cf. A., 1926, 105). Three groups, $H\rho$ 2418, 2670, 2772, were not found, two, 2149, 2456, are shown to be due to the transition Ac-*B* → Ac-*C*, and three, 1953, 2252, 2304, to Ac-*C* $\xrightarrow{\alpha}$ Ac-*C*″. C. A. S.

Radiations from radium-*D* and -*E*. J. A. GRAY (Nature, 1932, **130**, 738).—Ranges of the β-rays of Ra-*E* in various substances are given. Absorption of the γ-rays in Pb has been measured and a soft type of γ-ray, presumed to be the *M*-rays characteristic of at. no. 83, detected. *L*-Rays are emitted by approx. 30% of Ra-*D* atoms and primary rays by $< 4\%$; the primary rays consist apparently of a band extending from $\lambda < 0{\cdot}28$ Å. to $\lambda < 0{\cdot}30$ Å. The properties of the hard γ-rays of Ra-*E* indicate that they are excited by some of the β-rays after their escape from the nucleus. L. S. T.

Gamma-ray ionisation chamber. G. C. LAURENCE (Canad. J. Res., 1932, **7**, 103—105).—The chamber described is claimed to be as sensitive as a good gold-leaf electroscope, but the scale length is longer, permitting fewer readings each of longer duration. A. G.

γ-Rays of thorium-*B* and of the thorium-*C* bodies. C. D. ELLIS (Proc. Roy. Soc., 1932, **A**, **138**, 318—339).—The β-ray spectrum of Th-*B*+*C* has been studied and new measurements have been made of the energies of the β-ray groups. The relative $H\rho$ of the different groups were determined, also the abs. $H\rho$ of certain strong groups. The intensities of the groups were measured photometrically. The γ-rays associated with the disintegrating bodies have been deduced from these results. L. L. B.

Average life of activated atomic nuclei: probable cases of impossibility of γ-ray emission. F. PERRIN (Compt. rend., 1932, **195**, 775—778; cf. A., 1932, 5, 790).—Theoretical. Considering that oscillation of one constituent of a nucleus involves oscillation of the remainder, the calc. mean life of a state, *e.g.*, of Ra-*C*′, is greatly increased. Nuclei consisting of helions, Be^8, C^{12}, etc., or of helions and demihelions, Li^6, B^{10}, etc., ought not to emit γ-rays. C. A. S.

Ionisation by γ- and cosmic rays in oxygen and xenon. V. MASUCH (Z. Physik, 1932, **79**, 264—265).—Ionisation of O_2 and Xe is proportional to the density of the gas for the harder components of cosmic rays, but not for rays of smaller energy. A. B. D. C.

Secondary radiation produced by cosmic rays. J. M. BENADE (Nature, 1932, **130**, 699). L. S. T.

Light emission caused by electronic, ionic, and atomic collision. W. HANLE and K. LARCHE (Physikal. Z., 1932, **33**, 884—887).—The directional distribution of intensity for the three types of collision is investigated, and an arrangement of apparatus for studying this in ionic and at. collision is described. A. J. M.

Atomic eigenfunctions and energies. C. W. UFFORD and G. H. SHORTLEY (Physical Rev., 1932, [ii], **42**, 167—175; cf. A., 1931, 781).—Mathematical. N. M. B.

Breakdown discharge as statical ionisation. H. EISLER (Z. Physik, 1932, **79**, 266—274).—Breakdown discharge may be explained by a purely statical ionisation of the atoms or mols. of the dielectric. A. B. D. C.

Space charge and its relation to the chemical components of the atmosphere. R. STOPPEL (Z. Physik, 1932, **78**, 849—853).—Short-circuited electrometers show considerable variations of zero varying with the gas (H_2, N_2, O_2, and CO_2) surrounding the instrument. A. B. D. C.

Cosmic-ray ionisation as a function of pressure, temperature, and dimensions of the ionisation chamber. J. W. BROXON (Physical Rev., 1932, [ii], **42**, 321—335).—Investigations over a pressure range did not support the subsidiary radiation theory of cosmic-ray ionisation (cf. A., 1931, 3). N. M. B.

Magnetic spectrum of cosmic rays. P. KUNZE (Z. Physik, 1932, **79**, 203—205).—A Wilson chamber in an intense magnetic field showed curved traces of cosmic rays, positive particles being more frequent than negative; an energy spectrum is shown. A. B. D. C.

Air afterglow and active nitrogen. J. K. ROBERTSON (Canad. J. Res., 1932, **7**, 444—450).—The air afterglow spectrum in the visible range consists of a continuous faintly banded region 4400—5000 Å., and a pure continuum in the yellow and red. Evidence indicates that the yellow-red afterglow is due to N; the addition of Hg vapour at once destroys the glow. N. M. B.

Value of b_k and atomic radii of elements in relation to the periodic system. J. A. M. VAN LIEMPT (Rec. trav. chim., 1932, **51**, 1117—1130).—b_k is a periodic function of the at. no. Hence, in cases where its val. is unknown, b_k may be determined by interpolation in the b_k–at. no. curve. The vals. obtained are closely correlated with the at. and ionic radii. For any one element, the radius of the positive ion<that of the neutral atom<that of the negative ion, the difference becoming smaller with increasing at. no. of the element. The vals. with Ce^{++++}, Ce^{+++}, and Ce suggest that free Ce has the electronic structure 2 8 18 18 10 2, analogous to that of Ce^{++++} (2 8 18 18 8), whilst the Ce^{+++} ion has the structure 2 8 18 19 8. An attempt is made to correlate these at. radius relationships with superconductivity phenomena.

Eddington's theory and physical constants. G. S. R. KRISHNAN (Nature, 1932, **130**, 776).—Vals. have been calc. for the physical consts. Selected vals. are: at. wt. of H, $1{\cdot}00774\pm0{\cdot}00002$, e/m_0 $1{\cdot}77001\pm0{\cdot}00013\times10^7$ e.m.u., e $4{\cdot}81209\pm0{\cdot}00037\times10^{-10}$ e.m.u., N $6{\cdot}01132\pm0{\cdot}00089\times10^{23}$, and h $6{\cdot}64879\times10^{-27}$. vere found

Determination of e/m for "thread" ne at 169 SIEBERTZ (Physikal. Z., 1932, **33**, 895—897). were are obtained for e/m greater than for elec

N M B

Structure of line spectra in cr ane, ali-TOMASCHEK (Nature, 1932, **130**, 740).— **Relative** binations for Pr, Nd, Sm, and Er have b **Raman** es. (MISS)

Regularities in the line spectra of s, **54**, 4199— R. TOMASCHEK (Physikal. Z., 1932, **33**, of the lines The phosphorescence spectra of the r n-$C_6H_{13}Br$, CaO and MgO are investigated. s have been

Spectrum of chromium in c es character- DEUTSCHBEIN (Physikal. Z., 1932, **33**, gs. The re- The absorption and emission spectra of C brations are room temp. and at —180° to —190° wer ans, and the Cr is capable of producing phosphors c 2575 cm.$^{-1}$, isomorphous with the principal materia nd O–H fre- itself as larger mols. in the principal cr orce and ex- H_2S and the

Line spectrum of samarium ion i its variation with the temperatu a 5% change and J. G. HARWELL (Proc. K. Akad. e detected. sterdam, 1932, **35**, 979—994).—The ab G. A. G. of Sm^{+++} in hexagonal cryst. Sm(Et SCROFT and C. been determined parallel to the optic -575 2587).— and 169° abs. Absorption lines in t of H_2O drops 2200 Å. are tabulated. y with varying

Doublet separation of the BRUNETTI and Z. OLLANO (Nuovo f t e medium. 281—290; Chem. Zentr., 1932, i, to be identical solution of $Ce(NO_3)_3$ gives a Raman rticl b cm.$^{-1}$ and a $5{\cdot}6M$ solution of $CeCl_3$ cm.$^{-1}$ These are ascribed to the Ce at the transition $^2F_{5/2}$—$^2F_{7/2}$, in agreemen meters magnetic measurements, but not v I J P doublet formula.

benzophenone.

Absorption spectrum of o (J. Amer. Chem. **pressures and the existence of** light scattering **I. Ultra-violet bands between** is is contrary to W. FINKELNBURG and W. STEINEL, the discrepancy **79**, 69—88).—The absorption spec s. L. O. (c) atm. indicates that the O_4 mol. ex hanisms for the mols. united by van der Waals for pours by air.

Significance of ultra-violet ull Soc chi **h lides.** M BOR (he luminiscence 62—68).—The hypothesis that ul 30, 1255· 1931 bands of alkali halide crystals are unds The temp of two neighbouring ions within a re given for many to contradictions in the theory and ethers With removed by assuming that the ne low 300° probably an internal surface. peroxy-derivatives,

Molecular absorption of diate products are **cules in the vacuum ultra** D. R. D. and H SPONER (Z. Physik, 1 **er the influence of** were measu Elektrochem., 1932, 1560 Å. for ICl, IBr, and BrCl. t Brüninghaus (A.,

Absorption spectrum o D. D W. G. BROWN (Physical Rev. ROTHSCHILD 363).—Vibrational analysis lea addition of the IBr absorption spectrum CaS–Sm or SrS–Sm

phosphors greatly increases their efficiency, so that they can be excited by an ordinary electric lamp. The Bi must be fused with the phosphor, and probably acts as a sensitiser, taking up the incident radiation and passing it on to the phosphor. A. J. M.

Reflecting power of thin metallic films. P. ROUARD (Compt. rend., 1932, **195**, 869—870).—The reflecting power of the glass–metal surface of a Au film 9·5—10·4 mμ for λλ 5780, 5461, and 4358 Å. decreases with increasing thickness to min. for thicknesses $< 5{\cdot}2$ mμ, and then rises rapidly. Films of Ag and Pt behave similarly. C. A. S.

Variation of reflecting power of bismuth on magnetisation. E. ENGLERT and K. SCHUSTER (Z. Physik, 1932, **79**, 194—196).—Variation of resistance of Bi with temp. does not affect reflecting power. A. B. D. C.

Ionised gases in a magnetic field at pressures below 10^{-3} mm. Hg. T. V. IONESCU and C. MIHUL (Compt. rend., 1932, **195**, 765—767; cf. A., 1931, 285; 1932, 554).—The effects of pressure and H_2O vapour are examined. In the atm. waves of length > 10 m. are reflected where pressure is $< 10^{-4}$ mm. Hg, *i.e.*, at heights > 150 km. C. A. S.

Scattering of light by sound waves. P. DEBYE (Physikal. Z., 1932, **32**, 849—856).—Theoretical. A. J. M.

Selenium or selenide rectifier ? W. S. GRIPENBERG (Physikal. Z., 1932, **33**, 778).—Certain facts indicate that the rectifying properties of a Se rectifier are really attributable to a very thin surface layer of Fe selenide. W. R. A.

Selective photo-effect and optical absorption at composite photo-cathodes. W. KLUGE (Physikal. Z., 1932, **33**, 873—874).—The composite cathodes are made up of a layer of Ag, on which is deposited a layer of alkali oxide with alkali metal adsorbed. With such a cathode there are two max., one in the short-wave, the other in the long-wave region. By making the M_2O–M layer very thin, the long-wave max. gets weaker. It is also possible in this case to study both the photo-effect and optical reflexion. There is no min. of reflexion corresponding with max. of photo-electric efficiency. A. J. M.

Spectral sensitivity of [photo-electric] cells with copper electrodes covered with cuprous oxide. G. ATHANASIU (Compt. rend., 1932, **195**, 767—769).—Using electrodes of electrolytic Cu covered with Cu_2O prepared by (*a*) the author's method (cf. A., 1925, ii, 1067), (*b*) Garrisson's method (cf. A., 1923, ii, 728), and (*c*) heating to 1000° and cooling rapidly, and as electrolyte 0·1*N*-$CuSO_4$, -KCl, or -KNO_3, the e.m.f. of the photo-electric cell is with (*a*) negative, but with (*b*) and (*c*) positive or negative. The positive effect is due to CuO, which when alone produces an e.m.f. of sign opposite to that produced by Cu_2O. A similar explanation holds for the varying position of the max. sensitivity, that for Cu_2O being at 4600—4800 Å., but displaced towards red by CuO, the max. for (*b*) being at 5100—5800 Å. C. A. S.

Electrical and optical behaviour of semi-conductors. VII. Photo-electric properties of semi-conductor unidirectional layers. W. LEO (Ann. Physik, 1932, [v], **15**, 129—144).—The capacity and resistance of unidirectional layers of Cu_2O and Ag_2S are considered. W. R. A.

Relation of optical transparency of cuprous oxide to electrical conductivity. G. MÖNCH (Z. Physik, 1932, **78**, 728—733).—The absorption edge of Cu_2O lies at 638 mμ and is independent of the conductivity of the sample; the transparency of the sample was used to measure the O_2 content of the layer. A. B. D. C.

Electrostatic theory of the dependence on frequency of ionic mobility and dielectric constant in mixed solutions of strong electrolytes. I. General theory. H. FALKENHAGEN and W. FISCHER (Physikal. Z., 1932, **33**, 941—945).—The general solution of the differential equation connecting ionic mobility, dielectric const., and frequency is considered. A. J. M.

Dielectric constant. I. Variation of dielectric constant of quartz with applied potential. H. SAEGUSA and K. NAKAMURA (Sci. Rep. Tôhoku, 1932, **21**, 411—438).—Apparatus and technique for the accurate determination of dielectric const. are described. The dielectric const. of a quartz plate cut perpendicular to its optical axis increases exponentially with applied potential from about 2000 volts per cm. thickness, and increases rapidly with rising temp. When the quartz plate is cut parallel to the optical axis, no such effect is observed up to 12,000 volts per cm. E. S. H.

Electric moment of hydrogen peroxide. E. P. LINTON and O. MAASS (Canad. J. Res., 1932, **7**, 81—85).—The electric moments of H_2O_2 and of H_2O were measured by determinations of the dielectric consts. of solutions in dioxan at 25° and in Et_2O at 10° or 0°. The vals. obtained were 2·13 and $2{\cdot}06\times10^{-18}$ for H_2O_2 and 1·90 and $1{\cdot}71\times10^{-18}$ for H_2O. The lower val. obtained for H_2O in Et_2O may be due to its association being greater at the lower temp. or to experimental errors. The val. obtained for H_2O_2 favours the formula $H_2O\rightarrow O$. A. G.

Connexion between dipole moment and cohesive forces. A. E. VAN ARKEL (Rec. trav. chim., 1932, **51**, 1081—1107).—Calc. and observed vals. of b.p., dipole moment, and van der Waals *a* and *b* for org. liquids are compared. London's theory (A., 1930, 1239) is extended to more complicated mols. van Laar's law concerning the additivity of *b* (A., 1916, ii, 386) is obtained as a first approximation for substances of zero moment. For halogen atoms a/V^2 is const. (V=at. or mol. vol. at b.p.). For C tetrahalides (*e.g.*, CBr_3Cl) $T=(V_{\text{compound}}-V_C)/V_{\text{compound}}$ approx., where T=b.p. abs. It follows that the val. of the b.p. is approx. additive. For partly halogenated compounds (*e.g.*, $CHCl_3$) the b.p. is 45° > theory for compounds containing 1 H, 85° higher for those with 2 H, and 81° higher for those with 3 H, the val. of this increment increasing with dipole moment. The val. of *a* depends on the sum of the abs. partial moments and not on the total moment. For isomeric derivatives of C_6H_6 the b.p. rises with dipole moment. Of disubstituted C_2H_4 derivatives, the αα-compounds

have the lowest b.p.; when both substituents are the same, the *trans*-isomerides have lower b.p. than the *cis*. A study of C_2H_6 and C_3H_8 derivatives indicates that the more a group is surrounded by other atoms, the smaller is its effect on the cohesive forces. The b.p. of CF_4 is about −130°, and not −15° as stated by Moissan (A., 1890, 944). D. R. D.

Dielectric constant of ethyl alcohol vapour and possible effect of conductivity. H. L. KNOWLES (J. Physical Chem., 1932, **36**, 2554—2566).—Except near the saturation pressure $3(K-1)/(K+2)$, where K is the dielectric const., varies linearly with P, the ideal v.p. Near saturation the slope of the graph of K against P increases markedly. The val. of K, calc. from the slopes of the lower part of these curves, is $1{\cdot}686\times10^{-18}$. S. L. (*c*)

Dipole moments of quinoline and *iso*quinoline. R. J. W. LE FÈVRE and J. W. SMITH (J.C.S., 1932, 2810—2811).—New determinations of the dipole moments of quinoline and *iso*quinoline give vals. of $2{\cdot}18$ and $2{\cdot}52\times10^{-18}$ e.s.u., respectivelv. H. A. P.

Dielectric constants of liquid and solid ethyl ether and nitrobenzene. J. MAZUR (Spraw. Prace Polsk. Towarz. Ficyz., 1931, **5**, 181—200; Chem. Zentr., 1932, ii, 352—353).—For Et_2O, ε rises with fall of temp. and is max. (12·39) at −105·4°, thereafter falling rapidly until at −117·2° (solidification) it suffers sudden change. For solid Et_2O ε approaches 2·04 as the temp. falls below −118·9°. For $PhNO_2$, ε (35·41 at 30·01°) becomes max. at 9·6° (38·15) and then falls rapidly to 11·82 at 7·71°, finally approaching the val. 2·709. An anomalous val. is again obtained near the f.p. (Cf. this vol., 11.) A. A. E.

Ionised gases in a magnetic field at pressures above 10^{-3} mm. Hg. T. V. IONESCU and C. MIHUL (Compt. rend., 1932, **195**, 1008—1010).—The effects of pressures $>10^{-3}$ mm. Hg on the conductivity of ionised H_2, N_2, and air in fields $\not>80$ gauss for λ 250—660 cm. are examined, as also is the relation between conductivity and electronic current in various fields, and between dielectric const. and field at various pressures. Marked changes occur at pressures of 0·02—0·15 mm. Hg, which would favour propagation in the atm. of waves of λ 5—6 m. at 50—80 km. height at the expense of longer waves. C. A. S.

Electrical conductivity of palladium with occluded oxygen. D. P. SMITH (Z. Physik, 1932, **78**, 815—823).—O_2 lowers the electrical resistance of Pd independently of the presence of H_2.
A. B. D. C.

Electricity transport by oxygen in metals. A. COEHN (Z. Physik, 1932, **78**, 824—825).—Polemical against Smith (cf. preceding abstract). A. B. D. C.

Electrical resistance of titanium and zirconium nitrides and a new resistance effect. P. CLAUSING (Z. anorg. Chem., 1932, **208**, 401—419; cf. A., 1931, 921).—The nitrogenation of filaments of Ti or Zr can be followed by measuring the resistance for various filament currents. The formula ZrN has been established by synthesis. Resistivities of TiN and ZrN and their temp. coeffs. have been measured. Peculiar hysteresis effects in the change of resistance with temp. are described and attributed to traces of free metal in the nitrides. F. L. U.

Conductivity of corundum. H. VON WARTENBERG and E. PROPHET (Z. Elektrochem., 1932, **38**, 849—850).—The conductivity of corundum rises from $\kappa=1{\cdot}3\times10^{-7}$ at 1500° abs. to $5{\cdot}0\times10^{-6}$ at 1800° abs. Data are given for ruby. Artificial ruby may be prepared by heating Al_2O_3 with Cr_2O_3 (1%) at 1600° abs.
D. R. D.

Temperature coefficient of resistivity of silicon and a [new] thermo-electric phenomenon of unipolar substances. C. BEDEL (Compt. rend., 1932, **195**, 871—873).—The ends of a fragment of Si heated to a const. temp. exhibit p.d., *e.g.*, with pure Si in fragments 0·4 mv. at 100°, in crystal 8·6 mv. at 330°. Carborundum, pyrites, and galena behave similarly (cf. A., 1930, 402). This is due to the equal and opposite currents produced at the ends by the thermoelectric effect combined with the rectifying power of a unipolar substance. It is impossible therefore to determine the temp. coeff. of resistance of Si, as there are three superposed actions: the thermoelectric effect, dielectric conductivity at the contacts, and conductivity proper of Si; it is, however, certainly negative for pure Si. The resistivity of Si containing 0·1% Fe decreases continuously to 400°, but with 1·8% Fe there is a min. at 210°, above which it is positive (cf. A., 1910, ii, 481; 1931, 30). C. A. S.

Variation of the true and apparent electrical resistivity of quartz with temperature. S. SHIMIZU (Sci. Rep. Tohoku, 1932, **21**, 439—454).—The causes of the variation of resistivity with time have been investigated at different temp. (cf. A., 1932, 560). E. S. H.

Electrical conductivity of mercury at high temperatures and pressures. W. BRAUNBEK (Physikal. Z., 1932, **33**, 830—831). W. R. A.

Rotation of Rochelle salt in alkaline media. A. N. CAMPBELL and A. J. R. CAMPBELL (J. Physical Chem., 1932, **36**, 2610—2614).—The marked variation of rotation with [OH′], the reduction in [OH′] of aq. NaOH caused by the salt, the decrease in conductivity on mixing aq. Rochelle salt and NaOH, and the form of the equilibrium diagram point to complex formation. S. L. (*c*)

Spectrochemistry of compounds of the sterol group. K. VON AUWERS and E. WOLTER (Nachr. Ges. Wiss. Gottingen, 1931, 101—119; Chem. Zentr., 1932, i, 2595—2596).—Solutions of linalool (I), geraniol (II), farnesol (III), cinnamyl alcohol (IV), and their Ac derivatives, and triolein (V) in quinoline and 1-$C_{10}H_7$Me were examined. Of the homogeneous substances only (I), and its acetate, and (V) were normal. The solvents have a moderate effect; the exaltations of n are usually 0·2—0·3 and of the scattering power 5—10% > for the homogeneous materials; with (III) these are unchanged in solution, and with (IV) and its acetate somewhat diminished. Vals. for (II) in quinoline differed from those in 1-$C_{10}H_7$Me. Cholestane, cholestene, ψ-cholestene, α-cholesterylene, cholesterol, and cholesteryl butyrate and oleate were also examined; vals. of n in solution and in the fused state correspond, but those of dis-

persion exhibit variations. All the compounds tend towards depression of the mol. and sp. refractory power. Ergosterol (VI), ergosteryl acetate, palmitate, and benzoate, ergosteryl-B_3 acetate (VII), ergotetraene (VIII), suprasterol-I and -II, suprasteryl-I acetate, and an irradiation dihydro-derivative $C_{27}H_{44}O$ were studied. Ergosterol and its esters differ optically from the suprasterol group, the latter belonging to the cholesterol group and the former exhibiting exaltation. Hence (VI) contains a conjugated linking; two double linkings are considered to be conjugated and the third isolated. Windaus' formula (A., 1930, 1578) is not excluded. (VII) is also conjugated; in (VIII) either two double linkings are conjugated and the third is isolated, or three lie in a ring and the fourth is remote. In the suprasterols the three double linkings are isolated, whilst $C_{27}H_{44}O$ contains a conjugation. Hydroxycholestenone and dehydroergosteryl acetate were also examined. A. A. E

Refraction of gaseous acetaldehyde and ethyl acetate. H. Lowery (Phil. Mag., 1932, [vii], **14**, 743—745).—The gaseous refractive indices of MeCHO (for λ 5461 Å.) and of EtOAc (for λ 5461, 5893 Å.), and the dispersion of MeCHO between λ 4358 and 6708 Å., have been measured. H. J. E.

Dispersion of gases and vapours and its representation by the dispersion theory. III. Dispersion of oxygen between 6000 and 1920 A. R. Ladenburg and G. Wolfsohn (Z. Physik, 1932, **79**, 42—61).—Interferometer dispersion measurements give vals. which can be represented by a dispersion formula with three characteristic frequencies at 1899, 1468, and 544 Å. A. B. D. C.

Optical properties of carbonates. H. Brasseur (Z. Krist., 1932, **83**, 493—495).—The ionic refraction, R, of CO_3'' is taken as 10·88 or 8·38 according as the electric vector of the incident light is ∥ or ⊥ to the plane of the CO_3'' groups (cf. A., 1924, ii, 373). The birefringence of fourteen normal or basic carbonates is calc. as the difference between the vals. of n deduced from $R=M(n^2-1)/d(n^2+2)$ through use of the two vals. of R for CO_3''. The calc. birefringence exceeds the actual only for $(MgOH)_2Mg_2(CO_3)_3,3H_2O$ and $Na_2Ca(CO_3)_2,2H_2O$, but is less for all others, indicating respectively non-parallelism and parallelism of the CO_3'' groups. C. A. S.

Magnetic circular dichroism and anomalous magnetic rotatory dispersion in cobalt chloride solutions. M. Schérer (Compt. rend., 1932, **195**, 950—952).—With a field of 50 kilogauss and aq. $CoCl_2$ of d^{19} 1·122 positive magnetic circular dichroism and anomalous magnetic rotatory dispersion were detected. The ellipticity–λ curve shows a max. of $2\beta=1·50°$ for λ 5100 Å. (the wave-length for which absorption in the band λ 4350—5700 is a max.), and is steeper on the long-wave side. The rotation–λ curve has a point of inflexion at λ 5050, rotation being positive or negative as λ is > or < 5050 Å. (cf. A., 1925, ii, 478). C. A. S.

Magnetic circular dichroism and rotatory dispersion. A. Cotton (Compt. rend., 1932, **195**, 915—919).—The results reported in the preceding abstract are discussed with reference to the previous work of the author and others (cf. A., 1906, ii, 146; 1930, 668). The assumption that only paramagnetic atoms can give rise to the effects is questioned. C. A. S.

Magneto-optic rotation by condenser discharge. F. G. Slack and W. M. Breazeale (Physical Rev., 1932, [ii], **42**, 305—311; cf. Allison, A., 1930, 1541). N. M. B.

Mechanical double refraction of oils in relationship to the molecular form and association. III. D. Vorlander and J. Fischer (Ber., 1932, **65**, [*B*], 1756—1762; cf. A., 1931, 286).—Observations are recorded for many org. liquids of known mol. composition. The sp. double refraction $[D]_t$ vals. are much lower for aliphatic than for aromatic derivatives even when the internal friction of the oils is of the same order of magnitude. The $[D]_t$ vals. are regarded as an approx. mathematical expression of the relative tendency of the mols. towards association. With paraffin hydrocarbons, aliphatic dibromides, and dicarboxylic esters of the malonic series the influence of linear structure of normal C chains is obvious. The longer C chain of Me_2 succinate imparts a greater directive stability to the mol. than does the shorter C chain of the isomeric $(CH_2·OAc)_2$. *n*-Pentane and Et_2O show no D effect under the experimental conditions. C_6H_6 becomes positively double refractive, but no effect is observed with *cyclo*hexane. Homologues and substituted derivatives of C_6H_6 show a greater D effect than C_6H_6. Hydrogenation of homologues of C_6H_6 causes the disappearance of all D effect, which falls in the sequence 1-$C_{10}H_7Me$, tetra- and deca-hydronaphthalene. Cyclic hydroaromatic and open-chained, strongly-branched hydrocarbons cannot be distinguished from one another. The greater effect with $C_{10}H_8$ derivatives in comparison with C_6H_6 compounds shows that the two C_6 rings in $C_{10}H_8$ lie approx. in the same plane. The preponderating importance of the linear *para* position is observed. With PhCl, PhBr, PhI, the val. diminishes with increasing at. wt. of the halogen. The contrast between positive and negative substituents in C_6H_6 does not find expression. H. W.

Theory of diamagnetism of conductivity electrons. R. Peierls (Physikal. Z., 1932, **33**, 864).—A method of calculating diamagnetism of free electrons is indicated, which is free from the restriction that the wave-length of the electron must be small compared with the orbit radius. A. J. M.

Magnetic constants of benzene, naphthalene, and anthracene molecules. K. S. Krishnan (Nature, 1932, **130**, 698—699).—The principal susceptibilities of mols. of C_6H_6, $C_{10}H_8$, and anthracene have been calc. by a method previously given (A., 1932, 1078). The increase in susceptibility from C_6H_6 to $C_{10}H_8$ to anthracene is practically confined to a direction normal to the plane of the mols., which is also an axis of approx. magnetic symmetry. L. S. T.

Influence of light on paramagnetic susceptibility. O. Specchia (Nature, 1932, **130**, 697—698). L. S. T.

Transition from ferromagnetic to paramagnetic form for manganese arsenide and phosphide. A. SMITS, H. GERDING, and F. VERMAST (Rec. trav. chim., 1932, **51**, 1178—1192).—*V–T* curves indicate that the transition from ferro- to para-magnetic form in the case of MnAs and MnP is gradual. In the case of MnAs there is a temp. hysteresis. The equilibrium potentials of MnAs and MnP in aq. $MnCl_2$ containing HCl rise continuously with temp., but, in the case of MnAs, the potential obtained on rapid heating or cooling passes through a min. and temp. hysteresis is observed. D. R. D.

Diamagnetic susceptibilities of some sulphur compounds. J. FARQUHARSON (Phil. Mag., 1932, [vii], **14**, 1003—1012).—The mol. magnetic susceptibilities of SO_2, $KHSO_4$, K_2SO_3, $K_2S_2O_3$, $K_2S_3O_7$, $K_2S_2O_8$, and $K_2S_4O_6$ have been measured. The % differences between the experimental figures and those calc. by Pauling's and Slater's methods are in good agreement with each other and with theory. The changes in magnetic susceptibility which accompany the various stages in building up the mol. agree with theory and give the polarities of some of the linkings. J. W. S.

Dia- and para-magnetism of the metals. E. VOGT (Physikal. Z., 1932, **33**, 864—869).—There are two types of paramagnetism in metals, one dependent on temp., the other weak, and independent of temp. In the case of the transition metals the two types are not differentiated. The magnetism, in these metals, varies little with temp., with the exception of Pt and Pd, which can be explained by considering their at. structure. To test the views put forward, the susceptibility of mixed crystals of Au with Fe, Ni, Pd, and Pt is investigated. A. J. M.

Magnetic properties of some compounds of molybdenum, tungsten, and chromium in various states of valency of these elements. B. T. T. JABBES (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 693—700).—Twenty-two substances containing Mo, W, or Cr have been measured. $MoCl_4$, $MoCl_5$, and K_3CrO_8 are strongly paramagnetic; MoS_2 and Mo_3Br_6 are diamagnetic. Observed vals. for χ_A are compared with vals. deduced from the Hund and Bose–Stoner theories for Mo^{+6}, Mo^{+5}, Mo^{+4}, Mo^{+3}, Mo^{+2}, and discrepancies are discussed. Complex compounds in which the metal (M) is quinquevalent are strongly paramagnetic when they are of the MOX_3 type and diamagnetic when they are of the MO_2X type. Metallic Mo shows anomalous paramagnetism. W. R. A.

Magnetic behaviour of the oxygen molecule. R. EINAUDI (Atti R. Accad. Lincei, 1932, [vi], **16**, 133—139).—Mathematical. The behaviour of O_2 in magnetic fields of the order of 10^4 gauss is calc. O. J. W.

Compact molecules. J. J. VAN LAAR (Chem. Weekblad, 1932, **29**, 587).—A criticism of Backer's views (A., 1932, 679), and a claim for priority. H. F. G.

Polar valencies of carbon. T. MIŁOBĘDZKI (Rocz. Chem., 1932, **12**, 635—637).—The polar valencies of C in various compounds are classified with regard to their degree of oxidation, from $C^{-IV}H_4$ to $C^{+IV}Cl_4$, free C having the polar valency C^0. R. T.

Semi-classical theory of chemical binding. W. HEITLER (Z. Physik, 1932, **79**, 143—152).—A summary of a general theory of homopolar linkings which shows that the no. of linkings between two atoms is quantised as are the no. of light quanta according to Dirac's theory; the energy of linking is additive with respect to the no. of linkings. A. B. D. C.

Relationship between electrical potentials and chemical reactivity. L. KAHLENBERG (Science, 1932, **76**, 353—358).—An address. L. S. T.

Formation of double molecules in gases under the influence of an electric field. H. SENFTLEBEN (Physikal. Z., 1932, **33**, 826—829).—The influence of pressure, temp., and field strength on the effect has been investigated. The degree of association of $COMe_2$ and NO_2 is considered. W. R. A.

Five-electron problem in quantum mechanics, and its application to hydrogen–chlorine reaction. G. E. KIMBALL and H. EYRING (J. Amer. Chem. Soc., 1932, **54**, 3876—3885).—Slater's method (A., 1931, 1356) is used to solve the problem of five electrons with spin degeneracy. Rules are given for finding the proper functions corresponding with an arbitrary no. of valency linkings between atoms. The calc. activation energies of the reactions $Cl_3+H_2 \longrightarrow Cl_2+HCl+H$, $H+Cl_2+H_2 \longrightarrow 2HCl+H$, and $Cl+H_2O+H_2 \longrightarrow HCl+H_2O+H$ indicate that none of them takes part in the photochemical reaction between H_2 and Cl_2, and that the reaction proceeds through the Nernst chain. G. M. M. (*c*)

Single electron linking. R. F. HUNTER (Chem. and Ind., 1932, 939).—A review of published work supports the view of singlet sharing. E. S. H.

Spectroscopic determination of electron affinities. H. KUHN (Z. physikal. Chem., 1932, **B**, **19**, 217—218).—Lederle's theoretical methods (A., 1932, 791) are criticised. R. C.

Quantum mechanics treatment of the water molecule. A. S. COOLIDGE (Physical Rev., 1932, [ii], **42**, 189—209).—Mathematical. The interaction of the atoms in the H_2O mol., and the sources of the binding energy in various types of resonance or electron interchange, are investigated. N. M. B.

Angle between the oxygen linkings by the collision area method. W. A. HARE and E. MACK, jun. (J. Amer. Chem. Soc., 1932, **54**, 4272—4277; cf. A., 1932, 563, 566).—The viscosity of the vapours of Ph_2O and CH_2Ph_2 at temp. between 165° and 363° corresponds with the collision areas (theoretically almost equal) 36·13 and 36·40 Å.^{2}, and the Sutherland consts. 400 and 387, whilst the shadowgraphic collision areas of various mol. models agree with the angles 107° and 110°, respectively, between the O linkings. The Sutherland const. and collision area of Et_2O are 380 and 18·18 Å.^{2}, respectively, and the mol. is tightly coiled. The significance of these results is discussed. J. G. A. G.

Behaviour of liquid nitrobenzene in vicinity of m.p. J. WELLM (Z. physikal. Chem., 1932, **B**, **19**,

113—116; cf. A., 1932, 329).—The viscosity, d, and the dielectric const. are normal near the m.p. (Cf. this vol., 9.) R. C.

Supposed allotropy of liquid nitrobenzene. E. COHEN and L. C. J. TE BOEKHORST (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1016—1023).—Between 2° and 20° the sp. vol. and the fluidity of $PhNO_2$ (m.p. 5·77°) are expressed by $V=0{\cdot}81759_3+0{\cdot}000663t+0{\cdot}000{,}000{,}48t^2$ and $\phi=31{\cdot}98_9+0{\cdot}80348t+0{\cdot}002742t^2$ with errors of $\gtrless 2\times10^{-5}$ and $\gtrless 3\times10^{-2}$, respectively. No discontinuities are shown by the pure substance or when a trace of H_2O is added. A. G.

Parachor of rhenium. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (J.C.S., 1932, 2673—2676; cf. A., 1932, 585).—Measurements of density and surface tension (by capillary rise) on Re_2O_7, ReO_2Cl_3, and ReO_3Cl, at respective approx. temp. of 300°, 50°, and 30°, lead to vals. for the parachor of Re of 68·9, 78·9, and 76·4, respectively. N. M. B.

New X-ray interference method for complex crystals, in particular rolled and fibrous materials (object between two slits). H. SEEMANN (Physikal. Z., 1932, **33**, 755—763). W. R. A.

Use of monochromatic radiation in X-ray scattering in gases. W. VAN DER GRINTEN (Physikal. Z., 1932, **33**, 769—770).—Results obtained using monochromatic radiation and filtered radiation with CCl_4 are compared. W. R. A.

Influence of temperature on the scattering of X-rays by gas molecules. R. W. JAMES (Physikal. Z., 1932, **33**, 737—754).—The scattering curves for $SiCl_4$ vapour at 100° and 300° have been determined; no temp. effect has been observed. The curves substantiate the tetrahedral model for $SiCl_4$, and interat. distances, Cl—Cl 3·35, Si—Cl 2·17 Å., have been evaluated. The theory of the scattering of X-rays by a mol. with vibrating atoms has been considered. W. R. A.

New methods of mass-spectrometry. J. MATTAUCH (Physikal. Z., 1932, **33**, 899—903). A. J. M.

Corrections for Debye–Scherrer X-ray photographs. Z. NISHIYAMA (Sci. Rep. Tohoku, 1932, **21**, 364—384).—Different correction formulæ for the thickness of the specimen have been applied to results for Armco Fe and Al (99·95%). The author's formula (A., 1930, 148) gives the best agreement. The lattice consts. determined are Fe 2·861, Al 4·041 Å. E. S. H.

Determination of crystallographic constants. G. KALB (Z. Krist., 1932, **83**, 362—373).—Observed variations in such determinations far exceed experimental errors, and are due to vicinal faces (cf. A., 1903, ii, 472; 1932, 450). Averaging does not give a correct result, which is obtainable only by taking these faces into individual consideration. C. A. S.

Calculation methods in fine structure investigations. M. VON SCHWARZ and O. SUMMA (Z. Krist., 1932, **83**, 499—500). C. A. S.

Thermal dilation in crystals and Haüy's law. A. CAVINATO (Atti R. Accad. Lincei, 1932, [vi], **16**, 163—165).—A proof of the validity of Haüy's law for the thermal dilation of a crystal. O. J. W.

Atomic arrangement in glass. W. H. ZACHARIASEN (J. Amer. Chem. Soc., 1932, **54**, 3841—3851).—The atoms in a glass are linked by essentially the same forces as in a crystal. In both cases the linkings form three-dimensional networks, but the glass network is irregular in that it lacks the symmetry and periodicity of the crystal lattice. A glass network with an energy content comparable with that of the corresponding crystal can be formed only when the co-ordination nos. of the atoms involved are suitable. L. O. (c)

Carbon with metallic lustre; new form of carbon? S. B. HENDRICKS (Z. Krist., 1932, **83**, 503—504).—A grey, somewhat porous form of C (C 98·76—98·92, H 0·73—0·91%, no ash) is deposited in hot C tubes (800°) through which C_6H_6 vapour is passed; it is sometimes harder than corundum and takes a high polish (cf. A., 1892, 565; 1923, ii, 757). X-Ray examination shows patterns similar to those found in finely-divided graphite by Raman and Krishnamurti (cf. A., 1929, 984), which are, however, attributed to a modification of the ideal graphite lattice and not to "free electrons." C. A. S.

Unidimensional swelling of graphitic acid and graphite. U. HOFMANN [with A. FRENZEL, D. WILM, and E. CSALAN] (Kolloid-Z., 1932, **61**, 297—304).—A summary of published work. E. S. H.

Madelung constants for some cubic crystal lattices. J. SHERMAN (Phil. Mag., 1932, [vii], **14**, 745—746; cf. Wheeler, A., 1932, 793).—The const. for cuprite has been corrected. H. J. E.

Tetragonal and cubic martensites. K. HONDA and Z. NISHIYAMA (Sci. Rep. Tohoku, 1932, **21**, 299—331).—Tetragonal (α) martensite is the first product of quenching C steel and consists of an interstitial solid solution of C in Fe. Tempering the product at 100—150°, or shock such as grinding, converts it into cubic (β) martensite. X-Ray analysis shows that the lattice const. of β-martensite increases slightly with the content of C; it is therefore a solid solution of C in Fe and not a decomp. product of α-martensite. β-Martensite can also be obtained directly by quenching steel in rapeseed oil at 140°. A mechanism of the changes involved in quenching and tempering is suggested. E. S. H.

Blue sodium–tungsten bronze. W. F. DE JONG and H. J. STEK (Z. Krist., 1932, **83**, 496; cf. A., 1932, 450).—Blue Na–W bronze, probably $Na_2(WO_3)_5$, is tetragonal, with a 17·5, b 3·80 Å., d 7·3. C. A. S.

Crystal structure of hydrated cadmium sulphate. L. EGARTNER, F. HALLA, and E. SCHWARZ (Z. Krist., 1932, **83**, 422—425).—$3CdSO_4,8H_2O$ has a 14·65, b 11·84, c 16·35 Å., β 34° 48′, with 4 mols. in the unit cell, space-group C_{2h}^6. It is not piezoelectric. C. A. S.

Crystal structure and dehydration figures of alkali halide hydrates. W. A. WOOSTER (Nature, 1932, **130**, 698).—Weissenberg and oscillation photographs give for $NaBr,2H_2O$ a 6·59, b 10·20, c 6·51 Å., β 112·5°, $a:b:c$ 0·646 : 1 : 0·638, $d_{calc.}$ 2·28, 4 mols.

per unit cell; space-group C_{2h}^{5}—$P2_{1/a}$; and for $NaI,2H_2O$ a 6·85, b 5·76, c 7·16 Å., α 98°, β 119°, γ 68·5°, $a:b:c$ 1·190 : 1 : 1·243, $d_{calc.}$ 2·67, 2 mols. per unit cell; space-group C_1^1—P_1. L. S. T.

X-Ray examination of ammonium hydrogen fluoride. O. Hassel and N. Luzanski (Z. Krist., 1932, **83**, 448—459).—NH_4F,HF is rhombic with a 8·14, b 8·33, c 3·68 Å., d (by suspension method) 1·50, space-group V_h^{13}. It is not piezoelectric. C. A. S.

Structure of potassium osmiamate. F. M. Jaeger and J. E. Zanstra (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 610—624).—From aq. solution $KOsNO_3$ crystallises as yellow, hemihedral, tetragonal-bipyramidal crystals, $a:c=1:2{\cdot}3123$, space-group C_{4h}^{6}; d^{18} 4·49—4·51. Results for rotation, oscillation, and powder spectrograms are recorded and discussed. $KOsNO_3$ is a complex salt built up entirely of ions all of which have inert gas electronic configurations. The O and N ions are arranged around the Os ions at the corners of a tetragonal bisphenoid, disagreeing with structures suggested by Werner and Dinklage. W. R. A.

Structure of the ammonium, rubidium, and thallium osmiamates. F. M. Jaeger and J. E. Zanstra (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 787—798; cf. preceding abstract).—NH_4OsNO_3, $RbOsNO_3$, and $TlOsNO_3$ have each a rhombic-bisphenoidal pseudo-tetragonal structure, space-group V^4, the lattice consisting of the simple rhombic cell. There are 4 mols. in the unit cell, the dimensions of which are: NH_4OsNO_3 a 5·53, b 5·86, c 13·54 Å.; $RbOsNO_3$, a 5·57, b 5·84, c 13·64 Å.; $TlOsNO_3$, a 5·42, b 5·68, c 13·45 Å. J. W. S.

Structure of cerium osmiamate. F. M. Jaeger and J. E. Zanstra (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 779—786).—$CsOsNO_3$ is rhombic-bisphenoidal and pseudo-tetragonal in structure, a 8·08, b 8·35, c 7·22 Å. The space-group is V^2, and the unit cell contains 4 mols. (see preceding abstract). J. W. S.

Crystal structure of calcium metaborate. W. H. Zachariasen and E. Ziegler (Z. Krist., 1932, **83**, 354—361).—$Ca(BO_2)_2$ is rhombic, with a 6·19, b 11·60, c 4·28 Å., and 4 mols. in the unit cell, d 2·65, space group V^{14} (*Pnca*). Each Ca atom is surrounded by 8 O atoms at average distance 2·52 Å., each B by 3 O at 1·36 Å., two of the latter being shared by two BO_3 groups so that the BO_3 groups form endless chains. C. A. S.

Structure of potassium dithionate and measurement of integrated reflexion from a small crystal. G. V. Helwig (Z. Krist., 1932, **83**, 485—492; cf. A., 1931, 1115).—Further examination of small crystals by a new method for measuring the integrated reflexion and of a large crystal shows that the space-group is definitely D_3^2 (cf. A., 1932, 1079). A satisfactory structure similar to, but more symmetrical than, that of Huggins and Frank (cf. J. Min. Soc. Amer., 1931, **16**. 580) is deduced. C. A. S.

X-Ray analysis of iron pyrites by the method of Fourier series. H. M. Parker and W. J. Whitehouse (Phil. Mag., 1932, [vii], **14**, 939—961).—The lattice spacing in FeS_2 is 5·405 Å., the parameter of the S atom 0·114, the distance S—S 2·14 Å., and the distance S—Fe 2·26 Å. The predictions of Bragg and West (A., 1931, 26) concerning the diffraction effects in a Fourier analysis and the possibility of counting electrons are confirmed. The diffraction rings surrounding each peak were found to have the predicted radii. The Fe atom is found to have its full complement of 26 electrons, indicating the non-ionic nature of FeS_2. J. W. S.

Crystal structure of goethite. S. Goldstaub (Compt. rend., 1932, **195**, 964—967; cf. A., 1931, 1390).—The unit cell contains 2 mols. of Fe_2O_3,H_2O. The structure consists substantially of hexagonally close-packed O atoms with the Fe atoms in the octahedral interspaces, being closely related to hæmatite. C. A. S.

Crystal structure of bertrandite. T. Ito and J. West (Z. Krist., 1932, **83**, 384—393).—Bertrandite, $H_2Be_4Si_2O_9$, is rhombic pyramidal, with a 15·19, b 8·67, c 4·53 Å., and 4 mols. in the unit cell; space-group The structure differs fundamentally from that of hemimorphite (cf. A., 1889, 471; 1932, 987), and is represented by $Be_2(BeOH)_2SiO_5SiO_4$, the Si and Be atoms forming chains of Si with O and Be with O or O and OH, parallel to the c axis, thus explaining the predominating cleavage. C. A. S.

Structure of minerals of sodalite family. T. F. W. Barth (Z. Krist., 1932, **83**, 405—414).—The structures of sodalite, noselite, and hauynite all consist primarily of Si–Al–O chains forming a network of composition $(Al_6Si_6O_{24})^{VI}$, with internal spaces in which the larger ions Na^+, Ca^{++}, Cl', and SO_4'' can be packed. In sodalite all such are occupied by Cl' (with the Na^+ tetrahedrally around each Cl'); in noselite alternate spaces by SO_4'' (similarly surrounded); hauynite is intermediate with part of the Na_2O replaced by CaO, but also with more of the vacant spaces occupied by SO_4'' necessitating for electrovalent balance a further replacement of Na^+ by Ca^{++}. The formulæ for the unit cubes are $Na_8Al_6Si_6O_{24}Cl_2$, $Na_8Al_6Si_6O_{24}SO_4$, and $(NaCa)_{4\text{-}8}Al_6Si_6O_{24}(SO_4)_{1\text{-}2}$, respectively. They are isomorphous, space-group T_d^1, which for sodalite gives a structure almost identical with T_d^3 (cf. A., 1931, 289). A variate atom equipoint arrangement, similar to that in hauynite, applies to Al and Si in ultramarine (cf. A., 1929, 749), the framework of which is $[(AlSi)_{12}O_{24}]^n$, where the valency n, and consequently the content of Na and S, depend on the ratio Al : Si. C. A. S.

Structure of lead formate. F. Halla and L. Zimmermann (Z. Krist., 1932, **83**, 497—498; cf. A., 1929, 16).—Previous results are confirmed. The crystal is not piezoelectric; a structure is proposed. C. A. S.

X-Ray examination of mono- and poly-meric butenesulphones. E. Sauter (Z. Krist., 1932, **83**, 340—353).—The identity of polybutenesulphone before and after dissolution in H_2SO_4 or HNO_3 and repptn. by H_2O is confirmed. Δ^{β}-Butene-$\alpha\delta$-sulphone, d^{17} 1·50, is monoclinic, a 9·55, b 11·35, c 6·23 Å., β 131° 14′, 4 mols. in the unit cell, space-group C_{2h}^5; corresponding data for β-methyl-Δ^{β}-butene-$\alpha\delta$-sulphone (cf.

A., 1930, 1405) are 1·36, monoclinic sphenoidal, 6·60, 7·62, 6·67 Å., 110° 34′, 2, C_3^3; and for $\delta\gamma$-dimethyl-Δ^{β}-butene-$\alpha\delta$-sulphone, 1·34, rhombic, 7·55, 12·12, 7·39 Å., 90°, 4, V_h^8. All are non-piezoelectric. C. A. S.

X-Ray diffraction in ethyl ether near the critical point. F. H. W. NOLL (Physical Rev., 1932, [ii], 42, 336—339).—In the higher regions of the temp. range 25—210° at 43·5±0·7 kg. per sq. cm. pressure the ionisation curves are a combination of the liquid and polyat. gas types, the liquid type decreasing up to 155°. There is strong evidence of liquid, semi-orderly, cybotactic groups from room temp. to 199°. N. M. B.

Crystallographic relations of methylglucoses. E. VON SZADECZKY (Z. Krist., 1932, 83, 501—507).—4-Methylglucose dibenzylmercaptal, m.p. 96° (cf. A., 1932, 369), is monoclinic, $a:b:c=1·8230:1:1·8467$, β 100° 50′; the crystals are pseudo-hexagonal. The 2-Me derivative, m.p. 190—191°, is rhombic bipyramidal, $a:b:c=0·5331:1:1·0755$, in tabular crystals. C. A. S.

What causes the different X-ray spectra of natural starches? J. R. KATZ and J. C. DERKSEN (Naturwiss., 1932, 20, 851).—Natural starches give three types of X-ray spectra, designated *A*, *B*, and *C*, respectively. The *C* spectrum is probably a transition or mixed spectrum of *A* and *B*. Sol. starch was dissolved at 100° to form a 1 : 1 solution, and evaporated at 20°; the product gave the *B* spectrum. The same solution evaporated at 60° gave the *A* spectrum. The difference may arise owing to the existence of a different stereoisomeric form of the pyranoid ring in the starch crystals. A. J. M.

Röntgen diagram of stretched myosin threads. G. BOEHM and H. H. WEBER (Kolloid-Z., 1932, 61, 269—270).—Myosin threads, made by spraying from a capillary tube, give an X-ray diagram which is identical with that obtained from stretched frog-muscle. E. S. H.

Crystal threads and fibrous aggregation forms. H. W. KOHLSCHÜTTER (Kolloid-Z., 1932, 61, 270—280).—A discussion of the relations between the dendritic and similar crystal growths of metals and inorg. compounds and the thread-like structure of complex org. substances. E. S. H.

Linear and laminar fine structures. R. O. HERZOG (Kolloid-Z., 1932, 61, 280—297).—A lecture, in which is discussed the evolution of one- and two-dimensional structures from mols., through mol. aggregates, to the structural elements of histological specimens. E. S. H.

Polyoxymethylene films and threads. W. KERN (Kolloid-Z., 1932, 61, 308—310).—A review of published work, particularly on elasticity and plasticity. E. S. H.

Dependence of the susceptibility of bismuth single crystals on the field. W. J DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 454—458; cf. A., 1931, 411).—At 20·4° and 14·2° abs. the relation between diamagnetic magnetisation and field strength is linear except with fields of 12·5—14·5 and 21—28 kilogauss. H. J. E.

Spontaneous magnetisation and thermo-remanence in ferromagnetic single crystals. J. KOENIGSBERGER (Physikal. Z., 1932, 33, 763—767). W. R. A.

Ferromagnetic single crystals. R. GANS (Physikal. Z., 1932, 33, 924—928).—The ferromagnetic properties of single crystals can be most easily explained from (1) consideration of the symmetry of the crystal, and (2) Heisenberg's principle. A. J. M.

Elastic forces and magnetic properties. R. BECKER (Physikal. Z., 1932, 33, 905—913). A. J. M.

Permeability and hysteresis for magnetisation in the preferential direction for energy. F. PREISACH (Physikal. Z., 1932, 33, 913—923).—Experiments with permalloy are described and discussed. Preferential directions produced by directed cryst. and elastic forces affect the magnetisation in the same way. A. J. M.

Joule magnetostrictive effect in a group of cobalt-iron alloys. S. R. WILLIAMS (Rev. Sci. Instr., 1932, [ii], 3, 675—683).—A group of ferromagnetic rods, including Fe, Ni, Co, and Fe–Co alloys, has been found having a wide variation in change of length when magnetised longitudinally. A new extensometer and recording camera are described. C. W. G.

Resistivity of polycrystalline wires in relation to plastic deformation, and the mechanism of plastic flow. E. N. DA C. ANDRADE and B. CHALMERS (Proc. Roy. Soc., 1932, A, 138, 348—374).—Measurements have been made of the sp. resistivities of Cd, Cu, Al, and Sn wires at various stages of the plastic flow under large stresses. The sp. resistance of metals which crystallise in the cubic system is unaffected by the flow, but with metals crystallising with a unique axis of symmetry it changes by approx. 2% during the intermediate stage of flow at diminishing rate (the β-flow), although it remains unchanged during the immediate extension and during the final flow at const. rate. It is considered that the first immediate stretch takes place by break-up of the crystallites and movements of the fragments without distortion; that during the β-flow, rotation of the crystallites takes place with change of sp. resistance; and that in the final stage of steady flow slipping without rotation occurs. This hypothesis explains why an increase of sp. resistance with extension is found in metals of which the crystals have the slip-planes parallel to the unique axis, whilst there is a decrease with crystallites having the slip-plane normal to the unique axis. Further evidence in favour of this theory is afforded by low-temp. experiments, where there is marked immediate stretch but no β-stretch. Under these conditions, an extensive twinning takes place in the case of Cd, causing an increase of resistivity as opposed to the decrease found at room temp. L. L. B.

Rotatory magnetisation. H. BRION (Ann. Physik, 1932, [v], 15, 167—197).—The Barkhausen effect has been studied in relation to the position of the coil, to the density, and material of the target for layers of Ni, Fe, Fe–Si, and Cu–Ni–Fe alloys.

The rotatory moment of hysteresis can be approx. computed from the period of vibration. W. R. A.

Propagation of large Barkhausen discontinuities. II. K. J. SIXTUS and L. TONKS (Physical Rev., 1932, [ii], **42**, 419—435; cf. A., 1931, 791).—A new formula for the penetration time of large Barkhausen discontinuities is found. The behaviour of the discontinuity in a 15% Ni–Fe wire under various conditions was investigated. N. M. B.

Plasticity and creep in solids. H. JEFFREYS (Proc. Roy. Soc., 1932, **A**, **138**, 283—297).—A new derivation of the equations of plastic flow is given. A theory of creep is developed, and its relation to experimental evidence is discussed. The results are applied to certain geophysical problems. L. L. B.

Heat of loosening of the lead lattice. G. VON HEVESY, W. SEITH, and A. KEIL (Z. Physik, 1932, **79**, 197—202).—The heat of activation for the reaction constituted by interchange of lattice elements was determined from the temp. coeff. of diffusion velocity of a radioactive Pb isotope into Pb; its val. is 27,830 g.-cal. per mol., and it is no more sensitive to structure changes than the A const. of the diffusion equation. A. B. D. C.

Persistence of anisotropic structure in silica obtained from the action of acids on leucite. G. A. BLANC (Atti R. Accad. Lincei, 1932, [vi], **16**, 3—6; cf. A., 1931, 1253).—The crystal of hydrated SiO_2 obtained by the action of mineral acids on leucite retains under certain conditions the original cryst. form and structure of the complex $KAlSi_2O_6$. O. J. W.

Structural constant relative to changes of state. R. BIGAZZI (Atti R. Accad. Lincei, 1932, [vi], **16**, 48—53).—For a large no. of substances the relationship $TM/p^2=K$ is found to hold; T=abs. temp. of a change of state, b.p. or f.p., M=mol. wt., $p=d^{15}$. For substances having a similar structure but different composition K is approx. const. provided no change in M occurs during the change of state. If K is divided by a factor c, which depends on structural complexity of a particular mol., then $K'=K/c$ can be regarded as an approx. const. for a change of state. K' varies between 2 and 10 approx. for the substances tabulated. O. J. W.

Theory of superconductivity. R. DE L. KRONIG (Z. Physik, 1932, **78**, 744—750).—A metal conductor is represented as an electron lattice which "melts" at the temp. where superconductivity suddenly sets in. A. B. D. C.

Explanation of certain results on superconductivity. M. VON LAUE (Physikal. Z., 1932, **33**, 793—796).—The influence of a magnetic field on superconductivity and two experiments by Sizoo (cf. A., 1926, 667) are discussed. W. R. A.

Dispersion of sound in several gases, and its relation to the frequency of molecular collisions. W. T. RICHARDS and J. A. REID (Nature, 1932, **130**, 739).—The dispersion of sound in CO_2, CS_2, SO_2, and C_2H_4 is sensitive to pressure, and the velocity of sound at a given frequency increases as pressure is decreased until a const. val. is reached. Dispersion in mixtures of C_2H_4 and A or C_2H_4 and N_2 indicates that the vibrational energy of C_2H_4 is not excited by collisions with mols. of N_2 or A. In mixtures of C_2H_4 and H_2 it is necessary to suppose that a collision with a H_2 mol. is 10 times as likely to excite C_2H_4 as is a collision with another C_2H_4 mol. Air, N_2, A, C_3H_8, and C_5H_{12} appear to show no dispersion between 9 and 451 kilocycles. L. S. T.

Velocity of sound in nitrogen. W. H. KEESOM and J. A. VAN LAMMEREN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 727—736).—Using the method described previously (A., 1931, 792) the velocity of sound in N_2 has been measured over the temp. range −200° to 0°, and at different pressures. The Kirchhoff–Helmholtz formula holds very closely. J. W. S.

Optical properties of solid and liquid media under ultrasonic elastic vibrations. R. LUCAS and P. BIQUARD (J. Phys. Radium, 1932, [vii], **3**, 464 477).—Observations on Et_2O, paraffin, H_2O, and quartz as diffracting media show grating type diffraction patterns broadening into a mirage effect with increase of the elastic wave-length. N. M. B.

Heat capacity of iron. J. B. AUSTIN (Ind. Eng. Chem., 1932, **24**, 1225—1235).—The available data on the heat capacity of Fe are discussed thermodynamically. A heat capacity–temp. curve is given from 20° abs. to the m.p. of Fe, and is satisfactory up to 900°. There appears to be no discontinuous change in heat capacity at the magnetic inversion point, 768°, but there is a cusp in the heat capacity curve, and therefore a point of inflexion in the heat content–temp. curve, indicating that there is no latent heat of transformation in the ordinary sense. M. S. B.

Exact measurement of specific heats of solid substances at high temperatures. VI. Metals in stabilised and non-stabilised condition: platinum and silver. VII. Metals in stabilised and non-stabilised condition: copper and gold. F. M. JAEGER, E. ROSENBOHM, and J. A. BOTTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 763—771, 772—779).—VI. The sp. heat of Pt which has been heated to a high temp. and quenched is much < in the stable condition. The sp. heat of cold-plated Ag is also much < that of the fused and slowly cooled metal. The data obtained are compared with recorded vals.

VII. The sp. heat of rolled Cu is > that of the stabilised metal, and the sp. heat of cold-plated Au is slightly < that of the fused and solidified Au. J. W. S.

Change of the specific heat of tin when becoming superconducting. W. H. KEESOM and J. A. KOK (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 743—748).—Between 3·70° and 3·72° abs. the at. heat of Sn decreases from 0·0078 to 0·0054, the change coinciding with the transition of the superconducting to the non-superconducting state. A magnetic field impeding the production of superconductivity prevents also the change in sp. heat. Transition to the superconducting state is not associated with a heat of transition. J. W. S.

Exact measurement of specific heats of solid substances at high temperatures. XI. The

remarkable behaviour of beryllium after preliminary heating above 420°. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1055—1061).—The loss of heat from Be heated above 420° is abnormally slow, and this peculiarity is retained for several months at room temp. Other physical properties are also affected and there are unexplained lines in the *X*-ray spectrum. A. G.

Anomaly in the specific heat of liquid helium. W. H. KEESOM and (MISS) A. P. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 736—742).—The sp. heat of liquid He has a max. val. of about 3·0 at 2·19° abs., but falls to 1·1 certainly within 0·02° and probably within 0·002°. J. W. S.

Calculation of specific heats of diatomic gases by quantum statistics. C. GREGORY (Z. Physik, 1932, **78**, 791—800).—Quantum statistics are used to calculate the sp. heats from spectral data. A. B. D. C.

Specific heat and dissociation of gases at high temperatures. K. WOHL and M. MAGAT (Z. physikal. Chem., 1932, B, **19**, 117—138).—The effectiveness of the addition of H_2O vapour as a means of reducing heat losses in the explosion method of sp. heat determination (A., 1929, 1394) has been confirmed. The observed sp. heats of H_2O and H_2 agree within 1% with theoretical vals., whereas the observed vals. for N_2 and O_2 may be as much as 2·2% too small, probably because the time in which the exploding mixture is heated to and at its max. temp. is too short for the mol. vibrations to be fully excited. The thermal dissociation of H_2O into $\frac{1}{2}H_2$ and OH has been calc. from explosion data. The most probable heat effect of the reaction $2H_2O=H_2+2OH$ is −124 kg.-cal. R. C.

Specific heat of superheated water vapour for pressures of 120—200 atmospheres and for saturation temperatures up to 450°. W. KOCH (Forsch. Gebiet Ingenieurwesens, 1932, **3**, 1—10; Chem. Zentr., 1932, i, 1763).—Between 120 and 200 atm. c_p falls continuously with a rise in temp., and falls sharply at first with a rise in pressure. $c_p=0·49+(1·55\times10^7p+0·14\times10^9)T^{-3/5}+6·036\times10^{39}(p+80)^{5·58}\times T^{-10}+7·4302\times10^{130}(p-71)^{4·41}\times T^{-50}+7·9652\times10^{315}(p-19)^{21·79}\times T^{-130}$. The greatest measured val. is 4·249 at 200 atm. and 368·5°. L. S. T.

Definition and measurement of the distillation coefficient and the volatility constant of volatile substances in dilute solution. P. JAULMES (J. Chim. phys., 1932, **29**, 403—417).—Distillation coeff. is defined as the relation between the titre of a volatile acid in the distillate and that in the boiling liquid at the same instant. Volatility const. is defined as the corresponding relation between the vapour and the boiling liquid. Methods for determining these vals. are described. E. S. H.

Free energy of transition of iron ($\alpha\rightleftharpoons\gamma$). C. P. YAP (Trans. Faraday Soc., 1932, **28**, 781—788).—From published data for the sp. heat of Fe, the free energy of transition is calc. as 822 g.-cal. per g.-atom at 25°. The allotropy of Fe is discussed. E. S. H.

Fluorides of low b.p. M. MAGAT (Z. anorg. Chem., 1932, **209**, 11—12).—A reply to criticisms by Ruff, Ebert, and Menzel (A., 1932, 902). F. L. U.

Fusion curve of hydrogen up to 610 kg. per sq. cm. W. H. KEESOM and J. H. C. LISMAN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 607—610).—The fusion curve of H_2 up to 610 kg. per sq. cm. and in the temp. range 13·95—26·95° abs. is represented by $\log(a+p)=c\log T+b$, where $a=245$, $b=0·28771$, and $c=1·83435$. The difference between calc. and observed vals. of pressure is a function of temp. W. R. A.

Equation of the fusion curve. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 624—635).—Theoretical. The fusion curve of He is considered. W. R. A.

Thermal expansion of lead. P. HIDNERT and W. T. SWEENEY (Bur. Stand. J. Res., 1932, **9**, 703).—A curve is given indicating the thermal expansion of Pb from −253° to 300°, combining fresh data over the range 20—300° with published data. Cast Pb expands equally in all directions. D. R. D.

Origin of zero-point entropy. K. CLUSIUS (Nature, 1932, **130**, 775—776).

Density curve of liquid carbon monoxide and its saturated vapour, and the rectilinear diameter. E. MATHIAS, C. A. CROMMELIN, W. J. BIJLEVELD, and P. P. GRIGG (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 551—553).—CO obeys the law of rectilinear diameters approx. The crit. density is 0·3010. The results are tabulated. H. J. E.

Application of J. J. van Laar's theory concerning the additivity of b and $\sqrt{a}$ to boron, iron, nickel, osmium, and iridium compounds. J. A. M. VAN LIEMPT (Rec. trav. chim., 1932, **51**, 1108—1116; cf. A., 1916, ii, 386).—From published v.-p. and crit. point data for BF_3, $Fe(CO)_5$, $Ni(CO)_4$, OsO_4, and IrF_6, the at. consts. for B, Fe, Ni, Os, and Ir are deduced. The results indicate that BF_3, IrF_6, $Fe(CO)_5$, and $Ni(CO)_4$ have complete electron shells, but that OsO_4 has not, and that in the carbonyls the CO groups are linked directly to the central atom, cyclic formulæ being untenable. D. R. D.

Application of J. J. van Laar's theory concerning the additivity of b and $\sqrt{a}$ to aluminium compounds. J. A. M. VAN LIEMPT (Rec. trav. chim., 1932, **51**, 1131—1133).—$b_k=102\times10^{-5}$ for Al in Al_2Cl_6. The electron shells of the Al are complete, the structure being two tetrahedra with a common edge. D. R. D.

Properties of volatile hydrides. II. Preparation, [vapour] tensions, and densities of pure hydrogen sulphide. (At. wt. of sulphur.) A. KLEMENC and O. BANKOVSKI (Z. anorg. Chem., 1932, **208**, 348—366).—H_2S was prepared from H_2 and S and purified by fractional distillation. V.p. were determined between −120° and −60°. M.p. −85·6°, b.p. −60·7°. Gaseous H_2S does not attack Hg, but the liquid does. The dry gas does not react with solid KOH in absence of O_2. Density of liquid between 190° and 212° abs. is given by $d=0·9496\times[1+0·0018397(212·45-T)]$. The density of the gas

was determined at 0° and the wt. of a normal litre is given as 1·53623±0·00007 g. The corresponding at. wt. of S, calc. by using a linear extrapolation of the accepted compressibility to $p=0$, is 32·065± 0·0016. F. L. U.

Densities of saturated vapours. R. WRIGHT (J. Physical Chem., 1932, 36, 2793—2795).—Apparatus and procedure are described for the determination of d. The results indicate that there is no union between the mols. of $COMe_2$ and $CHCl_3$ in the vapour. E. S. H.

Thermal properties of substances of high mol. wt. A. W. HSIA (Z. ges. Kalte-Ind., 1931, 38, 150—154, 167—169; Chem. Zentr., 1932, ii, 344).—MeBr vapour is stable towards light. The v.p. (−76° to 30°) is given by: $\log p=10·3344-1375·625/T-1·11078\log T+8·559\times10^{-4}T$. Between −60° and 0° $d_{liq.}=624·98+1·1132(t_{crit.}-t)+153·72\times(t_{crit.}-t_{crit.}=194°$. The d of the gas was determined; the equation of state is $v=8·932T/P-0·1913/(T/100)^{4·9}$. The heat of volatilisation (at 50° 60·46; 0° 62·06, −50° 62·92, at b.p. 61·94 g.-cal. per g.), enthalpy, and entropy were determined. For *cis*-$C_2H_2Cl_2$ $\log p=11·23645-1702·5468/T-1·25137\log T+0·00023807T$; for *trans*-$C_2H_2Cl_2$ $\log p=1711·4651-11·9275/T-1·4394\log T+0·000569T$. The heats of vaporisation at the b.p. are 73·01 and $73·65_5$ g.-cal. per g., respectively. A. A. E.

Measurement of the total radiation of water vapour at temperatures up to 1000°. E. SCHMIDT (Forsch. Gebiet Ingenieurwesens, 1932, A, 3, 57—70; Chem. Zentr., 1932, ii, 832—833).

Glycerol viscosity tables. M. L. SHEELY (Ind. Eng. Chem., 1932, 24, 1060—1064).—Abs. viscosities for glycerol solutions at 20°, 25°, and 30° have been determined and tabulated for every 1% from 0 to 100% glycerol (interpolated from 55 experimental determinations). Vals. for 22·5° and 27·5° are given over the range 55—100% glycerol. The figures agree well with the experimental data of Archbutt and Deeley (within ±1·8%), but differ considerably from those of Herz and Wegner (B., 1925, 964). E. L.

Equation relating viscosity and surface tension. D. SILVERMAN and W. E. ROSEVEARE (J. Amer. Chem. Soc., 1932, 54, 4460).—By combining the equations of Batchinski (A., 1913, ii, 928) and of McLeod the equation $\gamma^{-1/4}=A/\eta+B$ is obtained, where γ is the surface tension, η is the viscosity, and A and B are consts. characteristic of the liquid. The curve of $\gamma^{-1/4}$ against fluidity for 25 liquids affords straight lines except in the cases of Et_2O and the alcohols. J. G. A. G.

Effect of a magnetic field on the viscosity of oxygen. M. TRAUTZ and E. FROSCHEL (Physikal. Z., 1932, 33, 947).—Using a transpiration method to measure the viscosity, $\Delta\eta/\eta$ was found to be −0·003 for fields of 10—15 kilogauss, a result agreeing with that of Engelhardt and Sack (A., 1932, 1081). A. J. M.

Viscosity, thermal conductivity, and diffusion gas mixtures. XXI. Absolute η-effective molecular theoretical significance of critical temperature, and the calculation of critical pressure from η. M. TRAUTZ (Ann. Physik, 1932, [v], 15, 198—218).—Theoretical. W. R. A.

Diffusion in liquids. I. R. FURTH. **II. Micro-diffusion apparatus for colourless liquids. III. Diffusion measurements on electrically neutral liquid mixtures and solutions.** R. ZUBER. **IV. Diffusion measurements on electrolytic solutions.** R. ZUBER and K. SITTE. **V. Theory of diffusion in solutions of strong electrolytes.** K. SITTE (Z. Physik, 1932, 79, 275—279, 280—290, 291—305, 306—319, 320—344).—I. A summary of present views on diffusion, and of possible applications of diffusion measurements to determine the mol. mechanism and states of aggregation in liquids.

II. Diffusion can be conveniently followed by observing in a low-power microscope the limit of the region of total reflexion.

III. The micro-diffusion method (see above) has been applied to aq. solutions of sucrose, carbamide, glycerol, and formamide. The results conform to Boltzmann's diffusion law, and show the dependence of the diffusion coeff. on the concn.; the size of the particles and its dependence on concn. are also deduced.

IV. The behaviour of aq. solutions of alkali halides agrees with Boltzmann's law, and this is shown to be expected theoretically. The diffusion coeff. first decreases and then increases with concn.; characteristic inflexions of the curve are subsequently shown. The experimental curve is explained by reference to Born's theory of ionic motion and to Bjerrum's theory of ionic association.

V. The formation of ionic clusters is considered with reference to Born's theory of ionic motion in dipolar liquids, the Nernst–Planck theory of diffusion of electrolytes in dil. solutions, and the diffusion of electrolytes in conc. solutions. The theoretical deductions agree well with observed results (see above), and are applied to obtain the degree of association of ions in aq. solutions of alkali halides at various concns. A. B. D. C.

Theory of diffusion. B. BRUŽS (Z. physikal. Chem., 1932, 162, 31—43).—By means of the theory previously elaborated (A., 1932, 123, 1000) and a thermodynamic treatment of osmotic pressure which takes into account the osmotic pressures of both solvent and solute and is applicable at all concns., an equation for diffusion coeffs. is obtained, which at low concns. agrees with Nernst's equation. Equations for liquid-junction potentials and Hittorf coeffs. are derived. R. C.

Diffusion of metals in the solid state. VI. Copper and aluminium. G. GRUBE and R. HAEFNER (Z. Elektrochem., 1932, 38, 835—842).—The diffusion of Cu and Al has been examined by micro-analysis of thin shavings after heating an Al cylinder electroplated with Cu at various temp. for a known time. Rapid diffusion occurs at 600°, being almost complete within 2 hr. If the metal be examined before diffusion is complete, the following layers are found: pure Cu, $CuAl_2$, eutectic with 32% Cu, η mixed crystals, pure Al. α Mixed crystals are formed

more slowly by diffusion of Al into Cu. In order to form a hard surface layer on Al, only η mixed crystals must be formed. For this purpose, the Al may be heated in a powdered mixture of $CuCl_2$ and Cu. Cu may be surface-hardened by heating it in a powdered mixture of NH_4Cl and Cu–Al alloy containing 80% Cu. D. R. D.

Law of additive atomic heats in intermetallic compounds. IX. Compounds of tin and gold, and of gold and antimony. X. Silver and gold. J. A. B. Bottema and F. M. Jaeger (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 916—928, 929—931).—IX. The existence of AuSn has been confirmed by *X*-ray analysis. Its structure is analogous to that of PtSn and the sp. vol. is about 12% < the mean of the sp. vols. of its components. Its true sp. heat is given by $c_p=0{\cdot}039649-0{\cdot}3356\times10^{-6}t+2{\cdot}9337\times10^{-8}t^2$. The mol. heat is < the sum of the at. heats of the components. The compound $AuSb_2$ exists in a γ form (below 358°), a β form (355—405°), and an α form (above 405°). The true sp. heats of these are given by: $\gamma c_p = 0{\cdot}043626 - 0{\cdot}189064\times10^{-4}t + 0{\cdot}79563\times10^{-7}t^2$, $\beta c_p = -0{\cdot}169785+0{\cdot}22014\times10^{-2}t-0{\cdot}42252\times10^{-5}t^2$, $\alpha c_p=0{\cdot}45389-0{\cdot}39127\times10^{-2}t+0{\cdot}70257\times10^{-5}t^2$. The sp. heats of Sb are given by: βc_p (below 413°)$=0{\cdot}0535656 - 0{\cdot}46635\times10^{-4}t + 0{\cdot}15497\times10^{-6}t^2$, αc_p (above 413°)$=0{\cdot}534496 - 0{\cdot}4522\times10^{-2}t + 0{\cdot}7944\times10^{-5}t^2$. In this case the mol. heat of $AuSb_2$ is > the sum of the at. heats of the constituents.

X. The sp. heat of the Au–Ag alloy containing 25·56 at.-% Au shows that the at. heat is not additive even in mixed crystals. The deviations increase with rise of temp. and are not appreciable below 600°. E. S. H.

Electrical conductivity and phase-rule diagrams of binary alloys. VII. System lithium–cadmium. G. Grube, H. Vosskuhler, and H. Vogt (Z. Elektrochem., 1932, **38**, 869—880).—The equilibrium diagram and the conductivity as well as the thermal expansion have been examined. Li melts at 179°, Cd at 321°, and LiCd at 549°. There are five series of mixed crystals, from two of which the *compounds* $LiCd_3$ and Li_3Cd separate on cooling. D. R. D.

Electrical properties of very dilute mixed-crystal alloys. III. Resistance of copper and gold alloys. Regularity of resistance increments. J. O. Linde (Ann. Physik, 1932, [v], **15**, 219—248).—Metals having at. nos. between 25 and 33, 45 and 51, and 77 and 80 were alloyed with Cu and the increase in resistance at 18° was measured. The solubility of Os, Ru, and Mo in Cu has been investigated. Similar experiments were conducted with Ag and Au. W. R. A.

Superconductivity of gold–bismuth [alloys]. W. J. de Haas and T. Jurriaanse (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 748—750; cf. A., 1931, 1224).—*X*-Ray diffraction measurements and chemical analysis show the presence of a phase Au_2Bi in Au–Bi alloys. This phase is responsible for the superconductivity in this system. The elementary cell of the cubic crystals has an edge of 7·94 Å. and contains 24 atoms. The sp. gr. is 15·46, which compares with 15·70 according to the *X*-ray measurements. J. W. S.

Magnetostriction of iron–cobalt alloys. Y. Masiyama (Sci. Rep. Tôhoku, 1932, **21**, 394—410).—The longitudinal and transverse effects for the whole series of alloys are opposite in character and the observed vol. change is a differential effect. A marked discontinuity at about 80% Co corresponds with the change of phase from α to γ solid solution. E. S. H.

Magnetic properties of the system Mn–Cu–Al. S. Valentiner and G. Becker (Physikal. Z., 1932, **33**, 872).—The unique position of the alloy $MnAlCu_2$ is shown also in its magnetic properties. A. J. M.

Lithium alloys. I. Thermal and *X*-ray analysis of the system lithium–tin. A. Baroni (Atti R. Accad. Lincei, 1932, [vi], **16**, 153—158).—Thermal data show the existence of Li_4Sn (m.p. 684°), Li_3Sn_2 (m.p. 483°), and $LiSn_4$, with eutectic points at 458°, 320°, and 214°, corresponding with 35, 58, and 94 at.-% Sn, respectively. *X*-Ray examination by the powder method confirms the first two, but not the third. The structures could not be determined. O. J. W.

Palladium–nickel alloys. A. T. Grigoriev (Ann. Inst. Platine, 1932, No. 9, 13—22).—The hardness–composition curve has a max. at 60 at.-% Pd, whilst the temp. coeff. of conductivity curve has two min., at 20·3 and at 80·8 at.-% Pd. The above data, in conjunction with the microcryst. structure of the etched alloys, indicate that the system consists of an unbroken series of solid solutions. R. T.

Platinum–cobalt alloys. V. A. Nemilov (Ann. Inst. Platine, 1932, No. 9, 23—30).—The fusion diagram indicates that the system consists of an unbroken series of solid solutions, with a min. m.p. for 25 at.-% Pt. Alloys of max. hardness contain 11·6 and 50·6 at.-% Pt. The microcryst. structure and the temp. coeff. of conductivity curve afford evidence for the transformation of one solid solution into another in alloys rich in Co. R. T.

Equilibrium diagram of the system iron–nickel–tungsten. K. Winkler and R. Vogel (Arch. Eisenhüttenw., 1932—1933, **6**, 165—172).—The space diagram of the ternary system shows four saturation surfaces corresponding with the separation of ternary α, ternary γ, Fe_3W_2, and a ternary W-rich solid solution, respectively. There are two planes of 4-phase equilibrium: (*a*) at 1455°, Fe_3W_2+liquid γ+W-rich solid solution, co-ordinates (i) 31·3% Fe, 68·7% W, (ii) 1% Fe, 1% Ni, 98% W, (iii) 52·5% Fe, 22% Ni, 25·5% W, (iv) 42·5% Fe, 27·5% Ni, 30% W; and (*b*) at 1465°, α+liquid γ+Fe_3W_2, co-ordinates (i) 56% Fe, 15% Ni, 29% W, (ii) 58·5% Fe, 10·5% Ni, 31% W, (iii) 61% Fe, 14% Ni, 25% W, (iv) 31·3% Fe, 68·7% W. The complete ternary diagram and many sections through it are shown and the structure and magnetic properties of the solid alloys are discussed. A. R. P.

Solid solutions [obtained] by precipitation and isomorphism between complexes of platinum and of quadrivalent tellurium. II. Cæsium chlorotellurite and the systems Cs_2PtCl_6–Cs_2TeCl_6 and Rb_2PtCl_6–Cs_2PtCl_6. G. Natta and

R. PIRANI (Atti R. Accad. Lincei, 1932, [vi], **16**, 265—270; cf. A., 1932, 564).—*X*-Ray investigation shows that Cs_2TeCl_6 crystallises in the cubic system, with 4 mols. in the unit cell: a 10·45±0·01 Å., v 1141·2×10^{-24} c.c., d 3·51. The space-group is O_h^5, and for u=0·25 the distances for Cl—Cs, Cl—Te, and Cl—Cl are 3·71, 2·62, and 3·72 Å., respectively. Crystallographic data for the two series of solid solutions show that Vegard's law is obeyed. O. J. W.

Binary mixtures. II. Viscosity of naphthalene solutions. L. PIATTI (Angew. Chem., 1932, **45**, 719—720).—The viscosities at 20° of solutions of $C_{10}H_8$ in C_6H_6, xylene, EtOH, 1-$C_{10}H_7Cl$, *m*-cresol, tolyl phosphate, and scrubbing oil have been determined. The influence of $C_{10}H_8$ in reducing the viscosity of the second component is greatest for liquids of high viscosity and is reversed for very mobile liquids. In the case of the oil the viscosity curve is very steep and the $C_{10}H_8$ content may be determined approx. from the viscosity. H. F. G.

Determination of facility of fractional distillation of liquid binary mixtures. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1932, **12**, 832—835).—Fractionation in its dependence on the relative v.p. is considered. R. T.

Dielectric constants of organic solvent–water mixtures at various temperatures. G. ÅKERLOF (J. Amer. Chem. Soc., 1932, **54**, 4125—4139).—By means of a resonance method the dielectric consts. of 0—100% mixtures have been determined at temp. between 20° and 100° for MeOH, EtOH, Pr$^{\alpha}$OH, Pr$^{\beta}$OH, CMe_3·OH, glycol, glycerol, $COMe_2$, mannitol, and sucrose. The variation of dielectric const., D, with abs. temp. is given by $D=ae^{-bT}$, where a and b are characteristic consts. J. G. A. G.

Partial molecular polarisation in solutions. W. J. C. ORR and J. A. V. BUTLER (Nature, 1932, **130**, 930—931).—Experimental and calc. vals. for Bu$^{\alpha}$OH in C_7H_{16} are compared. L. S. T.

Magnetic susceptibility of binary liquid mixtures. K. KIDO (Sci. Rep. Tohoku, 1932, **21**, 385—393).—The diamagnetic susceptibility of the mixtures H_2O–EtOH, H_2O–MeOH, H_2O–$COMe_2$, H_2O–HCO_2H, C_6H_6–EtOH, C_6H_6–$COMe_2$, $SnCl_4$–AcOH, and $SnCl_4$–HCO_2Et is a linear function of composition. Susceptibility is apparently not influenced by association or compound formation. E. S. H.

Solutions of ethyl alcohol in *cyclo*hexane, in water, and in *cyclo*hexane and water. R. D. VOLD and E. R. WASHBURN (J. Amer. Chem. Soc., 1932, **54**, 4217—4225; cf. A., 1931, 1225).—Equilibrium concns. and refractivities of single-phase saturated solutions have been determined at 25°. Cryoscopic data show that the mols. of EtOH are highly associated in *cyclo*hexane, whilst the distribution ratio of EtOH between H_2O and *cyclo*hexane indicates that EtOH has the same mol. form in the two phases. The results are discussed. J. G. A. G.

New equilibria at room temperature with three or four liquids together. E. JANECKE (Z. Elektrochem., 1932, **38**, 860—861).—$HCO·NH_2$–$PhNO_2$–paraffin oil, and $HCO·NH_2$–$PhNO_2$–C_6H_{14} form systems with three liquid phases. $HCO·NH_2$–H_2O–K_3PO_4 forms two phases. This mixture forms four liquid phases on mixing with $PhNO_2$–paraffin oil or $PhNO_2$–C_6H_{14}. These systems are not stable, since the $HCO·NH_2$ is slowly hydrolysed, forming HCO_2NH_4, which reacts with K_3PO_4, forming a ppt. which is probably a solid solution of the *trihydrate* K_3PO_4,$3H_2O$ in $(NH_4)_3PO_4$,$3H_2O$. D. R. D.

Influence of degree of dispersion on physicochemical constants. E. COHEN and C. THONNESSEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 441—453; cf. A., 1931, 677).—The solubility of salicylic acid in H_2O may be raised 15% by increasing the degree of dispersion, there being no evidence of a more sol. modification. *o*-Nitrobenzoic acid, acetylsalicylic acid, and phthalic acid behave similarly. H. J. E.

Influence of degree of dispersion on physicochemical constants. E. COHEN and C. THONNESSEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 798—802; cf. preceding abstract).—The influence of dispersion on the solubility of salicylic acid decreases with rise of temp. and finally disappears. This is attributed to the acceleration of recrystallisation at higher temp. The solubility data of Walker and Wood (J.C.S., 1898, **73**, 619) are inaccurate. J. W. S.

Solubility of succinic acid in binary mixtures. W. D. BANCROFT and F. J. C. BUTLER (J. Physical Chem., 1932, **36**, 2515—2520).—The max. solubility in $COMe_2$–H_2O mixtures alters with temp. The solubility does not change much with varying polymerisation of the alcohols. Some data for adipic acid have been obtained. Succinic and adipic acids are probably more sol. in depolymerised H_2O and $COMe_2$ than in the polymerised liquids. I. J. P. (*c*)

Hydrazine: solubility of hydrazinium salts in mixed solvents. E. C. GILBERT and E. H. HUFFMAN (J. Physical Chem., 1932, **36**, 2789—2792).—The solubilities of N_2H_4 picrate and trinitro-*m*-tolyloxide (I) have been determined in EtOH–H_2O mixtures at 20° and that of (I) in H_2O at temp. from 15° to 30°. The solubility curves show max. and min. and do not resemble those of the corresponding free acids; there is no evidence for the existence of a stable alcoholate. The salts retain H_2O of hydration even in 99·8% EtOH and the anhyd. salts take up H_2O from aq. EtOH. E. S. H.

Systems potassium stearate (palmitate)–alcohol–water. Separation of stearic and palmitic acids. K. SCHERINGA (Chem. Weekblad, 1932, **29**, 605—606).—At 18° the solubilities of K stearate in 94 and 66 wt.-% EtOH are 0·62% and 2·6%, respectively, and those of K palmitate 1·4% and 19%, respectively. In 49% EtOH K palmitate forms a colloidal solution. The solubility isotherms are very steep and indicate that rapid separation of the two acids may be effected by fractional crystallisation of the K salts from aq. EtOH. H. F. G.

Unusual crystal growth. H. G. TANNER (J. Physical Chem., 1932, **36**, 2639—2640).—By dissolving $Al(NO_3)_3$ in MeOH and adding NH_2Ph a gel was obtained from which a large tuft of white,

lustrous, hair-like crystals of NH_2Ph,HNO_3 was formed. The crystals grew in the gel to a certain size, when the gel shrank suddenly away from their sides, but the ends remaining in the gel continued to grow. F. L. B. (*c*)

Distribution ratios and association of carboxylic acids. A. E. SMITH and J. W. NORTON (J. Amer. Chem. Soc., 1932, **54**, 3811—3818).—The distribution at 0° between ββδ-trimethylpentane (I) and MeOH of HCO_2H, AcOH, BuOH, and octoic, lauric, palmitic, oleic, and 50% oleic–50% linoleic acids, and between (I) and MeCN of lauric, oleic, maleic, fumaric, and the phthalic acids indicates that CO_2H groups tend to associate in pairs. L. P. H. (*c*)

Distribution of solute between crystalline solid and liquid phases. VII. V. G. CHLOPIN and P. I. TOLMATSCHEV (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 43—49).—The partition of Ra between cryst. $Ba(NO_3)_2$ and its saturated solution acidified with HNO_3 is in accordance with the simple distribution law. R. T.

Rare gases. I. Permeability of various glasses to helium. W. D. URRY (J. Amer. Chem. Soc., 1932, **54**, 3887—3901).—The rate of diffusion of He, Ne, and H_2 through various glasses at comparatively low temp. and pressures has been determined. It seems that He is first adsorbed and H_2 absorbed on the glass surface. L. K. (*c*)

Diffusion of gases through fused quartz. L. S. T'SAI and T. R. HOGNESS (J. Physical Chem., 1932, **36**, 2595—2600).—Determinations of the rate of diffusion and permeability of quartz membranes for Ne and He at 180—980° suggest that quartz glass possesses channels which increase in clearance with rise in temp. SiO_2 glass, heated at high temp., undergoes a permanent change accompanied by an increase in permeability for He. The permeability of quartz glass for gases is greatest for atoms or mols. of small cross-section. S. L. (*c*)

Adsorption of platinum metals by active carbon. H. WOLBLING (Angew. Chem., 1932, **45**, 720—721).—Unlike "base" metals, Pt, Pd, and Os are adsorbed readily from dil. slightly acid solutions by active C, whilst Ir and Ru are incompletely adsorbed and 90—95% of any Rh present remains in solution. The adsorbed Pt may be extracted with hot conc. HCl or NaCl solutions, without detriment to the C, but after 1—2 days' treatment with H_2 this is no longer possible. Adsorbed Ir, Os, and Ru are but sparingly soluble in NaCl solution. Rh alone of the Pt metals is adsorbed rapidly and completely from ammoniacal solutions. Pt, Pd, and Os are completely adsorbed from solutions containing an excess of alkali iodide. From colloidal solutions prepared with $SnCl_2$, Pt and Pd are completely adsorbed in the cold; Os is partly adsorbed, and Rh is removed only on warming. Technical and analytical applications of these results are noted. H. F. G.

Precipitation and adsorption of small amounts of substances. VI. Inclusion of small amounts of lead in alkali halides. H. KADING (Z. physikal. Chem., 1932, **162**, 174—186; cf. A., 1930, 1365).—In the crystallisation of aq. NaCl, KCl, or KBr containing a very small amount of Pb (Th-*B*) the latter forms a solid solution, the distribution between the solid and liquid phases conforming to the simple distribution law. That solid solution formation rather than adsorption occurs is shown by radiographs and by the failure of attempts to realise adsorption displacement. The Pb enters into the solid phase as a complex anion, such as $PbCl_3'$; the plumbite complex is unable to do this. Pb is appreciably included only in halides with the rock-salt lattice; $NaCl,2H_2O$ and $NaBr,2H_2O$ take up no Pb. R. C.

Adsorption of crystal solution interfaces. VI. Macroscopic sodium nitrate crystals grown in the presence of dyes and other foreign materials. L. A. WEINLAND, sen., and W. G. FRANCE (J. Physical Chem., 1932, **36**, 2832—2839; cf. A., 1930, 1514).—The experiments indicate that the adsorption depends on the residual valency force fields, the interionic distances in the crystal face, and the polar nature of the adsorbed material. Adsorption is selective for crystal faces having stronger fields of force and modifies the crystal habit; the (100) faces are developed at the expense of the (111). *X*-Ray data indicate that the dye is adsorbed interstitially. Adsorption is independent of the degree of dispersion of the dye. E. S. H.

Sorption of tannic acid by proteins and the mechanism of vegetable tanning. W. GALLAY (Canad. J. Res., 1932, **7**, 349—363).—The sorption of tannic acid by gelatin and casein from aq. solution agrees with Freundlich's formula, the temp. coeff. being negative; from aq. EtOH and aq. $COMe_2$ the sorption follows Henry's law. Effects observed with hide powder as sorbent are also described. The viscosities of $EtOH–H_2O$ mixtures are related to the sorption effects which are observed with these liquids. N. M. B.

Theory of adsorption of gases on solids. R. S. BRADLEY (J. Physical Chem., 1932, **36**, 2674—2682).—The potential energy of an adsorbed mol. is considered to be represented by a simple harmonic formula, which corresponds with a "Morse curve." Formulæ are given for the no. of adsorbed mols. and for the correction for the finite size of the adsorbed mols. Frenkel's deduction of the mean life of an adsorbed mol. and the adsorption isotherm are revised. S. L. (*c*)

Adsorption. Availability and accessibility. (SIR) W. HARDY and (MISS) M. NOTTAGE (Proc. Roy. Soc., 1932, **A**, **138**, 259—283).—Measurements are recorded of the variation of static friction (μ) with temp. for solutions of a wax, $C_{15}H_{31}·CO_2H$, and $C_{16}H_{33}·OH$ in B.P. paraffin, over the range 10—106°. Variation is limited to a narrow temp. range (of about 15—20°), outside which μ is const. The limits of variation are the frictions of the pure solvent and solute, respectively, showing that the proportions of solvent and solute mols. in the adsorbed layer could be approx. determined from measurements of μ. At a given temp. μ is affected by the previous history and composition of the solution. The phenomena are

influenced by two changes: change in state of the bulk solution which fixes the "availability" of the solute for adsorption, and a change in the capacity of the solute for replacing adsorbed solvent, which is the "accessibility" of the solute. L. L. B.

Surface tension of caoutchouc solutions. E. VELLINGER (Compt. rend., 1932, **195**, 788—790).—The interfacial tensions between C_6H_6 solutions of caoutchouc (0·3%), and of its resin (0·02%) and an aq. solution of an electrolyte plotted against the p_H of the aq. solution show a max. at p_H 7 followed by rapid falls to zero at about p_H 11 and 12, respectively. The behaviour of caoutchouc closely resembles that of mineral oils. C. A. S.

Influence of cation exchange on the capillary rise of water in soil. O. BOTTINI (Atti Accad. Lincei, 1932, [vi], **15**, 883—887).—The rate of ascent of H_2O through specimens of a soil saturated, by the base-exchange method, with $Na^{\cdot}$, $NH_4^{\cdot}$, $K^{\cdot}$, $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Ba^{\cdot\cdot}$, or $H^{\cdot}$ varies according to the nature of the ion, being least for $Na^{\cdot}$ and rising to a max. at $H^{\cdot}$ in the order given. The effect is concerned primarily with the influence of the ions on the dispersion and swelling of the soil particles. H. F. G.

Surface films. XVI. Surface potential measurements on fatty acids on dilute hydrochloric acid. N. K. ADAM and J. B. HARDING (Proc. Roy. Soc., 1932, **A**, **138**, 411—430).—A description is given of apparatus for the simultaneous determination of the change in contact potential, ΔV, at the interface between aq. solutions and air, caused by a surface film, and the surface pressure of the film. With the acids $C_{13}H_{27}\cdot CO_2H$, $C_{15}H_{13}\cdot CO_2H$, $C_{17}H_{35}\cdot CO_2H$, and $C_{21}H_{43}\cdot CO_2H$, ΔV increases slightly with increasing length of the chain and shows a steady rise nearly proportional to the increasing no. of mols. in the film as the liquid-expanded film is compressed. The rise on compressing the condensed films is $<$ that corresponding with the no. of mols. in the film. The small change in the vertical component of the dipole moment per mol. (μ) as the expanded film is compressed indicates an approx. const. orientation of the CO_2H groups in the film throughout this region. A fall in μ of about 40% takes place on passing to the vapour state of the films, indicating some re-orientation of the CO_2H groups in the flat chains. L. L. B.

Surface potentials of unimolecular films. IV. Effect of underlying solution and transition phenomena in the film. J. H. SCHULMAN and A. H. HUGHES (Proc. Roy. Soc., 1932, **A**, **138**, 430—450).—The effect of the underlying solution on the surface potentials of unimol. films of several long-chain fatty compounds has been studied over a wide p_H range, with special reference to the mutual influence of the solution and the polar head-group of the film-forming material. Two-dimensional transitions of state are discussed in detail. L. L. B.

Measurement of superficial pressure of superficial solutions of soluble substances. A. MARCELIN and D. G. DERVICHAN (Compt. rend., 1932, **195**, 866—869).—A method is described for deducing the superficial pressure in the unimol. film formed by an insol. substance, *e.g.*, by oleic acid on H_2O, from the diameter of the clear circular space which is formed by a current of air of definite strength and width impinging vertically on the talc-powder covered film. The method is applicable to superficial solutions of sol. substances (the Gibbs layer). C. A. S.

Weakening of fine-structural cohesion by water and aqueous solutions. F. RINNE (Kolloid-Z., 1932, **61**, 304—308).—The high H_2O content of biological systems is regarded as the cause of their chemical lability. The high dielectric const. of H_2O causes a weakening of the electrical fields of the fine-structural units. This effect is illustrated by the influence of H_2O on the fine structure of cryst. bromophenanthrenesulphonic acid. E. S. H.

Spreading of ovalbumin. E. GORTER, J. VAN ORMONDT, and F. J. P. DOM (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 838—843).—Like caseinogen (cf. A., 1926, 1094) ovalbumin shows max. spreading on a solution of p_H 4—5, and min. spreading at about p_H 3. The effects of Cl', SO_4'', $CH(SO_3)_3'''$, $K^{\cdot}$, $Ba^{\cdot\cdot}$, and $Co(NH_3)_6^{\cdot\cdot\cdot}$ ions on the spreading favour the view that at the isoelectric point the neutral protein mol. spreads out in a thin layer, but addition of $H^{\cdot}$ or OH' ions diminishes the area occupied. The addition of negative ions on the acid side of the isoelectric point (below p_H 3) increases the surface by eliminating the charge of the protein ions. The same holds for the addition of positive ions in alkaline medium. The activity of ions is in the order ter-$>$bi-$>$uni-valent. J. W. S.

Proteins in unimolecular films. Measurements by the methods of du Nouy and Langmuir. E. GORTER and W. A. SEEDER (Kolloid-Z., 1932, **61**, 246—249).—Results obtained by the two methods are in agreement. E. S. H.

Films, threads, and colloid science. WO. OSTWALD (Kolloid-Z., 1932, **61**, 136—140).—Films and threads are discussed as difform systems, representing a transitional stage between massive and mol. matter. E. S. H.

Unimolecular surface films. N. K. ADAM (Kolloid-Z., 1932, **61**, 168—177).—A lecture on recent published work. E. S. H.

Examination of film structures by electrical and optical methods. E. K. RIDEAL (Kolloid-Z., 1932, **61**, 177—180).—A lecture. E. S. H.

Unimolecular layers of proteins. E. K. RIDEAL (Kolloid-Z., 1932, **61**, 218—222).—Resistance to compression is first observed in a film of gliadin when its concn. reaches $0{\cdot}36\times10^{-7}$ g. per sq. cm. The film is then easily compressible up to the val. $0{\cdot}7\times10^{-7}$, after which the compression rises rapidly to a concn. of about $1{\cdot}5\times10^{-7}$ g. per sq. cm., at which the film apparently assumes a two-dimensional gel structure. These data agree with vals. calc. on the assumption that the side-chains of the mol. contain $\cdot[CH_2]_2\cdot CO_2H$. The surface-potential method of examining the protein films is illustrated by experiments on the degradation of albumin by proteolytic enzymes, and the effect of irradiating a film of albumin by ultra-violet light is also described. E. S. H.

Gum surfaces. III. F. V. VON HAHN (Kolloid-Z., 1932, **61**, 222—234; cf. A., 1932, 1085).—The spreading of 37 org. substances and plant products on a surface of starch paste is related to the surface activity of the spreading solution by an S-shaped curve. Exceptions are noted in the case of substances having very high surface activity at low conens. (*e.g.*, soaps, saponin). E. S. H.

Solid properties and structure of cellulose nitrate films. A. V. BLOM (Kolloid-Z., 1932, **61**, 234—239).—Under increasing degree of stretching, films of cellulose nitrate pass through (*a*) an elastic region, (*b*) a transitional region, (*c*) a plastic region, (*d*) a region in which solid properties are developed as a result of increasing orientation of the micelles. Finally the films break. The breaking tension is not sufficient to characterise the cohesive forces operating in the chains of mols., but must be considered in relation to the whole of the stress–strain curve. The region (*d*) is more extended for samples of high viscosity than for those of low viscosity, and appears only in films of thickness $> 60\ \mu$. The development of birefringence supports the conclusions reached. E. S. H.

Physics of membranes. E. MANEGOLD (Kolloid-Z., 1932, **61**, 140—160).—Published work is summarised (cf. A., 1931, 905, 1007, 1128; 1932, 119, 691). E. S. H.

Membrane equilibria. F. G. DONNAN (Kolloid-Z., 1932, **61**, 160—167).—A lecture, with special reference to the biological significance. E. S. H.

Phase equilibrium in systems subdivided by membranes. R. EISENSCHITZ (Z. physikal. Chem., 1932, **162**, 216—222).—Equations are obtained which give the no. of degrees of freedom in systems subdivided by rigid impermeable and semipermeable membranes. R. C.

Osmotic pressure, and permeability of membranes. W. W. LEPESCHKIN (J. Physical Chem., 1932, **36**, 2625—2638).—The permeability of a membrane to a solute is expressed by $P_0=P(1-\mu)$, where P_0 is the suction of the solution, P its osmotic pressure, and μ the permeability factor, proportional to the permeability of the membrane to solute. The max. hydrostatic pressure, P_m, in an osmometer depends on the permeability of the membrane to both solute and H_2O, in accordance with $P_m=P(1-\mu)(1-\mu/\sigma)$, where σ is the H_2O-permeability factor. I. J. P. (*c*)

Osmotic systems in which non-diffusing substances may occur. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1038—1045).—If, in addition to diffusing substances, an osmotic system includes on the two sides of the membrane n and n' non-diffusing substances, respectively, it possesses $n+n'$ additional degrees of freedom. If the composition of the first side is fixed it still has n' degrees of freedom. A. G.

Osmosis in systems consisting of water and tartaric acid. III. F. A. H. SCHREINEMAKERS and J. P. WERRE (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 477—485; cf. A., 1932, 691).—Theoretical. H. J. E.

Osmotic systems containing water, sodium chloride, and sodium carbonate with one invariant liquid. F. A. H. SCHREINEMAKERS and L. J. VAN DER WOLK (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 938—947).—Theoretical. E. S. H.

Osmotic systems containing water, sodium chloride, and sodium carbonate with one invariant liquid. II. F. A. H. SCHREINEMAKERS and L. J. VAN DER WOLK (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1046—1054).—Osmotic effects with a membrane of pig's bladder are described. A. G.

Preparation and properties of proteo-cellulose membranes. J. LOISELEUR and L. VELLUZ (Bull. Soc. Chim. biol., 1932, **14**, 1210—1217; cf. A., 1931, 167).—Mixed solutions of (*a*) protein and cellulose acetate in glacial AcOH or 96—98% HCO_2H, and (*b*) protein in HCO_2H and cellulose acetate in $COMe_2$ with or without CH_2O, when evaporated at low temp. give rise to homogeneous membranes which are rendered static by the cellulose and show the xanthoproteic and biuret reactions. They adsorb reduced metals (Au, Ag) in colloidal form, dyes, and metallic ions. The adsorptive power increases with the proportion of protein to cellulose and varies with the nature of the protein. Membranes of caseinogen or ovalbumin adsorb dyes far more effectively than those containing gelatin, and this is attributed to the aromatic NH_2-acids which are present in the former but not in the latter. A. C.

Phenyl phosphate as a solvent in cryoscopy. I. F. GARELLI and G. RACCIU (Atti R. Accad. Lincei, 1932, [vi], **15**, 976—980).—Ph_3PO_4, m.p. 48·25°, is recommended as a cryoscopic solvent. The mean observed val. of K is 120 (calc. 117·6). The latent heat of fusion is 17·56 and the sp. heat 0·381. D. R. D.

Phenyl phosphate as a cryoscopic solvent. F. GARELLI and G. RACCIU (Atti R. Accad. Lincei, 1932, [vi], **16**, 54—56).—The lowering of the f.p. of Ph_3PO_4 leads to the formulæ: S_{10}; I_2; trimethylenetrinitrotetramine, $(CH_2{\cdot}N{\cdot}NO_2)_3$, and indigotin, $C_{16}H_{10}O_2N_2$. O. J. W.

Cryoscopy of some electrolytes in molten $CaCl_2,6H_2O$. E. DARMOIS and R. CHALIN (Compt. rend., 1932, **195**, 786—788; cf. A., 1931, 35).—Data are recorded for KNO_3, $Mg(NO_3)_2$, $La(NO_3)_3$, $Th(NO_3)_4$, KI, CdI_2, Na H and Na_2 malates, NH_4Br, $CdBr_2$, and LiI. C. A. S.

Determination of paramagnetic ionic moments in solutions. H. AUER (Physikal. Z., 1932, **33**, 869—872).—A crit. investigation of Quincke's method for determining paramagnetism has been made and the results are applied to salt solutions. The magnetic investigation of a salt solution is a sensitive test for inner mol. interaction, but the extrapolated vals. for moments of free ions derived in this way are doubtful. A. J. M.

Faraday effect of some uni-univalent electrolytes in aqueous solutions. I, II. E. B. ANDERSEN and R. W. ASMUSSEN (J. Physical Chem., 1932, **36**, 2819—2826, 2827—2831).—I. Technique for determining the magnetic rotation of the plane of polarisation of light by aq. salt solutions is described. Data are given for solutions containing different

compounds of $H^{\cdot}$, $Li^{\cdot}$, $Na^{\cdot}$, $Rb^{\cdot}$, $Cs^{\cdot}$, and $NH_4^{\cdot}$ with F', Cl', I', OH', ClO_3', BrO_3', and IO_3', which are all diamagnetic. The results indicate that the rotation of the compound is approx. equal to the sum of the rotations of the constituent ions. A change of the anion with the same cation gives a large change in the rotation, whilst only a slight effect is produced by a change of cation with the same anion. The rotation of H_2O is approx. one half the sum of that of $H^{\cdot}$ and OH', whilst that of aq. NH_3 is equal to the sum of rotations for $NH_4^{\cdot}$ and OH'.

II. Further measurements have been made, using mainly salts of alkali metals with oxy-acids of S. These results show that the effect of adding O or S to a mol. varies with the constitution. E. S. H.

Dusts, smokes, mists, and fogs. S. C. Blacktin (Chem. and Ind., 1932, 1006—1007).—Suspensions in gases may be classified as dusts, smokes, etc., according to their mode of formation, tendency of the particles to grow larger or smaller, and physical state of the particles. Abs. particle size is of minor importance. D. R. D.

Migration velocity of suspended dust particles in electro-filters. G. Mierdel (Physikal. Z., 1932, **33**, 823—824). W. R. A.

Influence of time on conductivity of colloid [suspensions] at different levels. Papayanno (Compt. rend., 1932, **195**, 1012—1014).—The conductivities at levels differing by 5—8 cm. of suspensions of mastic, collodion, and colloidal Ag plotted against time show that $(S-I)/I$, where S and I are the conductivities at the upper and lower level, respectively, is increasingly positive for mastic suspensions, whilst the reverse is true for collodion and colloidal Ag. It is zero for optically clear, but not for ordinary, conductivity H_2O. C. A. S.

Viscosity of lyophilic colloids. I, II. I. Sakurada (J. Soc. Chem. Ind. Japan, 1932, **35**, 445—453B).—I. Viscosity formulæ are discussed and relations between them are indicated.

II. Published data are used to derive the sp. vol. of colloid particles of cellulose nitrate in various dispersion media from the observed viscosity. The results obtained from different formulæ are compared and their relative validity is discussed. E. S. H.

Lyophilic colloids. XVI. Viscosity and sol concentration. H. G. B. de Jong, H. R. Kruyt, and J. Lens (Kolloid-Beih., 1932, **36**, 429—462; cf. A., 1932, 465).—The experiments show that gum arabic sols up to 30%, gelatin sols up to 17%, and coacervates of gum arabic–gelatin and gelatin–PrOH behave at 42° in accordance with the Hagen–Poiseuille law. Carragheen sols show a marked deviation. The relation between the viscosity of the hydrophilic sol, η_s, and the concn., C, is given by $\log[(\eta_s-\eta_0)/\eta_0 C]=aC+b$, where η_0 is the viscosity of the dispersion medium, and a and b are consts. The best agreement is found when considerable quantities of electrolyte are present, or at the isoelectric point, when the capillary-electric charge does not predominate. Application of the formula to published work shows that it is valid for organosols. The consts. a and b vary with the electrolytes present and with temp., but there is no simple relation between them. E. S. H.

Highly-polymerised compounds. LXXIII. Viscosity measurements with silicic acid solutions. R. Signer and H. Gross (Annalen, 1932, **499**, 158—168).—The viscosities of solutions obtained by hydrolysis of Me pentasilicate (A., 1930, 461) with 75% MeOH and containing 1·67—3·03% SiO_2 remain almost const. for a considerable time, then increase rapidly prior to gelation, and decrease immediately before complete gelation. The relation between max. viscosity and concn. ($K=\log \eta_r/c$) holds for solutions of varying concn. prepared from Me pyro-, penta-, and nona-silicates. Solutions of the same concn. prepared from different esters give the same curves for viscosity plotted against K_c ($=\log \eta_r$); the gelation times differ (the solution from the more highly polymerised ester gels more rapidly). The increase in particle size (leading to gelation) is probably due to the exclusive formation of thread-like mols. H. B.

Colloid-chemical study of a technical, high-molecular azo-dye. K. Brass and K. Eisner (Kolloid-Beih., 1932, **37**, 56—90).—The prep. of a black triazo-dye (no. 669 in Schultz–Lehmann's Tables, Berlin, 1931) and of some of its derivatives is described. Measurements of surface tension and viscosity failed to give characteristic results for the solutions. Diffusion experiments show that the particle size decreases progressively as the solution is purified, and increases with age. The technical preps. have a lower degree of dispersion than those prepared by the method described. The particle size of the acid dyes is about twice that of their Na and NH_4 salts. The acid dyes are adsorbed by cotton, wool, and animal C to a greater extent than are the NH_4 salts. The degree of adsorption decreases as the dyes are purified. Wool is coloured reversibly by these dyes at room temp., but irreversibly at higher temp. Addition of salts increases the adsorption and multivalent cations have a coagulating effect. E. S. H.

Electrical factors of colloid stability. E. S. Hedges (Chem. and Ind., 1932, 937—938).—A crit. review of recent work on the influence of non-electrolytes on electrokinetic potential, dielectric polarisation, and the relation between charge and hydration. E. S. H.

Emulsion persistence. W Clayton (Soc. Chem. Ind., Chem. Eng. Group, Nov. 25, 1932, advance proof, 19 pp.).—A survey and crit. discussion of published work on emulsifying agents, wetting, the "Bodenkorperregel," stability, viscosity, and electric charge, creaming (especially of milk), frothing, centrifugal separation, inversion, electro-osmotic behaviour (especially dehydration of crude petroleum), tests (especially for bituminous road emulsions). E. S. H.

Mechanism of the coagulation of sols by electrolytes. IV. Arsenic trisulphide sol. H. B. Weiser and G. R. Gray (J. Phvsical Chem., 1932, **36**, 2796—2812; cf. A., 1932, 994).—The changes in $[H^{\cdot}]$ in the titration of As_2S_3 sol with aq. $BaCl_2$, $SrCl_2$, $CaCl_2$, $AlCl_3$, or NH_4Cl have been followed by means of the glass electrode. The $H^{\cdot}$ displacement curve is similar in form to the adsorption curve. The

displacement is relatively greater at lower concns. and reaches a max. at or below the pptn. val. The amount of displaced $H^{\cdot}$ is 20—40% of the total [$H^{\cdot}$] of the liquid after coagulation of the sol, and is determined by the concn., size, and form of the particles; it is always < the amount of pptg. ion adsorbed. The order Al>Ba, Sr>Ca>NH_4 represents the displacing power, pptg. power, and adsorption of the several chlorides. E. S. H.

Influence of the anion on flocculation of colloidal clay by potassium salts. A. Demolon and E. Bastisse (Compt. rend., 1932, **195**, 790—792).—Experiments have been made with (*a*) colloidal clay from brick earth treated with 0·05*N*-HCl, and (*b*) the same freed from Fe_2O_3 by $H_2C_2O_4$. In the case of (*a*) the limiting val. for all K salts increases rapidly from neutrality to p_H 8·5 (cf. B., 1924, 721). OH ions show an optimum peptising concn. differing according to the base, *e.g.*, p_H 7·6 for K^+, 8·8—9 for Na^+. With fine kaolin the limiting val. increases continuously with p_H. In the case of (*b*) a higher limiting val. is found, but the fixing power for P_2O_5 is only 1/3 that of (*a*). C. A. S.

Lyotropic numbers and the properties of ions. E. H. Buchner, A. Voet, and E. M. Bruins (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 563—569; cf. A., 1932, 692).—Both cations and anions may be characterised by lyotropic nos., expressing their coagulating properties. These show a linear relation with the influence of the ions on the electrokinetic potentials of sols, with their catalytic activity in the inversion of sucrose and the hydrolysis of esters, and with their influence on the swelling of gelatin. H. J. E.

Lyotropic numbers and viscosity. E. H. Buchner, E. M. Bruins, and J. H. C. Merckel (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 569—575).—For concns. up to 1*N* there is a linear relation between the viscosity of dil. acids, or of salt solutions with a common cation, and the lyotropic nos. of the anions. The same holds for different cations with a common anion. Deviations occur in more conc. solutions. H. J. E.

Ionic interchange in sulphur sols. Lyotropic series and the mechanism of coagulation. T. R. Bolam and G. Bowden (J.C.S., 1932, 2684—2694).—The order of facility of replacement of $H^{\cdot}$ by cations, from the micelles of S sols stabilised by polythionic acid is $Mg^{\cdot\cdot}$>$K^{\cdot}$>$Na^{\cdot}$>$Li^{\cdot}$. Adsorption of total salt may also occur, the order for the alkali chlorides being K>Na>Li. If the concn. of acid is not too high, coagulation takes place at the concn. of salt which is just sufficient to liberate the whole of the $H^{\cdot}$; the concns. of LiCl and KCl which produce the first sign of coagulation liberate the same amount of $H^{\cdot}$. The occurrence of the lyotropic series observed in these phenomena is interpreted by reference to the Donnan equilibrium and the theory of surface dissociation. M. S. B.

Rhythmic precipitation of dyes by electrolytes. (Mlle.) S. Veil (Compt. rend., 1932, **195**, 781—783; cf. A., 1932, 693).—Neutral-red and toluidine-blue in presence of $K_2Cr_2O_7$ behave similarly to methylene-blue. Aq. $K_2Cr_2O_7$ dropped on gelatin impregnated with either forms Liesegang rings (cf. A., 1930, 1506). C. A. S.

Behaviour of metallic soaps with organic solvents. J. W. McBain and W. L. McClatchie (J. Physical Chem., 1932, **36**, 2567—2574).—The formation of jellies from soaps and org. solvents has been examined. For the Ag and Al soaps the best solvents are in general the least polar compounds. The Na soaps, although sol. in polar solvents, also dissolve and form jellies in the non-polar solvents. Swelling of jellies is attributed to direct combination, sorption, or polarisation of mols. or groups of mols. of solvent with exposed groups of the jelly for which the solvent has affinity, as well as to penetration of free mols. of solvent between the interlacing structure to release strains in the structure. The former factor corresponds with the thermodynamic properties represented by the v.p., whilst the latter is purely mechanical. F. L. B. (*c*)

Effect of *X*-radiation on viscosity of gelatin. H. Q. Woodard (J. Physical Chem., 1932, **36**, 2543—2553).—The viscosity, η, of dil. gelatin sols is decreased by intense irradiation by *X*-rays. When for a given sol η is reduced by heat, by p_H change, or by salts, the % reduction (A) due to subsequent irradiation is decreased. When η is reduced by ageing or by irradiation, (A) is decreased, but in a manner too irregular for quant. interpretation. When η is reduced by dilution, A is not changed. F. L. B. (*c*)

Effect of addition of salts on the isoelectric point of proteins. III. H. Andrzejewski (Biochem J., 1932, **26**, 1397—1405).—The concn. (*c*) of EtOH necessary for the flocculation of purified gelatin sols is smallest at the isoelectric point. Negatively-charged micelles are more readily coagulated by EtOH than are positively-charged ones. The val. of *c* at the isoelectric point is increased in the presence of $MgCl_2$ or Na_2SO_4, whilst $MgSO_4$ is without effect. At all p_H vals. salts giving rise to ions of the same valency do not affect the val. of *c*. At p_H < 4·8 salts yielding multivalent anions and univalent cations lower *c* at small concns. and slightly raise it at p_H > 4·8. This effect is due to the charge of the colloidal particles; the greater is the original charge the greater is the percentage recorded. Observations relating to anti- and iso-ions are also recorded. S. S. Z.

Heats of wetting of silica gel. R. Berthon (Compt. rend., 1932, **195**, 1019—1021).—Patrick and Grimm's hypothesis (cf. A., 1922, ii, 122) is incorrect; that of Bartell and Fu (A., 1930, 1246) errs in neglecting the effect of the curved surfaces of small capillaries in which the adsorption pressure P_a is > that on a plane surface. The energies of wetting, Q, have been determined for H_2O and 12 org. liquids, and compared with $W_a - W_c$ deduced from Bartell and Merrill's results (cf. A., 1932, 690), where W_a is the energy of adhesion of solid to liquid, W_b that of cohesion of the liquid. $W_a - W_c$ is much > Q for polar liquids such as MeOH, EtOH, and AcOH, for which the compression in the capillaries should be greatest. A thermodynamic theory of wetting must take into consideration the geometry of the surface. C. A. S.

Alkali cellulose. II. Application of phase theory to gel reactions. K. HESS, C. TROGUS, and O. SCHWARZKOPF (Z. physikal. Chem., 1932, **162**, 187—215; cf. A., 1932, 836).—Thermodynamic considerations applied to the system cellulose–NaOH–H_2O show that two solid phases may coexist in equilibrium with a liquid phase of variable composition and a vapour phase (cf. this vol., 22). Analytical and *X*-ray data show that two phases of const. composition (cryst. compounds) must be accompanied by at least one phase of variable composition. In the reaction between cellulose and NaOH changes on the micelle surfaces are accompanied by changes in the interior, so that the determination of the composition of a solid phase by analysis gives an average val., whilst *X*-ray methods can follow only the changes in the interior. Depending on the NaOH concn. there are formed several compounds for which Na/C=1/6. The formation of alkali cellulose is not covered by the theory of the Donnan equilibria, although the reaction of small parts of the cellulose agrees with this theory (cf. B., 1931, 920). As a whole the reaction may probably be regarded as a heterogeneous reaction on which are superimposed surface changes which probably have the character of Donnan equilibria. R. C.

Methane–carbon dioxide and carbon monoxide–hydrogen equilibrium. J. SCHMIDT and B. NEUMANN (Z. Elektrochem., 1932, **38**, 925—933).—The equilibrium $2CO+2H_2 \rightleftharpoons CH_4+CO_2$ has been investigated by a streaming method, using Ni pptd. on SiO_2 gel as catalyst. The results agree with theory above 600°. Various side-reactions occur. H_2O is formed by the reaction $CO_2+H_2 \rightleftharpoons H_2O+CO$ and reacts with CH_4, forming CO and H_2. Probably NiO is formed. The reaction $CH_4+CO_2=2CO+2H_2$ can be made to occur without pptn. of C. D. R. D.

Equilibrium between dimethyl ether, methyl alcohol, and water. N. G. GAJENDRAGAD, S. K. K. JATKAR, and H. E. WATSON (J. Indian Inst. Sci., 1932, **15A**, 59—69; cf. B., 1926, 565, 963).—For the conversion of MeOH into Me_2O an alum catalyst can be used at 170—250° or H_2SO_4 at 130°. In the former case the rate is much lower than with EtOH. The equilibrium const. is 15·4 at 230° and 48·5 at 130°. Equilibrium was approached from both sides. L U

Intermolecular force effects. III. Heat of combination and mode of combination of organic molecular compounds. G. BRIEGLEB and T. SCHACHOWSKOY (Z. physikal. Chem., 1932, **B**, **19**, 255—277; cf. A., 1932, 563).—From the extinction coeffs. for solutions of the binary compounds of *s*-trinitrobenzene (I) with Ph_2, $C_{10}H_8$, phenanthrene, and anthracene at various temp. in spectral regions in which the components do not absorb, the heats of dissociation have been calc. Combination is not due to any particular NO_2 group, but to the joint action of all such groups, and leads to the preferential formation of an average constellation in which the max. moment induced in the hydrocarbon lies in the direction of max. polarisability. The order of diminishing energy of combination is the same as the order of diminishing max. polarisability, as deduced from the Kerr const. The f.-p. diagram for Ph_2 and (I) shows that these combine to form an incongruently melting 1 : 1 compound. R. C.

Incomplete dissociation of typical binary salts and application of dilution law to their solutions in non-aqueous solvents. II. P. WALDEN (Z. physikal. Chem., 1932, **162**, 1—30; cf. A., 1930, 995).—Conductivity measurements over wide concn. ranges for salts behaving as typical strong electrolytes in aq. solution have shown that in solvents for which the dielectric const. is not too large these salts behave as weak electrolytes in respect of the validity of the dilution law. Various homopolar substances behave as weak electrolytes when dissolved in solvents such as N_2H_4, which by virtue of basic or acid properties are able to exert a sp. influence on the solute; such solvents usually have a fairly high dielectric const. The degree of dissociation as measured by the conductivity ratio seems to depend, not only on the dielectric const. of the solvent, but also on a mutual interaction of solvent and undissociated solute mols. R. C.

Autoxidation. VII. Absorption spectrum and dissociation constants of arsenious acid. P. GOLDFINGER and H. D. GRAF VON SCHWEINITZ (Z. physikal. Chem., 1932, **B**, **19**, 219—227; cf. A., 1932, 1006).—According to the titration curve the first dissociation const. is 2×10^{-10} to 8×10^{-10}, and spectroscopic measurements of the ionic concns. in presence of varying amounts of alkali give 1×10^{-14} to 6×10^{-14} for the second dissociation const. These vals. show that $HAsO_3''$ is responsible for the autoxidation of H_3AsO_3 (cf. A., 1925, ii, 308). The long-wave limit of continuous absorption in 1*M* solution is 2680 for H_2AsO_3' and 2800 Å. for $HAsO_3''$. R. C.

Acidity of thiophenol and of the isomeric dithiophenols. G. SCHWARZENBACH (Helv. Chim. Acta, 1932, **15**, 1468—1481).—The acidities determined potentiometrically in 60—100% aq. EtOH show that all the substances are stronger acids than the corresponding phenols, *o*-dithiophenol (I) being almost as strong as AcOH. The strengths decrease in the order *o*-, *m*-, *p*-, mono-. The results are discussed theoretically. In its behaviour towards solutions of metal salts, (I) shows a close resemblance to H_2S. F. L. U.

Acidic properties of metal salt hydrates. F. REIFF (Z. anorg. Chem., 1932, **208**, 321—347).—Acidities of aq. solutions of metal halides at various concns. have been determined electrometrically. The quotient $[H^+]$/concn. in general increases with concn., and the acidity is attributed mainly to the formation of aquo-acids, *e.g.*, $[ZnCl_2(OH)H_2O]H$. Metal salts of these acids cannot usually be isolated, but cryst. oxonium salts with cineole (=Ci), or more readily with 1 : 4-dioxan (=D), have been prepared. The following *compounds* are described:

$[MCl_2(OH)H_2O]H,D$ (M=Cu, Mn, Ni, or Co), $[CaCl_2(OH)]H,D$, $[LiCl(OH)]H,D$, $[(LiBr)_2O](H,D)_2$, $[LiI(OH)_2](H,D)_2$, $[NaI(OH)_2](H,D)_2$, $[SnCl_4(OH)_2](H,D)_2$, $[ZnCl_2(OH)_2]H_2,H_2O,Ci$, $2ZnBr_2,2H_2O,3Ci$, $(ZnI_2)_2,3H_2O,3Ci$, $[ZnBr_2(OH)H_2O]H,D$, $[(ZnI_2)_2O](H,D)_2$, $[AuCl_3(OH)]H,D$, $[AuCl_3O](H,Ci)_2$,

$[PtCl_4(OH)H_2O]H,D$. The acidity of equimol. solutions of chlorides increases with decreasing polarity and is parallel with the electrode potential of the metal. Acid properties of halide hydrates increase from chloride to iodide and with the valency of the metal. The suggested formation of an aquo-base by CsF in aq. solution is supported by the prep. of the *compound* CsF,2AcOH. The results are discussed. F. L. U.

Strength of semicarbazide—and a correction. N. F. HALL (J. Amer. Chem. Soc., 1932, **54**, 3961—3962).—Recalculation of Wood's val. gives 3·07 at 25° for the acid dissociation const. (pK_A). L. K. (*c*)

Simple basic indicators. II. Solutions in formic acid. L. P. HAMMETT and A. J. DEYRUP (J. Amer. Chem. Soc., 1932, **54**, 4239—4247; cf. A., 1932, 921).—Relative vals. of the basicity of a series of basic indicators in pure HCO_2H agree closely with those for aq. solutions. H_2SO_4 is a strong monobasic acid and $PhSO_3H$ is moderately strong, whilst HCO_2Na and NH_2Ph are strong bases. Ionisation consts. of HSO_4', EtCN, NHAcPh, and H_2O have been determined, and the ion product of the solvent corresponds with $-\log C_{H^+} \cdot C_{CO_2H'} = 6{\cdot}17$. J. G. A. G.

Existence of the phosphorus hexafluoride ion. W. LANGE (Z. anorg. Chem., 1932, **208**, 387—391; cf. A., 1930, 877).—Solutions of KPF_6 and of $KClO_4$ of the same concn. give the same depression of f.p. between 0·019 and 0·066*M*. The ion PF_6' is stable in aq. solution and its structure is regarded as symmetrical. F. L. U.

Compounds of tartaric acid and chromium. J. P. MATHIEU (Compt. rend., 1932, **195**, 1017—1019; cf. A., 1932, 111).—Changes in p_H, conductivity, and rotatory power when NaOH is added to solutions containing a fixed amount of tartaric acid with varying amounts of $Cr(OH)_3$ which have attained equilibrium by keeping for several months, indicate that the neutralisation of any excess tartaric acid is followed by the neutralisation of a very weak (violet) dibasic acid, $H_2[TCr]$, with formation of the (green) salt $Na_2[TCr]$; there is no pptn. of $Cr(OH)_3$. C. A. S.

Relation between the higher charge ions and the deviations from the first approximation of the Debye-Huckel theory. J. B. CHLOUPEK, V. Z. DANES, and B. A. DANESOVA (Coll. Czech. Chem. Comm., 1932, **4**, 473—479).—To test the validity of La Mer's development of the Debye-Huckel theory (A., 1928, 841; 1929, 1386, 1387), precise determinations of the solubility of $Ce(IO_3)_3$ from three different sources have been made in H_2O and in aq. solutions of KNO_3, K_2SO_4, $MgSO_4$, and $MgCl_2$ at 25·00±0·02°. M. S. B.

Glycine in water solution. J. Y. CANN (J. Physical Chem., 1932, **36**, 2813—2816).—Thermodynamic functions calc. from (unpublished) experimental data suggest that glycine in conc. aq. solutions is associated. E. S. H.

Activity coefficients of ions. K. HASS and K. JELLINEK (Z. physikal. Chem., 1932, **162**, 153—173).—The activity coeffs. of Cl', Br', I', SO_4'', CrO_4'', and C_2O_4'' for a wide range of concns. have been obtained from e.m.f. measurements with various salts at 25°, and the activity coeffs. of many of the salt cations have been deduced. Solubility products have been determined at 25°. R. C.

Behaviour of electrolytes in mixed solvents. IV. Free energy of zinc chloride in water–alcohol solutions. R. T. HAMILTON and J. A. V. BUTLER (Proc. Roy. Soc., 1932, **A**, **138**, 450—459; cf. A., 1930, 35).—The partial free energies of $ZnCl_2$ in H_2O–EtOH solutions, with $ZnCl_2$ concns. from 0·01 to 1·0*M*, have been measured at 15°. The vals. show that $ZnCl_2$ is almost completely ionised in H_2O and undissociated in EtOH. L. L. B.

Thermodynamic studies in silver chloride and silver bromide. F. L. E. SHIBATA and T. TAKETA (J. Sci. Hiroshima Univ., 1932, **2**, 243—268).—From measurements of the e.m.f. of cells of the type H_2(Pt)| aq. HCl(HBr)|AgCl(AgBr)|Ag between 4° and 30° the entropy of AgCl is calc. to be 24·3, and of AgBr 26·9 g.-cal. per degree at 25°. The effect on the e.m.f. of illuminating the cells was also studied. F. L. U.

Thermodynamic properties of liquid solutions of silver bromide with alkali bromides. J. H. HILDEBRAND and E. J. SALSTROM (J. Amer. Chem. Soc., 1932, **54**, 4257—4261).—The data obtained for AgBr diluted with LiBr, NaBr, KBr, and RbBr are interpreted on the view that the linking in the alkali bromides is completely ionic, whilst that in AgBr is incompletely ionic and is tightened by a large alkali ion, *e.g.*, Rb^+, in the AgBr liquid lattice, whereas a small alkali ion has the opposite effect. J. G. A. G.

Thermodynamic properties of fused salt solutions. VI. Rubidium bromide in silver bromide. E. J. SALSTROM (J. Amer. Chem. Soc., 1932, **54**, 4252—4256; cf. A., 1931, 1234).—The e.m.f. of the cell $Ag(s)|AgBr(l)$, $RbBr(l)|Br_2(g)$ has been determined between 456° and 622°, the mol. fraction of AgBr being varied between 0·352 and 1·0. Density data for the equimolar mixture are given for 514—624°. Free energies of formation and dilution, heats of formation, entropy changes, activities, and activity coeffs. are calc. The system shows a large negative deviation from Raoult's law. J. G. A. G.

Significance of solvent for solubility of salts, and activity coefficients of ions. J. N. BRONSTED, A. DELBANCO, and K. VOLQVARTZ (Z. physikal. Chem., 1932, **162**, 128—146; cf. A., 1929, 649).—The solubilities of several cobaltammine salts in MeOH solutions of various uni-univalent salts agree with Debye and Hückel's theory, but the solubilities in solutions of bi-bivalent salts do not. From the ratio of the solubilities of cobaltammine salts in H_2O and MeOH ionic distribution ratios have been calc. The relation between the solubility of $[Co(NO_2)_3,3NH_3]$ and that of flavotetranitrodiamminocobaltate in various solvents indicates that the solubilities of both substances are determined essentially by electric forces. Born's electrostatic formula is not generally valid for the ionic distribution ratio. R. C.

Thermodynamics of concentrated solutions. II. Calculation of entire crystallisation curves in binary eutectic systems. E. KORDES (Z. physikal. Chem., 1932, **162**, 103—127; cf. A., 1932, 228).—An equation has been derived for the calcul-

ation of the above curves and its validity confirmed by reference to existing data. The equation contains three consts., of which two can be calc., for f.-p. depressions in dil. solutions, from the latent heats of fusion and m.p. of the pure components, and the third is a factor which corrects for the positive or negative heats of mixture of the components in the molten state and can be calc. from a determination of crystallisation temp. at a single high concn. The equation is applicable to systems having a miscibility gap in the liquid state. R. C.

Thermochemistry and the periodic table. Energy of transfer of electrons on oxidation. T. C. SUTTON (Nature, 1932, **130**, 474—475).—The energy of linking with O is a periodic function of the at. no. in the two series C, N, O, and F, and Si, P, S, and Cl. It is proportional to the covalency of the atom, depends on the no. of electron shells in the atom, and is not directly affected by the nature of the nucleus. The energy of transfer of an electron on oxidation is approx. the same for all atoms with the same no. of electron shells and decreases as this no. increases. L. S. T.

Co-ordination. IV. Fluorides and chlorides and their complex ions. F. J. GARRICK (Phil. Mag., 1932, [vii], **14**, 914—937; cf. A., 1931, 547).—The energy of co-ordination (referred to abs. zero) in terms of the sizes, charges, and polarisabilities of the ions, is derived for the fluorides and chlorides of several metals and non-metals. In the case of those of B, Al, $Cr^{\cdots}$, Si, $Ti^{\cdots\cdot}$, and $Sn^{\cdots\cdot}$, and for PF_5 and SF_6 the same quantity is calc. from thermochemical data. There is satisfactory agreement between the two series of results. Conclusions are reached with regard to the stabilities of various known and hypothetical complex ions and salts, from considerations of the energies of hydration of complex ions, the lattice energies of complex salts, and the energies of co-ordination. E. S. H.

Heat of formation of hydrochloric acid and some related thermodynamic data. F. D. ROSSINI (Bur. Stand. J. Res., 1932, 9, 679—702).—The heat of formation of gaseous HCl from H_2+Cl_2 is given by $H_{298\cdot1}=-22{,}063\pm12$ g.-cal.[15] per mol. of HCl. Existing thermodynamic data for HCl and its aq. solution are compared and correlated. D. R. D.

Thermal data. I. Heat capacities, entropies, and free energies of seven organic compounds containing nitrogen. H. M. HUFFMAN and H. BORSOOK (J. Amer. Chem. Soc., 1932, 54, 4297—4301).—Data are recorded for *d*-alanine, *l*-asparagine, *l*-asparagine hydrate, *l*-aspartic acid, *d*-glutamic acid, creatine, and creatinine. J. G. A. G.

Vapour pressure of water over aqueous solutions of potassium hydroxide. Y. KOBAYASHI (J. Sci. Hiroshima Univ., 1932, 2, 269—274).—V.p. of aq. KOH at 25° have been calc. for concns. up to 20*M*. Tables and a curve are given. F. L. U.

Fusion diagrams of highly-refractory oxides. V. Systems with magnesium oxide. VI. Correction. H. VON WARTENBERG and E. PROPHET. H. VON WARTENBERG and H. J. REUSCH (Z. anorg. Chem., 1932, 208, 369—379, 380—381; cf. A., 1932, 913).—V. Revised m.p. of NiO, CoO, and Mn_3O_4 are 1990°, 1810°, and 1560°, respectively. Data for mixtures of MgO with Cu_2O, BeO, CaO, SrO, BaO, TiO_2, CeO_2, Cr_2O_3, Mn_3O_4, Fe_3O_4, NiO, and CoO are given. TiO_2 forms *compounds*, $2TiO_2,MgO$, m.p. 1680°, and TiO_2,MgO, m.p. 1840°. Mixed crystals are formed with NiO, CoO, Mn_3O_4, Fe_3O_4, and Cr_3O_4, the last-named being formed from Cr_2O_3 by loss of O_2 above 2300°.

VI. Fusion curves for mixtures of ZrO_2 and of Al_2O_3 with NiO, CoO, and Mn_3O_4 have been redetermined. F. L. U.

Iron nitrides. S. SATOH (Bull. Chem. Soc. Japan, 1932, 7, 315—333).—The structures of a series of Fe nitrides have been determined by *X*-ray analysis. The heat of formation of Fe_4N, calc. from the measured heat of dissolution in dil. H_2SO_4, is 4460 g.-cal. per g.-mol. Mol. heats of Fe_2N and Fe_4N have been calc., assuming Neumann and Kopp's law, and the equilibrium relations of the systems $Fe–Fe_4N–NH_3–H_2$ and $Fe_4N–Fe_2N–NH_3–H_2$ have been worked out. Fe nitride (containing no Fe) gives a potential −0·448 volt in *N*-$FeSO_4$ (free from $Fe^{\cdots}$), but in presence of 7% $Fe^{\cdots}$ the potential is +0·5708 volt. The presence of O_2 or $Fe^{\cdots}$ appears to convert the nitride into a passive state. Fe nitride does not provide a reversible electrode in solutions of NH_3 in MeOH, EtOH, or liquid NH_3 containing KNH_2. E. S. H.

Two-component salt mixtures of lead nitrate with thallium or silver nitrate. H. M. GLASS, K. LAYBOURN, and W. M. MADGIN (J.C.S., 1932, 2713—2715).—The f.-p. curves of the systems $Pb(NO_3)_2$–$AgNO_3$ and $Pb(NO_3)_2$–$TlNO_3$ both have a simple eutectic at 200·2° and 175·5°, respectively. The curves are limited by the decomp. of $Pb(NO_3)_2$ in mixtures containing < 60% $AgNO_3$ or 50% $TlNO_3$ (cf. A., 1932, 468). The decomp. temp. of $Pb(NO_3)_2$ rises with dilution. M. S. B.

Thermal dissociation of sodium hydrogen sulphate. F. ISHIKAWA, K. MASUDA, and H. HAGISAWA (Bull. Inst. Phys. Chem. Res., Japan, 1932, **11**, 1244—1253).—The dissociation pressure resulting from the reaction $2NaHSO_4 \rightleftharpoons Na_2S_2O_7+H_2O$ has been measured from 130° to 280°. The m.p. of $NaHSO_4$ is 182° and is not affected by addition of $Na_2S_2O_7$. $Na_2S_2O_7$ decomposes very slowly at 300° and rapidly above 400°. D. R. D.

Limits of the admissibility of co-ordinative and constitutional inferences from the composition of crystalline phases. E. HERTEL and A. DEMMER (Annalen, 1932, **499**, 134—143).—The equilibrium diagram for $TiCl_4$ (24—50 mol.-%) and EtCN shows the existence of six solid compounds and is more complex than would be expected from preparative results. The diagram for $TiCl_4$ (30—50 mol.-%) and PhCN indicates five compounds, whilst that for $TiCl_4$ (10—80 mol.-%) and *m*-$C_6H_4(NO_2)_2$ indicates six and these do not include the 2 : 1 compound (which can be isolated) owing to the metastability of this. Investigations on the mol. compounds of metal chlorides and NO_2-derivatives do not show whether N_2O_4 has a *s*- or *as*-constitution

(cf. Reihlen and Hake, A., 1927, 219). The following *compounds* are prepared: $TiCl_4$,3EtCN, m.p. 108°; $TiCl_4$,2PhCN, 173·5°; $TiCl_4$,3PhCN, 168°; $4TiCl_4$,*m*-$C_6H_4(NO_2)_2$, 115°; $TiCl_4$,*m*-$C_6H_4(NO_2)_2$, 116°; $TiCl_4$,3*p*-$C_6H_4(NO_2)_2$, 115°; $2TiCl_4$,*p*-$C_6H_4(NO_2)_2$, 130°; $TiCl_4$,2$COPh_2$, 150°. $TiCl_4$ forms 2 : 1, 1 : 1, and 1 : 2 *compounds*, m.p. 175°, 163°, and 136°, respectively, with Me fumarate; the use of an excess of the ester in cold C_6H_6 gives the 1 : 1 compound ($+2C_6H_6$), which when freed from C_6H_6 (in vac. during 4 weeks) affords the *substance*, $\overset{\cdot\cdot}{CH}\cdot CO^{2}>TiCl_2$ (?), m.p. 140°. Other mol. compounds (not new) are also described. H. B.

System $CS(NH_2)_2$–NH_3–H_2O. E. Janecke and A. Hoffmann (Z. Elektrochem., 1932, **38**, 880—883).—Solubility and v.-p. data are given over the range —78° to 181°. The *compounds* $CS(NH_2)_2$,3NH_3 and $CS(NH_2)_2$,NH_3 are stable at low temp. (decompose at —10° and 8°, respectively). D. R. D.

Reduction of zinc oxide by hydrogen. F. Schacherl (Gazzetta, 1932, **62**, 839—843).—The equilibrium const. ($1·3\times10^{-4}$ at 583°, $2·67\times10^{-6}$ at 393°) is not influenced by the presence of 33 mol.-% MgO in the ZnO. H. F. G.

Ternary system K_2SiO_3–Na_2SiO_3–SiO_2. F. C. Kracek (J. Physical Chem., 1932, **36**, 2529—2542).—The ternary system is of the simple eutectoid type with respect to the binary systems K_2SiO_3–SiO_2 and Na_2SiO_3–SiO_2, and no ternary compounds occur. In the disilicate region both $K_2Si_2O_5$ and $Na_2Si_2O_5$ take up a limited excess of K_2O, Na_2O, and SiO_2, depending on the composition of the liquid in equilibrium with the crystals. I. J. P. (*c*)

Solubility isotherms of complex inorganic thiocyanates. I. A. de Sweemer (Natuurwetensch. Tijds., 1932, **14**, 231—244).—The 25° isotherm of the system KCNS–$Co(CNS)_2$–H_2O indicates the existence of only one complex, viz., $K_2Co(CNS)_4$,$4H_2O$, the saturated solution of which contains 60·7%. The region in which the solid complex can exist is large compared with that of $K_4Ni(SCN)_6$,$4H_2O$, the only complex salt in the system KCNS–$Ni(CNS)_2$–H_2O at 25°. No complexes are formed in the system $Co(CNS)_2$–$Ni(CNS)_2$–H_2O at 25°. The analytical significance of the results is discussed. H. F. G.

Equilibrium in systems composed of sulphur dioxide and sodium, potassium, or ammonium thiocyanate. H. W. Foote and J. Fleischer (J. Amer. Chem. Soc., 1932, **54**, 3902—3906; cf. A., 1931, 799). G. M. M. (*c*)

Vapour lines of three-phase systems for the co-existence of two solid components with the vapour of a binary system. A. Smits and E. J. Harmsen (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 700—705).—In the region in which the vapour behaves as an ideal gas the mol. heat of sublimation of the least volatile component increases, thereby confirming the predictions of Wuite. W. R. A.

Limiting mobilities of some univalent ions and the dissociation constant of acetic acid at 25°. D. A. MacInnes, T. Shedlovsky, and L. G. Longsworth (Nature, 1932, **130**, 774—775).—A criticism (cf. A., 1932, 1089). The val. $K=1·753\times10^{-5}$ for AcOH (*ibid.*, 695) and not $1·776\times10^{-5}$ (*ibid.*, 1089) has been independently confirmed (*ibid.*, 695). L. S. T.

Irreversible processes in electrolytes. Diffusion, conductance, and viscous flow in arbitrary mixtures of strong electrolytes. L. Onsager and R. M. Fuoss (J. Physical Chem., 1932, **36**, 2689—2778).—Theoretical. The effects of the Coulomb forces on diffusion, electrolytic conduction, and viscous flow are considered from a common viewpoint. Previous results for simple electrolytes can be extended to mixtures containing an arbitrary no. of ionic species, and general limiting laws are derived. The electrostatic effects are proportional to the sq. root of the concn. The electrostatic contribution to viscosity is computed and the mechanism of force transfer is investigated. Kohlrausch's rule relating to the independent migration of ions is not valid for mixtures and the conductances are not additive. The general laws of diffusion are discussed. The rate of production of entropy in transport processes is a quadratic function of the velocities. Laws of combined diffusion and electrical conduction are formulated. E. S. H.

Influence of picric acid on the electro-capillary curve of mercury. H. Breindl and K. Sollner (Z. Elektrochem., 1932, **38**, 843—846).—Electrocapillary curves are given for Hg in contact with *N*/110-KCl, in H_2O, in *N*/1100-picric acid, and in *N*/1100-salicylic acid. Surface tension and e.m.f. data are also given for Hg in contact with dil. aq. $HgNO_3$ containing HNO_3 and KNO_3. D. R. D.

Electrokinetic phenomena. VIII. Surface conductance of cellulose and Smoluchowski's theory. H. A. Abramson (J. Physical Chem., 1932, **36**, 2141—2144).—Data for alkali chlorides and HCl show the classical theory to be inadequate. For $Li^{\cdot}$, $Na^{\cdot}$, and $K^{\cdot}$, but not for $Mg^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$, the quotient of the sp. surface conductance of cellulose by the ionic mobility is const. A modification of the theory is proposed which makes the surface conductance partly dependent on the abs. mobilities of the anions and cations (cf. A., 1931, 429). C. H. R. (*c*)

Unique electrode potential characteristic of a metal, and a theory for the mechanism of electrode potential. A. L. McAulay and E. C. R. Spooner (Proc. Roy. Soc., 1932, **A, 138**, 494—501).—A theory is advanced for the origin of the electrode potential of a metal immersed in an aq. solution. The bombardment, owing to heat motion, of polar H_2O mols. on the metal results in a stream of ions being drawn into the solution to a distance *t* from the electrode surface, and equilibrium is attained when their removal is balanced by their return under the field so produced. This results in a layer of ions of thickness *t*, surrounding the metal. Certain consequences of the theory which have been verified by experiment are described. L. L. B.

Potential [at metallic electrodes] in electrolytes with foreign ions. II. A. Schmid, P. Vogele, and W. Winkelmann (Helv. Chim. Acta, 1932, **15**,

1393—1398; cf. A., 1930, 705).—Potentials of Ag, Pb, and Cu in aq. solutions of their respective nitrates (Cu also in $CuSO_4$) have been determined at progressive dilutions of electrolyte. Ag behaves in accordance with Nernst's law down to about $10^{-5}N$, but is less negative at higher dilutions. Cu shows a similar deviation between 0·1 and 0·01N, whilst Pb is more negative from the start. In all three cases the potential–dilution curves possess a well-defined max. Potentials of Cu in Cu-free solutions of several acids and alkali salts are found to depend largely on the anion and very little on the cation present. Potentials in very dil. solutions and even in pure H_2O are definite and reproducible. F. L. U.

Influence of gases on normal potential of zinc electrode. F. H. GETMAN (J. Physical Chem., 1932, **36**, 2655—2663).—The initial val. of the potential of a Zn electrode in aq. $ZnCl_2$ is increased by air, N_2, and H_2, and decreased by O_2. This influence diminishes with time. The change in potential is much smaller than that produced by the same gases when the metal is immersed in aq. KCl. S. L. (*c*)

Normal potential and heat of dissolution of gallium. E. S. VON BERGKAMPF (Z. Elektrochem., 1932, **38**, 847—848).—Measurements with the cell Ga | $KGa(SO_4)_2$|Hg_2SO_4|Hg indicate that $E_0 = -0·52$ volt. Hence the heat of formation of $Ga^{\cdot\cdot\cdot}$ from Ga (solid) is 36 kg.-cal. The heat of dissolution of Ga in aq. HCl (1 mol. HCl : 8·81 mols. H_2O) is 32 kg.-cal. D. R. D.

Electrical measurement of cyanide solution activity. W. E. JOHN and E. BEYERS (J. Chem. Met. Soc. S. Africa, 1932, **35**, 27—34).—Measurements have been made of the potential of Au in 0·02—0·06% aq. KCN and the effect thereon of CaO, $Hg^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, and $Pb^{\cdot\cdot}$ was determined. With increasing concn. of KCN the potential becomes less negative, and finally reaches a positive val. in 0·037% aq. KCN. $Hg^{\cdot\cdot}$ in minute quantities raises the potential to a positive val. in all concns. of KCN, whereas CaO, $Fe^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, and $Pb^{\cdot\cdot}$ depress it to more negative vals. than in pure KCN. A. R. P.

Electrochemical investigation of solid cadmium–gold alloys. A. OLANDER (J. Amer. Chem. Soc., 1932, **54**, 3819—3833).—The e.m.f. of the cell Cd liquid|K(Rb)Cl,LiCl,$CdCl_2$|(Cd,Au) solid above 340° and the cell Cd solid|(K,Na,Cd)OAc|(Cd,Au) solid at 250—300° and the temp. coeffs. have been determined. With the completion of the phase diagram of the Au–Cd system three new transitions have been found. L. P. H. (*c*)

E.m.f. in liquid ammonia. G. I. COSTEANU (Compt. rend., 1932, **195**, 778—779).—For 0·1N solutions of the electrolytes the e.m.f. of the cells Pb|$Pb(NO_3)_2$,$AgNO_3$|Ag and Cd|$Cd(NO_3)_2$,$4H_2O$,$AgNO_3$|Ag between −65° and −35° are expressed by $0·462 + 0·0005(t+35°)$ and $0·963 - 0·00033(t+35°)$, respectively. C. A. S.

[Ammonium acetate as a buffer.] R. J. WILLIAMS and C. M. LYMAN (J. Amer. Chem. Soc., 1932, **54**, 4458; cf. A., 1932, 709).—The p_H of the solutions is liable to be < 7. J. G. A. G.

Indicators. XIX. Existence and significance of the "hydrogen effect." A. THIEL and G. COCH (Z. anorg. Chem., 1932, **208**, 397—400; cf. A., 1931, 1383).—When CO_2 is rigorously excluded an extremely small displacement of the p_H of solutions buffered to different extents is observed. This displacement, which may be of either sign, is independent of the presence of neutral salt. The contrary result obtained by Wolf is attributed to excessive platinising of the electrodes used. F. L. U.

Hydrogen over-voltage on mercury cathodes in presence of small amounts of platinum metals. I. SLENDYK and P. HERASYMENKO (Z. physikal. Chem., 1932, **162**, 223—240).—The current–voltage curves for the simultaneous separation of H and Pt on a dropping Hg electrode exhibit two periods of rapidly increasing current. The first corresponds with the separation of mol. H_2 catalysed by Pt already deposited, and the second with the discharge of H on the uncontaminated Hg surface. Even minute traces of Pt have an appreciable catalytic effect, and many published measurements of H over-voltage are doubtless in error as a consequence of this effect. Neutral salts cause considerable reduction in the catalysed separation of H. The variation with $[H^{\cdot}]$ of the limiting current and cathode potential for the catalysed separation can be accounted for by means of Langmuir's adsorption isotherm. Some other Pt metals, but not Pd or Rh, behave similarly to Pt. R. C.

Hydrogen over-voltage. T. ERDEY-GRUZ and H. WICK (Z. physikal. Chem., 1932, **162**, 53—62).—The slope, *b*, of the graph of the logarithm of the c.d. against the over-voltage of H on a C electrode with an uncontaminated surface is the same as for an indifferent metal electrode, and thus agrees with the theory (A., 1930, 1376). Compared with other metals, Pb and Ta give abnormal vals. of *b*, which is perhaps connected with the persistence on them of an adsorbed film even at H discharge potentials. R. C.

Discharge voltage of mercury on foreign electrodes. T. ERDEY-GRUZ and H. WICK (Z. physikal. Chem., 1932, **162**, 63—70; cf. A., 1932, 24).—The potential at which Hg starts to separate electrolytically on an electrode which it does not wet is calc. theoretically to be −0·34 volt, relative to the reversible potential of Hg in the same solution. With C electrodes coated with lustrous C separation begins at some parts of the surface of even the most inactive C at −0·21 volt, and this is ascribed to the presence of active spots. Discharge on the most inactive parts of the surface requires a potential of −0·23 to −0·27 volt. For Pt and Ta the discharge voltage is much smaller than for C. R. C.

Anodic film of aluminium. I. Effect of concentration of the electrolyte on the formation of anodic film. II. Anodic behaviour of aluminium in aqueous solutions of oxalic acid. S. SETOH and A. MIYATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **19**, 189—236, 237—291).—Experiments have been made with $H_2C_2O_4$ solutions and the influence of the concn. of the electrolyte on film formation has been examined. The thickness and electrical resistance of the Al_2O_3 film, resistance to corrosion, and

energy efficiency of film formation with d.c. and with superposed d.c. and a.c. have been measured. With a.c. no film is formed.

II. The porous active layer of Al_2O_3 is continuously renewed by combination of nascent O in the pores with the Al. At const. c.d. the rise of terminal voltage and the growth of the active layer are almost independent of the electrolyte used. The destructive power of the electrolyte on the active layer varies with the anion. Retardation of anodic corrosion by the electrolyte is effected by the screening action of O_2 occluded in the pores of the active layer. N. M. B.

Theory of passivity phenomena. XVII. Comparison of E. Müller and Schwabe's new theory of passivity and W. J. Müller's protective film theory with the experimental results of researches on passivity. W. J. MÜLLER (Z. Elektrochem., 1932, **38**, 850—860; cf. A., 1932, 473).—Experimental data for the electrolytic passivation of Pb, Cd, Cu, and Zn in saturated aq. solutions of their perchlorates and sulphates support W. Müller's theory. E. Müller and Schwabe's e.m.f.–c.d. curves (*ibid.*, 814) cannot be used as a basis for a theory of passivity. D. R. D.

Photovoltaic effect. R. T. DUFFORD (Trans. Electrochem. Soc., 1932, **62**, 345—351).—Work of the author and others on photovoltaic effects in cells containing ethereal solutions of Grignard compounds (A., 1927, 918; 1929, 1364; 1930, 846, 1126; 1931, 802) is reviewed and discussed. H. J. T. E.

Crossing of potential thresholds in chemical reactions. E. WIGNER (Z. physikal. Chem., 1932, **B**, **19**, 203—216).—The case where the reacting mols. have almost sufficient energy to cross the threshold mechanically, but a finite fraction of them have rather less energy and pass through the upper part of the energy hill non-mechanically, is worked out. The result is compared with Eckart's calculations (Physical Rev., 1930, [ii], **35**, 1303). Application of the quantum correction to the rate of transformation of para-H_2 into normal H_2 increases somewhat the deviation of the observed from the calc. vals. R. C.

Electrical ignition of explosive gaseous mixtures. G. I. FINCH (Nature, 1932, **130**, 929).—Crit. of the thermal theory of electrical ignition. L. S. T.

Lower pressure limit in the chain reaction between hydrogen and oxygen. C. N. HINSHELWOOD and E. A. MOELWYN-HUGHES (Proc. Roy. Soc., 1932, **A**, **138**, 311—317).—The influence of temp., H_2–O_2 ratio, presence of inert gases, and diameter of the explosion vessel on the lower limit of the low-pressure explosion region in the combination of H_2 and O_2 has been explored in detail (cf. A., 1931, 1244). The results can be explained on the hypothesis that the lower limit is determined by a balance between the branching of reaction chains and the destruction of chain carriers by diffusion to the walls of the vessel. L. L. B.

Internal energy of gases after explosion. W. T. DAVID, J. R. BROWN, and A. H. EL DIN (Phil. Mag., 1932, [vii], **14**, 764—777).—In CO–air and H_2–air explosions in spherical vessels 6 in. and 17·45 in. internal diameter with central ignition, heat losses up to the moment of max. pressure were approx. the same for each vessel. The higher pressure developed in the larger vessel is attributed to more complete combustion at the moment of max. pressure. Explosion experiments give too high vals. for sp. heats. H. J. E.

Explosive oxidation of carbon monoxide at lower pressures. G. HADMAN, H. W. THOMPSON, and C. N. HINSHELWOOD (Proc. Roy. Soc., 1932, **A**, **138**, 297—311).—Dry CO and O_2 combine explosively in SiO_2 vessels between certain pressure limits in the region of 700°. Outside these limits, which are independent of the degree of dryness, the reaction rate is very small. The effect of inert gases shows that the lower limit is determined by the diffusion of active centres of some kind to the vessel wall, and the upper limit to gas-phase deactivation. The lower limit is independent of temp., whilst the upper moves rapidly towards higher pressures as the temp. rises. CO may affect the wall of the vessel so that no explosion takes place, leading to a metastable state. The mechanism of the change is discussed. L. L. B.

Mechanism of flame movement. II. Fundamental speed of flame in mixtures of methane and air. H. F. COWARD and F. J. HARTWELL (J.C.S., 1932, 2676—2684).—During the uniform movement of flame, the vol. of gas burnt in unit time in the explosion of a given CH_4–air mixture is proportional to the area of the flame front. This relation holds for all inflammable CH_4–air mixtures and for all the explosion tubes used (diameters 2·5—10 cm.). From the results the speed of propagation in the direction normal to the flame front for a stationary gas mixture (the fundamental speed of flame) is calc. and a comparison made with the results given by Gouy's Bunsen flame method. F. J. W.

Propagation of flame in electric fields. II. Effects of transverse fields. E. M. GUENAULT and R. V. WHEELER (J.C.S., 1932, 2788—2793).—Changes in the speed of flames due to the imposition of a transverse electric field are caused by an increase in the surface area of the flame front. The field has no effect on the character or speed of the chemical reactions taking place in the flame. All changes in shape of the flame can be explained as due to a mechanical drag exerted by the field on the flame, which behaves as a positively-charged mass of gas. CO–air and C_2H_2–air mixtures were used. F. J. W.

Thermal decomposition of nitrous oxide. M. VOLMER and H. FROEHLICH (Z. physikal. Chem., 1932, **B**, **19**, 85—88; cf. A., 1931, 174).—At a temp. between 625° and 680° the graph of the reciprocal of the velocity coeff. against the reciprocal of the pressure between 2 and 300 mm. exhibits the curvature predicted theoretically, due to variation with pressure of the average mean life of the active mols. (A., 1927, 833). R. C.

Thermal decomposition of nitrous oxide. Effect of helium, argon, and oxygen. M. VOLMER

and H. FROEHLICH (Z. physikal. Chem., 1932, **B**, **19**, 89—96).—Measurements have been made at 625—670° with initial N_2O pressures of about 1—50 mm. The probabilities of activation per collision are: N_2O, 1/190; A, 1/1600; N_2, 1/800; He, 1/290; O_2, 1/830; CO_2, 1/145. R. C.

Reactions of hydrogen atoms with hydrazine and with ammonia. J. K. DIXON (J. Amer. Chem. Soc., 1932, **54**, 4262—4271; cf. A., 1932, 820).—Approx. 1 mol. of NH_3 and 1 mol. of permanent gas are produced in the decomp. of 1 mol. of N_2H_4 by a stream of at. H. The temp. coeff. between 0° and 22° is zero. With const. initial $[N_2H_4]$, the % of N_2H_4 decomposed and that of NH_3 produced decreases with [H]. H was, however, always in excess. With const. [H], the abs. wt. of N_2H_4 decomposed and of NH_3 formed decreased with initial $[N_2H_4]$, although the % decomp. increased. H_2O vapour does not affect the results. A weak green fluorescence occurs near the point of mixing of N_2H_4 and at. H; some of the lines in the spectrum were identified with the α-bands of the NH_3 flame. The reaction mechanism is probably $H+N_2H_4 \longrightarrow H_2+N_2H_3$, $2N_2H_3 \longrightarrow 2NH_3+N_2$, and the relation to the photochemical and electrical decomp. of NH_3 is discussed (cf. A., 1932, 705). Results observed with NH_3 may be due to the action of O atoms from the H_2O mixed with the at. H. J. G. A. G.

Reaction velocity of chloroalkyls with sodium vapour. H. VON HARTEL, N. MEER, and M. PÓLANYI (Z. physikal. Chem., 1932, **B**, **19**, 139—163).—The diffusion method for the determination of the velocity of gas reactions of Na vapour (cf. A., 1931, 174) does not give accurate vals. of the abs. velocity coeff., but is satisfactory for comparative purposes. The results show that the reaction inertia decreases in the order F, Cl, Br, I for the halides of a given radical, with increase in length of the C chain, with increase in the no. of Cl atoms, and the more so the closer these are together, and with introduction of carbonyl-O. It decreases in the order primary, *sec.*, *tert.*, but is not affected by branching of the C chain. The reaction is retarded by a double linking at the C atom to which the Cl is attached, but the inertia is reduced if the double linking occurs at the next C atom. A small reaction inertia seems to be associated with a large dipole moment. R. C.

Comparison of sodium vapour reaction with other organic chemical reactions. N. MEER and M. PÓLANYI (Z. physikal. Chem., 1932, **B**, **19**, 164—189; cf. preceding abstract).—The comparison is with published data for the ionic reactions (1) $A_I'+RA_{II} \longrightarrow RA_I+A_{II}'$ and (2) $R_1OR+H \longrightarrow R_1OH+R^{\cdot}$. Disregarding cases where there is possibly steric hindrance, the relations between reactivity and constitution are similar to those for Na vapour, except that lengthening the C chain causes considerable retardation. Assuming that under the influence of the electric forces of the dipole the reacting ion attacks that side of the atom to which it is to be attached which is remote from the linking to be severed, it may be deduced (*a*) that in (1), but not in (2), steric hindrance may operate, and (*b*) that in (1) optical inversion will occur when optically-active substances are involved. Of these (*b*) accords with the experimental data and explains the racemising action of halogen ions, assuming this to be based on atom-exchange reactions causing inversion and leading to equilibrium between the antipodes, and (*a*) probably accounts for the fact that in (1) the reactivity diminishes in the order primary, *sec.*, *tert.*, whereas the order for (2) is the same as for Na vapour. R. C.

Rate of fourth-order reaction between bromic and hydrobromic acids. Kinetic salt effect. H. A. YOUNG and W. C. BRAY (J. Amer. Chem. Soc., 1932, **54**, 4284—4296; cf. A., 1930, 713).—The velocity of the reaction $BrO_3'+3H_2O_2=3O_2+Br'+3H_2O$ between 0·0125—0·5*M*-$H^{\cdot}$, 0·005—0·01*M*-BrO_3', and 0·013—0·062*M*-H_2O_2, alone, and with the addition of 0·0008—0·008*M*-Br' and 0·07—0·7*M*-$NaClO_4$, at 25°, 45°, and 65°, is given by $-d[BrO_3']/dt = k_1[H_2O_2][BrO_3'][H^{\cdot}] + k[BrO_3'][Br'][H^{\cdot}]^2$. The heat of activation of the fourth-order reaction is 16,000±300 g.-cal. and that of the third-order 15,000±1000 g.-cal. The limiting law of the kinetic salt effect of the fourth-order reaction at 65° is $k/\gamma^2_{HBr}.\gamma^2_{HBrO_3}=\chi$, and the velocity at 25° for ionic strengths $< 0·2$ in $HClO_4$ or H_2SO_4 solutions is given by $-d[BrO_3']/dt = 540 \pm 15[BrO_3'][Br'][H^{\cdot}]^2\gamma^4_{HBr}$. The mechanism proposed for the autocatalytic reduction of BrO_3' by H_2O_2 involves a series of steps including the reduction of the intermediate compounds $HBrO_2$ and HOBr by H_2O_2. J. G. A. G.

Rate of reaction of disubstituted aminomethylsulphonic acids with iodine. T. D. STEWART and W. E. BRADLEY (J. Amer. Chem. Soc., 1932, **54**, 4183—4188).—The velocity of the reaction $R_2N^+H{\cdot}CH_2{\cdot}SO_3^- + I_3' \longrightarrow R_2N^+{:}CH_2 + SO_4'' + 3I' + 3H^{\cdot}$ is independent of [I], is of first order with respect to NH_2-acid, and decreases with increasing acidity. With a particular substituent group, R, the reaction velocity is the same whether I, Br, or H_2O_2 is used and the rate-determining step is probably an ionisation process, for which velocity coeff. and heats of activation are recorded for a no. of cases. J. G. A. G.

Kinetics of reaction between arsenious acid and iodine. II. Influence of neutral salts on velocity of reaction and equilibrium point. E. JÓZEFOWICZ (Rocz. Chem., 1932, **12**, 787—798).—K, Na, Li, Ba, Sr, Ca, and Mg chlorides and bromides (0·5—3*N*) and $NaNO_3$ and KNO_3 considerably reduce the velocity of oxidation of H_3AsO_3 by I, and slightly augment that of oxidation of HI by H_3AsO_4, thereby shifting the equilibrium point in the direction of H_3AsO_3 formation. This effect is due to reversal of the reaction $I_2+H_2O \rightleftharpoons HOI+HI$ in the presence of neutral salts. R. T.

Aldehyde hydrogen sulphites. II. Effect of varying temperature on equilibrium between benzaldehyde and hydrogen sulphite ion. III. Effect of changing hydrogen-ion concentration on specific reaction rate of addition of sodium hydrogen sulphite to benzaldehyde. IV. Discussion of equilibrium, rates, and temperature coefficients as affected by hydrogen-ion concen-

tration. T. D. STEWART and L. H. DONNALLY (J. Amer. Chem. Soc., 1932, 54, 3555—3558, 3559—3569; cf. A., 1932, 818).—II. Equilibrium data are given for p_H 0·0—13 at 0—58°.

III—IV. Data are given for the rate of reaction of PhCHO and $NaHSO_3$ at 21° for p_H 1·9 and 5·2. These permit the calculation at 21° for p_H 0—13 of the sp. rates of the reactions of PhCHO with SO_3'', HSO_3', and H_2SO_3, the sp. rates of dissociation of OH·CHPh·SO_3H (I) and its uni- and bi-valent ions, and the overall equilibrium const. (I) is a very strong monobasic acid, with a second dissociation const. of 7×10^{-10}; the activation energies and heats of dissociation are calc. The first dissociation const. of PhCHO as an acid is 5×10^{-13}.

H. A. B. (*c*)

Mechanism of oxidation process. XXXII. Enzymic oxidation of acetic acid by yeast. H. WIELAND and R. SONDERHOFF (Annalen, 1932, 499; 213—228).—Oxidation of AcOH [as NaOAc or $Ba(OAc)_2$ in buffered solutions] by "impoverished" yeast (I) (A., 1932, 303) and O_2 during about 24 hr. gives a solution containing unchanged AcOH, succinic acid (II) about 5% of AcOH consumed), and citric acid (III) (≡ about 10% of AcOH used). The oxidation is more dependent on the substrate concn. than in the case of EtOH (cf. *loc. cit.*); the velocity with $M/128$ solutions is about 75% of that with $M/4$ solutions. The time–O_2-consumption curves show that reaction undergoes self-acceleration owing to the intermediate products being oxidised faster than AcOH. The ratio CO_2 produced : O_2 consumed is approx. 1, whilst the mol. ratio O_2 : AcOH is 1·7—1·8. The intermediate production of glycollic acid or $H_2C_2O_4$ is improbable, since these acids are little or not affected by (I)+O_2. (II) is oxidised at a much slower rate than AcOH; it is considered that this does not disprove the intermediate formation of (II) from AcOH and it is suggested that the (II) produced during the dehydrogenation is "activated." Fumaric acid is oxidised by (I) and O_2 at about the same rate as (II). AcOH, (II), and malic acid are not dehydrogenated by (I) and methylene-blue. (III) may be produced by an aldol-like condensation of AcOH and oxaloacetic acid [formed from (II)]; this is supported by the observation that (III) is not produced from (II) and (I)+O_2. Oxidation of (III) by (I)+O_2 also proceeds slowly; the velocity of CO_2 evolution is very small during the initial stages, but subsequently increases rapidly. H. B.

Velocity of dissolution of carbon dioxide and ammonia in water and aqueous solutions. A. N. SCHUKAREV and M. V. BONDAREVA (Ukrain. Chem. J., 1932, 7, [Sci.], 1—11).—The velocity of dissolution (V) of CO_2 in H_2O is proportional to the velocity of stirring. For equiv. concns. of alkali $V_{NaOH}>V_{NH_3}$; the velocity coeff. diminishes with increasing concn. of alkali to N, above which it remains const. The velocity of dissolution of NH_3 in aq. acids (HCl, H_2SO_4, HNO_3) at first rises rapidly and then slowly with the concn. of acid; alkalis reduce the val. of V.

R. T.

Thermal decomposition of methane by a carbon filament. H. H. STORCH (J. Amer. Chem. Soc., 1932, 54, 4188—4198).—The decomp. of CH_4 by C filaments at 1457—2000° in bulbs cooled by liquid N_2, and at −183°, −78°, and 0°, has been investigated. The earliest products isolated are C_6H_6 and H_2, of which 95% yield is achieved with liquid N_2. At −183°, C_2H_4 and C_2H_2 are also obtained, whilst at the higher temp. the products are C and H_2. With < 8 cm. of CH_4, the reaction is of approx. first order and has a heat of activation of 77,170±10,000 g.-cal. At higher pressures, the reaction becomes of approx. second order, possibly owing to temp. gradient effects near the filament. The effect of H_2 on the reaction is in accord with the equation derived by Kassel (A., 1932, 1209) on the assumption of a series of dehydrogenations following the initial synthesis of C_2H_6.

J. G. A. G.

Oxidation of sulphur at low pressures. A. RITCHIE and E. B. LUDLAM (Proc. Roy. Soc., 1932, A, 138, 635—643).—The low-pressure oxidation of S, initiated on a hot surface and accompanied by a visible glow, has been studied experimentally. The rate is independent of the pressure of O_2, due to two compensating factors: (1) the rate of oxidation is proportional to the pressure of O_2, and (2) the rate of inhibition by SO_2 is inversely proportional to the pressure of O_2. A residual pressure is observed and an explanation is offered. L. L. B.

Kinetics of reactions governed by diffusion. J. PALACIOS (Anal. Fis. Quím., 1932, 30, 695—700).—The kinetics of reactions between a solid and a gas in which the velocity is determined by the relatively slow rate of diffusion of the gas through the layer of reaction product is considered. Such reactions proceed to completion in a finite time; if the surface is plane the velocity diminishes with time at a decreasing rate and then falls abruptly to zero at the instant of completion, whereas for cylindrical or spherical surfaces it falls continuously. H. F. G.

Intensive drying. I. Reaction between ammonia and phosphorus pentoxide. J. SANCHO and E. MOLES (Anal. Fís. Quím., 1932, 30, 701—719).—Very pure and dry NH_3 and P_2O_5 react vigorously at first, but after a few min. the velocity diminishes and several days are required for completion of the reaction. If more NH_3 is admitted to the vessel further absorption takes place. The composition of the product of the first reaction approximates to NH_3,P_2O_5, but with further NH_3 $(NH_3)_{1\text{-}2},P_2O_5$ is formed. The absorption obeys an equation of the Freundlich type, viz., $\delta=58t^{1/7\cdot6}$. H. F. G.

Kinetics of peptisation of hydrated chromic oxide. J. LISIECKI (Rocz. Chem., 1932, 12, 817—831).—Aq. HCl dissolves or peptises Cr_2O_3 hydrate gels, according to the structure and relative concn. of the gel and to [HCl]. NaOH in excess of the theoretical amount is required for peptisation, indicating the existence of the equilibrium CrO·ONa+H_2O ⇌ CrO·OH+NaOH. Peptisation by HCl or $CrCl_3$ leads to the production of $CrCl_2OH$. The reaction of peptisation by NaOH is of the autocatalytic type, and proceeds according to Ostwald's, Zawidzki's, and von Buzagh's kinetic equations. The velocity coeff. of the reaction is 0·133 at 18° and 0·525 at 38°; the temp. coeff. is 1·97 over the range 18—38°.

R. T.

Kinetics of the systems CaO–CO_2, and Cd–CO_2. S. BRETSZNAJDER (Rocz. Chem., 1932, **12**, 799—815).—The velocities of the reactions $CaO+CO_2 \rightleftharpoons CaCO_3$ and $CdO+CO_2 \rightleftharpoons CdCO_3$ vary with the pressure, temp., reacting surface (S) of the solid phase, and difference between the equilibrium pressure of CO_2 and that of the systems. At pressures considerably different from that of equilibrium the velocity is > theoretical, owing to the presence of active nuclei in the solid phase. The reaction is retarded by the formation of layers of reaction products on the oxides; the inhibitive action of these layers depends on their thickness and structure, and on previous treatment of the oxides. The val. of S depends on the dimensions and structure of the crystals of oxide. The velocity of reaction is not a simple function of the composition of the solid phase at a given temp. and pressure. R. T.

Galvano- and potentio-metric determination of corrosion. M. T. MICHAILOV (Korrosion u. Metallschutz, 1932, **8**, 85—89; Chem. Zentr., 1932, ii, 607).—Potential and c.d. measurements are inadequate. Todt's test is not universally applicable. A. A. E.

Methods for investigating the corrosion of metals. E. V. TZEKHNOVITZER (Soobshch. Vsesoy. Inst. Met., 1931, No. 1—2, 45—49).—A discussion. CH. ABS.

Corrosion of iron in mixtures of water vapour and air. E. I. DUIRMONT (Soobshch. Vsesoy. Inst. Met., 1931, No. 1—2, 37—45).—Corrosion is more rapid at higher temp. and in presence of CO_2 and O_2. The properties of the product depend on the temp. CH. ABS.

Rate of dissolution of carbonyl iron in hydrochloric and sulphuric acids. M. CENTNERSZWER and M. STRAUMANIS (Z. physikal. Chem., 1932, **162**, 94—102).—Dissolution in 10—11·45N-HCl is very slow, and there is a period of induction with one or more well-defined velocity max. Dissolution in H_2SO_4 is more rapid than in HCl of the same normality, but is qualitatively similar. The velocity fluctuations are ascribed to impurities, perhaps C. R. C.

Explosibility of systems of base metals and halogen compounds. F. LENZE and L. METZ (Chem.-Ztg., 1932, **56**, 921—923).—Mixtures of alkali or alkaline-earth metals with halogenated hydrocarbons are sensitive to shock, especially as the no. of halogen atoms is increased. Probably unstable intermediate compounds, such as C_2HCl and C_2Cl_2, are formed and lead to explosive decomp. of the whole. E. S. H.

Catalytic decomposition of hydrogen peroxide by ferric ions. W. LIMANOWSKI (Rocz. Chem., 1932, **12**, 782—786).—$Fe^{\cdot\cdot\cdot}$ catalyses the reduction of $KMnO_4$ by H_2O_2; H_2O_2 reduces $Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$, which is oxidised by $KMnO_4$. R. T.

Chemical reactions in concentrated electrolytes. XIV. Reaction between vanadic acid and hydrogen bromide, and the effect on it of acids, salts, and catalysts (2). M. BOBTELSKY and L. CHAJKIN (Z. anorg. Chem., 1932, **209**, 95—104; cf. A., 1932, 576).—When the Br formed is removed at a const. rate the influence of added substances is the more pronounced the smaller is the concn. of HBr. The reaction velocity increases with concn. of added H_2SO_4, being measurable only between the limits 35% and 48% H_2SO_4. All chlorides except $ZnCl_2$ and $CdCl_2$ accelerate the reaction. Sulphates exert little effect. F. L. U.

Catalytic effects produced by tartaric acid, sodium hydrogen tartrate, and by first- and second-stage tartrate buffers. H. M. DAWSON and E. SPIVEY (J.C.S., 1932, 2612—2620).—The catalytic coeffs. for the tartaric acid mol., the H tartrate ion, and the tartrate ion for the $COMe_2$–I reaction are $26{\cdot}0\times10^{-6}$, $8{\cdot}5\times10^{-6}$, and $1{\cdot}0\times10^{-6}$, respectively. The first-stage ionisation coeff. for tartaric acid is $k_1=8{\cdot}5\times10^{-4}$ in salt-free solutions. The influence of [NaCl] on k_1 is given by $\log k_1^x=\log k_1^0+0{\cdot}54\sqrt{x}-0{\cdot}24x$, where is the ionisation coeff. in $x$$M$-NaCl solution. The catalytic effects of first- and second-stage tartrate buffers can be represented by $v=v_h+v_{H_2T}+v_{HT'}+v_{T''}+v_{H_2O}+v_{OH}$, where the successive partial velocities are due respectively to $H^{\cdot}$, the tartaric acid mol., the H tartrate ion, the tartrate ion, the H_2O mol., and OH'. F. J. W.

[Effect of] hydrogen-ion concentration on degradation of uric acid. F. ROSENTHAL (Biochem. Z., 1932, **255**, 200—204).—Decomp. of uric acid, which increases with increasing p_H, can be detected in aq. solutions at p_H 7·5. The extent of decomp. is independent of concn. and is unaffected by the state of the dissolved acid. Inorg. catalysts ($FeCl_3$, $CuSO_4$, $KMnO_4$), methylene-blue, and glutathione do not accelerate the decomp., which does not take place between p_H 7·5 and 10·8 if O_2 (air) is absent. W.McC.

Effect of ions in sugar solutions and solvent mixtures. F. TODT (Z. Ver. deut. Zuckerind., 1932, **82**, 817—849).—The neutral-salt effect and the high activity of $H^{\cdot}$ in sugar solutions (especially with addition of EtOH) lead to the suggestion that these and allied effects are due to removal of H_2O of solvation from $H^{\cdot}$. E. S. H.

Decomposition of nitrous oxide on glowing platinum. G. M. SCHWAB and B. EBERLE (Z. physikal. Chem., 1932, **B**, **19**, 102—106; cf. A., 1932, 819).—O_2 formed by the reaction has a retarding action and is strongly adsorbed by the Pt wire, whereas added O_2 has no retarding action. R. C.

Catalysed hydrogenation of ethylene. M. TAUBER (Z. physikal. Chem., 1932, **B**, **19**, 97—101).—There seems to be no connexion between the activity of a Pt-black film and its volta potential. The activity is destroyed when the catalyst is exposed to a high vac., probably because of dehydration or the decomp. of surface oxides. R. C.

Heterogeneous chemical reactions in the silent electric discharge. I. S. MIYAMOTO (J. Sci. Hiroshima Univ., 1932, **2**, 217—242).—The following solid substances are reduced by gaseous H_2 in the silent discharge: S, I, $FeCl_3$, $CuCl_2$, CuCl, $HgCl_2$, Hg_2Cl_2, $SnCl_4$, $NaNO_3$, $AgNO_3$, $K_4Fe(CN)_6$, $KMnO_4$, $KClO_3$, KIO_3, HIO_3, $CuSO_4$, $KBrO_3$, As_2O_5,

As_2O_3, As_2S_3. Details with regard to the experiments and reaction products are given. F. L. U.

Boron hydrides. XVII. Electrolysis of solutions of boron hydrides in anhydrous ammonia. A. Stock and E. Wiberg [with H. Martini and A. Nicklas] (Ber., 1932, **65**, [*B*], 1711—1724; cf. A., 1931, 1248).—The initial reactions involved in the electrolysis of B_2H_6 in anhyd. NH_3 at −75° are $[B_2H_4]H_2+NH_3 \longrightarrow [B_2H_3(NH_2)]H_2$ (I) $+H_2$ and (I) $+NH_3 \longrightarrow [B_2H_2(NH_2)_2]H_2+H_2$. After this stage the reaction becomes very difficult, probably owing to internal salt formation of the compound. The second change, initially very slight but gradually increasing in importance and ultimately occurring almost exclusively, results in decomp. of NH_3 into N_2 and $3H_2$; its course as far as (I) is concerned is given by the scheme: $3(I) \longrightarrow 3B_2H_3(NH_3)'+3H^{\cdot}$; $3H^{\cdot}+3\ominus \longrightarrow 3H$; $3B_2H_3(NH_3)' \longrightarrow 3B_2H_3(NH_3)+3\ominus$; $3B_2H_3(NH_3)+NH_3 \longrightarrow 3(I)+N$. Hydrolysis of the residue left after electrolysis yields B_2O_3 and H_2, the total vol. of the latter being six times that of the B_2H_6. Electrolysis of solutions of B_4H_{10} is similarly accompanied by substitution and re-formation reactions. If the e.m.f. is sufficiently high all the H atoms of the anion B_4H_6 can be replaced with production of $[B_4(NH_2)_6]H_4$, but further replacement does not occur. Continued electrolysis at 10—16 volts results in slow evolution of H_2 without alteration in the B : NH_2 ratio until finally $B_4(NH_2)_6$ remains as a colourless, non-volatile substance, sol. in liquid NH_3. With medium voltages the first stage of the reaction ceases after introduction of about $4NH_2$ into the B_4H_{10} mol., and ultimately with small current practically only the mixture of 25% N_2 and 75% H_2 is evolved. Similar observations are made with $B_{10}H_{14}$. At 2—4 volts ammination appears to proceed to the stage $B_{10}(NH_2)_6H_8$, whereas at higher voltages 12 or more H atoms can be replaced. H. W.

Electrolytic oxidation. II. Electrolyte oxidation of sodium thiosulphate. S. Glasstone and A. Hickling (J.C.S., 1932, 2800—2807).—$(NH_4)_2MoO_4$ increases the yield of Na_2SO_4 obtained from the electrolytic oxidation of $Na_2S_2O_3$; MoO_3 similarly increases the formation of SO_4'' when $Na_2S_2O_3$ is oxidised by H_2O_2. During the oxidation of $Na_2S_2O_3$ at platinised Pt, Au, Ni, and gas-C anodes increase of p_H decreases the current efficiency for oxidation, but increases the ratio of Na_2SO_4 to $Na_2S_4O_6$ formed. $MnSO_4$ and $CoSO_4$, which catalyse the decomp. of H_2O_2, reduce markedly the oxidation efficiency at all the electrodes used. The results are in harmony with the view that the anodic oxidation of $Na_2S_2O_3$ is a secondary process in which H_2O_2 is the effective oxidising agent. F. J. W.

Theory of electrolytic formation of sodium persulphate. O. Essin and E. Alfimova (Z. physikal. Chem., 1932, **162**, 44—52).—Compared with the formation of $(NH_4)_2S_2O_8$ (A., 1926, 804) the formation of $Na_2S_2O_8$ is complicated by the production of H_2SO_5, which is responsible for the reactions $SO_5''-2\ominus \longrightarrow SO_4+\frac{1}{2}O_2$ and $SO_4+H_2O \longrightarrow SO_5''+2H^{\cdot}$, and $H_2SO_5+O \longrightarrow H_2SO_4+O_2$. The observed variation of current yield of active O with the concns. of SO_4'', SO_5'', and S_2O_8'' agrees with this view. R. C.

Electrolytic preparation of some complex salts of bivalent silver. G. A. Barbieri (Atti R. Accad. Lincei, 1932, [vi], **16**, 44—47).—Attempts to repeat Morgan and Burstall's prep. (cf. A., 1931, 234) of [Ag 3 dipy]$(NO_3)_2$ failed, the complex never containing more than 2 mols. of dipyridyl for 1 atom of Ag. By the anodic oxidation of Ag salts in acid solution in presence of dipyridyl the following complex *salts* of Ag^{II} were obtained: [Ag 2 dipy]$(NO_3)_2$, [Ag 2 dipy]$(ClO_4)_2$, and [Ag 2 dipy]$(SO_4H)_2$. O. J. W.

Silver plating. E. B. Sanigar.—See B., 1932, 1085.

Influence of magnetic field on electrolysis of nickel salts. H. Forestier (Compt. rend., 1932, **195**, 954—957; cf. A., 1930, 1002).—A field of 5200 gauss causes considerable retardation in the rate of deposition of Ni from 0·61% aq. $NiSO_4$ when $p_H < 2·3$, and stops it entirely for $p_H < 1$. For higher p_H there is slight acceleration. With increasing field and p_H 1·2 the rate decreases asymptotically to a min. With salts of Zn or Cu there is slight acceleration for all p_H. This enables Ni and Cu to be separated in solutions of p_H 1—2. C. A. S.

Gold plating solutions. O. Sizelove.—See B., 1932, 1085.

Possibility of use of chromium anodes in chromium plating. J. Korpium.—See B., 1932, 1085.

High-acid chromium [electrodeposition] process. Rassow and L. Wolf.—See B., 1932, 1085.

Distillation cathodes. W. Hinsch (Z. tech. Physik, 1931, **12**, 528—541; Chem. Zentr., 1932, i, 1757).—The emission of cathodes of Ba-coated Pt wires has been investigated. L. S. T.

Photochemical reaction of hydrogen and chlorine. A. J. Allmand and H. C. Craggs (Nature, 1932, **130**, 927).—Normal reaction rates are obtained even when special precautions to eliminate H_2O are taken. L. S. T.

Photochemical formation of hydrogen peroxide. A. L. Marshall (J. Amer. Chem. Soc., 1932, **54**, 4460—4461).—The quantum efficiency of the formation of H_2O_2 photosensitised by Hg is 2·5 and not 6·6 as previously reported (A., 1928, 30). Contrary to the observations of Frankenburger and Klinkhardt (A., 1932, 348), at least 75% of the product from moist H_2–O_2 mixtures is H_2O_2. J. G. A. G.

Photochemical reaction between bromine and potassium oxalate in visible and ultra-violet light. A. K. Bhattacharya, O. Prakash, and N. R. Dhar (Z. anorg. Chem., 1932, **209**, 139—144).—The reaction velocity is proportional to $I^{1/5}-I$ (where I is the intensity of the light), the temp. coeff. is > 1, and the quantum yield high. With increasing acceleration of the reaction the temp. coeff. falls, the quantum yield is increased, and the index of I reduced. Infra-red and red radiations accelerate the reaction probably by loosening the Br–Br linking.

Photochemical reduction of carbon dioxide. M. REGGIANI (Helv. Chim. Acta, 1932, **15**, 1383—1390).—Contrary to the observations of Rajvansi and Dhar (A., 1932, 480), exposure of CO_2 to sunlight or artificial light in presence of different optical sensitisers and of various inorg. and org. reducing agents for periods up to 48 hr. did not lead to the production of detectable quantities of CH_2O, HCO_2H, or CO. Negative results were also obtained when the CO_2 was in the form of K or Ca H carbonates or an aromatic org. acid. F. L. U.

Photochemical studies. XV. Germane. Decomposition of ammonia sensitised by mercury vapour. H. ROMEYN, jun., and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1932, **54**, 4143—4154).—GeH_4 does not absorb light of λ 7000—2100 Å., but radiation transmitted by a thin layer of quartz causes decomp. The unsensitised and Hg-sensitised decomp. conform approx. to the equation $GeH_4 = Ge + 2H_2$, but there is a deficiency of H_2 evolved, probably owing to adsorption. The sensitised reaction is approx. of first order and is not affected by added H_2 or N_2. The mechanism is discussed, and probably involves the initial formation of GeH_3 and H. J. G. A. G.

Photochemistry of phosphine. H. W. MELVILLE (Proc. Roy. Soc., 1932, **A**, **138**, 374—395).—The Hg-photosensitised decomp. of PH_3 has been studied and the kinetics of the reaction are compared with those of NH_3. From an investigation of the influence of the pressure of PH_3, H_2, O_2, and A on the reaction the following mechanism is suggested: the PH_3 mol. is dissociated, in the first place, by collision with excited Hg atoms into at. H and a residue which is probably PH_2. The dissociation products diffuse to the walls of the vessel, where they may recombine, as is shown by the fact that the reaction is retarded by at. H. Formation of PH_3 from red P or P vapour and at. H could not be detected. The lowering of the explosion limit of PH_3–O_2 mixtures by illumination with a Hg arc is due to a surface effect. The O_2 first attacks the products of dissociation, thus accelerating the rate of decomp., and the oxide mol. so formed (probably a P oxide) initiates a stable chain reaction between the remaining PH_3 and O_2, as is shown by the acceleration of this reaction by A. The effect can be reproduced by pretreatment of the walls of the tube with at. H. L. L. B.

"After effect" and "induction period" in the reversible photochemical reduction of tungstic acid sol. S. GHOSH and A. K. BHATTACHARYA (Bull. Acad. Sci. Agra and Oudh, 1932, **2**, 29—32).—A period of induction is observed in the photochemical reduction of tungstic acid by glucose and the reaction is of zero order (cf. A., 1930, 1533). On placing the reduction product in the dark, reoxidation takes place, but the rate of reaction, also zero-mol., is at first reduced owing to the "after effect" (cf. A., 1928, 720) or continuation of reduction in the dark after exposure to light. In an atm. of CO_2 the reaction is still zero-mol., but the rate is considerably increased. There is no reoxidation in the dark, but the "after effect" continues for some time, a stationary state being reached before reduction is complete. Reoxidation in the first case is apparently due to the presence of air and not to a reversal of the reaction. M. S. B.

Photoanisotropic effect (Weigert effect) with dyes. II. T. KONDO (Z. wiss. Phot., 1932, **31**, 185—199; cf. A., 1932, 1214).—Benzopurpurin, rhodulin-violet, orthochrome, pinacyanol, and metanil-yellow in collodion or gelatin emulsions have been examined in detail. With decreasing wave-length of activating polarised light, the max. of dichroism moves to shorter wave-lengths, but the max. dichroism obtainable is at a longer wave-length than the spectral absorption max. With orthochrome, the shape of the dichroism curve alters with the wave-length of activation. Metanil-yellow shows both dichroism and strong double refraction, the max. of the latter being at a longer wave-length. Circularly polarised light has no effect. The effects vary greatly from collodion to gelatin emulsions. J. L.

Activation of nuclei. LUPPO-CRAMER (Z. wiss. Phot., 1932, **31**, 200—202).—So-called "Siede-emulsionen" (neutral, *i.e.*, free from NH_3, during ripening) and certain special emulsions (cf. A., 1931, 579, 806) are activated by immersing, before exposure, in 0·5% aq. NaOH, or in 1% aq. NH_3 (then washing for 1 hr. and drying). Treatment of these activated plates, after exposure and before development, with a solution of 2% KBr+2% H_2SO_4, or 2% KBr+0·3% H_2O_2, or with $(NH_4)_2S_2O_8$ solution causes some destruction of the latent image and considerable fog. J. L.

Desensitising [with] sensitisers. LUPPO-CRAMER (Z. wiss. Phot., 1932, **31**, 203—207).—The Capri-blue effect (cf. B., 1932, 162; A., 1931, 806) also appears with physical development; methylene-blue, phenosafranine, and Janus-green B behave similarly. Ordinary diapositive plates treated with Capri-blue solutions are increasingly desensitised to white light at concns. $> 1 : 10^7$, but they are sensitised to red light at concns. of 1 : 20,000 to $1 : 10^9$, with a max. between $1 : 2 \times 10^6$ and $1 : 10^7$. Erythrosin and neocyanine (ællocyanine) solutions behave similarly, the latter sensitising to a high degree for red and infra-red light at a concn. of $1 : 10^6$. J. L.

Lattice disturbances. LUPPO-CRAMER (Z. wiss. Phot., 1932, **31**, 208—209). Gelatin emulsions of HgI_2 are only slightly light-sensitive; addition of TlI sensitises the emulsion up to 50° E.-H., developed in metol–quinol, or, better, amidol. Addition of Na_2CO_3 to amidol developer causes fogging and reversal. Immersing plates in 3% $NaNO_2$ or $NaHSO_3$ solution has no sensitising effect. J. L.

Hypersensitisation. III. Influence of silver ions on the spectral sensitivity of dyed [sensitised] silver bromide plates [emulsions]. J. I. BOKINIK and Z. A. ILJINA (Z. wiss. Phot., 1932, **31**, 210—215; cf. A., 1932, 581).—Slow plates were sensitised with dyes and hypersensitised with 0·01% $AgNO_3$ solution. Acid dyes, which do not sensitise, are not hypersensitisable. Plates sensitised with basic dyes, *e.g.*, pinacyanol, pinachrome, fuchsin, auramine, etc., are mostly hypersensitised over the same spectral region. Plates desensitised with pina-cryptol-yellow or -green are nevertheless resensitised

and hypersensitised by $AgNO_3$. These results support the theory that metallic Ag is produced by photochemical decomp. of Ag ion–dye complex. J. L.

Photochemical reaction involving zinc oxide and oxygen. J. McMorris and R. G. Dickinson (J. Amer. Chem. Soc., 1932, **54**, 4248—4252).—NO_2 and not O_3 (A., 1932, 130) was found in O_2 which had passed over ZnO [prepared from $Zn(NO_3)_2$] strongly irradiated with near ultra-violet light from a Hg arc. Visible radiation is ineffective. J. G. A. G.

Decompositions by light in aqueous solutions. I. Decomposition of trichloroacetic acid and ferric thiocyanate. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1932, **209**, 123—128).—The rate of decomp. of $CCl_3{\cdot}CO_2H$ (I) and $Fe(CNS)_3$ (II) in light of various wave-lengths has been measured at 15—55°; the temp. coeff. is > 1, but decreases with increasing rate of decomp. The quantum yields of photochemical decomp. are high and increase with rise in temp. and acceleration of the reaction. The relation between the rate of decomp. and the light intensity or absorbed radiation varies from $I^{1/3}$ to I for (I) and from $I^{1/4}$ to I for (II). In presence of H_2O light seems to loosen the C·Cl, C·O, and C:N (in presence of $Fe^{\cdots}$) linkings, so that decomp of (I) is accelerated in visible, and decomp. of (II) in red and infra-red, light. A. R. P.

Photobromination of benzene. E. Rabinowitsch (Z. physikal. Chem., 1932, **B**, **19**, 190—202).—The quantum yield is 0·4—0·9 at room temp., and its temp. coeff. is 1·6. It varies little with the light intensity or the wave-length between 3000 and 5500 Å., although there is a fall on approaching the dissociation limit of Br, and it increases with the Br concn. The dissolved Br mols. are attached to C_6H_6 mols., with which they react on light absorption. $C_6H_6Br_6$ is formed chiefly by reaction of the activated Br mols. PhBr results from the reaction with free Br atoms: $C_6H_6+Br=Ph+HBr$, $Ph+Br_2=PhBr+Br$, the former of these requiring thermal activation, which accounts for the high temp. coeff. of the photochemical reaction and the disappearance of the temp. coeff. on dilution with CCl_4 (cf. A., 1929, 1153). A monochromator giving light of considerable intensity is described. R. C.

Radio-sensitivity from a chemical viewpoint. G. Harker (J. Cancer Res. Comm., Sydney, 1932, **4**, 109—117).—When Pd deposited on C is exposed to X-rays in an atm. of H_2 a reaction is sometimes initiated which yields MeNC. Once started, the reaction proceeds to completion after the rays are switched off if conditions are favourable, and under some conditions it occurs without X-ray treatment. A. G.

Liquefaction of helium. F. Simon (Z. ges. Kälte-Ind., 1932, **39**, 89—90; Chem. Zentr., 1932, ii, 578).—He released from an insulated vessel at 50 atm./12° abs. is quickly cooled to the b.p. and about 50% of the He remains liquefied in the vessel. By diminution of pressure a temp. of $< 2°$ abs. is easily reached. A. A. E.

Preparation of liquid hydrogen with neon as intermediary. K. Clusius (Z. ges. Kälte-Ind., 1932, **39**, 94—97; Chem. Zentr., 1932, ii, 579).—Ne is cooled in liquid air and expanded from 190 atm., whereby it is partly liquefied and is used to effect the liquefaction of H_2. The process is considered thermodynamically. A. A. E.

Fixation of hydrogen by highly-dispersed metals. Synthesis of ammonia. E. Müller and K. Schwabe (Z. Elektrochem., 1932, **38**, 861—868).—On shaking with H_2, liquid Zn amalgam absorbs H_2, forming a greyish-yellow solid. Zn also combines with H_2, when it is distilled with NaCl in H_2 at low pressure, using Frankenburger's method (A., 1931, 1120) with improved technique. Under these conditions, W did not distil and no H_2 was absorbed. Frankenburger's results on Fe were confirmed. Traces of NH_3 are formed when the experiment is conducted in an atm. of N_2+H_2. Palladised $BaSO_4$ catalyses the reaction $N_2+3H_2=2NH_3$ at room temp. D. R. D.

Relative stability of copper derivatives of β-diketo-compounds. T. S. Moore and (Miss) M. W. Young (J.C.S., 1932, 2694—2709).—The equilibria existing between β-diketo-compounds and the Cu derivatives of other diketo-compounds, together with the equilibria between two Cu derivatives, have been studied mainly in C_6H_6 solution. The results are quantitatively consistent with the equations $CuA_2+HB \rightleftharpoons CuAB+HA$; $CuAB+HB \rightleftharpoons CuB_2+HA$, and $CuA_2+CuB_2 \rightleftharpoons 2CuAB$. The vals. of the equilibrium consts. indicate that the co-ordinating affinity of the β-diketo-compounds in their Cu derivatives follows the same order as the percentage of enol contained in the pure compounds. No evidence was obtained of the existence of compounds, such as CuA_2,HB, containing 6-covalent Cu. F. J. W.

[Explosive decomposition of alkaline ammoniacal silver solutions.] W. Coltof (Chem. Weekblad, 1932, **29**, 737).—An alkaline NH_3–Ag solution prepared exactly as described by Tollens (A., 1882, 1329) exploded violently within 1 hr., when the containing vessel was moved, although no ppt. and the merest trace of film were present (cf. A., 1932, 582). S. C.

New complex compounds of silver cyanide with sodium cyanide. G. A. Barbieri and A. Tettamanzi (Atti R. Accad. Lincei, 1932, [vi], **15**, 965—967).—$NaAg(CN)_2$ and the *compounds* $Na_2Ag(CN)_3,3H_2O$ and $Na_3Ag(CN)_4,5H_2O$ separate on crystallising a solution of AgCN in aq. NaCN. D. R. D.

Cæsium polybromides. I. W. H. Harris (J.C.S., 1932, 2709—2713).—The system CsBr–Br–H_2O has been examined at 0° and 25°. The only polybromide existing at both temp. is $CsBr_3$. Fresh evidence is given confirming the formula $Br_2,10H_2O$ for Br hydrate. F. J. W.

Ternary compound $4CaO,Al_2O_3,Fe_2O_3$. S. Solacolu (Zement, 1932, **21**, 301—305; Chem. Zentr., 1932, ii, 851).—The existence of brown-millerite, $4CaO,Al_2O_3,Fe_2O_3$, is confirmed. The substance is stable in presence of excess of CaO. Its isomorphism with $2CaO,Fe_2O_3$ is confirmed. A. A. E.

Reaction between calcium oxide and silica in relation to the hardening of Portland cement. A. J. P. VAN DER BURGH (Chem. Weekblad, 1932, **29**, 616—618).—When CaO is added to SiO_2 gel in contact with H_2O the CaO concn. of the solution remains approx. const. at 0·002*M* until the gel has absorbed about 0·9 mol. of CaO per mol., and thereafter rises rapidly until the ratio $CaO : SiO_2$ in the solid phase is about 1·4 : 1. The voluminous product does not change with time. The reactions at the membrane formed when $Ca(OH)_2$ solution is brought into contact with SiO_2 are discussed in their bearing on the hardening of Portland cement. H. F. G.

Hydrothermal synthesis of calcium silicates under ordinary pressure. VI. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, **35**, 439—443B; cf. A., 1932, 1007, 1008).—$CaSiO_3$ is obtained by heating CaO and SiO_2 (1 : 1) at or above 1200°. Ca_2SiO_4 is produced by heating CaO and SiO_2 (2 : 1) at or above 1250°. $Ca_3Si_2O_5$ is formed under intermediate conditions, but is mixed with other silicates from which separation is difficult. E. S. H.

Synthetic bianchite. C. ANDREATTA (Atti R. Accad. Lincei, 1932, [vi], **16**, 62—69; cf. A., 1930, 1397).—By crystallisation at 30° from a solution containing $ZnSO_4$, $FeSO_4$, and H_2SO_4, $(Zn,Fe)SO_4,6H_2O$, which has approx. the composition of natural bianchite, was obtained. The green transparent monoclinic crystals have *H* 2—3, *d* 2·031+0·005. Crystallographic and optical data are given. O. J. W.

Alkaline-earth silicides. L. WÖHLER and W. SCHUFF (Z. anorg. Chem., 1932, **209**, 33—59; cf. A., 1926, 368).—The *compounds* SrSi and BaSi are obtained from the elements by brief heating at 1000° and subsequent quenching. By heating at 1200—1400° the above are converted slowly, and CaSi readily, into the disilicides. The latter are also produced from Si and the corresponding oxides or peroxides by Goldschmidt's method. Ba also forms the *compound* $BaSi_3$, and the existence of still higher silicides is probable. The chemical behaviour of the compounds has been studied. The following heats of formation were determined: CaSi 85·3, $CaSi_2$ 161·5, SrSi 112·8, $SrSi_2$ 147·4, BaSi 181·5, $BaSi_3$ 399·2 kg.-cal. Observations on the thermal decomp. of Ca, Sr, and Ba oxalates are recorded. F. L. U.

Action of ammonia on mercurous chloride. C. RENZ (Helv. Chim. Acta, 1932, **15**, 1316—1320).—The grey residue left after dissolving NH_2HgCl by aq. HCl from Hg_2Cl_2 which has been blackened in aq. NH_3 is but slightly attacked by dil. or conc. HNO_3. A second treatment with aq. NH_3 produces further blackening. The product is regarded as a "photochloride" consisting of Hg finely dispersed in unchanged Hg_2Cl_2. F. L. U.

Potassium iodomercurate. F. GALLAIS (Compt. rend., 1932, **195**, 875—878).—The conductivity curve of mixed solutions, 0·01*M*, of KI and $HgCl_2$ indicates a min. for $KI+0·22HgCl_2$ when the solvent is H_2O, but for $KI+0·25HgCl_2$ in EtOH, and in both cases a second discontinuity for $KI+0·50HgCl_2$. It is concluded that K_2HgI_4 is formed but destroyed immediately without formation of $KHgI_3$ (cf. A., 1928, 20): $0·25K_2HgI_4+0·25HgCl_2=0·50HgI_2+0·50KCl$. The limit mol. conductivity of the iodomercurate indicates formation of three ions, $2K^{\cdot}+HgI_4''$ (cf. A., 1921, ii, 57; 1925, ii, 887); moreover, $AgNO_3$ ppts. Ag_2HgI_4 from EtOH solution of the iodomercurate. Although the anion HgI_4'' predominates in a solution of iodomercurate it must be capable of furnishing compounds in which the anion contains only I_3 (cf. A., 1931, 1318). C. A. S.

Chlorination of aluminium oxide with chlorine and carbon monoxide. W. D. TREADWELL and L. TEREBESI (Helv. Chim. Acta, 1932. **15**, 1353—1362).—The rate of chlorination of γ-Al_2O_3 has been studied in the range 325—980°. The course is autocatalytic up to 800°, the more markedly so the lower is the temp. Above 800° the curve is linear until the solid is nearly used up. The velocity–temp. curves show a max. at about 550° and a min. at about 650°, the latter corresponding with transformation of γ-Al_2O_3 into the less reactive α-form. The observed autocatalysis is attributed to formation of active C at the reacting surface. When $COCl_2$ is used the reaction is more rapid and also shows max. velocity at 550°. F. L. U.

Structure of kaolins from the viewpoint of the chemistry of ultramarine. I. Action of dealkalising factors on sodium kaolinates. M. DOMINIKIEWICZ (Rocz. Chem., 1932, **12**, 836—853).—$Na_6Al_6Si_6O_{24}$ (I) and $Na_{12}Al_6Si_6O_{27}$ (II) have been prepared from kaolin and Na_2CO_3. Thugutt's nepheline hydrate (cf. A., 1911, ii, 298) is identical with the trihydrate of (I). Na cannot be removed from (I) by treatment with SO_2Cl_2, AcCl, Ac_2O, AcOH, S, NH_4Cl, SO_2, and H_2S at red heat; HCl at 175° converts it into $Na_4Al_6Si_6O_{23}$ (III). (II) is converted by SO_2Cl_2, AcCl, and Ac_2O into $Na_8Al_6Si_6O_{24}$, which yields (I) with S, NH_4Cl, or HCl at 110°, and this, as before, gives (III) on treatment with HCl at 175°, whilst the trihydrate of (I) yields that of (III) under similar conditions. The above results support the view that the basis of all aluminosilicates is hexa-aluminosilicic acid, and that this acid possesses three types of OH groups, of different acidity. The existence of the compound $Na_8Al_6Si_6O_{22\cdot5}$, described by Silber (A., 1881, 684) is not confirmed. R. T.

Separation of rare earths by basic precipitation. X. Preparation of pure ytterbium oxide. W. PRANDTL (Z. anorg. Chem., 1932, **209**, 13—16; cf. A., 1931, 813).—Yb can be separated from Tm and Lu by repeated electro-reduction of $Yb_2(SO_4)_3$ to the slightly sol. $YbSO_4$. Details are given. F. L. U.

Acid fluorides of thallium and ammonium and their mixed crystals. O. HASSEL and H. KRINGSTAD (Z. anorg. Chem., 1932, **208**, 382—386; cf. A., 1930, 1099).—The substance obtained by crystallising a solution of TlF in excess of aq. HF at room temp. is shown by analysis to be $H_2TlF_3,0·5H_2O$. The *compound* $H_2(NH_4)F_3,0·5H_2O$ can be similarly prepared. The two salts form a continuous series of mixed crystals. F. L. U.

Active charcoal. E. LANDT (Kolloid-Beih., 1932, **37**, 1—55).—A survey of published work on prep.,

chemical composition, electrical conductivity, wettability, apparent and true sp. gr., heat of wetting, sedimentation vol., porosity, surface development, electric charge, isoelectric point, coagulation and peptisation, and adsorption of acids, bases, salts, org. electrolytes, and non-electrolytes. Application to the sugar industry is discussed. E. S. H.

Transformation of amorphous carbon into graphite. H. ISHIKAWA (Elec. Rev., Japan, 1931, **19**, 419, 493, 690, 726, 824, 884).—Graphitisation of amorphous C with 8% SiO_2 at 1850° for 24 hr. affords 77—80% of graphite. Experiments with C and 5% of SiO_2, Al_2O_3, Fe_2O_3, and WO_3 gave higher % of graphitisation than those with C free from these oxides (about 30% yield). Transformation of amorphous C into graphite probably takes place around impurities as nuclei. CH. ABS.

Nitrogen compounds of germanium. III. Germanous imide. W. C. JOHNSON, G. H. MOREY, and A. E. KOTT (J. Amer. Chem. Soc., 1932, **54**, 4278—4284).—GeI_2 is prepared by the interaction of GeS with conc. HI, and crystallised from the solution at −80°. With precautions, gaseous NH_3 at −33·5° reacts quantitatively with GeI_2 thus: $GeI_2+3NH_3=GeNH+2NH_4I$. GeNH is insol. in liquid NH_3, reacts with H_2O or dil. NaOH to give NH_3 and $Ge(OH)_2$, and reacts violently with O_2. J. G. A. G.

Separation of hafnium and zirconium. I. W. PRANDTL (Z. anorg. Chem., 1932, **208**, 420—426; cf. A., 1931, 813).—A solution of mixed ZrO_2 and HfO_2 in dil. H_2SO_4 containing $H_2C_2O_4$ is treated with $Na_4Fe(CN)_6$, when the ppt. contains a greater proportion of Hf than the original mixture. F. L. U.

Basic lead salts. P. JOLIBOIS and L. CLOUTIER (Compt. rend., 1932, **195**, 795—796).—Using the method previously described (cf. A., 1920, ii, 107) addition of aq. $Pb(NO_3)_2$ to aq. $K_2Cr_2O_7$ containing increasing amounts of KOH gives successively $PbCrO_4$, $PbCrO_4$,$Pb(OH)_2$, and $PbCrO_4$,$2Pb(OH)_2$ (cf. A., 1906, ii, 757). Similarly the following only were obtainable: $2PbCO_3$,$Pb(OH)_2$, $PbCl_2$,$Pb(OH)_2$, $PbCl_2$,$6Pb(OH)_2$, $PbSO_4$,$3Pb(OH)_2$, $2SiO_2$,$3Pb(OH)_2$, B_2O_3,$Pb(OH)_2$, and $2B_2O_3$,$7Pb(OH)_2$. No basic iodide was obtained (cf. A., 1904, ii, 258). C. A. S.

Principles of the genetic development of material. VII. Conversion of lead oxide into carbonate. Chemistry and morphology of white lead. V. KOHLSCHÜTTER [with H. HOSTETTLER] (Helv. Chim. Acta, 1932, **15**, 1425—1449; cf. A., 1932, 131).—The course of the reaction and the nature of the product obtained when PbO is acted on by CO_2 and H_2O under various conditions have been studied by measurements of vol. change, p_H of liquid, by chemical and *X*-ray analysis, and by microscopical examination. Products approximating to white lead were obtained only when the PbO was in a finely-dispersed form. The reaction is considered to take place in a layer of solution adherent to the particles, and to be preceded by a local peptisation of the PbO. The character of the product is largely determined by the concn. of CO_2. F. L. U.

Thorium sulphide. PICON (Compt. rend., 1932, **195**, 957—959; cf. A., 1930, 582).—ThS_2, prepared by passing H_2S over ThO_2 in a graphite boat at 1600°, black, vitreous, has d_0^{θ} 7·234, m.p. 1925±25°, at which temp. it is slightly volatile. On heating in vac., S is evolved at 2800°, ThC_2 being formed from the graphite of the crucible. Cl_2 attacks it at 250°; Br, if moist, slowly at room temp.; O_2 at 400°; aq. HF and (slowly) aq. HCl at room temp.; dry HCl at 300°; SO_2 at 400° forms S and ThO_2; conc. H_2SO_4 has no action, but dil. acid gives $Th(SO_4)_2$; 10% HNO_3 gives $Th(NO_3)_4$; CO_2 above 440° gives $ThO_2+2CO+S$; Mg has no action at 800°. Aq. NaOH has very little action in the cold; fused NaOH attacks it rapidly. $K_4Fe(CN)_6$ at room temp. gives ThO_2 and S, but H_2O_2 and $KMnO_4$ form $Th(SO_4)_2$. C. A. S.

Hyponitrites. II. Metallic salts. III. Esters. J. R. PARTINGTON and C. C. SHAH (J.C.S., 1932, 2589—2597).—The hyponitrites of Ca, Sr, and Ba decompose on heating, forming chiefly the monoxide, N_2, and N_2O, together with some nitrite and nitrate, and NO. The hyponitrites of Pb and Cu do not give any nitrite or nitrate. Alkalis convert them partly into hydroxides; acids give chiefly N_2O. $KMnO_4$ and NaOCl oxidise them incompletely to nitrates. Mol. wt. determinations on C_6H_6 solutions of Et, Pr, Bu, and CH_2Ph esters of $H_2N_2O_2$ indicate the formula $R_2N_2O_2$. They decompose at temp. as low as 15°, giving N_2. H_2O, alkalis, and acids produce hydrolysis to the alcohol, aldehyde, and N_2. Reducing agents give alcohol and N_2. F. J. W.

Basic phosphates. P. JOLIBOIS and L. CLOUTIER (Compt. rend., 1932, **195**, 1027—1029; cf. this vol., 38).—Similar methods failed to yield any basic phosphate of Pb, Cu^{II}, Fe^{III}, Al, Zn, Ag, Mn, Cr, or U, the tribasic salt only being formed mixed with varying amounts of the hydroxide, or, if NaOH was in great excess, the hydroxide only. C. A. S.

Ammonolysis of antimony trichloride. R. SCHWARZ and A. JEANMAIRE (Ber., 1932, **65**, [*B*], 1662—1664; cf. A., 1932, 1100).—$SbCl_3$ absorbs rather more than 3 mols. of NH_3 without appearing to yield a definite ammonate. The initial product appears to be Sb(NH)Cl which, when washed with liquid NH_3 (for removal of NH_4Cl), continuously loses Cl until finally orange SbN remains. It is unusually sensitive to moisture. Decomp. into Sb and N commences at 500° and is complete at 750°. H. W.

Desulphurisation of antimony trisulphide with carbon monoxide. E. V. BRITZKE and M. V. ZAETEV.—See B., 1932, 1077.

Sulphurous acid and its salts. XII. Action of hydrogen sulphide on potassium hydrogen sulphite solutions. F. FOERSTER and O. SCHMITT (Z. anorg. Chem., 1932, **209**, 145—174).—The reaction products of H_2S and 0·5*M*-$KHSO_3$ under various conditions comprise S_2O_3'', S_3O_6'', S_4O_6'', S_5O_6'', SO_4'', S (ppt.), and $H^{\cdot}$, and evidence is adduced to show that their formation can be explained on the assumption of the existence of the intermediate compound SO. Curves showing the proportion of the above substances produced under different conditions and methods of analysing the solutions are given. A. R. P.

Thionitrososulphonium chloride, $(SN)_3SCl$ (thiotrithiazyl chloride). A. MEUWSEN (Ber., 1932, **65**, [*B*], 1724—1733).—$(SN)_3SCl$ is obtained in 90% yield by digestion of S_4N_4 (purified by sublimation in high vac.) with S_2Cl_2 in CCl_4 or by the action of excess of $SOCl_2$ on S_4N_4; poor yields of impure product are obtained from S_4N_4 and AcCl. Since the presence of 4 SN groups in S_4N_4 and $(HSN)_4$ is regarded as established and these do not suffer disruption under the action of Cl, it is assumed that they are present in S_4N_3Cl formed by the much milder action of S_2Cl_2. The product is therefore considered to be thionitroso- or *iso*thiazyl-sulphonium chloride. This conclusion is strengthened by its stability to Cl, which demonstrates the absence of S·S linkings, by the quant. evolution of N as NH_3 when acted on by alkali and by absence of separation of I after addition of KI. Cautious warming of $(NSCl)_3$ with S_2Cl_2 gives the very unstable, rust-brown $N_2S_3Cl_2$, which regenerates $(NSCl)_3$ when treated with Cl_2 in CCl_4 and passes, when heated with S_2Cl_2 in CCl_4, into $(SN)_3SCl$; the last-named substance is also obtained directly by prolonged warming of $(NSCl)_3$ with S_2Cl_2 in CCl_4. The reactions of $N_2S_3Cl_2$ are readily explained by the constitution $(NS)_2SCl_2$. H. W.

Chemically different and differently-coloured chromic hydroxides. A. HANTZSCH and E. TORKE (Z. anorg. Chem., 1932, **209**, 60—94).—When aq. $[Cr(H_2O)_6]Cl_3$ is added to 2*N* aq. NH_3 containing 25% NH_4Cl at room temp. a bright bluish-green ppt. (*A*), readily sol. in dil. HCl, AcOH, or NaOH, is obtained. Similar treatment of aq. $[Cr(H_2O)_4Cl_2]Cl,2H_2O$ yields a dark green ppt. (*B*) of the same empirical composition, $Cr(OH)_3,3H_2O$, but less readily sol. in the above reagents. The acid solutions of (*A*) are blue, of (*B*) green. On dehydration both (*A*) and (*B*) give the same green $Cr(OH)_3,H_2O$, but the isobaric dehydration curve is stepped with (*A*) and continuous with (*B*). (*A*) is completely converted into (*B*) when left for 8—10 months at room temp. (*A*) does and (*B*) does not react with 100% AcOH or Ac_2O. From their chemical behaviour the constitution of (*A*) appears to be $Cr(OH)_3,3H_2O$, and of (*B*) $[Cr(H_2O)(OH)_3],2H_2O$. No hydrate with a larger proportion of H_2O could be isolated. F. L. U.

Bivalent chromium compounds. G. A. BARBIERI and A. TETTAMANZI (Atti Accad. Lincei, 1932, [vi], **15**, 877—882).—The following *compounds* are described: $[Cr(C_{10}H_8N_2)_3]Br_2,6H_2O$, from 2:2′-dipyridyl, $Cr(OAc)_2$, and NaBr; $[Cr(C_{10}H_8N_2)_3](ClO_4)_3$; $Cr(SCN)_2,2(C_6H_{11}N_4,HSCN)$, from $(CH_2)_6N_4$,HSCN and $Cr(OAc)_2$, and the analogous *Fe* and *Mn* derivatives; $CrCl_2,2HCl,C_6H_{12}N_4,4H_2O$, and the corresponding *Mn*, *Ni*, *Fe*, and *Co* compounds. H. F. G.

Permolybdates and pertungstates and the structure of perchromates. A. ROSENHEIM, M. HAKKI, and O. KRAUSE (Z. anorg. Chem., 1932, **209**, 175—203).—Alkali and alkaline-earth molybdates and tungstates dissolved readily in 30% H_2O_2 at 0°, giving blood-red and pale yellow solutions, respectively, from which the following *compounds* have been isolated: K_2MoO_8, $K_2WO_8,0{\cdot}5H_2O$, $Rb_2WO_8,3H_2O$, Na_2WO_8,H_2O, $BaWO_8,4H_2O$; all these compounds explode on rubbing or warming. The following stable *compounds* have been prepared in a similar way from polymolybdates and polytungstates:

$5(NH_4)_2O,12MoO_3,12O,21H_2O$,
$5(NH_4)_2O,12MoO_3,3O,12H_2O$,
$5(CH_6N_3)_2O,12MoO_3,3O,11H_2O$,
$5(CH_6N_3)_2O,2MoO_3,3O,3H_2O$,
$5BaO,12MoO_3,3O,18H_2O$, $5Ag_2O,12MoO_3,3O,12H_2O$,
$BaO,2MoO_3,4O,4H_2O$, $K_2O,2MoO_3,4O,4H_2O$,
$K_2O,3MoO_3,4O,H_2O$, $K_2O,3MoO_3,O,4H_2O$,
$K_2O,2WO_3,4O,4H_2O$, $BaO,2WO_3,4O,8H_2O$,
$(CH_6N_3)_2O,2WO_3,4O,H_2O$. From RC_2O_4, H_2MoO_4 and H_2O_2 at 0° *compounds* of the type RC_2O_4, H_2MoO_4,2O [R=Ba, K_2, or $(NH_4)_2$] and $K_2C_2O_4,MoO_5$, have been prepared. Corresponding W *derivatives* of K_2, $(NH_4)_2$, Rb$_2$, Ba, and $(CH_6N_3)_2$ are also described. The constitution of the above compounds and of perchromates is discussed and it is concluded that in all cases the metal atom is sexavalent, the permolybdates and pertungstates having the formula $(O_2)_2{:}M{:}(O_2R)_2$, the perchromates the formula $(O_2){:}[Cr(:O){:}(O_2K)_3]_2$, and the oxalato-complexes the formula $R_2[(O_2)_2M(C_2O_4)(H_2O_2)]$ (M=W or Mo). A. R. P.

Oxidations with fluorine. XIX. Action of fluorine on aqueous solutions of ammonia and of ammonium carbonate. F. FICHTER and A. GOLDACH (Helv. Chim. Acta, 1932, **15**, 1511—1520; cf. A., 1931, 1022).—Passage of F_2 through aq. NH_3 at temp. between −8° and 35° gives rise to O_2, N_2, N_2O, NH_4NO_2, and N_2H_4. Aq. $(NH_4)_2CO_3$ yields NH_4NO_3 in addition to the above No NH_2OH could be detected. Yields of all products were quantitatively determined. A mechanism is suggested whereby all the observed products can be accounted for by assuming the initial reaction $NH_3+F_2=2HF+{\cdot}NH{\cdot}$. F. L. U.

p_H values of hypochlorite solutions. L. P. LYNCH and C. R. NODDER (J. Text. Inst., 1932, **23**, 309—318T).—The excess of alkali present in stock solutions of NaOCl may be determined after decomp. of the OCl′ with neutral H_2O_2, but the p_H val. of dil. solutions cannot, in general, be determined after such decomp. A simple method of finding the approx. p_H vals. of dil. hypochlorite liquors is described. Equations are evolved from which the shift in p_H val. produced by adding the Na or K salt of a weak acid to a buffer solution may be determined. The shifts observed on addition of several of such salts to OAc′ and PO_4''' buffers, and the calc. vals. for the effect of the addition of NaOCl, are recorded. A method of determining the dissociation const. of a weak acid is indicated. B. P. R.

Anti-corrosive effect of addition of water-glass to bromine water, chlorine water, or bleaching-powder solutions. H. BOHNER (Hausz. V.A.W. Erftw. Aluminium, 1931, **3**, 347—348; Chem. Zentr., 1932, i, 1823).—The corrosion of Al, silumin, or lautal by Cl_2-H_2O or Br-H_2O is markedly diminished by the presence of 0·5 or 5%, respectively, of Na silicate. Attack by bleaching-powder solution is

also considerably repressed by the presence of Na silicate. A. A. E.

Thioper-rhenates. H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart (J.C.S., 1932, 2811—2812).—A correction. F. J. W.

Fluorination of rhenium. O. Ruff and W. Kwasnik [with E. Ascher] (Z. anorg. Chem., 1932, **209**, 113—122).—In a current of F at 125° Re forms ReF_6 as a colourless gas, which solidifies to light yellow crystals, m.p. 26·4°. Moisture hydrolyses ReF_6 to $HReO_4$ and ReO_2,H_2O and in contact with quartz at 20° it is slowly converted into an oxyfluoride. Most metals reduce ReF_6 to lower fluorides at 500° and eventually to metal at higher temp. No higher fluoride could be prepared. A. R. P.

Effect of silica on the dissociation of ferric oxide. J. Kleffner and E. J. Kohlmeyer (Metall u. Erz, 1932, **29**, 189—194; Chem. Zentr., 1932, ii, 974).—The conversion $Fe_2O_3 \longrightarrow Fe_3O_4$ at 1600° is unaffected by SiO_2, but Fe_3O_4 reacts with it under these conditions. Fe_3O_4 has m.p. 1580°. A. A. E.

Calcium salt of a complex ferriphosphoric acid. A. Sanfourche and B. Focet (Compt. rend., 1932, **195**, 873—875).—On adding 14 g. of $FePO_4$ to 145 g. of aq. solution of 35·4 g. of $CaH_4(PO_4)_2$ and 8·1 g. of H_3PO_4 the liquid rapidly gelatinises, but soon deposits white crystals of the complex $Ca[H_2Fe(PO_4)_2]_2$, containing 3—6% $CaHPO_4$. With less $FePO_4$ the above transformations occur less rapidly, but more so with rise in temp. The stability of the gel stage is much increased if $AlPO_4$ is substituted for part of the $FePO_4$ (cf. A., 1923, ii, 31). C. A. S.

Preparation of nickel-free cobalt salts through cobalt complexes. J. V. Dubsky and V. Dostal (Chem. Listy, 1932, **26**, 593—595).—The salts $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5OH_2]_2(SO_4)_3$, $[Co(NH_3)_4(NO_2)_2]Cl$, $[Co(NH_3)_4CO_3]_2SO_4$, $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_3(NO_2)_3]$, $[Co(NH_3)_2(NO_2)_4]K$, and $[Co(CN)_6]K_3$, prepared from Co salts containing Ni, were free from Ni, whilst $[Co(C_2O_4)_3]K_3$ and $[Co(CNS)_4]K_2$ were contaminated with Ni. R. T.

Substituted complex cobalticyanides. I. Hexapotassium dicobalti-μ-sulphito-decacyanide. P. Ray (Z. anorg. Chem., 1932, **208**, 392—396; cf. A., 1931, 1140).—An orange-red cryst. *compound*, to which the formula $K_6[(CN)_5{\cdot}Co{\cdot}SO_3{\cdot}Co{\cdot}(CN)_5]$ is assigned, is obtained by adding a solution of $CoCl_2$ saturated with SO_2 to aq. KCN cooled to −10°. The Pb, Hg^{II}, Cu^{II}, Cd, Zn, Fe^{III}, Mn^{II}, Co^{II}, and Ni^{II} *salts* are described. F. L. U.

Cobaltic pentammines. (Mme.) R. Duval (Ann. Chim., 1932, [x], **18**, 241—301).—In part a more detailed account of previous results (A., 1929, 1254; 1931, 53), including a reply to Klement (A., 1931, 1140), showing that persulphatopentamminecobaltic sulphate must possess the structure originally assigned. By application of the method previously described (*loc. cit.*) 30 types of pentamminecobaltic compounds have been prepared and are described, the following being new: *formatopentamminecobaltic dithionate* and *chloride*, $[CoCO_2H(NH_3)_5]Cl_2$; *oxalatopentamminecobaltic oxalate*, $[CoC_2O_4(NH_3)_5]C_2O_4,3H_2C_2O_4$; *tartropentamminecobaltic nitrate*, $[CoC_4H_4O_6(NH_3)_5]NO_3$, and *citratopentamminecobaltic citrate*, probably $[CoX(NH_3)_5]+[Co(XH_2)_3(NH_3)_5]+[Co(XH_2)_3(NH_3)_5]$ ($X=C_6H_5O_7$) (cf. Duff, J.C.S., 1923, **123**, 568); *chloratopentamminecobaltic chlorate*, $[CoClO_3(NH_3)_5](ClO_3)_2,2H_2O$, and *cobaltinitrite*; *perchloratopentamminecobaltic perchlorate*, $[CoClO_4(NH_3)_5](ClO_4)_2$, differing from the compound $[Co(H_2O)(NH_3)_5](ClO_4)_3$ obtained by Hassel (A., 1929, 18); *bromatopentamminecobaltic bromate*, $[CoBrO_3(NH_3)_5](BrO_3)_2$, obtained by loss of $2H_2O$ from $[Co(H_2O)(NH_3)_5](BrO_3)_3,H_2O$; *iodatopentamminecobaltic iodate*, $[CoIO_3(NH_3)_5](IO_3)_2,HIO_3$; *dithionatopentamminecobaltic dithionate*, $[CoS_2O_6(NH_3)_5]S_2O_6,2H_2O$, which reacts with $[Co(NH_3)_5Cl]Cl_2 \longrightarrow 2[CoS_2O_6(NH_3)_5]Cl$ (+$3H_2O$) + $[CoCl(NH_3)_5]S_2O_6$. With Na_3PO_4 $[Co(H_2O)(NH_3)_5](OH)_3$ (I) gives $[CoPO_4(NH_3)_5]$ (cf. Duff, *loc. cit.*, and Klement, A., 1926, 1219), but with H_3PO_4 followed by NH_4NO_3 is obtained the double *salt* $[CoH_2PO_4(NH_3)_5](H_2PO_4)_2,3NH_4NO_3$. (I) with K chromioxalate gives a *compound*, which may be $[Co(H_2O)(NH_3)_5][Cr(C_2O_4)_3]$, $[Cr(C_2O_4)_3]K_3,6H_2O$, or $[Co(NH_3)_5Cr(C_2O_4)_3][Cr(C_2O_4)_3]K_3,6H_2O$, and with K cobaltioxalate are obtained $[Co(C_2O_4)_3][Co(H_2O)(NH_3)_5]$, $[Co(H_2O)(NH_3)_5][Co(C_2O_4)_3]K_3,6H_2O$, and $[Co(C_2O_4)_3][Co(H_2O)(NH_3)_5],10H_2O$. *Aquopentamminecobaltic cobaltinitrite*, $[Co(H_2O)(NH_3)_5][Co(NO_2)_6]$, and *hexamminecobaltic formate*, $[Co(NH_3)_6](CO_2H)_3$, are also described. J. W. B.

Phosphides of nickel: reaction between phosphorus and nickel carbonyl. C. M. W. Grieb and R. H. Jones (J.C.S., 1932, 2543—2546).—P does not react with liquid $Ni(CO)_4$, but with the vapour forms a black cryst. *substance*, NiP, m.p. > 50°. It is sol. in HNO_3 and aqua regia, but insol. in HCl. Heating in air causes the loss of P and the formation of $Ni_3(PO_4)_2$. Bubbling $Ni(CO)_4$ vapour through liquid P or a solution of P in turpentine gives a black unstable *substance* containing NiP_4. F. J. W.

Nickelo-hexanitrites. M. Mousseron and R. Cariteau (J. Pharm. Chim., 1932, [viii], **16**, 382—387).—The following salts were prepared from Ni (freed from Co and AcOH) $[X=Ni(NO_2)_6]$: (*a*) hydrolysed by cold H_2O, K_4X, Na_4X, Li_4X K_2Li_2X, and K_3NaX; (*b*) stable to cold, but hydrolysed by hot, H_2O, Ca_2X, Ba_2X, Sr_2X, SrCaX, BaSrX, CaBaX, K_2CaX (+$3H_2O$, lost at 180° in vac.), K_2BaX, K_2SrX, and $Ca(NH_4)_2X$; (*c*) stability not defined, K_2MgX, K_2CdX, K_2PbX, K_2HgX, and Na_2HgX. All these salts form orange to red octahedra, and are best washed with $COMe_2$. Cuttica's results (A., 1923, ii, 77) were vitiated by washing the ppts. with EtOH–Et_2O, in which KNO_2 is insol. R. S. C.

Iridium tetrahydroxide. N. K. Pschenitsin and C. E. Krasikov (Ann. Inst. Platine, 1932, No. 9, 135—136).—$Ir(OH)_4$ is prepared from KOH and K_2IrCl_6. R. T.

Preparation of iridium tetrachloride. N. K. Pschenitsin and C. E. Krasikov (Ann. Inst.

Platine, 1932, No. 9, 133—134).—$IrCl_4$ is prepared from Cl_2 and $(NH_4)_2IrCl_6$. R. T.

Thermal decomposition of bivalent platin-ammines. A. A. GRUNBERG and B. V. PTITSIN (Ann. Inst. Platine, 1932, No. 9, 73—90).—The decomp. temp. of a no. of salts of the type $[Pt4NH_3]X_2$ diminish in the order $SO_4 < CrO_4 < Cl_2 < Br_2 < (NO_2)_2 < I_2 < (CNS)_2$, and of the type $[Pt2NH_3X_2]$ in the order: *cis*-isomeride: $Cl_2 < Br_2 < (NO_2)_2 < I_2$; *trans*-isomeride: $Br_2 < Cl_2 < I_2$. The *trans*- are more stable than are the corresponding *cis*-isomerides. Traces of H_2O greatly reduce the thermostability of the above compounds. R. T.

Green salt of Magnus and some related compounds. E. G. COX, F. W. PINKARD, W. WARDLAW, and G. H. PRESTON (J.C.S., 1932, 2527—2535).—Magnus' green salt $[Pt,4NH_3][PtCl_4]$ is pyramidal, space-group C_4^1 ($P4$), a 6·29, c 6·42±0·02 Å., with 1 mol. per unit cell; the salt is therefore not polymerised. The ions $[PtCl_4]$ and $[Pt4NH_3]$ have the same form as in K_2PtCl_4 and $[Pt,4NH_3]Cl_2$, except that the NH_3 groups in the cation are not rotating. The Pd analogue has the same structure. The supposed pink isomeride of Magnus' green salt is actually Cleve's salt, $[Pt,3NH_3,Cl]_2[PtCl_4]$. Under experimental conditions not fully understood, the true pink isomeride is obtained; this is orthorhombic, a 7·9, b 8·2, c 7·9 Å., with 2 mols. of $[Pt,4NH_3][PtCl_4]$ in the unit cell. Both pink forms are convertible into the green salt. F. J. W.

Systematic measuring out of samples as a practical help in volumetric and gravimetric analysis. P. FUCHS (Chem.-Ztg., 1932, **56**, 941—943).—In order that burette readings may be numerically equal to the percentage of the substance under determination present in the sample, the mass of sample taken should be equal to the quantity of the pure substance which would react with 100 c.c. of the solution in the burette. A similar relationship applies in gravimetric analysis, in order that the mass of ppt.=% of substance in the sample. D. R. D.

Equilibria in reduction, oxidation, and carbonisation processes in iron. XII. R. SCHENCK and T. DINGMANN (Z. anorg. Chem., 1932, **209**, 1—10).—Technique of micro-analysis of gas mixtures is described. F. L. U.

Determination of hydrogen-ion concentration. B. ELEMA (Chem. Weekblad, 1932, **29**, 638—643).—Largely a review of the characteristics of the MacInnes and Dole glass electrode. Details are given of the prep. of the electrode and of its use for small vols. of liquid. The use of the Ag|AgCl electrode is recommended; if the HCl is covered with paraffin to prevent evaporation, the potential of the glass electrode remains const. for at least 6 months. H. F. G.

New indicators for the determination of halogens by Fajans' method. L. BELLADEN and G. PIAZZA (Annali Chim. Appl., 1932, **22**, 631—637).—Using Orsella brillante C and Chromotrop F.4 C as indicators, halogen ions may be determined by Fajans' method (A., 1924, ii, 60, 776) with zero error at dilutions down to about 0·01N and with an error $\gtrsim$0·2% at dilutions to 0·003N. I′ in presence of Cl′ may be determined with zero error when KCl:KI is $\gtrsim$1 and with 0·3% error when KCl:KI=3. In presence of Orsellab rillante C, Ag is determinable exactly with standard KBr solution, either in neutral solution or in presence of HNO_3 up to N/3 concn. T. H. P.

Determination of very small quantities of bromide. Z. SZABÓ (Z. anal. Chem., 1932, **90**, 189—193).—The Br′ solution is treated with 1 g. of $KHCO_3$ and a measured vol. of Cl_2-H_2O (5 mg. Cl_2 per c.c.), the solution evaporated to dryness, and the residue dissolved in H_2O; 5 c.c. of 1% PhOH, 2—5 mg. of KI, and 5 c.c. of 20% H_2SO_4 are added, and the liberated I is titrated with 0·001N-$Na_2S_2O_3$. A correction is applied for the amount of Cl_2 used (table given). A. R. P.

Use of calcium carbonate in the determination of iodides. C. STAINIER and L. LECLERCQ (J. Pharm. Belg., 1932, **14**, 265—270; Chem. Zentr., 1932, ii, 1049).—Na phosphate interferes with the titration of I with $Na_2S_2O_3$. The solution is conveniently neutralised with $CaCO_3$. A. A. E.

Colorimetric determination of fluorine in [natural] water with ferric thiocyanate. (MISS) M. D. FOSTER (J. Amer. Chem. Soc., 1932, **54**, 4464—4465).—The complex ion formed by interaction of a fluoride and $FeCl_3$ does not give the characteristic Fe colour with NH_4CNS. By careful control of acidity, temp., and concn., the bleaching produced in $FeCl_3$–NH_4CNS solution by 0·025 mg. of F′ in 100 c.c. H_2O can be determined. J. G. A. G.

Thiosulphate solutions of permanent titre. R. A. KOLLIKER (Z. anal. Chem., 1932, **90**, 272—277).—The storage bottle, burette, and $Na_2S_2O_3$ solution are sterilised by live steam and maintained under aseptic conditions. Apparatus and procedure are described. The change in normality of solutions so prepared was 0·1% after 500 days. F. L. U.

Analytical notes. L. ROSENTHALER (Pharm. Zentr., 1932, **73**, 737—738).—CH_2O can be detected in presence of $(CH_2)_6N_4$ by phloroglucinol and NaOH. α-Naphthoflavone can be used as indicator for I–$Na_2S_2O_3$ titrations in acid, but not in $NaHCO_3$ solution. R. S. C.

Determination of arsenic, antimony, tin, and zinc in ores and alloys by titration with potassium iodate. Y. Y. LURE.—See B., 1932, 1083.

Determination of silicon, aluminium, fluorine, and orthophosphoric acid in the presence of one another. I. T. MILLNER and F. KUNOS (Z. anal. Chem., 1932, **90**, 161—170).—For the determination of SiO_2 and Al_2O_3 in alkali fluorides, fluosilicates, or cryolite the substance is evaporated to dryness in a Pt crucible with HCl, H_3BO_3, and Na_2HPO_4 to expel F as BF_3, and the residue heated at 130° to dehydrate SiO_2. The filtrate from the SiO_2 is evaporated with HNO_3 and the P_2O_5 removed with $(NH_4)_2MoO_4$: Al_2O_3 is then determined in the usual way with or without a preliminary separation of Mo. A. R. P.

Volumetric determination of alkali sulphates. J. FIALKOV and M. STSCHIGOL (Pharm. Zentr., 1932,

73, 563—566).—The neutral solution is treated with an excess of 0·1*N*-$BaCl_2$, the excess of $Ba^{"}$ is pptd. from the boiling solution by an excess of 0·1*N*-alkali (1 : 2 mixture of Na_2CO_3 and NaOH), and an aliquot part of the solution is filtered and titrated with 0·1*N*-HCl. A. R. P.

Determination of potassium, using lead-containing complexes. II. $Na_2PbCo(NO_2)_6$. P. S. SERGIENKO (Ukrain. Chem. J., 1932, 7, [Sci.], 36—41).—The reagent (*A*) is prepared by adding a saturated solution of 11·5 g. of $Pb(NO_3)_2$ to 15 g. of $NaNO_2$ and 10 g. of $Co(NO_3)_2,6H_2O$, adding H_2O to 100 c.c., and filtering from the ppt. which forms after a time. The neutral solution under examination is freed from NH_3, and 15 c.c. of (*A*) are added per 20 mg. of K, when a dark green ppt. of $K_2PbCo(NO_2)_6$ separates. The washed ppt. is boiled with 50—100 c.c. of 0·1*N*-$KMnO_4$ and 15—20 c.c. of 30% H_2SO_4, and then with 0·1*N*-$Na_2C_2O_4$, excess of which is titrated with 0·1*N*-$KMnO_4$. The experimental error is +1—2% for 0·1—0·3 g. of K. R. T.

Volumetric determination of small quantities of sodium. S. RUSZNYAK and E. HATZ (Z. anal. Chem., 1932, 90, 186—189).—See A., 1932, 1152. A. R. P.

Rapid macro- and micro-determination of silver. G. SPACU and P. SPACU (Z. anal. Chem., 1932, 90, 182—185).—The hot neutral or slightly ammoniacal $AgNO_3$ solution is treated with KI sufficient to redissolve the AgI ppt., then with an excess of aq. $[Cu\ pn_2]SO_4$ (pn=propylenediamine), whereby on cooling the whole of the Ag separates as pale violet crystals of the *compound* $[Cu\ pn_2](AgI_2)_2$. The crystals are washed with 1% aq. KI containing 0·5% of the precipitant, then with 96% EtOH and Et_2O, and dried in vac. for weighing; they contain 23·07% Ag. The sensitivity of the test is 1 part of Ag in 200,000 parts. A. R. P.

Volumetric determination of calcium and magnesium in presence of each other. E. VON MIGRAY (Chem.-Ztg., 1932, 56, 924).—The boiling solution is treated with *N*-$(NH_4)_2C_2O_4$ and aq. NH_3, and acidified with 2*N*-AcOH; Na_2HPO_4 is added and the solution made alkaline with NH_3. The ppt. is suspended in H_2O, and the liquid titrated at 80—90° with 0·1*N*-HCl, using Me-red to determine Mg. 0·1*N*-$KMnO_4$ is then added to determine Ca. E. S. H.

Potentiometric determination of zinc. I. TANAEV.—See B., 1932, 1084.

Separation of group III metals. R. RIPAN (Bul. Soc. Stiinte Cluj, 1931, 6, 280—285; Chem. Zentr., 1932, i, 1806).—Zn, Al, Cr, Mn, and Fe are separated from Co and Ni by treating the sulphides pptd. by alkaline $(NH_4)_2S$ with 10% HCl, and Co is confirmed by the blue colour formed when a drop of KCNS and EtOH or $COMe_2$ is added to the Co and Ni solution. The HCl extract is neutralised with Na_2CO_3 and the Zn removed as $[Zn(NH_3)_4]Cl_2$ by boiling with a small amount of Cl_2-H_2O and excess of NH_3. Boiling with conc. NaOH removes Al from the residue, whilst boiling with KOH and Cl_2-H_2O removes Cr as chromate. The residual Fe and Mn are dissolved in HCl and the Fe is pptd. with NaOAc. Al is best identified by pptn. with $(NH_4)_2CO_3$. L. S. T.

Separation of common elements into groups. II. Separation by means of sodium hydroxide and sodium peroxide. E. H. SWIFT and R. C. BARTON. **III. Separation of zinc, cobalt, nickel, and iron from aluminium, chromium, and manganese.** E. H. SWIFT, R. C. BARTON, and H. S. BACKURS (J. Amer. Chem. Soc., 1932, 54, 4155—4161, 4161—4172; cf. A., 1932, 827).—II. Details of two procedures for separating Mn, Fe, Co, and Ni from Al, Cr, and Zn by means of NaOH and Na_2O_2 are given. With solutions of pairs of metals the separation of Zn or of Cr, unless originally present as CrO_4'', is very unsatisfactory, but that of Al from Fe or Mn is nearly complete.

III. By the following method, < 1 mg. of Al, Cr, or Mn is carried down with ppts. of Zn, Co, Ni, or Fe from solutions containing 250 mg. each of two metals, one from each "group," in 100 c.c. of 0·3*M*-HCl. The solution is almost neutralised with 6*N*-aq. NH_3 10 g. of $(NH_4)_2C_2O_4$ are added, and the solution is exactly neutralised with $NaHCO_3$. H_2S is passed for 3—5 min. and the temp. is then raised to 60°. Acidity is neutralised by adding 1 g. of $NaHCO_3$ and H_2S is again passed, the process being repeated until the solution remains alkaline. 1 mg. of a metal of one "group" can be separated from 500 mg. of one from the other. J. G. A. G.

Simultaneous electrolytic determination of lead and copper. H. BILTZ (Z. anal. Chem., 1932, 90, 277—278).—A claim for priority over Bjørn-Andersen (A., 1932, 1011). F. L. U.

Registering potentiometric determination of small quantities of dissolved copper. L. TRONSTAD (K. Norske Vidensk. Selsk. Forhandl., 1931, 4, 20—23; Chem. Zentr., 1932, ii, 575).—Vals. from the empirical e.m.f.–Cu concn. curve are subject to a relative error of about 10%. Hence for 0·002—0·05 g. per litre they are at least as accurate as iodometric vals. Variations in the total concn. of the electrolytic bath and small temp. variations do not greatly affect the error. Other e.m.f. vals. are obtained, however, in 0·002*N*-Na_2SO_4, but they are reproducible, and Cu can be determined potentiometrically. A. A. E.

Quantitative emission-spectral analysis. III. Determination of copper in high-grade aluminium. J. CLERMONT.—See B., 1932, 1083.

Micro-chemical reaction of copper salts. I. M. KORENMAN (Pharm. Zentr., 1932, 73, 738—741). —NH_2Ph in H_2O (*A*) or conc. aq. NH_2Ph,HCl (*B*), saturated with NH_4CNS, gives a characteristic cryst. ppt. with Cu salts. (*A*) is most suitable for conc. solutions or in presence of Cd, (*B*) for dil. solutions (min., 0·00000005 g. Cu). Cd salts give a ppt. with (*B*) only, readily distinguished from the Cu ppt., but much Cd obscures the crystal form of the latter. The ppt. is not formed in presence of Bi, Sb, or Sn, but (*A*) and (*B*) are the only reagents sp. for Cu. A solution of cinchonine and NH_4CNS in dil. HNO_3 gives a cryst. ppt. only with Cu salts, but certain other salts interfere. R. S. C.

Gasometric determination with a ureometer of calcimeter type. G. D'ESTE (Boll. Chim. farm.,

1932, **71**, 717—728).—Full details are given of the application of the author's apparatus (A., 1932, 550) to the determination of CeO_2, MnO_2, and MnO_4', with H_2O_2; H_2O_2, BaO_2, etc., and HBO_3, with $KMnO_4$; Pb_3O_4, with HNO_3; Fe, Zn, etc. and $CaCO_3$ etc. with HCl; and V_2O_5 and S_2O_8'' with N_2H_4. H. F. G.

Determination of indium and gallium with 8-hydroxyquinoline. W. GEILMANN and F. W. WRIGGE (Z. anorg. Chem., 1932, **209**, 129—138).—In is completely pptd. as $In(C_9H_6NO)_3$ at 70—80° from a solution containing 2% NaOAc and 2% AcOH, and Ga as $Ga(C_9H_6NO)_3$ from feebly ammoniacal tartrate solution. The ppts. are dried at 105—120° for weighing. Both compounds are volatile, so that the metals can be recovered only by destroying org. matter with H_2SO_4 and HNO_3 and treating the solution with aq. NH_3. A. R. P.

Colour reaction between rhenium heptoxide and hydrogen peroxide. Rhenium peroxide. H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1932, **208**, 367—368).—Solid Re_2O_7 gives with conc. H_2O_2 a deep red solution. The coloured product is stable except towards H_2O, and is sol. in EtOH or Et_2O, but not in hydrocarbons, $CHCl_3$, CCl_4, or $COMe_2$. The white oxide formulated by I. Noddack and W. Noddack (A., 1929, 411) as Re_2O_8 did not yield the red compound except with H_2O. This and other experiments indicate that the white oxide is a modification of Re_2O_7. F. L. U.

Colorimetric determination of iron with 2 : 2′-dipyridyl. F. FEIGL, P. KRUMHOLZ, and H. HAMBURG (Z. anal. Chem., 1932, **90**, 199—202).—A 1% solution of 2 : 2′-dipyridyl in 0·1*N*-HCl gives an intense red colour with Fe'' salts. Fe''' salts must first be reduced with Na_2SO_3. In presence of Mn the solution must be at least 0·2*N*-HCl, and in presence of Zn, which gives a colourless complex with the reagent, a large excess of a 2·5% solution of reagent must be used. Hg'' forms an insol. complex with dipyridyl, but this is converted into a complex Hg sulphite if the acidity of the solution does not exceed 0·1*N*. A. R. P.

7-Iodo-8-hydroxyquinoline-5-sulphonic acid as a reagent for colorimetric determination of ferric iron. J. H. YOE (J. Amer. Chem. Soc., 1932, **54**, 4139—4143).—The addition of 0·1 p.p.m. of Fe''' to aq. 7-iodo-8-hydroxyquinoline-5-sulphonic acid (2 g. per litre) changes the colour from yellow to blue or green. The sensitivity is greatest in solutions slightly acid to Me-orange and the colour is stable to light. A large no. of colourless ions give no colour reaction, and coloured ions at sufficiently low concn. do not interfere. Salts of Sn, Ti, and especially Cu interfere. J. G. A. G.

Micro-electrolytic determination of iron. A. OKAC (Chem. Listy, 1932, **26**, 595—597).—0·3—0·5 g. of $(NH_4)_2C_2O_4$ is added to a small vol. of H_2O, the solution (1—10 mg. Fe) is added, and the vessel is warmed to complete dissolution of oxalate. The electrodes are then placed in the vessel, and H_2O is added to allow complete immersion of the cathode (total vol. of electrolyte 6 c.c.). A current of 0·3—0·6 amp. is passed during 10—20 min. to decolorise the electrolyte, and 5 min. later H_2O is gradually added to 150 c.c., when the current is cut off. The cathode is washed with H_2O and EtOH, dried during 15 min. at 80°, and weighed. The analytical error is 0·1—1%. R. T.

Determination of iron carbonyl in gases. E. POHLAND and W. HARLOS (Z. anal. Chem., 1932, **90**, 193—199).—For small quantities of gas the $Fe(CO)_5$ is converted into Fe_2O_3 by exposing a mixture of the gas and O_2 to direct sunlight or to the light of the Hg vapour lamp. The Fe_2O_3 is dissolved in HCl and determined volumetrically or colorimetrically. The $Fe(CO)_5$ may also be converted into $FeBr_3$ by shaking the gas with Br-H_2O. To determine $Fe(CO)_5$ in a gas stream the gas is passed through MeOH or H_2SO_4. $Fe(CO)_5$ has been found in compressed H_2 and always in CO stored in Fe cylinders. A. R. P.

Electrographic determination of nickel in nickel steels. A. GLAZUNOV and J. KŘIVOHLAVÝ.—See B., 1932, 1121.

Rapid colorimetric determination of nickel in alloys. I. V. P. OCHOTIN and A. P. SYSTCHOV.—See B., 1932, 1121.

Colorimetry of titanium. II. General colorimetric procedure. H. GINSBERG (Z. anorg. Chem., 1932, **209**, 105—112; cf. A., 1931, 814).—Systematic errors in the colorimetric determination of Ti in solutions containing < 3 mg. Ti per 100 c.c. have been traced to the optical behaviour of the solid glass dipping rods of the Duboscq colorimeter. Similar errors are to be expected when dealing with other solutions having very slight colour. F. L. U.

Precipitation method for determining vanadium [in steel]. S. M. GUTMAN.—See B., 1932, 1083.

Electrometric determination of vanadium in self-hardening steels. S. M. GUTMAN and N. V. MIKEEVA.—See B., 1932, 1083.

Determination of antimony in commercial copper. H. BLUMENTHAL.—See B., 1932, 1121.

Ceric sulphate in volumetric analysis. X. Determination of antimony and arsenic. N. H. FURMAN (J. Amer. Chem. Soc., 1932, **54**, 4235—4238).—Contrary to Willard and Young (A., 1928, 725), but in agreement with Rathsburg (*ibid.*, 1207), Sb is oxidised rapidly by $Ce(SO_4)_2$ at room temp., in absence of a catalyst, if 30—50 vol.-% of HCl (*d* 1·19) is initially present. As in relatively high concn. interferes, but in lower concns. may be determined, after the end-point of oxidation of Sb has been found, by adding ICl as catalyst and continuing the $Ce(SO_4)_2$ titration to the second end-point. J. G. A. G.

Electrolytic determination of bismuth in lead alloys. L. LUCCHI and A. BARTOCCI.—See B., 1932, 1121.

Drop method of approximate determination of gold. N. A. TANANAEV and E. V. VASILIEVA (Ukrain. Chem. J., 1932, **7**, [Sci.], 50—54).—The coloration given by a drop of solution on benzidine paper is matched with those given by a series of standard Au solutions. The error rises from ±2% for 0·1 mg. to ±20% for 0·06 mg. of Au. R. T.

Heat loss from Dewar flasks. K. S. COLE and R. H. COLE (Rev. Sci. Instr., 1932, [ii], **3**, 684—686).—Newton's law of cooling is obeyed if the contents are stirred. The heat loss coeff. is independent of the vol. of the contents between 50% and 90% capacity. C. W. G.

Reduction of platinum resistance thermometers to the international temperature scale. G. S. CALLENDAR (Phil. Mag., 1932, [vii], **14**, 729—742).—The reduction of measurements and their accuracy are discussed. H. J. E.

Constancy of the rotatory power of quartz plates. K. SANDERA (Z. Zuckerind. Czechoslov., 1932, **57**, 41—44).—To investigate the cause of variations in the rotatory power of quartz control plates, a set of four plates first calibrated in 1914 were read in March, 1931, August, 1931, and March, 1932. Inappreciable differences were observed in the readings, the mean of all being about 0·005° V. Severe mechanical effects, as grinding and compression, caused some variation of the readings, but these reverted to the original val. J. P. O.

Optical-electric colorimeter. B. LANGE (Chem. Fabr., 1932, 457—459).—A lamp is placed between two test glasses, the light passing through suitable filters, then through the liquids to be compared, and on photo-electric cells. The instrument is particularly suitable for matching faint colorations, being much more sensitive than the eye. If a mirror galvanometer is used for current measurement the colour of $10^{-5}N$-$KMnO_4$ can be detected. Turbidities may be readily compared even when rapidly settling ppts. are concerned. The apparatus may be used for the determination of one component in a coloured solution, *e.g.*, Fe in a dye, or of the val. of coloured solutions. C. I.

Surface microscopy. H. WAGNER and M. ZIPFEL (Chem. Fabr., 1932, 421—423).—Various methods of illuminating opaque objects are described, and their application to the study of paint films etc. is discussed. H. F. G.

Christiansen filter for ultra-violet light. H. KOHN and K. VON FRAGSTEIN (Physikal. Z., 1932, **33**, 929—931).—The filter is made by mixing a solution containing 56% C_6H_6 and 44% EtOH with amorphous SiO_2. The point of intersection of the dispersion curves of the liquid mixture and the SiO_2 is at 360 mμ at 20°, and this is the wave-length of the light transmitted. The filter is very sensitive to temp. A. J. M.

Photochemical technique. III. Quartz capillary arc lamps of bismuth, cadmium, lead, mercury, thallium, and zinc. R. M. HOFFMAN and F. DANIELS (J. Amer. Chem. Soc., 1932, **54**, 4226—4235; cf. A., 1932, 827).—Full details of the construction and operation of an inexpensive, easily repaired, quartz capillary lamp containing molten Bi, Cd, Pb, Tl, or Zn are given. Energy distribution curves were determined by a modified method for recording thermopile–galvanometer deflexions. J. G. A. G.

Quantitative crystal analysis by *X*-rays. M. E. NAHMIAS (Z. Krist., 1932, **83**, 329—339).—Sources of error in previous methods (cf. B., 1925, 546; 1931, 350) are discussed, and improvements suggested. The essential difference in the new method is that the intensities of the lines of the substance to be determined are not compared directly with those of that pure substance, but both are compared with the lines of a third substance, *e.g.*, Al. The powdered materials are stuck on fine (0·03 cm. diam.) Al wire which is moved helicoidally, thus averaging the composition of the material examined and diminishing errors due to heterogeneity. With quartz and kaolin and quartz and mullite results accurate to 10%, or with practice to 5%, are readily obtained. C. A. S.

Simple photographic method of measuring the persistence of spectral lines. A. OCCHIALINI and G. M. RANGHIASCI (Atti Accad. Lincei, 1932, [vi], **15**, 875—876).—A series of photographs is taken at short time intervals on one plate as the source of light is gradually moved away from the slit. The no. of spectra in which the line in question is visible gives a measure of the intensity. The method is applicable to the analysis of alloys. H. F. G.

Thermionic potentiometer for the measurement of p_H. A. E. J. VICKERS, J. A. SUGDEN, and R. A. BELL (J.C.S., 1932, 2812).—A reply to Morton (A., 1932, 1105). F. J. W.

Fractional distillation. G. O. THACKER.—See B., 1932, 1107.

Extractors and condensers. O. HAGEN (Chem. Fabr., 1932, 424—427).—Several modified types of Soxhlet extraction apparatus are described, and an account is given of a condenser in which the vapour is caused to follow a helical path by means of a screw-shaped central portion through which the cooling H_2O flows. The loss of solvent with this type is about 50% of that with the ordinary Allihn condenser. H. F. G.

Soxhlet with three-way tap. H. WASSERFUHR (Asphalt u. Teer, 1932, **32**, 358—360; Chem. Zentr., 1932, ii, 1109).—The lower part of the siphon tube is fitted with a 3-way tap so that the apparatus can be used in the usual way, there is a continuous flow of solvent into the flask, or the solvent can be removed during extraction. A. A. E.

Check valve for water filter-pumps. G. BALZ (Z. Elektrochem, 1932, **38**, 868—869).—A Hg trap is employed, the sucking-back of Hg being prevented by means of a sintered glass filter plate. D. R. D.

Experiments with capillary jets. E. TYLER and F. WATKIN (Phil. Mag., 1932, [vii], **14**, 849—881). J. W. S.

Measurement of vapour pressure by transference and its application to the pneumatolytic transference of aluminium oxide by hydrogen chloride or chlorine. W. FISCHER and R. GEWEHR (Z. anorg. Chem., 1932, **209**, 17—32; cf. A., 1929, 31).—Apparatus for the quant. collection of volatile solid products arising from the interaction of Al_2O_3 and HCl or Cl_2 is described. Results obtained at temp. between 1000° and 1200° indicate that with HCl the reaction is $Al_2O_3+6HCl \rightarrow 2AlCl_3+3H_2O$, but that with Cl_2 at least one oxychloride is formed. F. L. U.

Dissociation pressures of nitrates and sulphates. I. Apparatus. B. NEUMANN and A. SONNTAG (Z. Elektrochem., 1932, **38**, 934—936).—The ordinary type of apparatus with a paraffin oil or H_3PO_4 trap and Hg manometer is described. D. R. D.

Theory of drying. J. FRITH and F. BUCKINGHAM.—See B., 1932, 1107.

Measurement of viscosity. K. FISCHER (Chem. Fabr., 1932, 459—461, 471—473).—Capillary viscosimeters are best operated under pressure, in which case the effect of the changing liquid head becomes negligible. These instruments give only kinematic viscosities which often cannot be converted into abs. units. Falling-ball or -cylinder viscosimeters also require a knowledge of d; they are limited in that they cannot be used with corrosive liquids. Fifteen types of viscosimeter are tabulated, the accuracy, time required, and other particulars being given. C. I.

Use of Wilson cloud chamber for measuring the range of α-particles from weak sources. F. N. D. KURIE (Rev. Sci. Instr., 1932, [ii], **3**, 655—667).—Two photographs of the chamber are taken simultaneously at right angles by means of a single lens, and are examined after development by using the camera as a projector. C. W. G.

Physico-chemical and physiological researches relating to organic colouring matters. A. MEYER (Bull. Soc. chim., 1932, [iv], **51**, 1202—1205).—The use of impure and inadequately defined dyes in physico-chemical and physiological work is deprecated. H. B.

Early chemistry of gold. A. KENT (Proc. Roy. Phil. Soc. Glasgow, 1932, **60**, 101—112).

Geochemistry.

Determination of atmospheric ozone by visual photometry. J. GAUZIT (Compt rend., 1932, **195**, 892—894).—A spectrophotometer enabling the optical density, and thence the O_3 content, of the atm. to be determined photometrically by means of visual rays (λλ 6800—4900) is described. The equiv. thickness of the O_3 layer at Montpellier on Jan. 30 and 31, and Sept. 14, 1932, thus determined was 0·31, 0·35, and 0·235 cm. ±10%, respectively (cf. A., 1926, 1080; 1927, 808). C. A. S.

Inert gas content and radioactivity of natural Italian hydrocarbon gases. M. G. LEVI, A. G. NASINI, and P. DE CORI (Gazzetta, 1932, **62**, 799—821).—Analyses are given of 23 samples of natural gas from different districts. The total inert gas content (vol.-%) ranged from 0·004 to 1·4, the content of A from 0·003 to 1·28, and that of He from 0·0005 to 0·12. The radioactivity varied from 0·02 to 17·8 millimicrocuries per litre. H. F. G.

Helium content of beryllium. W. D. URRY (Nature, 1932, **130**, 777—778).—The possible mechanisms discussed are all insufficient to account for the abnormally high He content of several palæozoic beryls (A., 1910, ii, 920; 1928, 1341). L. S. T.

Tian-Shan gaseous springs. P. I. TOLMATSCHEV (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 51—64).—The gases associated with 55 Tian-Shan (Turkestan) thermal springs contained H_2S 0—1·6, CO_2 0—7·3, CO 0—13·6, O_2 0—18·8, CH_4 0—35·4, C_2H_6 0—41·3, higher paraffins 0—11·7, and N_2 and inert gases 15—100%. Apart from the above springs, the Bezbeltschir spring gas had CO_2 93·5, O_2 0·4, and N_2 6·5%, a Shor-Su spring H_2S 47·7, CO_2 2·3, CO 2·5, O_2 1·1, CH_4 20·6, and higher hydrocarbons 11·7%, and a Tschadai spring CO_2 1·0, CO 0·4, O_2 1·2, CH_4 69·1, and N_2 28·3%. R. T.

Analysis of the acid water of Slatina Radenci. S. S. MIHOLIC (Jub. Fest. 50 Slatina Radenci, 1932, 16 pp.).—Analyses of various waters, made during the last 60 years, are summarised. Little change in composition appears to have occurred during the period. The dissolved substances in the waters are of mixed origins. H. F. G.

Cruz del Aire meteorites. R. E. S. HEINEMAN (Amer. J. Sci., 1932, [v], **24**, 465—470).—A description and analysis are given. C. W. G.

Occurrence of potassium in Tarapacá province [Chile]. K. V. AREND (Bol. min. Soc. Nac. Min., 1931, **43**, 784—790; Chem. Zentr., 1932, ii, 853).

Crystal morphology of faujasite and linnæite. W. WITTEBORG and W. BARMEN (Z. Krist., 1932, **83**, 374—381).—Examination of recently-found crystals of faujasite (a variety of analcite) and of linnæite, CoS,Co_2S_3, and in particular of their vicinal faces, confirm them as holohedral cubic, O^h. C. A. S.

Crystal structure of dickite. J. W. GRUNER (Z. Krist., 1932, **83**, 394—404; cf. B., 1930, 832; A., 1932, 987).—Dickite is monoclinic with a 5·14, b 8·94, c 15·42 Å., β 96° 50′, and 4 mols. of $Al_2Si_2O_5(OH)_4$ in the unit cell, d_{theor} 2·589, space-group C_s^4. C. A. S.

Structural relations between phosphates (triphylite) and silicates (olivine): composition of ardennite. B. GOSSNER and H. STRUNZ (Z. Krist., 1932, **83**, 415—421).—Triphylite has a 4·67, b 10·34, c 6·00 Å., d 3·56; 4 mols. of $Li(FeMn)PO_4$ in the unit cell; space-group v_h^{16} (cf. olivine; A., 1926, 995); The mean of two closely agreeing analyses of ardennite gives SiO_2 28·76, As_2O_5 4·30, V_2O_5 4·90, Al_2O_3 24·65, Fe_2O_3 0·08, FeO 0·96, MnO 26·41, MgO 2·08, CaO 2·56, H_2O 5·08%, corresponding with $(SiO_4)_5(AsO_4)Al_3Mn(AlOH)_2Mn_4,2H_4O$, with which is compared zoisite, $(SiO_4)_6Al_4(AlOH)_2Ca_4$, indicating equivalence between $Si^{IV}+Al^{III}$ and As^V+Mn^{II}. Ardennite has a 18·56, b 5·83, c 8·72, d 3·610—3·645, with 2 mols. in the unit cell, space-group v_h^{12}, showing some similarity to zoisite. C. A. S.

Twin structure of amethyst quartz with reference to the temperature of origin. O. MÜGGE (Z.

Krist., 1932, **83**, 460—484).—From the character and interrelations of the different forms of twinning exhibited by such quartz it can be determined whether it has been formed below or above 573°. C. A. S.

Mixed crystals in the ternary system An–Ab–Cg. E. Dittler and A. Kohler (Tsch. Min. Petr. Mitt., 1932, **43**, 352—361).—Fusions of various composition ranging from $An_{80}Ab_{10}Cg_{10}$ to $An_{50}Ab_{10}Cg_{40}$ yielded crystals of basic plagioclase in which no appreciable amount of the carnegieite mol. ($NaAlSiO_4$) could be detected. This separated out in the groundmass as nepheline. When this mol. is present in larger amount the nepheline takes up some anorthite and becomes isotropic or optically positive, and the crystals show signs of unmixing. L. J. S.

Peridotite of Kaersut (Greenland) and associated dyke rocks. F. K. Drescher (Tsch. Min. Petr. Mitt., 1932, **43**, 207—270).—The residual liquid from the crystallisation of the peridotite has penetrated along veins, giving kaersutite- and augite-pegmatites which are relatively richer in alkalis than the parent rock. Analyses are given of the rocks and their constituent minerals. L. J. S.

Scapolite, zoisite, and secondary albite from the Lampi-Varaka (N. Karelia) pegmatite vein. S. M. Kurbatov (Bull. Acad. Sci. U.R.S.S., 1932, No. 2, 241—257).—The vein originally consisted of plagioclase, which as a result of autopneumolysis underwent conversion into scapolite, and this, in turn, under the influence of hydrothermal factors, yielded zoisite, calcite, and albite. R. T.

Stanniferous region of Nam Pha Thene (Laos). J. Fromaget (Compt. rend., 1932, **195**, 967—969).—The chief feature is an intrusive mass of monzonitic granite containing SiO_2 67·14, Al_2O_3 15·71, Fe_2O_3 0·96, FeO 2·83, MgO 1·20, CaO 4·18 Na_2O 3·21, K_2O 3·60, TiO_2 0·46, P_2O_5 0·16, H_2O+ 0·61, H_2O- 0·22, MnO 0·12%. This is in close relationship with quartzitic microdiorite. Both are traversed by veins of microgranite containing up to 2% cassiterite which has resulted from metallic emanations which have also converted the felspar of the microgranite into damourite. C. A. S.

Sierra Nevada as a co-magmatic region. A. A. Fitch (Amer. J. Sci., 1932, [v], **24**, 481—495).—The Sierra Nevada province has been characterised since the early Mesozoic by a suite of rocks for which Al, Fe+Mg, and Ca+Na+K are sensibly invariant, Ca showing a progressive decrease with time and Na+K an increase. C. W. G.

Calcareous rock of the apex of the black stones in the Gargano region. M. Coppola (Annali Chim. Appl., 1932, **22**, 638—641).—This contains about 20% of clay, 65·5% $CaCO_3$, 7·9% $MgCO_3$, etc., together with 2·2% C, which may have been produced either from CO or CO_2 or by profound igneous distillation. T. H. P.

Sp. gr. of Japanese acid clay. K. Yamamoto and H. Ishikawa (Bull. Waseda Appl. Chem. Soc., 1932, **17**, 1—8).—The clay has d^{25} 2·4—2·5; after acid treatment it has d^{25} 2·2—2·4. d increases above 120°, is max. at 200°, and decreases slowly to 400° and rapidly from 600° to 800°. The change at 120—200° is attributed to the effect of adsorbed H_2O, and that at 600—800° to structural change. Ch. Abs.

Physico-chemical properties of Japanese acid clay. VI. *X*-Ray studies. II. K. Yamamoto (J. Soc. Chem. Ind. Japan, 1932, **35**, 482—486B; cf. A., 1931, 1266).—The clay contains cryst. $Al_2O_3,4SiO_2,H_2O$. The lattice consts. of the hexagonal crystals have been determined. The clay has d 2·4—2·6; after treatment with alkali it is higher, but lower after treatment with acids. These effects are due to the content of colloidal SiO_2. d increases by heating the clay up to 200°, through loss of H_2O; above 400° d decreases through a change in structure. After heating at 1200° for 4—5 hr. the diffraction pattern is changed completely and then is identical with that of opal. E. S. H.

Microbiological characteristics of certain Crimean and Caucasian hill and steppe soils. T. L. Simakova (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 71—83).—Nitrifying bacteria and *Azotobacter* are present in the surface layers of Crimean soils (*A*) but not in Caucasian mountain soils (*B*); this is ascribed to the low $CaCO_3$ content and high acidity of (*B*). Denitrifying bacteria are present only in the upper 25 cm. of (*B*), and at all depths examined of (*A*). *Clostridium pasteurianum* and anaerobic but not aerobic cellulose-destroying bacteria were present in both (*A*) and (*B*). R. T.

Chemical and morphological examination of the origin of forest humus. W. Grosskopf (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 176—178).—Forest humus consists largely of lignin or its transition products. A. G. P.

Swedish soils. O. Tamm (Ernähr. Pflanze, 1932, **28**, 297—308).—Geological formations are described and profiles of typical soils recorded. A. G. P.

Geochemistry of oil formation. S. Zuber (Petroleum, 1932, **28**, 1—5).—A discussion of theories. E. S. H.

Organic Chemistry.

Graphical study of the composition of organic compounds. IV. T. Higasi (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 1254—1265).—The compositions of C–H–O compounds are indicated on a trilinear diagram and certain deductions made. D. R. D.

Two "methyl" groups of normal saturated hydrocarbons. R. Reinecke (Chem.-Ztg., 1932, **56**, 932—933).—The van 't Hoff conception of the C tetrahedron can be brought into harmony with recent discoveries if the two tetrahedra in, *e.g.*, C_2H_6 are conceived of as united, not corner to corner, but one

corner to the centre of a face. For many purposes it is more convenient to represent mols. by cubes of which the diagonals of the faces form the tetrahedra. The theory is developed and illustrated by the properties of substituted derivatives of C_2H_6, and its possibility of extension to ring mols. such as graphite, C_6Me_6, and to such compounds as stearic acid is pointed out. C. I.

Absorption in the ultra-violet of methane, ethane, and butane. W. KEMULA and S. MRAZEK. —See this vol., 6.

Action of sulphur on hydrocarbons. F. J. NELLENSTEYN and D. THOENES (Chem. Weekblad, 1932, **29**, 582—587).—The reaction between S and paraffins, paraffin oils, and lubricating oils at 260—300° yields C and almost all the S as H_2S, only traces of org. compounds of S being formed; it involves the complete breaking down of $\cdot CH_3$, $:CH_2$, and $\cdot CH$ groups. The mechanism of the reaction is discussed. H. F. G.

Synthesis of highly-chlorinated hydrocarbons and the catalytic action of aluminium chloride. H. J. PRINS (Rec. trav. chim., 1932, **51**, 1065—1080). —Certain chloro-methanes, -ethanes (less readily), -ethylenes, and -propylenes, and $C_3H_3Cl_5$ in presence of $AlCl_3$ condense with polychlorohydrocarbons containing a double linking and a neighbouring CCl_2 or CCl_3 group. $C_3H_2Cl_6$ reacts only at higher temp. with previous loss of HCl. The action is ascribed to the formation, *e.g.*, from $CHCl_3$, of $[AlCl_4]^-$ and $[CHCl_2]^+$, the latter being the active agent. The formation of higher condensation products in certain cases is due to loss of HCl from the saturated chlorohydrocarbons first produced. The action may be reversed. Octachloropentadiene is converted by $AlCl_3$ into octachloro*cyclo*pentene. Reagents which remove halogens give with polychlorohydrocarbons, besides the normal coupled products, coloured unsaturated substances containing only C and Cl. The colour intensity of $AlCl_3$ complexes with chlorohydrocarbons passes through a max. with increasing Cl content. A. A. L.

Action of chlorine on acetylene and the preparation of tetrachloroethane and trichloroethylene. N. A. VALIASCHKO and K. G. KOSENKO (Ukrain. Chem. J., 1932, **7**, [Sci.], 12—35).—The yield of $C_2H_2Cl_4$ from C_2H_2 and Cl_2 is 71—81%, and 88% when the catalysts are respectively Fe or Fe oxides and $SbCl_5$. 87% yields of C_2HCl_3 are obtained by treating $C_2H_2Cl_4$ with $Ca(OH)_2$. R. T.

Derivatives of tribromoethanol (avertin). II. S. CHECHIK (J. Amer. Pharm. Assoc., 1932, **21**, 1007—1009; cf. A., 1932, 367).—*Benzyl* ββ*β-tribromoethyl ether*, b.p. 172—174°, and β-bromo-ββ-dibenzyloxyethyl alcohol, b.p. 194—196° (*Ac* derivative), are described. E. H. S.

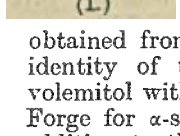
Dehydration of βγδ-trimethylpentan-γ-ol. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1932, **54**, 4392—4393).—Dehydration of βγδ-trimethylpentan-γ-ol with a little I at the b.p. gives the normal products, β-*iso*propyl-Δ^{α}-*iso*pentene and βγδ-trimethyl-Δ^{β}-pentene, in the ratio 1 : 2; the structures are determined by ozonolysis. H. B.

Rearrangement of unsaturated αδ-glycols. β-Methyl-Δ^{β}-butene-αδ-diol. A. F. SHEPARD and J. R. JOHNSON (J. Amer. Chem. Soc., 1932, **54**, 4385—4391).—αδ-Dibromo-β-methyl-Δ^{β}-butene (isoprene dibromide) and KOAc in AcOH at 100° give the *diacetate* (I), b.p. 120·5—122·5°/10 mm., of β-*methyl*-Δ^{β}-*butene*-αδ-*diol* (II), b.p. 127·5—128°/7 mm. (II) is reduced catalytically (PtO_2) to β-methylbutanediol, the diacetate of which is obtained by similar reduction of (I). (II) is readily converted by halogen acids or $ZnCl_2$ into tiglic aldehyde (α-methyl-Δ^{α}-butenal) [mixture of *dibromides*, b.p. 71—73° (corr.)/3·5 mm.], also formed from (I) and MeOH–HCl; the suggested mechanism is: $OH\cdot CH_2\cdot CH{:}CMe\cdot CH_2\cdot OH \longrightarrow CH_2{:}CH\cdot CMe{:}CH\cdot OH \longrightarrow CHMe{:}CMe\cdot CHO$. H. B.

Octadecane-ακ-diol. W. SECK and F. DITTMAR (Chem. Umschau, 1932, **39**, 226—229).—*Octadecane-ακ-diol*, m.p. 65° (corr.) (*diacetate*, b.p. 201°/0·2 mm.), has been prepared by hydrolysing ακ-dibromo-octadecane (cf. A., 1932, 1109) with KOAc and AcOH, or with AgOAc (yield 90%). Smaller yields of the glycol (16—20%) are obtainable by the reduction of Et ι-hydroxystearate, or its acetate with NaOBu. E. L.

Synthesis of *allo*dulcitol. LESPIEAU and WIEMANN (Compt. rend., 1932, **195**, 886—888).—Griner's mixture (I) of divinyl glycols and Br give two solid *dibromides* and a liquid. The higher-melting dibromide (m.p. 174°) with Zn dust and EtOH gives a pure *divinyl glycol* (II), m.p. 18°, b.p. 100°/14 mm., hydrogenated (Pd) to γδ-dihydroxy-*n*-hexane, m.p. 88·5° (A., 1928, 151). The formula $CH_2{:}CH\cdot\overset{H}{\underset{OH}{C}}\text{—}\overset{H}{\underset{OH}{C}}\cdot CH{:}CH_2$ for (II) is proved by the higher m.p. of the dibromide and the oxidation of (II) by $AgClO_3$ and osmic acid to allo*dulcitol* (III), m.p. 144—146° [*dibenzylidene* derivative, m.p. 246° (block)]. Oxidation of an erythritol (A., 1930, 450) probably gives the corresponding dicarboxylic acid. Oxidation of (I) gives a mixture of (III), mannitol, and a third isomeride. R. S. C.

Identity of volemitol (α-sedoheptitol) and β-*d*-mannoheptitol. V. ETTEL (Coll. Czech. Chem. Comm., 1932, **4**, 504—512).—Epimerisation of α-*d*-mannoheptonic acid affords the β-acid, m.p. 155°, $[\alpha]_D^{20}$ −2·9° in H_2O (*Ca* and *Ba* salts), reduced by Na–Hg to β-mannoheptose, m.p. 140°, $[\alpha]_D^{20}$ −7·61° in H_2O [p-*bromophenylhydrazone*, m.p. 191—193° (decomp.)], and to β-*d*-mannoheptitol (I), m.p. 150°, $[\alpha]_D$ +1·9° in H_2O, which with PhCHO and 50% H_2SO_4 gives a *tribenzylidene ether*, m.p. 210°, $[\alpha]_D^{20}$ −42·8° in C_5H_5N, and an *ether* (not pure), m.p. 190—195°, $[\alpha]^{20}$ −72·60° in C_5H_5N. The identity of these derivatives with those similarly obtained from volemitol (A., 1929, 798) proves the identity of this alcohol with (I). Interaction of volemitol with MeCHO under conditions used by La Forge for α-sedoheptitol (A., 1917, i, 118) gives, in addition to the triethylidene ether, m.p. 161—162°, $[\alpha]_D^{20}$ −74·3° in $CHCl_3$, previously obtained (*loc. cit.*), an isomeric *ether*, m.p. 210°, $[\alpha]^{20}$ −51·9° in $CHCl_3$, identical with that obtained by Bougault and Allard



(A., 1903, i, 62), thus removing the discrepancy previously observed, and confirming the identity of volemitol with α-sedoheptitol (A., 1928, 1213). J. W. B.

Aromatic esters of monoalkyl ethers of ethylene and diethylene glycols. R. C. CONN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1932, 54, 4370—4372).—The following esters are prepared from $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OAlk$ and $OH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OAlk$ by the C_5H_5N method: β-methoxyethyl benzoate, b.p. 251·6—252·6°/738·5 mm., and p-*nitrobenzoate*, b.p. 158·3—160·3°/4 mm., m.p. 50·5°; β-*ethoxyethyl benzoate*, b.p. 260—261°/738·5 mm., and p-*nitrobenzoate*, b.p. 163·5—164·5°/4 mm.; β-*butoxyethyl benzoate*, b.p. 156·5—157°/14·5 mm., 131·6—132·6°/3 mm., and p-*nitrobenzoate*, b.p. 179—180°/3·5 mm.; -*ethoxyethoxyethyl benzoate*, b.p. 160—161°/14·5 mm., 141—143°/2 mm., and p-*nitrobenzoate*, b.p. 207—209°/4 mm.; β-β′-*butoxyethoxyethyl benzoate*, b.p. 179·3—181·3°/4 mm., and p-*nitrobenzoate*, b.p. 230—232°/4 mm. Various physical data are given. H. B.

Interaction of etherates of magnesium halides and ethylene oxides. II. Interaction of magnesium bromide etherate and some monosubstituted aliphatic ethylene oxides. I. RIBAS and E. TAPIA (Anal. Fís. Quím., 1932, **30**, 778—791; cf. A., 1930, 1403).—Ethylene oxide, epichlorohydrin, and αβ-oxido-γ-methoxypropane react in Et_2O with $MgBr_2$ to give *products* $CH_2Br{\cdot}CHR{\cdot}O{\cdot}MgBr,Et_2O$ (R=H, CH_2Cl, or $CH_2{\cdot}OMe$), white cryst. substances decomposed by moisture with formation of the compounds $CH_2Br{\cdot}CHR{\cdot}OH$ and $MgBr_2+Mg(OH)_2$. Apparently identical products are formed by interaction of MgEtBr and the compounds $CH_2Br{\cdot}CHR{\cdot}OH$. Half the Br in these products appears as Br′ ion when dissolved in dil. HNO_3 under conditions in which the interaction of $MgBr_2$ with the ethylene oxide to give the bromohydrin is negligible. Confirmatory determinations are made of the $Mg(OH)_2$ formed.

$MgBr_2$ reacts with excess of the above ethylene oxide derivatives to give *products* $(CH_2Br{\cdot}CHR{\cdot}O)_2Mg$. No evidence was obtained of the formation of additive compounds of the type $MgBr_2$+ethylene oxide+Et_2O even at −21°. R. K. C.

Mechanism of hydrolysis of dialkylaminomethyl ethers. T. D. STEWART and W. E. BRADLEY (J. Amer. Chem. Soc., 1932, **54**, 4172—4183).—The preps. of the following are described: *diethylaminomethyl Me*, *Et*, *Bu*$^{\alpha}$, and n-*heptyl ethers*, b.p 115—115·8°/755 mm., 132—134°/756 mm., 172—173°/758 mm., and 112·5°/15 mm., respectively, and *di*-n-*propyl*-, b.p. 87°/42 mm., *diiso*propyl-, *di*-n-*butyl*-, b.p. 116°/11 mm., *diiso*butyl-, b.p. 92°/5 mm., *di*-n-*amyl*-, b.p. 28°/5 mm., *phenylmethyl*-, *diallyl*-, b.p. 89°/11 mm., and *dimethyl*-, b.p. 128°/756 mm., -*aminomethyl Bu*$^{\alpha}$ *ethers*. n-*Butoxymethylpiperidine*, b.p. 82°/5 mm., and 3-β-*hydroxyethyloxazolidine*, b.p. 78°/2 mm., were prepared.

That the hydrolysis of these ethers to CH_2O, alcohol, and *sec.*-amine probably involves the primary formation of the *N*-dialkylmethyleneiminium ion, which subsequently adds OH′ to form the amine and CH_2O, is supported by the isolation of $NEt_2{\cdot}CH_2Cl,6H_2O$ and $(NBu^{\beta}_2{\cdot}CH_2)_2PtCl_6$, and a study of the reaction between CH_2O and $NHEt_2$ in dil. aq. solution. J. G. A. G.

Chlorides of arylsulphurous acids and the mixed aryl alkyl sulphites. P. CARRÉ and D. LIBERMANN (Compt. rend., 1932, **195**, 799—801).—$SOCl_2$ and diaryl sulphites afford the chlorides of arylsulphurous acids which are not purified, but afford with alcohols, in presence of C_5H_5N, arylalkyl sulphites. The following are described: *Ph Me*, b.p. 128—130°/20 mm., *Ph Et*, b.p. 142—144°/25 mm., *Ph Bu*$^{\alpha}$, b.p. 170—173°/20 mm., o-*tolyl Me*, *Et*, b.p. 145—147°/20 mm., and *Bu*$^{\alpha}$, b.p. 170—173°/13 mm., m-*tolyl Me*, b.p. 137—140°/25 mm., *Et*, b.p. 147—150°/25 mm., and *Bu*$^{\alpha}$, b.p. 178—180°/20 mm., p-*tolyl Me*, b.p. 134—136°/20 mm., *Et*, b.p. 146—149°/20 mm., and *Bu*$^{\alpha}$, b.p. 175—177°/25 mm., *sulphite*. J. L. D.

Action of acid chlorides on orthoformic ester. Preparation of symmetrical esters of sulphuric acid. R. LEVAILLANT (Compt. rend., 1932, **195**, 882—884).—$CH(OEt)_3$ (I) (1 mol.) and $CCl_3{\cdot}COCl$ (1 mol.) at 95—100°, and later at 160°, give EtCl, HCO_2Et, and $CCl_3{\cdot}CO_2Et$ (yield > 90%). $CH_2Cl{\cdot}COCl$ at 100—110° gives similarly $CH_2Cl{\cdot}CO_2Et$, and BzCl at 125—130° in presence of a little $ZnCl_2$ gives BzOEt (92% yield). *p*-$C_6H_4Me{\cdot}SO_2Cl$ at 110°, and $PhSO_2Cl$ at 150—155° ($ZnCl_2$) give good yields of the Et esters. Addition of $SOCl_2$ (1 mol.) to (I) (2 mols.) at 0° and gradual heating to 100° yields SO_2Et_2 (80% yield). SO_2Cl_2 (1 mol.) and (I) (1 mol.) give $ClSO_3Et$ and a little Et_2SO_4. Esters of $ClSO_3H$ give good yields of symmetrical esters of H_2SO_4, *e.g.*, $ClSO_3Et$ (1 mol.) and (I) (1 mol.) give a 90% yield of Et_2SO_4. R. S. C.

Reaction between neutral lead mercaptides and sulphur. W. E. DUNCAN and E. OTT (J. Amer. Chem. Soc., 1932, **54**, 4463).—The basic Pb derivative of *sec.*-BuSH and S in C_6H_6 give (cf. A., 1930, 1405) a mixture of basic Pb polysulphides; individual compounds could not be isolated. H. B.

Thioethers of pentaerythritol. II. H. J. BACKER, P. TERPSTRA, and N. D. DIJKSTRA (Rec. trav. chim., 1932, **51**, 1166—1172).—The following tetrathioethers of pentaerythritol are prepared as previously described (A., 1932, 363), % yields being given in parentheses: *Bu*$^{\beta}$, b.p. 221—223°/2 mm. (80), n-*amyl*, b.p. 241—243°/2 mm. (80), n-*hexyl*, b.p. 206—208°/0·0001 mm. (80), n-*heptyl*, b.p. 222—224°/0·0001 mm. (93), n-*octyl*, b.p. 238—240°/0·0001 mm. (77), n-*nonyl*, b.p. 251—253°/0·0001 mm. (79), n-*decyl*, m.p. 19°, b.p. 259—261°/0·0001 mm. (87), n-*undecyl*, m.p. 28° (74), and n-*dodecyl*, m.p. 35—36° (92). The *tert.*-Bu ether exists in two forms, m.p. 116·4° and 123·6°. *X*-Ray data are given for this substance and the Ph. and tetrabenzyl ethers. A. A. L.

Tetrasulphones derived from carbontetramethanethiol. H. J. BACKER and N. D. DIJKSTRA (Rec. trav. chim., 1932, **51**, 1173—1177).—Tetrathioethers of pentaerythritol (cf. preceding abstract) with H_2O_2 in AcOH give the following tetrasulphones: *Me*, decomp. > 300°, *Et*, m.p. 185·5°, *Pr*$^{\alpha}$, m.p.

126·5°, *Pr*$^{\beta}$, m.p. 220·5°, *Bu*$^{\alpha}$, m.p. 111·5°, *Bu*$^{\beta}$, m.p. 134°, sec.-*Bu*, m.p. 115°, tert.-*Bu*, decomp. > 300°, n-*amyl*, m.p. 83·5°, n-*hexyl*, m.p. 85·5°, n-*heptyl*, m.p. 72°, n-*octyl*, m.p. 80°, n-*nonyl*, m.p. 76°, n-*decyl*, m.p. 78·8°, n-*undecyl*, m.p. 72·5°, n-*dodecyl*, m.p. 78·3°, *Ph*, m.p. 244°, *benzyl*, m.p. 179·5°, β-*phenylethyl*, m.p. 183°. A. A. L.

Resolution of chloroiodomethanesulphonic acid. J. Read and (Miss) A. M. McMath (J.C.S., 1932, 2723—2727).—Optically impure NH_4 *d*- and *l*-chloroiodomethanesulphonate (J.C.S., 1914, **105**, 811) in H_2O when repeatedly pptd. with brucine sulphate affords, after treatment with dil. NH_3, *NH*$_4$ d-*chloroiodomethanesulphonate*, m.p. 229—230° (decomp.), $[\alpha]_D$ +13·2° in H_2O {*Ba* salt, $[\alpha]_D$ +11·0°; *strychnine* salt, m.p. about 227° (decomp.), $[\alpha]_D$ −14·6°; l-*hydroxyhydrindamine* salt, m.p. 204° (decomp.), $[\alpha]_D$ −6·0°; d-*hydroxyhydrindamine* salt, m.p. 194° (decomp.), $[\alpha]_D$ +23·6°}, and *NH*$_4$ l-*chloroiodomethanesulphonate*, $[\alpha]_D$ −13·0° in H_2O [*strychnine* salt, m.p. about 227° (decomp.), $[\alpha]_D$ −26·5°; l-*hydroxyhydrindamine* salt, m.p. 194° (decomp.), $[\alpha]_D$ −46·9° in $COMe_2$]. The NH_4 salts described are less easily racemised than the chloroiodoacetates (A., 1927, 445). J. L. D.

Conductometric determination of small amounts of fatty acids by the visual method. G. Jander and K. F. Weitendorf (Angew. Chem., 1932, **45**, 705—707).—Small amounts (10—25 mg.) of fatty acids are determined by extraction from H_2O with light petroleum, evaporation to dryness, dissolution in EtOH purified over CaO and H_2O, and conductometric titration with 0·1*N*-NaOH in MeOH after addition of a little HCl. CO_2 must be excluded. A. G.

Reaction of carboxylic acids with phosphorus pentoxide. K. C. Laughlin and F. C. Whitmore (J. Amer. Chem. Soc., 1932, **54**, 4462).—$CMe_3{\cdot}CO_2H$ and P_2O_5 give CO and polymerides of *iso*butene; $PrCO_2H$ gives CO and CO_2 in the ratio 1 : 5 and tar, whilst $Pr^{\beta}CO_2H$ gives CO and CO_2 in the ratio 5 : 1 and tar (in presence of xylene the ratios of CO and CO_2 remain the same, but the yield is diminished to 0·07 and 0·14%, respectively). Gas is not evolved when BzOH is heated with an excess of P_2O_5 in xylene. H. B.

***n*-Decyl series.** G. Komppa and Y. Talvitie (J. pr. Chem., 1932, [ii], **135**, 193—203).—The following are described: n-*decyl chloride*, b.p. 223—223·5°/760 mm., 105—105·5°/15·5 mm., from the alcohol and PCl_5 in CCl_4; n-*decyl bromide* (I), b.p. 117·6—118°/15·5 mm., 104—104·4°/8 mm., from the alcohol, Br, and red P; *Et* n-*decylacetoacetate*, b.p. 171—171·5°/9 mm., from $CHNaAc{\cdot}CO_2Et$, (I), and NaI in EtOH, hydrolysed (very dil. H_2SO_4 at 200°) to Me *n*-undecyl ketone; *Me* n-*decyl ether*, b.p. 213·3—213·5°/760 mm., 100·5°/15·5 mm., from Na decyloxide (II) and Me_2SO_4 in C_6H_6; *Et* n-*decyl ether*, b.p. 223·5—224°, 99·6—99·8°/8 mm., from NaOEt and *n*-decyl iodide (III); *Pr*$^{\alpha}$ n-*decyl ether*, b.p. 242·5°/760 mm., 122·5°/15·5 mm., from NaOPr and (III); *di*-n-*decyl ether*, b.p. 196°/15·5 mm., in poor yield from (II) and (III) in xylene; *Ph* n-*decyl ether*, b.p. 178°/15 mm., m.p. 8—10°, from NaOPh and (III); n-*decyl formate*, b.p. 105·1—105·3°/9 mm., acetate, b.p. 244°/760 mm., 125·6—125·8°/15·5 mm. (lit. 125—126°/15 mm. and 187—190°/720 mm.), *propionate*, b.p. 138·2—138·6°/15·5 mm., 123·9—124·3°/8 mm., n-*butyrate*, b.p. 149·8°/15·5 mm., 134·8—135°/8 mm., *palmitate*, m.p. 30°, pyruvate, decomp. on attempted distillation (*semicarbazone*, m.p. 143°), *benzoate*, b.p. 195·8°/8 mm., p-*nitrobenzoate*, m.p. 30·2°, p-*aminobenzoate hydrochloride*, m.p. 161° (not sharp), *cinnamate*, b.p. 224°/11 mm., m.p. 7°, *phenylcarbamate*, m.p. 59·6°, and *naphthylcarbamate*, m.p. 71·4°; N-n-*decylphthalimide*, m.p. 56°, from *o*-$C_6H_4(CO)_2NK$ and (III) at 200°, hydrolysed (conc. HCl at 200°) to *n*-decylamine (*phenylcarbamyl*, m.p. 84·2°, and α-*naphthylcarbamyl*, m.p. 129·5°, derivatives). Numerous spectrochemical data are recorded. H. B.

α-Bromo-*n*-butyric acid. I. Preparation, purity, and velocity of hydrolysis. R. Ahlberg (J. pr. Chem., 1932, [ii], **135**, 282—304).—Partly a more detailed account of work previously reviewed (A., 1931, 574). The reaction, which proceeds 500 times as rapidly as the other (cf. *loc. cit.*) during the hydrolysis of an aq. solution of Ba α-bromobutyrate, is due to the presence of an unstable impurity in the α-bromobutyric acid (I) used. Such impurity is found when the $PrCO_2H$ used is prepared by fermentation (not with the synthetic acid); it is removable by neutralisation of the Br-acid with aq. Na_2CO_3, keeping the solution for 3—4 days, and then acidifying. The rate of hydrolysis of pure (I) (details of prep. by the Hell–Volhard method given) (as neutral salt) is practically independent of the concn. and is $k\times10^6$= 16·8—17·2 at 25° and 511—527 at 45°; the temp. coeff. in the range 25—45° is 5·53. H. B.

Esters of α-hexabromostearic acid. K. E. Stanfield and E. R. Schierz (J. Amer. Chem. Soc., 1932, **54**, 4356—4359).—The following esters are new: n-, m.p. 143—143·1°, and tert.-, m.p. 162—162·5°, -*Bu*; α-*ethylpropyl*, m.p. 135·8—135·9°; iso*amyl*, m.p. 135—135·1°; α-*methylbutyl*, m.p. 135·7—135·9°; *dimethylethylcarbinyl*, m.p. 159—159·5°; β-*methylbutyl* (?), m.p. 133·4—133·8°; *hexyl*, m.p. 132·6—132·8°; *heptyl*, m.p. 130·6—130·8°; α-*propylbutyl*, m.p. 135·1—135·2°; *octyl*, m.p. 128—129°; α-*methylheptyl*, m.p. 129·1—129·2°; *benzyl*, m.p. 140·4—140·5°. The m.p. of the esters decreases with increase in the no. of C atoms of the alkyl group; the esters from *tert.*-alcohols have abnormally high m.p. and are less sol. in org. solvents than those from primary and *sec.*-alcohols. H. B.

Autoxidation of unsaturated fatty acids. II. Action of carotenoids. W. Franke (Z. physiol. Chem., 1932, **212**, 234—255; cf. A., 1932, 1112).—Carotenoids, including vitamin-*A* and carotene, accelerate the oxidation of fatty acids but not of the glycerides. In presence of hæmin the lipochromes produce considerable autoxidation not in the free fatty acids, but in the neutral oils, which may be due to the formation of an additive compound between hæmin and carotenoid. In C_5H_5N but not in other solvents the lipochromes restrict autoxidation of unsaturated fats and fatty acids. In $NPhMe_2$ in

presence of hæmin autoxidation of the lipochromes and of the unsaturated fatty acids is extremely rapid. The autoxidation was also studied in xylene with and without hæmin. J. H. B.

Composition of illipé butter. Study of αα-dilauro-β-azelain and αα-dilaurin. G. SHUSTER (J. Pharm. Chim., 1932, [viii], **16**, 421—431; cf. A., 1931, 712, 1199).—The Hilditch process for the examination of fats has been modified by pre-oxidation of the fat in $COMe_2$ solution by $KMnO_4$. Illipé butter contains tristearin 1·4%, palmitodistearin 5·2%, dilauro-β-olein 21·3%, distearo-β-olein 40·2%, β-monostearo-αα-diolein 5·4%, β-palmito-αα-diolein 3·5%, and triolein 12·22%. The following have been synthesised: *αα-distearo-β-azelain*, m.p. 67°; *β-stearo-αα-diazelain*, m.p. 61°; *β-palmito-αα-diazelain*, m.p. 57°. αα-Dilauro-β-azelain, m.p. 44°, can be partly hydrolysed to αα-dilaurin, m.p. 22—23°. T. McL.

Elæostearic acids. I. Isomerism of the elæostearic acids. E. ROSSMANN (Chem. Umschau, 1932, **39**, 220—224).—The properties of the isomeric acids and their esters, and the irreversible isomerism of the α- to the β-form, support a conception of the β-acid as an extended *trans*-form chain mol., whilst the α-acid is regarded as a *cis*-form coiled chain. It is improbable that couepic acid is a geometrical isomeride of elæostearic acid. E. L.

Acylacetic esters. J. DÉCOMBE (Ann. Chim., 1932, [x], **18**, 81—187).—Distillation of acylacetic esters in specially washed Pyrex flasks at a rate of 6—8 drops a min., termed "slow distillation," gives distillates containing much enolic form, without changing the proportions of the isomerides in the residues, whence it is concluded that enolisation takes place in the vapour state. The following figures give the percentages of enolic form (determined by Br titration) present in the equilibrium mixture and obtainable by "slow distillation," respectively, the temp. given in parentheses being the apparent b.p. at 11 mm. during "slow distillation": Et acetoacetate (I), 7·4, 98—99·5 (42—46°); Et propioacetate [from MgEtI and $CN{\cdot}CH_2{\cdot}CO_2Et$ (II) in 70% yield], b.p. 84°/15 mm., 6·9, 94—95 (60—62°); Et butyroacetate [from MgPrI and (II) in 55% yield], 8·48, 60—64 (80—82°); Et valeroacetate [from MgBuI and (II) in 25% yield], b.p. 107—108°/15 mm., 11·5, 30—34 (100°/14 mm.); Et hexoylacetate (by hydration and esterification of Δ^{α}-heptinenoic acid in 50% yield), b.p. 115—116°/14 mm., 16·3, —. The preps. of the esters [except (I)] are modified; those prepared from (II) are best purified by way of the Mg derivatives, which are pptd. by aq. NH_3–NH_4Cl–$MgCl_2$, which diminishes the yields by 10—15%. The preps. of the following Et esters are modified: sodioformylacetate (III), α-methylformylacetate (b.p. 154—162°), α-phenylformylacetate (forms, b.p. 144—145°/6 mm. and m.p. 69—71°), benzoylacetate (from BzOEt and EtOAc) (b.p. 140—144°/6 mm., 70% yield). Equilibration of the enolic form of (I) is irregular and catalysed by forces beyond control, although the results of K. Meyer are in the main confirmed. The enolic form of (I) does not react immediately with NH_3, whilst the equilibrium mixture in ordinary Et_2O at 0° gives with NH_3 a cryst. intermediate *compound*, rapidly decomposed above 0°. It is concluded that reaction takes place by Michael addition to the ketonic form and that the product is Et β-aminocrotonate and not β-iminobutyrate. A trustworthy method of obtaining the form of m.p. 32° is given. (III) and NH_3 under various conditions give only Et_3 trimesate, but the following *Et* esters were prepared from the appropriate acylacetate and base: *β-dimethylaminoacrylate*, b.p. 97—98°/0·5 mm., cryst. in a freezing mixture (giving with boiling H_2O $NHMe_2$ and Et_3 trimesate); β-anilinoacrylate, colourless needles, m.p. 114—115°, and yellow plates, m.p. 116°; *β-butylaminoacrylate* (impure), cryst. (reduced by Na and EtOH to γ-benzylaminopropyl alcohol); *β-dimethylamino-*, b.p. 121°/15 mm., and *β-benzylamino-α-methylacrylate*, b.p. 146—148°/1 mm.; *β-amino-*, b.p. 142—149°/0·5 mm. [from Et α-phenylformylacetate and liquid and cryst. forms of (IV), *β-methylamino-*, b.p. 140—142°/3 mm. [from (IV)], *β-dimethylamino-*, b.p. 184—185°/16 mm. [from (IV)], and *β-benzylamino-α-phenylacrylate*, m.p. 64—65° [from (IV)]; *β-dimethylamino-*, b.p. 135°/21 mm., β-diethylamino-, b.p. 153°/20 mm., β-anilino-, b.p. 142—145°/5 mm., β-benzylamino-, and *β-dibenzylamino-crotonate*, m.p. 110—111°; *β-amino-*, b.p. 105—108°/10 mm. (prepared in presence of NH_4NO_3), and *β-dimethylamino-Δ^{α}-pentenoate*, b.p. 134—135°/21 mm.; *β-amino-Δ^{α}-hexenoate*, b.p. 105—107°/10 mm. (I) does not condense with NHPhMe or $NHPh_2$. Et α-methylformylacetate with NH_3, Et propioacetate with $NH_2{\cdot}CH_2Ph$, and Et butyroacetate with $NHMe_2$ give mixtures. Et benzoylacetate and NH_2Me in Et_2O give a cryst. *compound*, which loses NH_3 when heated, and when kept gives an oil, decomposed by distillation. Attempts to reduce Et β-aminocrotonate, m.p. 32° or 18°, or its Ac derivative, catalytically and with Al amalgam failed. The azine of (I) cannot be reduced, but the phenylhydrazone is reducible by Al amalgam. The best results for (I) and other esters are obtained by reduction of the acetyl- or benzoylhydrazones (not necessarily pure) with Al amalgam, the product being purified by way of the oxalate. The following *Et* esters were thus prepared: *β-amino-α-methylpropionate*, an oil (*chloroplatinate*; *hydrochloride*, m.p. 130°); β-aminobutyrate, b.p. 68—69°/17 mm. (*chloroplatinate*; *oxalate*, m.p. 88—90°; *phenylcarbamide*, m.p. 110°); *β-amino-n-valerate*, b.p. 83—84°/17 mm. (*chloroplatinate*); *β-amino-n-hexoate*, b.p. 102—104°/25 mm. (*chloroplatinate*; *oxalate*, m.p. about 155° after sintering from 130°) (other conditions give *3-n-propyl-5-pyrazolone*, m.p. 125°); *β-amino-n-octoate*, b.p. 132—133°/25 mm. (*chloroplatinate*; *phenylcarbamide*, m.p. 114°; *oxalate*). The method failed with Et benzoylacetate, which gives only the pyrazolone. The *acetylphenylhydrazones* of (I) and Et propioacetate have m.p. 90° and 93°, respectively. The following *Et* esters were prepared by hydrogenation (PtO_2), best in EtOH, of the unsaturated compounds, although the method failed in many other cases: *β-dimethylamino-α-phenylpropionate* (impure), b.p. 142—147°/15 mm. (*hydrochloride*, m.p. 150—151°); *β-dimethylamino-*, b.p. 81·5°/21 mm. [*chloroplatinate*; *hydrochloride*, m.p. 136—137° (block), 125° (tube)], *β-diethylamino-*, b.p. 98°/vac. (*chloroplatinate*, decomp. about 170°; *hydrochloride*, hygroscopic), *β-benzylamino-*, b.p. 172—174°/24 mm. (formed

equally easily from the α- and β-forms of β-benzylaminocrotonate) [*hydrochloride*, m.p. 112—114°; *chloroplatinate*; slowly hydrolysed by hot H_2O to the corresponding *acid*, m.p. about 191° (block)], and *β-dibenzylamino-butyrate*, b.p. 195—200°/5 mm. (*chloroplatinate*); *β-dimethylaminovalerate*, b.p. 100°/30 mm. [*chloroplatinate*; *hydrochloride*, m.p. 160° (block), 150° after sintering (tube)], hydrolysed by hot H_2O to the corresponding *acid*, m.p. 90—91°. Alkylation of the saturated primary NH_2-esters by alkyl iodides under various conditions led to mixtures; *e.g.*, Et β-aminobutyrate gives, amongst other products, the β-*NHMe*-compound, b.p. 77—81°/20 mm., and then Et crotonate and probably the NMe_2-compound (*methiodide*, cryst.). The following *Et* esters were prepared in about 60% yield by hydrogenation (PtO_2) of mixtures of the primary base and MeCHO in EtOH (Skita's method): *β-ethylaminobutyrate*, b.p. 74—75°/12 mm. (*hydrochloride*; readily hydrolysed by hot H_2O to the corresponding *acid*, m.p. 169—170°); *β-ethylaminohexoate*, b.p. 110—111°/20 mm. (*hydrochloride*); *β-ethylamino-octoate*, b.p. 134—135°/20 mm. (*hydrochloride*). Attempts to alkylate the *sec.*-bases by alkyl iodide led to much deamination, whilst Skita's method gives mixtures; the latter method gives slowly a little *Et β-ethylbutylaminobutyrate*, b.p. 118—119°/15 mm. (*hydrochloride*, an oil; *chloroplatinate*). Reduction of the NH_2-esters by Na and EtOH often leads to unsaturated compounds, depending on the substituents attached to the N and α-C atoms; the following were prepared by this method: *γ-benzylaminopropyl alcohol* (from the acrylate), b.p. 132°/2 mm. (*hydrochloride*, m.p. 84—85°; *hydrochloride* of the *Bz* derivative; *phenylcarbamide-phenylurethane*, m.p. 107°); *γ-benzylamino-*, b.p. 126°/1 mm. [*hydrochloride*, m.p. 101°; *hydrochloride* of the *Bz* derivative, m.p. 129—130°; *phenylcarbamide-phenylurethane*, m.p. 126° (block), 119—120° (tube)], and *γ-dimethylamino-isobutyl alcohol* (from the crotonates), b.p. 163—164° (*hydrochloride* of the *Bz* derivative); *γ-methylamino-*, b.p. 125—129°/3 mm. [*hydrochloride*, m.p. about 80°; *hydrochloride* of the *Bz* derivative, m.p. 131—132° (decomp.) (block), softening from 120° to 125° (tube); *phenylcarbamide-phenylurethane*, m.p. about 150° (block), softening from 138° (tube)], *γ-dimethylamino-*, b.p. 134°/8 mm., m.p. 35—36° [*hydrochloride*, an oil; *hydrochloride* of the *Bz* derivative, m.p. 172—173° (block)], and *γ-benzylamino-β-phenylpropyl alcohol* (from the acrylates), m.p. 64° (*hydrochloride*, m.p. 135—136°; *phenylcarbamide*, m.p. 135—136°; *O*-derivatives could not be obtained); the last-named ester was accompanied by some *β-benzylamino-α-phenylpropionic acid*, m.p. 225—226° (block), 190—195° (tube); *γ-dimethylamino-*, b.p. 82—85°/25 mm. (*hydrochloride* of *Bz* derivative, hygroscopic), and *-benzylamino-n-butyl alcohol* (from the butyrates), . p. 173—174°/23 mm. (*phenylcarbamide*, m.p. 110°; no *O*-derivatives could be obtained); *γ-dimethylamino-n-amyl alcohol* (from the pentenoate), b.p. 79°/20 mm. [*hydrochloride*, m.p. about 102—103°; *hydrochloride* of the *Bz* derivative, m.p. about 117—118° (block), hygroscopic]; γ-methylamino-γ-phenylpropyl alcohol, b.p. 125—130°/2 mm., m.p. 57—58°, hygroscopic (from the cinnamate in poor yield). Et propio- and butyro-acetates with MeCHO and a little $NHMe_2$ at −10° give *Et_2 ethylidenebispropio-* and *ethylidenebisbutyro-acetate*, m.p. 121° and 131°, respectively. In the latter case the yield is better in aq. solution, whence it is concluded that MeCHO reacts in the hydrated form. The yield in this condensation decreases as the length of the C chain increases, and is 0 with Et valeroacetate. Esters containing high proportions of the enolic form give better yields than the equilibrium mixtures. The ethylidene esters do not decolorise Br in EtOH and are, therefore, considered to be diketonic forms, in agreement with previous views. From these results, which are confirmed by experiments with (I), it is concluded that the enolic form of the acylacetic ester condenses with hydrated MeCHO by Michael addition. R. S. C.

Mode of formation of disubstituted malonic ester derivatives. M. S. Dunn, C. E. Redemann, and S. Lauritsen (J. Amer. Chem. Soc., 1932, **54**, 4335—4337).—The mol. ratios of Et benzyl- (I) and dibenzyl-malonate formed from equimol. amounts of Na, $CH_2(CO_2Et)_2$, and CH_2PhCl when the reaction is carried out in MeOH (or EtOH) and PhMe are 2 : 1 and 2·1—12·5 : 1, respectively; with no solvent the ratio is 1·2 : 1. The results support Leuchs' view that disubstituted malonic esters may be formed directly from the reactants. CH_2PhCl does not react with $CH_2(CO_2Et)_2$ or (I) in boiling PhMe. H. B.

Cleavage of disubstituted malonic esters by sodium ethoxide. A. C. Cope and S. M. McElvain (J. Amer. Chem. Soc., 1932, **54**, 4319—4325).—The following reactions occur when disubstituted malonic esters are heated with dry NaOEt: (i) $CR_2(CO_2Et)_2 \longrightarrow CHR_2{\cdot}CO_2Et + CO + CO_2 + C_2H_4$ etc.; (ii) $CR_2(CO_2Et)_2 + NaOEt \longrightarrow CO_2Et{\cdot}CR_2{\cdot}C(ONa)(OEt)_2 \longrightarrow Et_2CO_3 + CR_2{:}C(ONa){\cdot}OEt$; the extent of reaction (i) is determined by the yield of $CHR_2{\cdot}CO_2Et$ and that of (ii) by the wt. of Et_2CO_3. Thus $CEt_2(CO_2Et)_2$ at 220—230° gives $CHEt_2{\cdot}CO_2Et$ (67%) and Et_2CO_3 (16%); Et ethyl*iso*amylmalonate similarly affords Et α-ethyl*iso*heptoate (66%) and Et_2CO_3 (12%), whilst Et ethyl-α-methylbutylmalonate yields Et β-methyl-α-ethylhexoate (64%) and Et_2CO_3 (4%); $CPhEt(CO_2Et)_2$ at 120°/24 mm. furnishes Et α-phenylbutyrate (38%) and Et_2CO_3 (58%); Et ethylvinylmalonate gives Et_2CO_3 (38%) and 35% of recovered ester at 100°/14 mm.; $CPh_2(CO_2Et)_2$ at 100°/20 mm. affords Et_2CO_3 (90%). The following cleavages by EtOH–NaOEt are reported: $CPh_2(CO_2Et)_2$ to $CHPh_2{\cdot}CO_2Et$; $CEt_2(CO_2Et)_2$ (at 250°) to $CHEt_2{\cdot}CO_2Et$; $CHEt(CO_2Et)_2$ at 250° to $PrCO_2Et$. 5 : 5-Diethylbarbituric acid (65%) is obtained from $CEt_2(CO_2Et)_2$, $CO(NH_2)_2$, and dry NaOEt at 170°; $CPh_2(CO_2Et)_2$ similarly gives (mainly) $CHPh_2{\cdot}CO{\cdot}NH_2$ and some $CHPh_2{\cdot}CO_2H$. H. B.

Synthesis of ethylvinylmalonic ester and incidental compounds. A. C. Cope and S. M. McElvain (J. Amer. Chem. Soc., 1932, **54**, 4311—4319).—$CNaEt(CO_2Et)_2$ and CHBr:CHBr in Et_2O give about 25% of *Et ethyl-β-bromovinylmalonate*, b.p. 117—120°/1 mm., reduced catalytically (Adams) to $CEt_2(CO_2Et)_2$ and by Zn dust and 95% EtOH at 170° to *Et ethylvinylmalonate* (I), b.p. 122—124°/30

mm., also reduced catalytically to $CEt_2(CO_2Et)_2$. Other products formed in the above condensation are Et_2CO_3 (7%) and *Et* Δ$^{\gamma}$-*octene*-$\gamma\zeta\zeta$-*tricarboxylate* (II) (30·7%), b.p. 150—152°/2 mm., 304—306°/740 mm.; (II) is reduced catalytically (Cu–Cr oxide) to *Et octane*-$\gamma\zeta\zeta$-*tricarboxylate*, b.p. 154—156°/2 mm., which when hydrolysed and then decarboxylated gives αα′-diethyladipic acid. The formation of (II) involves the changes: $CHBr{:}CH{\cdot}CEt(CO_2Et)_2$ + EtOH ⟶ Et_2CO_3 + $CHBr{:}CH{\cdot}CHEt{\cdot}CO_2Et$ (III); (III) ⟶ $CH_2Br{\cdot}CH{:}CEt{\cdot}CO_2Et$ (IV); $CNaEt(CO_2Et)_2$ + (IV) ⟶ $CO_2Et{\cdot}CEt{:}CH{\cdot}CH_2{\cdot}CEt(CO_2Et)_2$; the EtOH is produced by reduction of the original $CHEt(CO_2Et)_2$ with 23% of the Na used. (I) and EtOH–NaOEt give the unstable *Et* γ-*ethoxy*-α-*ethylcrotonate*, b.p. 96—99°/14 mm., reduced (Cu–Cr oxide catalyst) to $CHEt_2{\cdot}CO_2Et$ and *Et* γ-*ethoxy*-α-*ethylbutyrate*, b.p. 90—92°/14 mm., which is also prepared by way of *Et ethyl*-β-*ethoxyethylmalonate*, b.p. 142—143°/17 mm. [from $CHEt(CO_2Et)_2$ and $OEt{\cdot}CH_2{\cdot}CH_2Br$], and γ-*ethoxy*-α-*ethylbutyric acid*, b.p. 138—139°/18 mm. (I) could not be converted into a barbituric acid by $CO(NH_2)_2$ in EtOH–NaOEt; α-ethoxycrotonamide results by alcoholysis of (I) and subsequent rearrangement of the intermediate ester to $CHMe{:}CEt{\cdot}CO_2Et$, which then reacts with $CO(NH_2)_2$ (or NH_3). Et ethyl-β-bromoethylmalonate (V), b.p. 128—130°/3 mm., when heated, passes into α-*carbethoxy*-α-*ethylbutyrolactone*, b.p. 265—267°/740 mm., 135—138°/9 mm. [the Et ethyl-β-hydroxyethylmalonate of Shonle *et al.* (A., 1930, 1047) is probably this lactone]. (V) and NMe_3 in EtOH at 130° give NMe_4Br and Et ethyl-β-dimethylaminoethylmalonate [hydrochloride, m.p. 147—148° (lit. 154°)]. H. B.

Phenacyl and *p*-bromophenacyl esters of dibasic organic acids. T. L. Kelly and P. A. Kleff (J. Amer. Chem. Soc., 1932, **54**, 4444—4445).—The following are prepared essentially by Reid's method (A., 1919, i, 157; 1920, i, 480): phenacyl adipate, m.p. 87·6°, pimelate, m.p. 72·4°, suberate, m.p. 102·4°, azelate, m.p. 69·7°, sebacate, m.p. 80·4°, phthalate, m.p. 154·4°, *iso*phthalate, m.p. 191°, terephthalate, m.p. 192·2°; *p*-bromophenacyl glutarate, m.p. 136·8°, adipate, m.p. 154·5°, pimelate, m.p. 136·6°, suberate, m.p. 144·2°, azelate, m.p. 130·6°, itaconate, m.p. 117·4°, *l*-malate, m.p. 179°, phthalate, m.p. 152·8°, *iso*phthalate, m.p. 179·1°, terephthalate, m.p. 225°. H. B.

Colour reactions and autoxidation of hydropolyenecarboxylic esters. R. Kuhn, P. J. Drumm, M. Hoffer, and E. F. Moller (Ber., 1932, **65**, [*B*], 1785—1788).—Dihydrocrocetin Me_2 ester in C_5H_5N gives a dark blue colour on addition of 2*N*-NaOH; the solution becomes orange-red when shaken and gives the crocetin spectrum. In high vac. the blue solution is stable, but addition of O causes immediate production of crocetin Me_2 ester. Methyldihydrobixin similarly affords an emerald-green solution from which β-methylbixin, m.p. 202°, separates on access of air. C_5H_5N can be replaced by quinoline, $COMe_2$, or COPhMe, but not by EtOH or EtOAc; alkali metal can be used in place of the hydroxide. Et dihydromuconate (I) with cold NaOEt–EtOH or C_5H_5N–2*N*-NaOH gives a dark red sodio-compound from which (I) can be readily recovered; the colour changes after a time to brownish-yellow. The intensely-coloured compounds are regarded as double enolates. Autoxidation of methyldihydrobixin in presence of amines proceeds to the absorption of 10 O without coming to a definite end; with NaOH rapid absorption of 2 O takes place, followed by a much slower O consumption. The process is accompanied by production of H_2O_2. H. W.

Plant dyes. XLVI. Constitution of crocetin and bixin. Synthesis of perhydronorbixin. P. Karrer, F. Benz, R. Morf, H. Raudnitz, M. Stoll, and T. Takahashi (Helv. Chim. Acta, 1932, **15**, 1399—1419; cf. A., 1932, 1234).—The results of Kuhn *et al.* (A., 1931, 1067) on the analysis of crocetin (I) and perhydrocrocetin (II) and the quant. CrO_3 oxidation of (I) are confirmed. Formulation of (I) as αεxξ-tetramethyltetradecaheptaene-αξ-dicarboxylic acid and of norbixin (III) as γημπ-tetramethyloctadecanonaene-ασ-dicarboxylic acid instead of the older unsymmetrical formulæ is supported by the degradative experiments, (*a*)—(*d*), and (*e*) by synthesis of perhydronorbixin (IV). (*a*) (II), red P, and Br give the αα′-*Br*$_2$-*acid* (not obtained pure), changed by boiling, dil. alkali into the αα′-(*OH*)$_2$-*acid* (not obtained pure), the *Me*$_2$ ester, b.p. 165°/0·04 mm. (prepared by CH_2N_2), of which with MgMeI yields the *diglycol*, $[OH{\cdot}CMe_2{\cdot}CMe(OH){\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}]_2$ (cannot be distilled); this with $Pb(OAc)_4$ in C_6H_6 at 45° gives $COMe_2$ and β*o*-*diketo*-ζλ-*dimethyl*-n-*hexadecane*, b.p. 132—135°/0·05 mm. (*disemicarbazone*, m.p. 168°), shown by colour reactions not to be an aldehyde. (*b*) (IV) gives similarly the impure αα′-*Br*$_2$- and αα′-(*OH*)$_2$-*acid*; the *Me*$_2$ ester of the latter, b.p. 213—216°/0·14 mm., gives the *diglycol*, $[OH{\cdot}CMe_2{\cdot}CH(OH){\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}]_2$, and thence γημπ-*tetramethyloctadecane*-ασ-*dialdehyde*, b.p. 185°/0·3 mm., which gives colour reactions of aldehydes and is oxidised to the corresponding *dicarboxylic acid*, b.p. 220°/0·1 mm. (*amide*, m.p. 127°). (*c*) Na–Hg and bixin in hot EtOH–C_5H_5N with a little H_2O give αα′ -*tetrahydro*- and (possibly) αα′ββ′γγ′-*hexahydro*-*norbixin*, an oily mixture, oxidised by alkaline $KMnO_4$ to succinic acid. (*d*) The Me_2 ester of (I) gives a similar mixture of *tetra*- and *hexa*-*hydro*-derivatives, oxidised to methylsuccinic acid. (*e*) The Et_2 ester, b.p. 135°/12 mm., of αα′-dimethylpimelic acid, solid, b.p. 208°/12 mm. (obtained in 60% yield from $CH_2(CH_2Br)_2$ and Et_2 sodiomethylmalonate), yields by reduction βζ-*dimethylheptane*-αη-*diol*, b.p. 117°/0·45 mm., which with PBr_3 or, better, gaseous HBr gives αη-*dibromo*-βζ-*dimethylheptane*, b.p. 135°/10 mm. This with NaOEt and $CH_2(CO_2Et)_2$ affords γη-*dimethylnonane*-αι-*dicarboxylic acid*, the *Et*$_2$ ester, b.p. 129°/0·2 mm., of which by partial hydrolysis gives the *Et* ester, b.p. 159°/0·2 mm., electrolysis of which affords *Et*$_2$ γη-*dimethyldecoate*, b.p. about 80°/0·3 mm. (with possibly a little Δ$^{\theta}$-ester), and the Et_2 ester of (IV). Natural and synthetic (IV) give the same diamide, m.p. 110·5°, and *di-tribromoanilide*, m.p. 83°. The new formulæ for (I) and (III) necessitate the following constitutions for their derivatives: crocetane, βζλο-

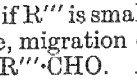
tetramethylhexadecane; bixane, δθνρ-tetramethyleicosane; dibixane, 4 : 8 : 13 : 17 : 22 : 26 : 31 : 35-octamethyloctatriacontane. R. S. C.

d-Galacturonic acid and its methylation products. K. Smoleński and M. Cichocki (Coll. Czech. Chem. Comm., 1932, **4**, 500—503).—*d*-Galacturonic acid monohydrate (A., 1927, 229), $[\alpha]_D^{\theta}$ +77·93° to +52·24° in 24 hr., with 0·25% HCl in MeOH at 100° affords the *Me* ester (I), m.p. 137—138°, $[\alpha]_D^{20}$ +124·9° in H_2O, of *α-methyl*-d-*galacturonic acid*, m.p. 115—116°, $[\alpha]_D^{20}$ +138·5°, which is isolated from its *Ba* salt, $[\alpha]_D^{20}$ +103·9°, obtained by hydrolysis with $Ba(OH)_2$. The mother-liquor from (I) affords the impure syrupy *Me* ester, $[\alpha]_D^{20}$ −36·92°, of *β-methyl*-d-*galacturonic acid*, $[\alpha]_D^{20}$ −32·3° (*Ba* salt, $[\alpha]_D^{20}$ −38·6°). J. W. B.

Crystalline *d*-mannuronic acid. K. P. Link (Science, 1932, **76**, 386).—*d*-Mannuronic acid, m.p. 165°, has been obtained [by E. Schoeffel] by decomposing the Ba salt at −10° in presence of EtOH; [α] −50° ⟶ −20° in 2 hr. L. S. T.

***iso*Propylidenehexuronic acid.** L. von Vargha (Nature, 1932, **130**, 846—847).—When shaken for 24 hr. with $COMe_2$ in presence of $CuSO_4$ or when 5% H_2SO_4 is added to its $COMe_2$ solution, hexuronic acid (I) yields the iso*propylidene* derivative, m.p. 220—222° (decomp.), $[\alpha]^{20}$ +20°, +15°, and +28° in H_2O, EtOH, or MeOH, respectively, the corresponding vals. for (I) being +24°, +58°, and +50°. L. S. T.

Action of sodium ethoxide on ethyl *l*-α-benzenesulphonylbutyrate. W. C. Ashley and R. L. Shriner (J. Amer. Chem. Soc., 1932, **54**, 4410—4414).—Et benzenesulphonylacetate (from $PhSO_2Na$ and $CH_2Cl{\cdot}CO_2Et$ in EtOH) and EtI in EtOH–NaOEt give Et α-benzenesulphonylbutyrate, m.p. 63—64°; the free acid, m.p. 123—124° (*amide*, m.p. 169—170°), is resolved by brucine into l-α-*benzenesulphonylbutyric acid* (I), m.p. 105—107° (softens at 60°), α_D^{27} −27·3° in EtOH (*brucine* salt), which is converted through the chloride into the *Et* ester (II), m.p. 44·5—45·5°, α_D^{25} −32·48°. Treatment of (II) with EtOH–NaOEt at −10° gives an inactive Na derivative. The half-life periods of (I) and (II) in EtOH at 27° are 1350 and 80 hr., respectively; racemisation is ascribed to the change $PhSO_2{\cdot}CHEt{\cdot}CO_2R$ ⟶ $PhSO_2{\cdot}CEt{:}C(OH)(OR)$. H. B.

Glycidic synthesis of aldehydes. G. Darzens (Compt. rend., 1932, **195**, 884—886).—Hydrolysis of glycidic esters 
gives the ketone, CHR′R″·COR‴, if R‴ is small (cf. A., 1912, i, 627), but when R‴ is large, migration occurs with formation of aldehyde, CR′R″R‴·CHO. *Et α-chlorolaurate* (I), b.p. 132—133°/4 mm., $COMe_2$, and NaOEt in EtOH at −10° give the *glycidic* ester, b.p. 162—165°/5 mm., easily hydrolysed by NaOH–EtOH to the *glycidic acid*, m.p. 22°, b.p. 184—185°/15 mm. When the acid is distilled at atm. pressure, it gives CO_2 and *αα-dimethyldodecaldehyde*, b.p. 156—160°/16 mm. (*semicarbazone*, m.p. 59·5°). (I) and *cyclo*hexanone yield similarly the *glycidic* ester, b.p. 173—176°/5 mm., and 1-n-*decyl*cyclo*hexan*-1-*aldehyde*, b.p. 166—170°/15 mm. (*semicarbazone*, m.p. 98·5°), whilst with PhCHO the *glycidic* ester, b.p. 185—190°/5 mm., and *α-phenyl-α-methyl*-n-*dodecaldehyde*, b.p. 178—180° (pressure not stated), m.p. 49° (*semicarbazone*, m.p. 195°), are formed. R. S. C.

Polyene compounds. II. Condensation products of crotonaldehyde. Production of alicyclic compounds. K. Bernhauer and G. Neubauer (Biochem. Z., 1932, **251**, 173—186; cf. A., 1932, 834).—The condensation product contains two aldehydes (I and II). (I), $C_8H_{10}O$, b.p. 71—73°/12 mm. (*p*-nitrophenylhydrazone, m.p. 142°; semicarbazone, m.p. 196°; stable H sulphite compound), yields on reduction with H_2 in presence of Pd–$CaCO_3$ a *substance*, $C_8H_{12}O$, m.p. 98—101°, b.p. 75—76/12 mm. (*p*-nitrophenylhydrazone, m.p. 160—163°), which yields an isomeric *aldehyde* (*p*-nitrophenylhydrazone, m.p. 213—214°; semicarbazone, m.p. 171—172°) when boiled at atm. pressure. On oxidation with Ag_2O (I) yields an acid, $C_8H_{10}O_2$ (probably dihydro-*o*-toluic acid), m.p. 62—63° (Br_2-derivative, unstable, m.p. 134°), which, on dehydrogenation with HBr or Pd–$BaSO_4$, yields *o*-toluic acid, m.p. 102°. (I) is probably dihydro-*o*-tolualdehyde. (II) is less stable. On oxidation with Ag_2O it yields a dibasic unsaturated *acid*, with one double linking, $C_8H_{12}O_4$, m.p. 124—125°, and an unsaturated monobasic acid, $C_8H_{10}O_3$, b.p. 140—145°/3 mm. Possible mechanisms for the reactions involved in the conversion of unsaturated aliphatic aldehydes into alicyclic and aromatic compounds are discussed. W. McC.

Polyene compounds. III. Condensation products of crotonaldehyde. K. Bernhauer and K. Irrgang (Biochem. Z., 1932, **254**, 434—437).—A fraction of the condensation product, b.p. 81—95°/12 mm., gave on oxidation with Ag_2O–Na_2O_2 *p*-toluic acid and was probably dihydro-*p*-tolualdehyde. P. W. C.

Three-carbon series. I. Synthesis of glyceraldehyde and glycerol. II. Chemical and biochemical production of alkyl ethers of dihydroxyacetone. III. Crystalline α-phenylglycerol. Detection of acraldehyde and of methylglyoxal. I. S. Neuberg (Biochem. Z., 1932, **255**, 1—26; cf. A., 1930, 1164).—I. The yield of cryst. glyceraldehyde (I) from fresh 10% acraldehyde and activated Na or Ba chlorate is 14%, but can be increased if the dinitrophenylhydrazone is used for purification. Reduction of (I) yields glycerol in 60% yield.

II. The α-Me ether of dihydroxyacetone [2 : 4-dinitrophenylhydrazone, m.p. 175° (corr.); 2 : 4-*dinitrophenylosazone*, m.p. 272—280° (decomp.)] and the α-Et ether [2 : 4-*dinitrophenylhydrazone*, m.p. 167° (corr.); 2 : 4-*dinitrophenylosazone*, m.p. 265—275° (decomp.)], are obtained as syrups by the action of *Bacterium suboxidans* or (less effectively) of *B. xylinum* or by oxidation with NaOBr. By the biochemical method the yield is ≯20% and less by the chemical method.

III. α-Phenylglycerol prepared by the method of Moureu and Gallagher (A., 1922, i, 34) crystallises after 8 months in the dark, m.p. 100·5° (corr.). The 2 : 4-dinitrophenylhydrazones of glyceraldehyde and dihydroxyacetone give 31—44% yields of AcCHO on

treatment with hot dil. H_2SO_4. *Acraldehyde*-2 : 4-*dinitrophenylhydrazone*, m.p. 166—167°, has very low solubility in aq. liquids. The *compound* OH·CMe(SO_3Na)·CH(OH)·SO_3Na is pptd. from aq. solution by EtOH. W. McC.

Colour reaction of ketones. K. Taufel and H. Thaler (Z. physiol. Chem., 1932, **212**, 256—262).—A sensitive colour reaction consists in treating 50 mg. of substance with 0·4 c.c. of pure *o*-OH·C_6H_4·CHO, adding 4 c.c. of H_2O, shaking, adding 2 c.c. of conc. H_2SO_4, and again shaking.. A red colour in the upper layer usually indicates the presence of the group ·CH_2·CO·CH_2·. J. H. B.

Phytochemical reduction of heptan-α-ol-β-one. P. A. Levene and A. Walti (J. Biol. Chem., 1932, **98**, 735—738).—dl-α-*Chloroheptan*-β-*ol*, b.p. 93°/13 mm., from CH_2Cl·CHO and Mg amyl bromide, is oxidised to α-*chloroheptan*-β-*one*, b.p. 80°/13 mm., transformed by HCO_2K in MeOH into α-*hydroxyheptan*-β-*one* (I), b.p. 95°/20 mm. (I) is reduced by a fermenting mixture of sugar and yeast to d-*heptane*-αβ-*diol*, b.p. 121—122°/12 mm., $[\alpha]^{25}$ +16·81° in EtOH (*diphenylurethane*, m.p. 111—112°, $[\alpha]^{23}$ +12·14° in EtOH; α-*bromoheptan*-β-*ol*, b.p. 75°/15 mm., $[\alpha]^{22}$ +2·0°). R. N. C.

Recovery of sugars from their hydrazones. H. Collatz and I. S. Neuberg (Biochem. Z., 1932, **255**, 27—37).—Carbohydrates (*e.g.*, glycollaldehyde, glyceraldehyde, dihydroxyacetone, *l*-arabinose, *d*-mannose) can readily be obtained pure (often cryst.) and in good yield by decomposing their phenyl-, diphenyl-, or dinitrophenyl-hydrazones with MeCHO. In some cases other carbonyl compounds of low mol. wt. (*e.g.*, $COMe_2$) may replace MeCHO and sometimes other substances (*e.g.*, uronic acids) may also be obtained pure in this way. Almost the whole of the MeCHO hydrazone produced may be recovered. *Glycollaldehyde*-2 : 4-*dinitrophenylhydrazone* has m.p. 155—156° (corr.); glycer-2 : 4-dinitrophenylosazone has m.p. 275—277° (corr.). W. McC.

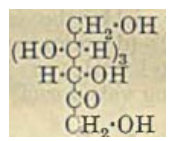
Active reductant of glucose and first steps in its oxidation. J. M. Ort (Proc. Staff. Mtgs. Mayo Clinic, 1932, **7**, 203—204).—Activation of glucose proceeds by (1) ionisation as a weak acid, (2) momentary formation of -enediol. Mild oxidising agents attack this, but not normal glucose. At p_H 7—10 in absence of air, H is the only reductant accumulating appreciably in slightly alkaline solutions in 1—2 days; at p_H 10 the H_2 (pressure 0·01 atm.) can be removed with a pump. When air, H_2O_2, or other oxidants are added, provided these are not able to break the entire -enediol double linking, a glucose oxide and a peroxide are formed. Ch. Abs.

Substitution of glucose in position 4. I. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1932, **97**, 763—775).—4 : 6-Benzylidene-β-methylglucoside 2 : 3-dibenzoate with HCl in $COMe_2$ gives β-*methylglucoside* 2 : 3-*dibenzoate* (I), $[\alpha]_D^{20}$ +92·8° in $CHCl_3$ [Ac_2 derivative, m.p. 131—132° (sinters 123°)], $[\alpha]_D^0$ +79·8° in $CHCl_3$ (cf. A., 1929, 428)]. Partial benzoylation of (I) gives β-*methylglucoside* 2 : 3 : 6-*tribenzoate*, m.p. 144·5—145·5°, $[\alpha]_D^{20}$ +82·0° in $CHCl_3$ [*Ac* derivative, m.p. 156—157°, $[\alpha]_D^{20}$ +96·0° in $CHCl_3$ (not identical with 6-acetyl-β-methylglucoside 2 : 3 : 4-tribenzoate); 4-p-*toluenesulphonate*, m.p. 191—192° (decomp.), $[\alpha]_D^{20}$ +43·0° in $CHCl_3$; *Me ether* (II); $[\alpha]_D^{21}$ +58·5° in $CHCl_3$. β-Methylglucoside 2 : 3 : 6-triacetate (*Bz* derivative, m.p. 98—99°, $[\alpha]^{20}$ −61·0°) (cf. A., 1927,1174), is similarly obtained. (II) on hydrolysis and acetylation gives 4-*methyl*-β-*methylglucoside* 2 : 3 : 6-*triacetate*, m.p. 107—108°, $[\alpha]_D^0$ −32·8° in $CHCl_3$, also obtained from the Ac_4 derivative of 4-methylglucose (A., 1925, i, 1242) through the acetobromo-derivative. A. A. L.

Oxidation of β-glucosan. B. Hvistendahl (Svensk Kem. Tidskr., 1932, **44**, 231—235).—Oxidation of β-glucosan with $KMnO_4$ gives $(CHO)_2$ at moderate temp., with org. acids, principally $H_2C_2O_4$; if a large excess of $KMnO_4$ be used, and the temp. raised, only $H_2C_2O_4$ results. No evidence could be obtained of the formation of the diketonic substance mentioned by Pictet (A., 1920, i, 819). Oxidation of glucose and galactose under similar conditions yields only $H_2C_2O_4$. H. F. H.

Configuration of sedoheptose. V. Ettel (Coll. Czech. Chem. Comm., 1932, **4**, 513—520).—The identity of volemitol with β-*d*-mannoheptitol (this vol., 47) renders La Forge's configuration for sedoheptose (A., 1917, i, 444; 1920, i, 595) incorrect.

(I.) CH_2·OH
(HO·C·H)$_3$
H·C·OH
HO·C·H
CH_2·OH



(II.)

Consideration of the possible theoretical configurations for this heptose and of known data indicate that β-sedoheptitol is identical with β-*l*-guloheptitol (I) (Wherry, A., 1920, i, 595) and α-sedoheptitol with *d*-mannoheptitol, whence sedoheptose is a *d*-altro-ketoheptose (II). J. W. B.

Glucosides. IX. Methyl salicylate vicianoside (? violutoside). A. Robertson and R. B. Waters (J.C.S., 1932, 2770—2771).—The 2 : 3 : 4-triacetyl-β-glucoside of Me salicylate (A., 1931, 1400) and *O*-triacetylarabinosidyl bromide in dry C_6H_6 containing Ag_2O afford during 65 min. the O-*hexa-acetyl*-β-*vicianoside* of Me salicylate, m.p. 158°, deacetylated by NH_3 in MeOH to *Me salicylate* β-*vicianoside*, m.p. 173° after sintering at 168—169°, probably identical with violutoside (A., 1926, 715). J. L. D.

Crystalline Kombe strophanthin. J. S. Meulenhoff (Pharm. Weekblad, 1932, **69**, 1161—1173).—The crystals which separate when the solution of the mixed glucosides in a small quantity of H_2O is preserved are extracted with $COMe_2$; Et_2O is added to the dried solution and the fairly pure cryst. ppt. is removed. A purer product is obtained by adding H_2O to an EtOH extract of the crude material; cymarin may be removed by recrystallisation from H_2O or by extraction with $CHCl_3$. If the EtOH solution is not kept cold, decomp. occurs, and the pure substance can no longer be isolated. The material described by Jacobs contains an appreciable quantity of cymarin. H. F. G.

Microscopical detection of glycogen and galactogen and their separation. F. May and F.

KORDOWICH (Z. Biol., 1932, **93**, 233—238).—Galactogen differs from glycogen in giving no colour reaction with I, but no satisfactory differentiation is at present available. P. G. M.

Mol. wt. and chemical structure of cellulose and starch. I. R. MOROZOV (J. Appl. Chem., Russia, 1932, **5**, 211—216).—Formulæ [both $(C_6H_{10}O_5)_{64}$] are proposed for cellulose and starch. CH. ABS.

Highly-polymerised compounds. LXXII. Dependence of the viscosity of cellulose solutions on temperature. H. STAUDINGER (Ber., 1932, **65**, [*B*], 1754—1756).—A reply to Hess and Rabinovitsch (A., 1932, 1117). H. W.

Differentiation of hemicelluloses. L. F. HAWLEY and A. G. NORMAN (Ind. Eng. Chem., 1932, **24**, 1190—1194).—The term hemicellulose is used to include incrusting substances not closely associated with cellulose and generally containing a uronic acid and also substances contained in the Cross and Bevan cellulose fraction which are free from uronic acids. It is suggested that the former class be termed polyuronides and the latter cellulosans. A. G.

Hemicelluloses of wood. (MISS) M. H. O'DWYER (Chem. and Ind., 1932, 968—971).—A review of recent work.

Fission of quaternary ammonium compounds by hydrogenation. XI. Ethylenic and carbon–nitrogen linkings. H. EMDE (Helv. Chim. Acta, 1932, **15**, 1330—1336; cf. A., 1912, i, 801).—A lecture. The following is new. [With H. KULL.] A C–N linking in quaternary NH_4 salts is broken by hydrogenation (Pd–C or Pd–$BaSO_4$) in purified AcOH, AcOH–NaOAc, aq. NaOAc, or H_2O. Thus, $CH_2Ph{\cdot}NPhMe_2Cl$ in AcOH (Pd–$BaSO_4$) yields PhMe and $NPhMe_2$. R. S. C.

Synthesis of β-ethoxyamines. I. J. WERNERT and W. R. BRODE (J. Amer. Chem. Soc., 1932, **54**, 4365—4369).—β-Ethoxyamines, $OEt{\cdot}CHR{\cdot}CH_2{\cdot}NH_2$ [accompanied by $(OEt{\cdot}CHR{\cdot}CH_2)_2NH$], are prepared from $OEt{\cdot}CHR{\cdot}CH_2Br$ (Boord *et al.*, A., 1930, 1269; 1931, 709; 1932, 361) and MeOH–NH_3 at about 25° or, better, 90—100° under pressure. The following are described: β-ethoxy-β-phenylethylamine, b.p. 107—109°/12 mm.; β-ethoxybutylamine, b.p. 138·5—140·5°; ββ′-diethoxydibutylamine, b.p. 132—135°/31 mm.; *β-ethoxyamylamine*, b.p. 56—56·5°/15 mm.; *-diethoxydiamylamine*, b.p. 133·5—134·5°/14 mm.; *β-ethoxy-γ-methylamylamine*, b.p. 64—65°/13 mm.; *ββ′-diethoxy-γγ′-dimethyldiamylamine*, b.p. 144—147°/14 mm.; *β-ethoxyhexylamine*, b.p. 68—69°/13 mm.; *-diethoxydihexylamine*, b.p. 151—154°/12 mm. *N-β-Ethoxybutylaniline*, from β-ethoxybutyl bromide and NH_2Ph in MeOH, has b.p. 153·5°/21 mm. H. B.

Preparation of diethyl*iso*propylamine. S. CASPE (J. Amer. Chem. Soc., 1932, **54**, 4457).—$Pr^{\beta}Br$ heated with $NHEt_2$ and glycerol [or $(CH_2{\cdot}OH)_2$] for 72 hr. gives 60% of *diethylisopropylamine*, b.p. 108°. H. B.

Mode of union of the glucosamine residues in chitin. L. ZECHMEISTER, W. GRASSMANN, G. TÓTH, and R. BENDER (Ber., 1932, **65**, [*B*], 1706—1708).—Chitodextrin, the most sparingly sol. product of the action of superconc. HCl on chitin (cf. A., 1931, 935), is readily hydrolysed by emulsin as shown by the rapid increase of the I val. (Willstätter–Schudel). Increase in acidity is not observed and acetglucosamide is stable towards emulsin. The experiments afford further evidence of the β-glucosidic nature of chitin. H. W.

Reaction of formaldehyde with glycine. E. GUBAREV and A. BYSTRENIN (Biochem. Z., 1932, **255**, 92—102).—The extent to which glycine and CH_2O interact and the rate of reaction vary greatly with the proportions of the reactants. Equilibrium is attained in from 1 to more than 30 days. If the medium is alkaline the extent of reaction is increased but the attainment of equilibrium is retarded. W. McC.

Cupric complexes of glycine and alanine. H. BORSOOK and K. V. THIMANN (J. Biol. Chem., 1932, **98**, 671—705).—Absorption spectra indicate the existence of at least four types of complex of both glycine and alanine with Cu, and the absorption spectra of each in the pure state have been determined. The constitution of each has been determined from potentiometric and spectrophotometric data. The no. of H ions set free in the formation of all except the two basic compounds and the orders of magnitude of the instability consts. were determined. H. G. R.

Aminolysis of aspartic acid. E. BAUR and K. WUNDERLY (Naturwiss., 1932, **20**, 873).—Aspartic acid in saturated aq. solution in absence of air, and in contact with C at 40—80°, yields NH_4 lactate, CO_2, and small amounts of $AcCO_2H$ and MeCHO in addition to NH_4 malate (cf. A., 1924, 847). W. O. K.

Syntheses of peptides of *d*-lysine; *d*-lysyl-*d*-glutamic acid and -*l*-histidine. M. BERGMANN, L. ZERVAS, and J. P. GREENSTEIN (Ber., 1932, **65**, [*B*], 1692—1696; cf. A., 1932, 935).—*Me* d-αε-*diaminohexoate dihydrochloride*, m.p. 212° (corr.), is converted through the *dibenzylcarbonato*-compound into *dibenzylcarbonato*-d-*lysinehydrazide* (I). Successive treatment of (I) with $NaNO_2$ and Et_2 *d*-glutamate affords *Et*$_2$ *dibenzylcarbonato*-d-*lysyl*-d-*glutamate*, m.p. about 105° after softening at 95°, whence the corresponding *acid*, m.p. about 130° after softening at 96°, and d-*lysyl*-d-*glutamic acid* (II), $NH_2{\cdot}[CH_2]_4{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}[CH_2]_2{\cdot}CO_2H$, m.p 197° (corr.), $[\alpha]^{18}$ +22·9° in H_2O. (II) is almost neutral to litmus, behaves as a dicarboxylic acid in EtOH in presence of thymolphthalein, and is not affected by animal proteolytic enzymes. (I) when transformed into the azide and coupled with histidine Me ester affords *dibenzylcarbonato*-d-*lysyl*-l-*histidine Me* ester, m.p. 138—140°, hydrolysed to *dibenzylcarbonato*-d-*lysyl*-l-*histidine*, m.p. 157—162°, whence d-*lysyl*-l-*histidine sulphate*, $C_{12}H_{21}O_3N_5,H_2SO_4$, m.p. 205°, $[\alpha]_{\mathrm{I}}^{20}$ +35·3° in H_2O. H. W.

Optical rotation of *d*-talonamide and of salts of *d*-talonic acid. A. G. RENFREW and L. H. CRETCHER (J. Amer. Chem. Soc., 1932, **54**, 4402—4404).—*d*-γ-Talonolactone (A., 1932, 602) and EtOH–NH_3 give d-*talonamide* (I), m.p. 118—120° (softens at 116°), $[\alpha]_{\mathrm{D}}^{20}$ −13·1° in H_2O (*hydrate*, m.p. 100—102°); *NH_4 d-talonate*, m.p. 148°, $[\alpha]_{\mathrm{D}}^{20}$ +2·9° in H_2O, is

obtained, using conc. aq. NH_3. Na *d*-talonate has $[\alpha]_D^5$ +2·5° in H_2O. The lævorotation of (I) is in accordance with Hudson and Komatsu's rule (A., 1919, i, 524). (I) exhibits slow mutarotation probably owing to the formation of the NH_4 salt. H. B.

Applicability of Artmann and Skrabal's iodometric method for ammonia to the determination of carbamide. K. Wolfel (Z. anal. Chem., 1932, 90, 170—181).—Oxidation of $CO(NH_2)_2$ with NaOBr results in 9—14% of the N being converted into CNO′, but good results (±0·5%) may be obtained by Artmann and Skrabal's method (A., 1907, ii, 196) if the solution is made acid with HCl, after the first reaction ceases, to convert the CNO′ into $NH_4^{\cdot}$, and then again made alkaline so that the regenerated NaOBr oxidises the $NH_4^{\cdot}$. The solution is finally acidified, treated with KI, and the I corresponding with the excess OBr′ titrated with $Na_2S_2O_3$. Addition of Na_2HPO_4 prevents "after-blueing." A. R. P.

Imperfect silver [nitrate]-guanidine complex. M. Lesbre (Compt. rend., 1932, **195**, 880—882).—Guanidine (I) and aq. $AgNO_3$ form a ppt., which redissolves in excess of (I). Electrometric measurements show that the solution contains a complex ion, $[Ag(CH_5N_3)]^{\cdot}$, which, as the concn. of (I) decreases, is in equilibrium with increasing amounts of $[Ag(CH_5N_3)_3]^{\cdot}$. k for the former ion is $5{\cdot}14\times10^{-10}$. Beyond a certain limiting concn. $Ag(CH_5N_3)NO_3$ is pptd. R. S. C.

Ethylenic nitriles. α-Methyl-Δ$^{\alpha}$-octenonitriles and α-hexylacrylonitrile. J. Varhulst and C. Glorieux (Bull. Soc. chim. Belg., 1932, **41**, 501—509).—Oxidation of methylhexylcarbinol with Cr_2O_3 affords *Me hexyl ketone*, b.p. 173·6—174°/770 mm. [*cyanohydrin*, b.p. 131—132°/11 mm., which with $SOCl_2$ and then with HCl yields β-*chloro*-α-*methyloctonitrile* (I), b.p. 113—114°/10 mm., and α-*chloromethyloctonitrile* (II), b.p. 121—122°/10 mm.]. (I) with C_5H_5N gives cis-α-*methyl*-Δ$^{\alpha}$-*octenonitrile*, b.p. 201·2—201·8°/767 mm., and the trans-*form*, b.p. 219—219·6°/767 mm., hydrolysed by cold H_2SO_4 to *amides*, m.p. 68·2—68·6° (III) and 53·2—53·6°, respectively. (II) with C_5H_5N affords α-*hexylacrylonitrile*, b.p. 200·6—201·2°/766 mm., hydrolysed by cold H_2SO_4 to (III). J. L. D.

Applications of thallium compounds in organic chemistry. VIII. Molecular association of dialkylthallium chelate compounds. E. R. Wiltshire and R. C. Menzies (J.C.S., 1932, 2734—2739; cf. A., 1932, 1269).—Chelate dialkyl Tl compounds formed from β-diketones show an association in freezing C_6H_6 varying approx. between 1 and 2. The effect of the alkyl groups on the association is small, the nature of the diketone being the important factor. Association is probably due to the marked tendency of the Tl atom to increase its outer electronic shell to 12. The following are described: *Me* (*dimethylthalli*)-, m.p. 184°; *Me* (*diethylthalli*)-*acetoacetate*, m.p. 127°; *Et* (*dimethylthalli*)-, m.p. 133°; *Et* (*diethylthalli*)-*benzoylacetate*, m.p. 95°; (*dimethylthalli*)-, m.p. 173—175°; (*diethylthalli*)-*dibenzoylmethane*, m.p. 112°. J. L. D.

Reactions of Δ$^{1:3}$-*cyclo*hexadiene. P. Bedos and A. Ruyer (Compt. rend., 1932, **195**, 802—804).—Interaction of Δ$^{1:3}$-*cyclo*hexadiene (I) with HOCl affords the *monochlorohydrin*, $C_6H_8Cl{\cdot}OH$, (II), b.p. 98°/18 mm., m.p. 28—29°, small amounts of *dichlorohydrin*, m.p. 123°, and two *dichlorides*, b.p. 68—69°/12 mm. and 73—77°/12 mm., respectively. (I) and HOI give an *iodohydrin*, transformed, as is (II), into the *monoxide*, C_6H_8O (III), b.p. 45°/22 mm. (III) or a *dioxide*, b.p. 66°/11 mm., is obtained from (I) and BzO_2H. J. L. D.

Mechanism of nitration of benzene. B. V. Tronov and L. V. Ladygina (Ukrain. Chem. J., 1932, 7, [Sci.], 55—63).—The reaction is assumed to be one between double mols. of HNO_3 and C_6H_6, with the formation of an intermediate residual valency complex. R. T.

Catalytic oxidation of *p*-cymene in the liquid phase. C. E. Senseman and J. J. Stubbs (Ind. Eng. Chem., 1932, **24**, 1184—1186).—When O_2 is bubbled through *p*-cymene containing MnO_2 or Mn *p*-toluate the principal product of oxidation is *p*-toluic acid, the max. yield of which is 50% of the *p*-cymeno consumed. Cr_2O_3, Co_2O_3, CeO_2, Fe_2O_3, Ni_2O_3, and CuO are less active catalysts. A. G.

Additive products of styrene and aromatic hydrocarbons. A. Spilker and W. Schade (Ber., 1932, **65**, [*B*], 1686—1689).—Addition of 93% H_2SO_4 and styrene to C_6H_6 at 30—35° yields $CHPh_2Me$, b.p. 148°/15 mm. (oxidised to $COPh_2$), in about 25% yield. α-*Phenyl*-α-p-*tolyl*-, α-*phenyl*-α-3 : 4-*dimethylphenyl*-, α-*phenyl*-α-2 : 4-*dimethylphenyl* and α-*phenyl*-α-2 : 5-*dimethylphenyl-ethane* are prepared similarly. $C_{10}H_8$, styrene, and 93% H_2SO_4 in CCl_4 yield α-*phenyl*-α-2-*naphthylethane*, b.p. 220—222°/15 mm., m.p. 69° (oxidised to *Ph* β-*naphthyl ketone*, m.p. 81°), and non-cryst. α-phenyl-α-1-naphthylethane. H. W.

Rearrangements of poly-inenes. II. *s*-Tetraphenyldiphenylethinylethane. H. E. Munro and C. S. Marvel (J. Amer. Chem. Soc., 1932, **54**, 4445—4450).—Na diphenylphenylethinylmethyl (I), prepared by the method of Moureu *et al.* (A., 1927, 355) or from triphenylpropargyl Me ether and 40% Na–Hg, with $ClCO_2Me$ gives *Me* ααγ-*triphenyl*-Δ$^{\beta}$-*butinenoate*, b.p. 98—105°/2—3 mm., and is converted by $CMe_2Br{\cdot}CMe_2Br$ in Et_2O into the unstable (not isolated) *s*-tetraphenyldiphenylethinylethane (αγγδδζ-hexaphenyl-Δ$^{\alpha\epsilon}$-hexadi-inene) (II). (II) absorbs O_2 rapidly (but does not give a stable peroxide) and is cleaved by 40% Na–Hg to (I). (II) rearranges readily into the hydrocarbon $C_{42}H_{30}$ (III), m.p. 172—173°, described by Moureu *et al.* (*loc. cit.*; cf. Wieland and Kloss, A., 1929, 1053) as (II). (III) does not absorb O_2 and is not cleaved by 40% Na–Hg, but gives a compound, $C_{42}H_{30}Na_2$, which is converted by H_2O into a *hydrocarbon*, $C_{42}H_{32}$, m.p. 239—241°, and by $ClCO_2Me$ into an impure *ester*, $C_{42}H_{30}(CO_2Me)_n$, m.p. 90—93°. H. B.

Proposal to adopt the stem "xen" of A. W. Hofmann's xenyl as basis for nomenclature of diphenyl and its derivatives. W. J. Hale (J. Amer. Chem. Soc., 1932, **54**, 4458—4459).—The following nomenclature is suggested: xenene for diphenyl; xenyl for diphenylyl; xenols for hydroxy-

diphenyls; xenylenediamines for diaminodiphenyls; xenenecarboxylic (or xenoic) acids for diphenylcarboxylic acids; chloroxenenes for chlorodiphenyls.

H. B.

Nitration of 4 : 4′-dichlorodiphenyl. C. C. VERNON, A. REBERNAK, and H. H. RUWE (J. Amer. Chem. Soc., 1932, **54**, 4456—4457).—The results of Shaw and Turner (A., 1932, 259) are confirmed.

H. B.

Rearrangements of poly-inenes. III. Synthesis of 1 : 1′-bis-(1 : 3-diphenylindenyl). L. F. HALLEY and C. S. MARVEL (J. Amer. Chem. Soc., 1932, **54**, 4450—4454).—1-Lithio-1 : 3-diphenylindene (from 1 : 3-diphenylindene and LiBu in C_6H_6 and N_2) and $CMe_2Br{\cdot}CMe_2Br$ give 1 : 1′-*bis*-(1 : 3-*diphenylindenyl*), $(C_6H_4{<}^{CPh}_{CPh}{>}CH)_2$, m.p. 190—191°, which is not identical with the hydrocarbon $C_{42}H_{30}$ (I), m.p. 172—173°, obtained by rearrangement of αγγδδζ-hexaphenyl-Δ$^{\alpha\zeta}$-hexadi-inene (this vol., 56). Oxidation of (I) with CrO_3 in AcOH gives *o*-$C_6H_4Bz{\cdot}CO_2H$, whilst treatment with HCl in boiling AcOH affords a hydrocarbon, m.p. 261—262°, and a small amount of a substance, m.p. 290°. It is improbable that (I) and related compounds (A., 1932, 505) are di-indenyls.

H. B.

Derivatives of 2-ethylnaphthalene. G. LÉVY (Compt. rend., 1932, **195**, 801—802).—Nitration of 2-$C_{10}H_7$-Et in AcOH at 3—10° affords 1-*nitro*-2-*ethylnaphthalene*, m.p. 49·5—50°, reduced by Fe in boiling AcOH during 4 hr. to 2-*ethyl*-α-*naphthylamine*, m.p. 25—28° (*Ac* derivative, m.p. 156·2°), decomp. of the diazonium sulphate affording 2-ethyl-α-naphthol (A., 1932, 734).

J. L. D.

Chlorination of fluorene. J. BUFFLE (Helv. Chim. Acta, 1932, **15**, 1483—1495).—2-Chlorofluorene is best prepared from fluorene and Cl_2 in C_6H_6 or AcOH at 80—90° in presence of I. Some 2 : 7-Cl_2-derivative is also formed. Purification is best effected by distillation.

R. S. C.

Alkylphenanthrenes. V. 9-Methyl-, 1 : 9-dimethyl-, and 1 : 2 : 8-trimethyl-phenanthrenes. R. D. HAWORTH and C. R. MAVIN (J.C.S., 1932, 2720—2723; cf. following abstract).—1-$C_{10}H_7Me$ affords with succinic anhydride, AcCl, and $AlCl_3$ in $PhNO_2$, 4-methyl-α-naphthyl Me ketone (*picrate*, m.p. 101—102°) and β-(4-*methyl*-1-*naphthoyl*)*propionic acid*, m.p. 168—169° [*semicarbazone*, m.p. 202—203°; *Me* ester, m.p. 45—47° (I)]. (I) is reduced by Clemmensen's method and cyclised to 1-*keto*-9-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 74—75° (*semicarbazone*, m.p. 255—257°), which, with MgMeI and subsequent dehydrogenation, affords 1 : 9-*dimethylphenanthrene*, m.p. 87—88° (*picrate*, m.p. 160°). 5-*Cyano*-1-*methylnaphthalene*, m.p. 92—93° (from the 5-NH_2-compound), in boiling PhMe with MgMeI during 3 hr. affords 5-*methyl*-α-*naphthyl Me ketone*, m.p. 44—46°, the oily ω-Br-compound of which with $CMeNa(CO_2Et)_2$ in C_6H_6 during 12 hr., followed by alkaline hydrolysis and heating at 160°, affords β-(5-*methyl*-1-*naphthoyl*)-iso*butyric acid*, m.p. 160—161°, converted into 1-*keto*-2 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II), m.p. 108—109° [*semicarbazone*, m.p. 256—258° (decomp.)]. Interaction of (II) with MgMeI in Et_2O and of the product with Se affords 1 : 2 : 8-trimethylphenanthrene, identical with methylpimanthrene (A., 1931, 359).

J .L. D.

Alkylphenanthrenes. IV. 7-Methyl-1-ethyl- and 1-ethyl-7-*iso*propyl-phenanthrenes: constitution of abietic and *d*-pimaric acids. R. D. HAWORTH (J.C.S., 1932, 2717—2720; cf. A., 1932, 1024).—7-Methyl-1-ethyl- and 1-ethyl-7-*iso*propyl-phenanthrene obtained from 4-keto-7-methyl-1-ethyl- (*semicarbazone*, m.p. 198—200°) and 4-keto-1-ethyl-7-*iso*propyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (*semicarbazone*, m.p. 225—226°) are identical respectively with methylpimanthrene and methylretene, which arise from abietic and *d*-pimaric acids (formulæ suggested) probably by a Wagner–Meerwein change (cf. *ibid.*, 949).

J. L. D.

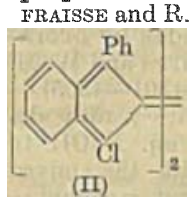
Resin acids. II. 1-Methyl-7-*iso*propylphenanthrene (retene). J. C. BARDHAN and S. C. SENGUPTA (J.C.S., 1932, 2798—2800; cf. A., 1932, 1241).—Reduction of Et γ-*iso*propylidenepimelate (J.C.S., 1907, **91**, 1743) with H_2 affords *Et* γ-iso*propylpimelate*, b.p. 170°/27 mm., which with Na in C_6H_6 gives *Et* 4-iso*propyl*cyclo*hexan*-1-*one*-2-*carboxylate* (I), b.p. 130—132°/10 mm. The K derivative of (I) affords, with β-*o*-tolylethyl bromide in boiling C_6H_6 during 28 hr., *Et* 4-iso*propyl*-2-(β-*o*-*tolylethyl*)cyclo*hexan*-1-*one*-2-*carboxylate*, b.p. 195—197°/2 mm., reduced by Na–Hg to *Et* 4-iso*propyl*-2-(β-*o*-*tolylethyl*)-cyclo*hexan*-1-*ol*-2-*carboxylate*, b.p. 200—205°/2 mm., which, when treated successively with P_2O_5 and Se, affords 1-methyl-7-*iso*propylphenanthrene, identical with retene from abietic acid (A., 1932, 839).

J. L. D.

Trihalides of perylene. K. BRASS and E. CLAR (Ber., 1932, **65**, [*B*], 1660—1662).—Treatment of perylene in C_6H_6 with excess of Br in C_6H_6 ppts. a *compound*, $C_{20}H_{12}Br_3$, m.p. 162° (decomp.) after softening at 157°, from which 1 Br is removed in $PhNO_2$ by $Na_2S_2O_3$. It appears probable that after removal of 1 Br atom, the residual two add to the perylene mol. with production of a dibromide. A less stable *tri-iodide*, partly molten at 190° after softening at 170° (vac.), is obtained from which I is completely removed by $Na_2S_2O_3$.

H. W.

Dissociable organic oxides. Extension of methods of preparation of rubrene. Synthesis of a dichlorodiphenylrubene, $C_{30}H_{18}Cl_2$, and its preparation from dibenzoylmethane. C. DUFRAISSE and R. BURET (Compt. rend., 1932, **195**, 962—964).—Ph phenylethinyl ketone and PCl_5 give a *compound* (I), $C_{30}H_{20}Cl_4$, m.p. 310° (previous decomp.), which when heated loses 2HCl to form 1 : 1′-*dichloro*-3 : 3′-*diphenylrubene* (II), garnet-red, m.p. 251°. (I) [and hence (II)] is also formed from CH_2Bz_2 and PCl_5 (by way of $CClPh{:}CH{\cdot}COPh$) (cf. A., 1932, 616).



H. B.

Sulphonation of aromatic amines by the so-called "baking process." W. HUBER (Helv. Chim. Acta, 1932, **15**, 1372—1383).—To obtain good yields of sulphonic acid by heating the acid sulphate it is necessary to use pure base, to ensure homogeneity of the salt and avoid excess of H_2SO_4, and to remove H_2O

(which causes hydrolysis of the acid and consequent further sulphonation) as it is formed. Addition to the melt of substances, *e.g.*, $H_2C_2O_4$, which yield H_2O by decomp. is disadvantageous. Pure H sulphates are not obtained by the methods given in the lit. They are best obtained by adding the liquid base to the theoretical amount of 70% H_2SO_4, or a solution of the base in AcOH to the theoretical amount of conc. H_2SO_4, and drying the product in vac. Salts thus prepared give the following yields of sulphonic acid when heated at 180°/12—15 mm. in a special apparatus; the temp. given in parentheses are the approx. m.p. of the H sulphates: NH_2Ph (160°), 97·9; *o*-, *m*-, (I), and *p*-toluidine (145°, 120°, and 175°, respectively), 96·2—96·3; 1 : 3 : 4- and 1 : 4 : 2-xylidine (135° and 160°, respectively), 96·0 and 96·4; α- and β-naphthylamine (170° and 205°, respectively), 93·3 and 89·0 (β-salt heated at 220—230°); dehydrothio-*p*-toluidine, 92 (heated at 210—220°); 1-aminoanthraquinone, 90·3% (heated at 200°). Small amounts of base were recovered in each case. Contrary to statements in the lit., (I) gives the 6-sulphonic acid, whilst sulphonation of *m*-nitrotoluene occurs in the 5- (75%) and 6- (25%) positions, and the toluidines and xylidine are sulphonated with oleum at low temp., *m*- as well as *p*- to the NH_2 group. R. S. C.

Action of ω-aminoacetophenone and of piperidine on aromatic nitro-compounds. M. Giua and G. Reggiani (Atti R. Accad. Sci. Torino, 1932, **67**, 51—56; Chem. Zentr., 1932, ii, 875).—ω-Aminoacetophenone hydrochloride in EtOH in presence of NaOAc with 2 : 4 : 5-trinitrotoluene causes substitution of 5-NO_2; with chloro-2 : 4-dinitrobenzene and picryl chloride the phenacylamine residue substitutes the Cl atom. 4 : 6-Dinitro-*N*-phenacyl-*m*-toluidine, m.p. 194°; 2 : 4-dinitro-, m.p. 178°, and 2 : 4 : 6-trinitro-*N*-phenacylaniline, m.p. 170°. *N*-4 : 6-Dinitro-, m.p. 111°, and 2 : 6-dinitro-*m*-tolylpiperidine, m.p. 99·5°. A. A. E.

Rearrangements by the action of nitrous acid on amines of the type CHPhMe·CH$_2$·NH$_2$. P. A. Levene, R. E. Marker, and A. Rothen (J. Amer. Chem. Soc., 1932, **54**, 4463—4464).—Active CHPhMe·CH_2·NH_2 and NOCl give (active) CHPhEtCl (cf. A., 1930, 1287); a similar rearrangement occurs with α-phenyl-α-methylpropylamine (cf. A., 1931, 1413). Dextrorotatory substituted phenylacetic acids are now correlated with lævorotatory substituted β-phenylpropionic acids. H. B.

Desulphurisation of thiocarbamides by bromate and iodate solutions. H. H. Capps and W. M. Dehn (J. Amer. Chem. Soc., 1932, **54**, 4301—4305).—Arylthiocarbamides, NH_2·CS·NHAr, are readily desulphurised by $KBrO_3$ or KIO_3 in aq. NaOH to the corresponding cyanamides, whilst the mixed thiocarbamides, NHR·CS·NHAr (except α-phenyl-γ-benzylthiocarbamide of those studied), give the corresponding carbamides. The following are new: α-*phenyl*-γ-2 : 4-, m.p. 168°, and -2 : 5-, m.p. 168°, *-dichlorophenyl-*, -γ-*o-ethoxyphenyl-*, m.p. 145°, and -γ-4-*hydroxy*-2-*methylphenyl-*, m.p. 177°, *-thiocarbamides*; *anisyl-*, m.p. 210°, and 2 : 5-*dichlorophenyl-*, m.p. 185°, *-thiocarbamides*; α-*o-tolyl*-γ-m-4-*xylylthiocarbamide*, m.p. 162°; α-phenyl-γ-2 : 4-dichlorophenyl-, m.p. 208°, and -γ-m-4-*xylyl-*, m.p. 226°, and α-*o-tolyl*-γ-*p-chlorophenyl-*, m.p. 212°, *-carbamides*. Thiocarbamides often show varying m.p. owing to decomp.; they are best crystallised from PhMe. H. B.

Rearrangement of *o*-amino-sulphones. L. A. Warren and S. Smiles (J.C.S., 1932, 2774—2778; cf. A., 1932, 735).—*o*-Nitrophenyl-*o*-aminoarylsulphones rearrange under the influence of alkaline reagents into the corresponding sulphinic acids: NHR·Ar·SO_2·C_6H_4·NO_2 ⟶ SO_2H·Ar·NR·C_6H_4·NO_2. A similar rearrangement, leading eventually to the disulphide, is undergone by a similarly substituted sulphoxide [cf. (III) ⟶ (VIII) below]. The N-*Me* derivative (Me_2SO_4 and NaOH), m.p. 84°, of *o-nitrobenzenesulpho*-p-*toluidide*, m. p. 116°, is converted by conc. H_2SO_4 at 100° (cf. A., 1915, i, 228) into *o-nitrophenyl* - 4 - *methylamino* - m - *tolylsulphone*, m.p. 122°. This is not demethylated by HBr in AcOH; it is converted slowly by 2*N*-NaOEt in EtOH and rapidly by 50% aq. KOH at 70—80° into *K* *o-nitrophenyl-methylamino*-m-*tolylsulphinate* (I) and a little (II) (below). With MeI in aq. MeOH (I) gives 4-*o-nitrophenylmethylamino*-m-*tolylmethylsulphone*, m.p. 120°, with SO_2 and a little HI in EtOH it gives 4-*o-nitrophenylmethylamino*-m-*tolyl disulphide*, m.p. 132—133°, and with warm AcOH (with loss of HNO_2) 3 : 6-*dimethylthiodiphenylamine dioxide* (II), m.p. 153°.

o-Nitrophenyl 2-*acetamido*-1-*naphthyl sulphoxide* (III), m.p. 198° (decomp.), is obtained from the corresponding sulphide, H_2O_2, and AcOH at 100°; further oxidation at 100° gives the *sulphone* (IV), m.p. 160°, hydrolysed by EtOH–H_2SO_4 to *o-nitrophenyl*-2-*amino*-1-*naphthylsulphone* (V), m.p. 171°. This is isomerised by *N*-NaOH in aq. EtOH to 2-*o-nitroanilinonaphthyl*-1-*sulphinic acid* (VI), m.p. 210° (decomp.) [*methylsulphone* (VII), m.p. 125° (MeI and NaOMe in MeOH)]. The *Ac* derivative of (VI) is similarly formed from (IV), but was not isolated pure, being identified by methylation to 2-*o-nitrophenylacetamido*-1-*naphthylmethylsulphone*, m.p. 195°, which is readily hydrolysed to (VII) by NaOH in EtOH, and is converted by HI in AcOH into N-*o-nitrophenyl*-1-*methyl*-β-*naphthathiazyl periodide*, $\left|C_{10}H_6\begin{matrix}S\\<\\N(C_6H_4\cdot NO_2)\end{matrix}>CMe\right|I_3$, m.p. 183. 2-*o-Nitroanilino*-1-*naphthyl disulphide* (VIII), m.p. 235° (decomp.), is obtained either from (VI) with HI (*d* 1·7) in $COMe_2$ or as a product of rearrangement of (III) by warm 2*N*-NaOH. (VI) is converted by AcOH at the b.p. into *bis*-2-*o-nitroanilino*-1-*naphthyl sulphoxide* (IX), m.p. 225° (decomp.), and *o-nitrophenyl*-β-*naphthylamine*, m.p. 110°; the last-named and H_2S are also formed by reduction of (VIII) or (IX) with HI in AcOH at the b.p. H. A. P.

Bromination of β-naphthylamine. F. Bell (J.C.S., 1932, 2732—2734).—Bromination of *p*-toluenesulphon-2-naphthalide in $CHCl_3$ gives the 1 : 6-*Br*$_2$-derivative (I), m.p. 145°, whilst in C_5H_5N the 1 : 3-*Br*$_2$-derivative (II), m.p. 163°, is formed. (II) is also formed by bromination of the 1-*Br*-compound, m.p. 100° (from 1-bromo-β-naphthylamine and $C_6H_4Me\cdot SO_2Cl$), in C_5H_5N, in which no further bromination occurs; in $CHCl_3$, (II) is attacked slowly by Br, some 1 : 3 : 6-tribromo-β-naphthyl-

amine being isolated. Further action of Br in $CHCl_3$ on (I) gives the 1 : 3 : 6-*Br*$_3$-derivative, m.p. 184°. 1 : 3-*Dibromo*-β-*naphthylamine*, m.p. 119° (*Ac* derivative, m.p. 201°), is prepared by hydrolysis of (II). 1 : 6-Dibromo-β-naphthyl Me ether gives with Br in $CHCl_3$ the 1 : 4 : 6-*Br*$_3$-compound. Nitration of β-naphthol in AcOH gives the 1 : 6-$(NO_2)_2$-derivative; its *m*-nitrobenzenesulphonate, however, gives a mixture of 8-*nitro*-, m.p. 144—146°, and 5-*nitro*-, m.p. 166°, -2-*naphthyl* m-*nitrobenzenesulphonates*. H. A. P.

Chemical behaviour of Millon's base. II. A. Bernardi and M. A. Schwarz (Gazzetta, 1932, **62**, 905—908).—Millon's base does not react with benzenesulphonic or sulphanilic acids. With naphthionic and naphthylamine-2 : 3-disulphonic acids in EtOH in presence of $ZnCl_2$ it gives additive *compounds*, $3Hg_2O_2,NH_3,C_{10}H_6(NH_2)\cdot SO_3H$ and $5Hg_2O_2,NH_3,C_{10}H_5\cdot NH_2(SO_3H)_2$, respectively, and with G and R acids *compounds*, $5Hg_2O_2,NH_3,2C_{10}H_5\cdot OH(SO_3H)_2,4H_2O$, formed by addition and condensation. All are insol. and unstable in air, but can be kept over $CaCl_2$ in vac. E. E. J. M.

Reaction products from hippuryl chloride. P. Karrer and V. Itschner (Helv. Chim. Acta, 1932, **15**, 1420).—"*NN'*-Dibenzoylglycine anhydride" (A., 1913, i, 968) is 1 : 3-dibenzamido-2 : 4-dihydro-*cyclo*butadiene, identical with that obtained from Et hippurate and NaOEt (A., 1889, 249) or hippuryl chloride, C_5H_5N, and Cu (A., 1928, 428). R. S. C.

Purification of aromatic amines. A. Weissberger and E. Strasser (J. pr. Chem., 1932, [ii], **135**, 209—210).—A solution of the amine in dil. HCl is treated with 0·05—0·1 part of $SnCl_2$ at about 50° and the Sn pptd. with H_2S (this process is repeated if necessary), NaCl is then added, the resultant colourless solution made alkaline (H_2S is removed if necessary with Na_2SO_3), and extracted with Et_2O (if the amine is not pptd.). *m*- and *p*-$C_6H_4(NH_2)_2$, benzidine, tetramethylbenzidine, 4 : 4'-diaminodiphenic acid, aminoquinol Me_2 ether, *p*-$NH_2\cdot C_6H_4\cdot OH$, and NHPhEt are readily purified by this process. H. B.

Nitro-dye from *m*-phenylenediaminesulphonic acid and chlorodinitrobenzene. V. G. Gulinov and V. L. Bunitski (Ukrain. Chem. J., 1932, **7**, [Tech], 9—16).—Na 2 : 4-*di*-2' : 4'-*dinitroanilinobenzenesulphonate*, a golden-brown dye for wool, is obtained from 1-chloro-2 : 4-dinitrobenzene and Na 2 : 4-diaminobenzenesulphonate. R. T.

Spectrochemistry and configuration of azoxybenzenes and stilbenes. K. von Auwers (Annalen, 1932, **499**, 123—133; cf. A., 1928, 688).—Spectrochemical data are recorded for "normal" and *iso*-azoxybenzenes, -*o*-, -*m*-, and -*p*-azoxytoluenes, -*o*-azoxyanisoles, and -2 : 2'-dichloroazoxybenzenes, and 2-chloro-2'-bromoazoxybenzene (Müller, A., 1932, 263, 734) in quinoline. The exaltations in refractive power of the *iso*-forms are usually about half those of the "normal." Muller's conclusion (*loc. cit.*) that the pairs are *cis–trans*-isomerides is correct. The "normal" form is designated *anti* and the *iso*- as *syn*. The sp. exaltation of *trans*-stilbene differs from that of *iso*stilbene in the same manner (but more markedly) as with the azoxybenzenes. *cis*- and *trans*-αβ-Dimethylstilbenes do not show any appreciable difference in their sp. exaltations. Data for βγ-diphenylbutadiene and βγ-diphenylbutane are also given. H. B.

Azo-derivatives of trinitromethane. A. Quilico (Gazzetta, 1932, **62**, 912—927; cf. A., 1915, i, 1011; 1916, i, 609).—Solutions of diazonium salts react with NH_4 nitroformate in presence of cryst. NaOAc giving *benzene*-, p-*nitro*-, p-*bromo*-, and p-*chloro-benzene*-, and β-*naphthalene-azotrinitromethanes*, R·N:N·$C(NO_2)_3$, and 4 : 4'-*diphenyldisazotrinitromethane*; all are yellow and explode on heating or percussion. With $SnCl_2$ in HCl they give the amine corresponding with the diazonium salt used, CO_2, and NH_3. When heated in solution in an inert solvent, *e.g.*, AcOH, or left for several days they lose 2 NO_2, giving the following *carbonitrosohydrazines*, R·N(NO)·N:CO: *phenyl*-, m.p. 85°; p-*nitro*-, m.p. 160°; p-*bromo*-, m.p. 145°, and p-*chloro-phenyl*-, m.p. 133°; β-*naphthyl*-, m.p. 115°, and 4 : 4'-*diphenylyl*-, decomp. about 260°. These are colourless and stable; with $SnCl_2$ in HCl they give the hydrazines and with hydrolysing agents the diazoimides corresponding with the radical R. E. E. J. M.

Structure of Para-red and related dyes. F. A. Mason (J. Soc. Dyers and Col., 1932, **48**, 293—295).—Sudan-I (benzeneazo-β-naphthol) readily forms a *compound*, $C_{16}H_{11}ON_2SnCl_3$, with $SnCl_4$ in PhMe at room temp., and also a *boroacetate*, m.p. 204—206° (shrinks 198°). Similarly, Para-red (*p*-nitrobenzeneazo-β-naphthol) forms a *compound*, $C_{16}H_{10}O_3N_3SnCl_3$, and a *boroacetate*, m.p. 260—265° (decomp.). A chelated structure is therefore assigned to these dyes, and the formation (or otherwise) of Cr lakes by *o*-hydroxyazo-dyes is ascribed to the degree of stability of the chelate ring. H. A. P.

Resistance of the linking between the arylazo-group and the nucleus in aminoazo-derivatives. G. B. Crippa and P. Galimberti (Gazzetta, 1932, **62**, 937—944; cf. A., 1929, 181).—When 1-benzeneazo-β-naphthylamine is heated with $H_2C_2O_4$ at 135—180°, fission between the NPh:N group and naphthalene occurs, giving β-naphthyloxamic acid and oxalonaphthalide, with phenol. 4-Benzeneazo-α-naphthylamine, *o*-aminoazobenzene, and chrysoidine condense with $H_2C_2O_4$, giving *bis*-4-*benzeneazo*-1-*oxalonaphthalide*, m.p. 180°, *bis*-o-*benzeneazo-oxanilide*, m.p. 279° (I), and *dioxalylbis*-2 : 4-*diamino*-1-*benzeneazobenzene*, m.p. 229°. The relatively weak attachment of the NAr:N group to the naphthalene nucleus when in the *ortho* position to NH_2 is explained on the theory of covalency. (I) with Fe in boiling AcOH gives 2 : 2'-*dibenziminazole*. E. E. J. M.

Azo-dyes and their intermediate products. XI. *peri*-Bisazo-dyes. II. P. Ruggli and A. Courtin (Helv. Chim. Acta, 1932, **15**, 1342—1352; cf. A., 1932, 264).—An azo-group in the α-position in $C_{10}H_8$ derivatives hinders, but does not prevent, coupling in the *peri*-position. The bisazo-dyes thus obtained are, if sol., brown to violet-brown dyes for wool. PhN_2Cl and 7-hydroxy-α-naphthylamine (I), m.p. 206—207° (decomp.) [Ac derivative (II),

m.p. about 194° (decomp.) (lit. 165°)], in NaOH at —4° give *7-hydroxy-8-benzeneazo-α-naphthylamine* (III) [*Ac* derivative, similarly obtained from (II)], which with $SnCl_2$ and HCl in HCO_2H gives some NH_2Ph and *2-hydroxy-1 : 8-perimidine (hydrochloride)*, readily oxidised to 1 : 8-perimidinequinone, decomp. 200—212°; reduction in AcOH gives the corresponding *Me* derivatives. Diazotised (III) and β-naphthol in neutral aq. EtOH give the *1 : 8-bisazo-dye*. (II) and diazotised Na sulphanilate at —4° give *Na 7-hydroxy-8-benzeneazo-1-acetnaphthalide-4'-sulphonate*, hydrolysed to the *NH_2*-compound [also obtained from (I) at —10°]. The last-named gives a diazo-compound which is stable to H_2O, with hot EtOH and Cu_2O gives Orange II, with boiling 10% H_2SO_4 gives *Na 2 : 8-dihydroxy-1-benzeneazonaphthalene-4'-sulphonate*, and couples with β-naphthol or resorcinol in EtOH–NaOAc to give *peri-bisazo-dyes*. R. S. C.

Mechanism of catalytic hydrogenation of phenol under high pressure. II. S. ANDO (J. Soc. Chem. Ind. Japan, 1932, **35**, 455—458B; cf. B., 1931, 1085).—The reaction of PhOH with 3 H_2 at 150—250° in an autoclave and in presence of a Ni catalyst gives rise to *cyclo*hexanol. At higher temp. *cyclo*hexane, *cyclo*hexene, and C_6H_6 are formed. *cyclo*Hexene can be formed from *cyclo*hexanol in presence of Al_2O_3 as catalyst. E. S. H.

Dielectric constant as a means of organic analysis. A. CHRETIEN and P. LAURENT (Compt. rend., 1932, **195**, 792—794).—When the dielectric const. of a C_6H_6 solution (0·1—0·25*M*) of a mixture of an acidic and basic org. substance is plotted against the mol.-% composition of the mixture the curve consists of one straight line if no compound is formed, or of two or more such lines meeting at points denoting the composition of the resulting compounds. In this way the existence is indicated in C_6H_6 solution of equimol. compounds of PhOH with quinoline; C_5H_5N with PhOH, β-naphthol, and pyrrole; 2 : 4-dinitrophenol with NH_2Ph; *o*-NO_2·C_6H_4·OH with NHPh·NH_2; of 1 mol. of pyrocatechol or of dimethylglyoxime with 2 mols. of C_5H_5N; 1 of phloroglucinol with 2 and 3 of C_5H_5N; and of 2 and 1 of 2 : 4-dinitrophenol with 1 of phenazine. No compounds are indicated between PhOH and $NPhMe_2$; *o*-NO_2·C_6H_4·OH and $NHPh_2$ or $NPhMe_2$; or β-naphthol and NH_2Ph or C_5H_5N. C. A. S.

Dibromopicric acid. H. WILLSTAEDT and F. REUTER (J. pr. Chem., 1932, [ii], **135**, 211—214).—3 : 5-$C_6H_3Br_2$·OH (prepared in 20% yield by decomp. of the diazonium sulphate) and HNO_3 (*d* 1·52) in AcOH give *dibromopicric acid* (I), m.p. 165°. Trinitroanisole and Br in presence of Fe afford picric acid. Extraction of the anthocyanin of red cabbage is best accomplished by an aq. solution of (I) (rather than picric or dichloropicric acids). H. B.

Structure of amber musk. I. *tert.*-Butyl-*m*-tolyl methyl ether and its nitration products. II. O. A. SEIDE and B. M. DUBININ (J. Gen. Chem. Russ., 1932, **2**, 455—471, 472—477).—I. *m*-Tolyl Me ether and $Bu^{\beta}Cl$ condense ($AlCl_3$) to the *tert.*-Bu compound (I), more easily prepared from *m*-tolyl Me ether, *iso*butylene, and $AlCl_3$, b.p. 223°, m.p. 23—24°. The mixture obtained by the nitration of (I) can be separated by vac. distillation into amber musk (II), b.p. 185°/16 mm., m.p. 85°, and 4 : 6-dinitro-*m*-tolyl Me ether (III), b.p. 202—203°/16 mm., m.p. 101°. The lower b.p. of (I) makes Barbier's formula (A., 1928, 291) for it improbable. (II) can be obtained by the nitration of acetyl-*tert.*-butyl-*m*-tolyl Me ether (IV) (*loc. cit.*) together with 2 : 4-dinitro-6-acetyl-*m*-tolyl Me ether, the structure of which is established; the former is produced by the replacement of the Ac and the latter of the *tert.*-Bu group of (III) by NO_2. The *tert.*-Bu in (IV) cannot therefore occupy position 6, since this is occupied by the Ac group and the only possible position is 4. It follows that (II) is 2 : 6-dinitro-4-*tert.*-butyl-*m*-tolyl Me ether and (I) is 4-*tert.*-butyl-*m*-tolyl Me ether. This has been proved as follows: 4-nitro-*m*-tolyl Me ether is reduced to the 4-*NH_2*-compound, b.p. 109°/11 mm. (*picrate*, decomp. 198—199° with previous darkening), and converted by the Sandmeyer reaction into *4-bromo-m-tolyl Me ether*, b.p. 107—109°/11 mm.; the Br is replaced (Grignard) by *tert.*-Bu, giving (I) nitrated to (II). (IV) must therefore be 6-acetyl-4-*tert.*-butyl-*m*-tolyl Me ether.

Nitration of (I) yields, in addition to the products already isolated (*loc. cit.*), a *quinone*, m.p. 96°, in the fraction b.p. 135—145°/14 mm., and a *mononitro*-derivative (V), m.p. 81—82°, in the fraction 145—171°/14 mm.; these become the sole products with HNO_3 *d* 1·38—1·42. The quinone is 4-tert.-*butyltoluquinone*, reduced by NHPh·NH_2 to the *quinol*, m.p. 122—123°, and forming the *quinhydrone*, violet plates, m.p. 116°, on mixing with the latter. (V) gives (II) on further nitration and must therefore be either the 2- or the 6-*NO_2*-derivative; as some 4 : 6-dinitro-*m*-tolyl Me ether is formed at the same time (by displacement of the CMe_3 group), the former possibility is ruled out. The nitration of (I) is accompanied by an intense coloration, due to the formation of an oxonium salt, isolated as the *perchlorate* (VI), $C_{24}H_{34}O_7NCl,0·5H_2O$, probably 2: 2'-dimethyl-5 : 5'-di-*tert.*-butyl-4 : 4'-dimethoxydiphenylhydroxylamine-*N*-oxide perchlorate. (VI) is hydrolysed by dil. H_2SO_4 to the above quinone and accounts for its formation.

II. A repetition of Darzens and Levy's synthesis of amber musk (A., 1931, 1152) shows that the *tert.*-butyl-*m*-tolyl Me ether (VII) obtained by their method has b.p. 102—104°/8 mm., m.p. 6°, and is nitrated to an isomeride (VIII) of (II), m.p. 111°, possessing a much weaker musk odour than (II). No coloured oxonium salt is formed during the nitration. A *NO_2*-compound m.p. 82—83° (IX), not identical with the 6-*NO_2*-derivative (cf. above) and devoid of musk odour, is also formed; a compound of m.p. 72° was not isolated. It is suggested that (VII) is 6-*tert.*-butyl-*m*-tolyl Me ether, (IX) the 4-*NO_2*- and (VIII) the 2 : 4-*$(NO_2)_2$*-derivative. The statement (*loc. cit.*) that the odour of musk is due to two NO_2 groups *ortho* to the OMe is evidently incorrect. G. A. R. K.

Nitro-dye from aminophenolsulphonic acid and chlorodinitrobenzene. V. G. GULINOV (Ukrain. Chem. J., 1932, **7**, [Tech.], 5—8).—A

golden-yellow dye for wool, *Na* 2 : 4-*dinitroanilino-phenol*-m-*sulphonate*, is obtained from 1-chloro-2 : 4-dinitrobenzene and Na *p*-aminophenol-*m*-sulphonate. R. T.

Reaction of primary and secondary amino-alcohols and aminophenols with arylsulphonyl chlorides. K. H. SLOTTA and R. BEHNISCH (J. pr. Chem., 1932, [ii], **135**, 225—236).—β-Aminoethyl alcohol (I) (1 mol.), obtained in 80% yield from $(CH_2)_2O$ and cold conc. aq. NH_3, and *p*-$C_6H_4Me{\cdot}SO_2Cl$ (II) (1 mol.) at 130° give p-*toluenesulphon*-β-*chloroethylamide*, m.p. 101°; with 0·5 mol. of (II) at 100°, p-*toluenesulphon*-β-*hydroxyethylamide* (III), b.p. 250°/10 mm., m.p. 56° (*Na* and *K* salts), also prepared from equimol. amounts of (I) and (II) in C_5H_5N, results. *Benzenesulphon*-β-*hydroxyethylamide*, b.p. 247—248°/10 mm. (*Na* salt), is obtained from (I) and $PhSO_2Cl$ at 100°. (II) and (III) in boiling C_5H_5N afford β-p-*toluenesulphonamidoethylpyridinium* p-*toluenesulphonate*, m.p. 193—194° (sinters at 188°) (corresponding *picrate*, m.p. 165°), also obtainable directly from (I), (II), and C_5H_5N. β-*Benzenesulphonamidoethylpyridinium benzenesulphonate*, m.p. 180° (corresponding *picrate*, m.p. 110°), is similarly prepared. β-Methylaminoethyl alcohol and (II) at 100° give p-*toluenesulphon*-N-*methyl*-β-*hydroxyethylamide*, b.p. 250°/20 mm., 180—185°/3·5 mm. (O-*Ac* derivative, b.p. 150°/0·3 mm., m.p. 58°), also prepared by the Schotten–Baumann method and from *p*-$C_6H_4Me{\cdot}SO_2NHMe$, $CH_2Cl{\cdot}CH_2{\cdot}OH$, and EtOH–KOH at 170°. *p*-$NMe_2{\cdot}C_6H_4{\cdot}OH$, prepared from *p*-$NMe_2{\cdot}C_6H_4{\cdot}OMe$ and HBr (*d* 1·49) in AcOH, and (II) in C_5H_5N afford p-*dimethylaminophenyl* p-*toluenesulphonate*, m.p. 130° (*hydrochloride*, m.p. 188°; *picrate*, m.p. 146°). Piperazine formation is not observed in the above cases as with $NR_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (A., 1932, 1042). H. B.

Diphenyl sulphide. W. W. HARTMAN, L. A. SMITH, and J. B. DICKEY (Ind. Eng. Chem., 1932, **24**, 1317—1318).—The prep. of Ph_2S using C_6H_6, S_2Cl_2, and $AlCl_3$ is described and references are given to 22 other methods. On a semi-commercial scale a yield of 83·3% is obtained. S. M.

4-Hydroxy-3-methoxystyrene (4-vinylguaiacol). T. REICHSTEIN (Helv. Chim. Acta, 1932, **15**, 1450—1453).—Vanillin and MgMeI (3 mols.) give 4-hydroxy-3-methoxyphenylmethylcarbinol ("apocynol," J.C.S., 1908, **93**, 1520), b.p. about 180°/12 mm., m.p. 102·5—103°, or, under other conditions, *4-hydroxy-3-methoxystyrene* (I), b.p. about 120°/12 mm. [and a (?) dimeric distillation residue] (also obtained from ferulic acid by NaOH at 300° or, better, Cu powder and quinoline at 240°) [*benzoate*, m.p. 112°; p-*nitrobenzoate*, m.p. 107°; *Et glycollate*, m.p. (from H_2O) 85°, (anhyd.) 110°; *carbonate*, m.p. 104°; *phosphate*, m.p. 67—70° (uncorr.); *Me ether* (3 : 4-*dimethoxystyrene*), b.p. 85°/1 mm.]. Fromm's phenol (A., 1927, 968) from coal tar is, therefore, not (I). The following m.p. are recorded: creosol [*benzoate*, m.p. 76°; p-*nitrobenzoate*, m.p. 109°; *Et glycollate*, m.p. (from H_2O) 99—103°, (anhyd.) 117°; *carbonate*, m.p. 148°; *phosphate*, m.p. 103°]; 4-hydroxy-3-methoxy-1-ethylbenzene [*benzoate*, m.p. 64°; p-*nitrobenzoate*, m.p. 100°; *Et glycollate*, m.p. (from H_2O) 68°, (anhyd.) 86°; *carbonate*, m.p. 118°]; 3-hydroxy-4-methoxy-1-ethylbenzene (by Clemmensen reduction of *iso*acetovanillone), m.p. 37—38·5°, b.p. 73—78°/1 mm. [*benzoate*, m.p. 52°; p-*nitrobenzoate*, m.p. 67°; *Et glycollate*, m.p. (anhyd.) 89—92°; *carbonate*, m.p. 95°]; eugenol (*benzoate*, m.p. 70°; p-*nitrobenzoate*, m.p. 80·5°); *iso*eugenol [*benzoate*, m.p. 104°; p-*nitrobenzoate*, m.p. 124°; *Et glycollate*, m.p. (from H_2O) 86—88°, (anhyd.) 118°; *carbonate*, m.p. 106°]. All m.p. are corr. R. S. C.

Condensation of phenols with aliphatic aldehydes. W. C. HARDEN and E. E. REID (J. Amer. Chem. Soc., 1932, **54**, 4325—4334).—The following are prepared usually from the phenol and Alk·CHO in presence of conc. HCl: (*a*) from PhOH: 4 : 4′- (Br_4-derivative, m.p. 226°) and 2 : 4′-dihydroxydiphenylmethane (Br_4-derivative, m.p. 193°); αα-di-*p*-hydroxyphenyl-ethane, m.p. 122° (Br_4-derivative, m.p. 140°), -propane, m.p. 129° (Br_4-derivative, m.p. 150°), -butane, m.p. 137° (Br_4-derivative, m.p. 152°), -pentane, m.p. 120° (Br_4-derivative *diacetate*, m.p. 168°), -hexane, m.p. 110·5° (Br_4-derivative *diacetate*, m.p. 129°), and -heptane, m.p. 120° (lit. 103°) (Br_4-derivative *diacetate*, m.p. 111°); (*b*) from *o*-cresol; 4 : 4′-dihydroxy-3 : 3′-dimethyldiphenylmethane (Br_2-derivative, m.p. 173·5°); αα-*di*-(4-*hydroxy*-3-*methylphenyl*)-*ethane*, m.p. 100° (Br_2-derivative, m.p. 77°), -*propane*, m.p. 94° (Br_2-derivative, m.p. 111°), -*butane*, m.p. 135° (Br_2-derivative, m.p. 104°), -*pentane*, m.p. 97° (Br_2-derivative *diacetate*, m.p. 150°), -*hexane*, m.p. 78° (Br_2-derivative *diacetate*, m.p. 121°), and -*heptane*, m.p. 85° (Br_2-derivative *di*-p-*nitrobenzoate*, m.p. 215°); (*c*) from *m*-cresol: 4 : 4′-*dihydroxy*-2 : 2′-*dimethyldiphenylmethane*, m.p. 113° (Br_4-derivative, m.p. 185°); αα-*di*-(4-*hydroxy*-2-*methylphenyl*)*ethane*, m.p. 128° (Br_2-, m.p. 189°, and Br_4-, m.p. 207°, derivatives), -*propane*, m.p. 140° [Br_4-derivative, m.p. 121° (*diacetate*, m.p. 81°)], -*butane*, m.p. 145° (Br_4-derivative, m.p. 142°), -*pentane*, m.p. 149° (Br_4-derivative *diacetate*, m.p. 78°), -*hexane*, m.p. 152° [Br_4-derivative, m.p. 119° (*diacetate*, m.p. 142°)], and -*heptane*, m.p. 156° (Br_4-derivative, m.p. 67°); (*d*) from resorcinol: 2 : 4 : 2′ : 4′-tetrahydroxydiphenylmethane (Br_4-derivative); αα-*di*-(2 : 4-*dihydroxyphenyl*)-*ethane*, -*propane*, -*butane*, -*pentane*, -*hexane*, and -*heptane*, all of which have m.p. > 300° and give Br_4-derivatives; (*e*) from chloral: ββ-trichloro-αα-di-*p*-hydroxyphenyl-, m.p. 199—200°, -αα-*di*-(4-*hydroxy*-3-*methylphenyl*)-, m.p. 121—122°, m.p. (+C_6H_6) 91°, -αα-*di*-(4-*hydroxy*-2-*methylphenyl*)-, m.p. 162—163°, and -αα-*di*-(4-*hydroxy*-2-*methyl*-5-iso*propylphenyl*)-, m.p. 193·5°, -*ethanes*. Data on the solubility, bactericidal action towards *S. aureus*, and toxicity towards goldfish and seedlings of *Lupinus albus* of the above compounds are given. In general, bactericidal action increases with length of the C-chain [except in (*c*) and (*d*), where max. activity is with the -butane and -pentane, respectively] and is a function of the lipoid solubility. H. B.

Tetralin peroxide. M. HARTMANN and M. SEIBERTH (Helv. Chim. Acta, 1932, **15**, 1390—1392).—Tetralin (I) and air (with or without a catalyst, *e.g.*, Zn turnings) at room temp. or 70—80° gives gradually the *peroxide* (II), m.p. 53—54°, which is given the formula $C_6H_4{<}\begin{matrix}CH(O{\cdot}OH){\cdot}CH_2\\ CH_2\text{———}CH_2\end{matrix}$, since it is sol. in NaOH

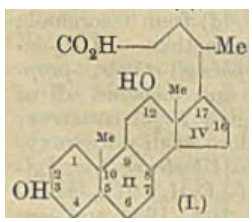
and pptd. therefrom by CO_2 or acids, liberates I from HI, oxidises leucomethylene-blue, gives α-tetralol with Zn dust and 50% AcOH, and α-tetralone with aq. $FeSO_4$. (II) explodes in contact with conc. H_2SO_4 or when strongly heated, and with aq. $NaHSO_3$ gives the *Na* salt of a *sulphonic acid*, which with acids gives dihydronaphthalene. (II) may be isolated as Na salt when (I), which has been kept in air for some time, is shaken with aq. NaOH, or by removing unchanged (I) at 50—70°/2—3 mm. Distillation residues of old specimens of (I) may explode when heated.

R. S. C.

Size of ring II in cholesterol. R. Criegee (Ber., 1932, **65**, [*B*], 1770—1772).—The oxidation of *cis*-glycols with $Pb(OAc)_4$ proceeds more rapidly than that of *trans*-compounds and the magnitude of the difference in the rate of reaction depends above all on the magnitude of the ring in which the glycol grouping occurs. The ratio of the rates of oxidation of the isomeric glycols $k_{cis} : k_{trans}$ is recorded for the following compounds, the size of the ring being placed in parentheses: *cyclo*hexane- (6), 23; tetrahydronaphthalene- (6), 21·6; hydrindene- (5), 55,000; acenaphthene- (5), 130,000, -diol: methylmannofuranoside (5) and ethylglucofuranoside carbonate (5), > 90,000; mannono-γ-lactone (5) and arabono-γ-lactone (5), > 20,000. Since the ratio for the *cis*- and *trans*-glycols of cholesterol is about 36,000, ring II must be five-membered unless the improbable hypotheses be accepted that, unlike other 6-membered rings, its structure is plane and fixed. Oxidation of the glycols shows that the double linking of cholesterol cannot be in the αβ position to a OH group.

H. W.

Ring system of sterols and bile acids. II. O. Rosenheim and H. King (Chem. and Ind., 1932, 954—956).—The views previously expressed (A., 1932, 736, 1131) are supplemented. Deoxycholic, chenodeoxycholic, and hyodeoxycholic acids are now postulated as 3 : 12- (I), 3 : 7-, and 3 : 6-dihydroxycholanic acids, respectively; cholic acid remains 3 : 7 : 12-trihydroxycholanic acid, but its distinctive OH group is now at C_7 instead of C_{12}. The attachment of the side-chain at C_{17} explains the *X*-ray crystallographic measurements of Bernal (*ibid.*, 327) and unpublished results on *apo*cholic (II) and dihydroxycholenic (III) acids. Since reduction of (III) gives (I), it follows that (II) does not arise by ring formation between position 17 and the sp. OH group of cholic acid (cf. *loc. cit.*). (II) is convertible by HCl into (III); it is suggested that a bridge linking between C- and C_9 in (II) gives rise to a double linking between C_8 and C_9 in (III). A similar scheme explains the production of α-ergostenol from ergosterol if the conjugated double linkings of the latter are $C_5{\cdot}C_6{\cdot}C_7{\cdot}C_8$. Migration of the *tert.*-Me group from C_{10} to C- would make ring II aromatic and thus explain the production of toluenetetracarboxylic acid from ergosterol, etc. (*ibid.*, 612). The postulation of ring IV as five-membered (Wieland and Dane, *ibid.*, 1131) is favoured; evidence supporting this view is quoted. The ultra-violet absorption spectrum of the hydrocarbon $C_{18}H_{16}$, obtained by dehydrogenation (Se) of cholesterol and ergosterol, is similar to that of chrysene and is intermediate between that of the latter and octahydrochrysene.



H. B.

Tachysterol. A. Windaus, F. von Werder, and A. Luttringhaus (Annalen, 1932, **499**, 188—200).—Acetylation (Ac_2O) of the adduct formed when irradiated ergosterol is treated with citraconic anhydride (I) (A., 1932, 311) gives the *adduct*, $C_{15}H_{20}O_5$, m.p. 161—162°, $[\alpha]_D^{20}$ +75·2° in $CHCl_3$, of (I) and tachysteryl acetate, which when heated at 165—190°/0·001 mm., regenerates its components. Treatment of the crude irradiation product (freed from ergosterol) (*loc. cit.*) with 2 : 6-dinitro-*p*-toluoyl chloride in C_5H_5N at 70°, gives *tachysteryl* 2 : 6-*dinitro*-p-*toluate*, m.p. 154—155° (and vitamin-D_2 2 : 6-dinitro-*p*-toluate), hydrolysed by 3% MeOH–KOH in N_2 to *tachysterol* (II), $[\alpha]^{18}$ −70° in "benzine," which has not been obtained cryst. (II) is isomeric with ergosterol (as shown by analysis of the adduct), consumes 4—5 O when titrated with BzO_2H, is oxidised (O_3) to α-methyl*iso*valeraldehyde, does not give toluenetetracarboxylic acid with HNO_3, and undergoes autoxidation (O_2 in MeOH) to a *product* (III), $C_{28}H_{44}O_7$, decomp. 130° (sinters at 98°). (II) has no antirachitic action, but when irradiated gives vitamin-D_2 and both suprasterols. The following changes occur when ergosterol is irradiated: ergosterol ⟶ lumisterol ⟶ tachysterol ⟶ vitamin-D_2 ⟶ suprasterols. When (II) is heated at 190°/6 hr. (sealed tube), the dextrorotatory *pyrotachysterol* (IV), $C_{28}H_{44}O$, is produced. (IV) is not activated by irradiation and does not give an adduct with (I). Absorption curves are given for (II), (III), (IV), and the mixture obtained when (II) is treated with Na and PrOH.

[By E. Fernholz.] The mother-liquors from the prep. of dihydrovitamin-D_2 allophanate (*loc. cit.*) contain (after hydrolysis with MeOH–KOH) an alcohol, which gives a 3 : 5-*dinitrobenzoate* $C_{35}H_{46(48)}O_6N_2$, m.p. 164—165°, $[\alpha]_D^{18}$ +138° in $COMe_2$. *Dihydrovitamin*-D_2 3 : 5-*dinitrobenzoate* has m.p. 95°, $[\alpha]_D^{16}$ +32·2° in $CHCl_3$.

H. B.

Light-absorption and constitution. VI. Light-absorption of conjugated systems. A. Burawoy (J. pr. Chem., 1932, [ii], **135**, 145—154).—Polemical (cf. Dilthey, A., 1932, 1028).

H. A. P.

Alkali-fastness of Patent-blue dyes. G. Heller (Chem.-Ztg., 1932, **56**, 902—903).—The fastness to alkalis of $CHPh_3$ dyes containing a SO_3H group *ortho* to the central C atom is probably a steric effect, wandering of the OH group from the N atom to this C atom being hindered.

C. I.

Nitriles and amides of cinnamic acid. J. Ghosez (Bull. Soc. chim. Belg., 1932, **41**, 477—500).—Fractional distillation and crystallisation of the mixture of cinnamonitriles (prep. described from PhCHO and cyanoacetic acid) affords a trans-*isomeride*, b.p. 263·8°/756 mm., and a cis-*isomeride*, b.p. 249—249·4°/756 mm. β-*Phenylglutaronitrile*, m.p. 26°, b.p. 207·5—208·5°/12—13 mm., was also isolated. Hydrolysis of the *cis*-nitrile with H_2SO_4 affords cis-*cinnamamide*, m.p. 199—202°.

J. L. D.

Colour and properties in the cinnamic series. (MME.) RAMART-LUCAS and TRIVEDI (Compt. rend., 1932, **195**, 783—785).—Introduction of an α- or β-methyl group into Ph·CH:CH·COR (R=OH, OEt, NH_2) shifts the absorption bands towards the ultra-violet and diminishes their intensity, and also depresses the reactivity of the group ·COR. J. L. D.

8-Bromo- and -iodo-naphthoic acids. H. GOLDSTEIN and P. FRANCEY (Helv. Chim. Acta, 1932, **15**, 1362—1366).—Na 8-amino-1-naphthoate (modified prep. from naphthastyril) gives by diazo-reactions 8-bromo-1-naphthoic acid (*chloride*; *anilide*, m.p. 151°) and 8-*iodo*-1-*naphthoic acid*, m.p. 164·5° [*Me* and *Et* esters, from the Ag salts (not by EtOH and acid), m.p. 59° and 64·5°, respectively; *chloride*; *anilide*, m.p. 171·5°]. R. S. C.

Transformation products of bromonaphthastyril. H. GOLDSTEIN and P. FRANCEY (Helv. Chim. Acta, 1932, **15**, 1366—1372).—Bromonaphthastyril (I) (modified prep.) [N-*Ac* derivative (II), m.p. 161·5°] and boiling aq. NaOH give 5-bromo-8-amino-1-naphthoic acid (III), which regenerates (I) slowly in vac. and rapidly at 250° or in hot EtOH, and with hot Ac_2O gives (II). (III) with alkaline Me_2SO_4 yields N-*methylbromonaphthastyril*, m.p. 139·5°, and, when diazotised and heated at 60°, the *lactone*, m.p. 192°, of 5-*bromo*-8-*hydroxy*-1-*naphthoic acid*, formed by bromination of naphtholactone (cf. A., 1889, 153); the acid regenerates the lactone at 210°, and with an excess of alkaline Me_2SO_4 gives *Me* 5-*bromo*-8-*hydroxy*-1-*naphthoate*, m.p. 124°. (II) affords by diazo-reactions 5 : 8-*dibromo*-1-*naphthoic acid*, m.p. 227·5° (*Me* and *Et* esters, m.p. 73° and 74°, respectively; *chloride*; *anilide*, m.p. 212°), and 5-*bromo*-8-*iodo*-1-*naphthoic acid*, m.p. 250° (*Me*, m.p. 122°, and *Et*, m.p. 89·5°, esters, from Ag salt; *chloride*; *amide*, m.p. 230°; *anilide*, m.p. 190·5°). R. S. C.

Reactivity of *peri*-substituted naphthalenes. II. Replacement of halogen in 8-halogeno-1-naphthoic and *o*-halogenobenzoic acids. H. G. RULE and A. J. G. BARNETT (J.C.S., 1932, 2728—2732).—The reactivity towards ·ONa compounds in the presence of Cu-bronze of the 8-halogeno-1-naphthoic acids is in general greater than that of the corresponding *o*-halogenobenzoic acids, the same type of replacement occurring in the former case with the Br compounds as in the latter with the I compounds. Na *o*-bromobenzoate is, however, readily converted by NaI and Cu-bronze in PrOH at 80° into the iodobenzoate, whilst attempts to carry out this reaction with the naphthoate resulted in partial dehalogenation; Na *o*-iodobenzoate, but not the bromonaphthoate, is converted into the NO_2-compound by $NaNO_2$. Condensation could not be brought about between the bromonaphthoate and $CHNa(CO_2Et)_2$ or $CHAcNa{\cdot}CO_2Et$, either dry or in EtOH, and Na 8-chloro-1-naphthoate is inert under the conditions studied. The following are described: 8-n-*propoxy*-, m.p. 176—177°, 8-n-*butoxy*-, m.p. 154—155°, 8-l-*menthoxy*-, m.p. 206—207°, 8-*phenoxy*-, m.p. 139—140°, and 8-*benzyloxy*-, m.p. 125—126°, -1-*naphthoic acids*. H. A. P.

Stereochemistry of diphenyls. XXV. Relative interfering effects of the groups F, OMe, Cl, and Br as determined by the relative rates of racemisation of 2′-substituted 2-nitrodiphenyl-6-carboxylic acids. R. W. STOUGHTON and R. ADAMS. **XXVI. Effect of substitution on rate of racemisation of optically active diphenyls.** H. C. YUAN and R. ADAMS (J. Amer. Chem. Soc., 1932, **54**, 4426—4434, 4434—4443).—XXV. *Me* 2-*bromo*-3-*nitrobenzoate* (I), m.p. 78—78·5° (by esterification of the acid), *o*-$C_6H_4I{\cdot}OMe$, and Cu-bronze at 240—250° give (after hydrolysis) 2-*nitro*-2′-*methoxydiphenyl*-6-*carboxylic acid*, m.p. 196·5—197° (corr.), resolved by brucine into the d-*form*, m.p. 196—197°, $[\alpha]_D^{20}$ +29·5° (initial) in EtOH [*brucine* salt (+0·5H_2O), m.p. 219—220°, m.p. (anhyd.) 223—224°]. 4-Chloro-3-iodotoluene and (I) similarly give 2 : 2′-*dichloro*-5 : 5′-*dimethyldiphenyl*, m.p. 85—86°, and 2′-*chloro*-2-*nitro*-5′-*methyldiphenyl*-6-*carboxylic acid*, m.p. 234—234·5° (corr.), which is resolved into d-, $[\alpha]_D^{20}$ +18·6° in EtOH (*brucine* salt, m.p. 220—221°), and l-*forms*, m.p. 234·5° (slight softening at 180°), $[\alpha]_D^{18}$ −68·9° (initial) in AcOH [*brucine* salt (+0·75H_2O), m.p. (anhyd.) 215—217°]. 4-*Bromo*-3-*iodotoluene*, b.p. 145—150°/20 mm. (from the 4-NH_2-compound), and (I) afford 2′-*bromo*-2-*nitro*-5′-*methyldiphenyl*-6-*carboxylic acid*, m.p. 228—229° (corr.), resolved into d-, m.p. 226·5—228° (softens at 177°), $[\alpha]_D^{20}$ +27·5° in EtOH (*brucine* salt, m.p. 228—229°), and l-*forms*, m.p. 227—228° (softens at 177°), $[\alpha]_D^{18}$ −58·4° (initial) in AcOH [*brucine* salt (+H_2O), m.p. 203° (softens at 150°), m.p. (anhyd.) 219°]. 3-*Iodo*-4-*fluorotoluene*, b.p. 122—125°/30 mm. (from the 4-NH_2-compound), and (I) give 2′-*fluoro*-2-*nitro*-5′-*methyldiphenyl*-6-*carboxylic acid* (II), m.p. 187—188° (corr.) [*brucine* salt (+0·25H_2O), m.p. 213—214·5° (softens at 150°), m.p. (anhyd.) 214—215°, $[\alpha]_D^{20}$ +15° (calc.) ⟶ −3·4° (5 hr.) in $CHCl_3$; *quinine* salt (+2H_2O), m.p. 135—140°, m.p. (anhyd.) 138—140°, $[\alpha]_D^{20}$ −125° (calc.) ⟶ −82·5° (5 hr.) in $CHCl_3$; *strychnine* salt, m.p. 194—196°, $[\alpha]_D^{20}$ −31·2° in $CHCl_3$], which could not be obtained in an active form. The rates of racemisation of the active acids in various solvents show that the interfering effect of the 2′-substituent is Br>Cl>OMe>F. (II) warmed with conc. H_2SO_4 gives 4-*fluoro*-5-*nitro*-1-*methylfluorenone*, m.p. 204—205°.

XXVI. 3-Iodo-4-methoxytoluene, (I) (above), and Cu-bronze at 240—260° give (after hydrolysis) a little 6 : 6′-dinitrodiphenic acid (III) and 2-*nitro*-2′-*methoxy*-5′-*methyldiphenyl*-6-*carboxylic acid*, m.p. 182—183°, resolvable into the l-*form*, m.p. 180—182°, $[\alpha]_D^{25}$ −20° (initial) in EtOH (*brucine* salt, m.p. 146—150°). 4-Chloro-2-iodoanisole and (I) similarly give (III), 5 : 5′-*dichloro*-2 : 2′-*dimethoxydiphenyl*, m.p. 144·5—145·5°, and 5′-*chloro*-2-*nitro*-2′-*methoxydiphenyl*-6-*carboxylic acid*, m.p. 174—175°, which is resolvable into the l-*form*, m.p. 173—175°, $[\alpha]_D^{17}$ −115° (initial) in EtOH [*brucine* salt (+H_2O), m.p. 148—153°]. 4-Bromo-2-iodoanisole and (I) afford 5′-*bromo*-2-*nitro*-2′-*methoxydiphenyl*-6-*carboxylic acid*, m.p. 186—187° (*Me* ester, m.p. 148—149°), resolved into the l-*form*, m.p. 185—187°, $[\alpha]_D^{25}$ −84° (initial) in EtOH (*brucine* salt, m.p. 162—165°), whilst 2-iodo-4-nitroanisole and (I) give 2 : 5′-*dinitro*-2′-*methoxydiphenyl*-6-*carboxylic acid*, m.p. 202—203°, resolvable into the l-*form*, m.p. 201—202°, $[\alpha]_D^{25.5}$ −93° (initial) in EtOH [*brucine*

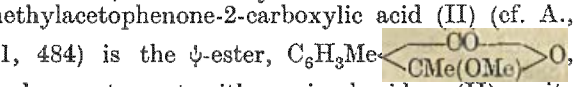
salt (+3H_2O), m.p. 179—183°]. The rates of racemisation of the above active acids and of *l*-2-nitro-2′ : 5′-dimethoxydiphenyl-6-carboxylic acid (A., 1932, 945) are compared with that of 2-nitro-2′-methoxydiphenyl-6-carboxylic acid (Part XXV). The half-life periods for the free acids in EtOH at 26° increase in the order: 5′-substituent=H, OMe, Me, Cl, Br, NO_2. All the above brucine salts exhibit mutarotation, but the 5′-NO_2-acid salt has a much smaller half-life period than the other four salts (which have approx. the same val.). The Na salts racemise less readily in H_2O (but more readily in EtOH) than the acids in org. solvents. The possible causes of the differences in the rates of racemisation of the free acids are discussed; the dipole moments of the *p*-substituted anisoles (*i.e.*, the variable part of the above acids, which are 4-substituted-2-2′-nitro-6′-carboxyphenylanisoles) parallel the rates of racemisation (these decrease with rise in the moment). There appears to be some relation between the rate of racemisation and the polarity of the 5-′group. H. B.

Phenacyl and *p*-bromophenacyl esters of monosubstituted benzoic acids. T. L. Kelly and H. W. Howard (J. Amer. Chem. Soc., 1932, **54**, 4383—4385).—The following are prepared essentially by Reid's method (A., 1919, i, 157; 1920, i, 480): (*a*) phenacyl esters: *o*-, m.p. 83·2°, and *m*-, m.p. 113·4°, -bromobenzoates; *o*-, m.p. 83°, *m*-, m.p. 116·4°, and *p*-, m.p. 87·6°, -chlorobenzoates; *o*-, m.p. 71°, *m*-, m.p. 115·6°, and *p*-, m.p. 101° (decomp.), -iodobenzoates; *o*-, m.p. 124·5°, and *m*-, m.p. 104·5°, -nitrobenzoates; *m*-, m.p. 146·5°, and *p*-, m.p. 178°, -hydroxybenzoates; *o*-, m.p. 126°, *m*-, m.p. 145·5°, and *p*-, m.p. 146·2°, -nitrocinnamates; (*b*) *p*-bromophenacyl esters: *o*-, m.p. 101·6°, *m*-, m.p. 126·4°, and *p*-, m.p. 133·8°, -bromobenzoates; *o*-, m.p. 106°, *m*-, m.p. 117·2°, and *p*-, m.p. 126°, -chlorobenzoates; *o*-, m.p. 110·2°, *m*-, m.p. 127·6°, and *p*-, m.p. 146·4°, -iodobenzoates; *o*-, m.p. 100·6°, *m*-, m.p. 133·6°, and *p*-, m.p. 134°, -nitrobenzoates; *m*-, m.p. 168°, and *p*-, m.p. 184°, -hydroxybenzoates; *o*-, m.p. 141·5°, *m*-, m.p. 177·5°, and *p*-, m.p. 190·5°, -nitrocinnamates. p-*Bromophenacyl* o-, m.p. 172°, m-, m.p. 190°, and p-, m.p. 200°, -N-p-*bromophenacylamidobenzoates* are prepared, using an excess of *p*-$C_6H_4Br{\cdot}CO{\cdot}CH_2Br$. H. B.

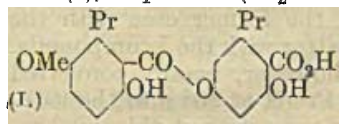
Preparation of stereoisomeric methoxyphenylacetic acids by resolution of the racemic acid. E. Bamann and J. M. Portmann (Arch. Pharm., 1932, **9**, 513—519).—Crystallisation of the quinine (I), quinidine, cinchonine, or cinchonidine salts of *dl*-methoxyphenylacetic acid (modified prep.) gives the salt of the *d*-acid; the morphine (II) or strychnine salt leads to that of the *l*-acid. (I) and (II) (recryst. from H_2O) are most suitable for prep. of the active acids (cf. A., 1932, 269). R. S. C.

Benzylidenepyruvic acid. II. L. Musajo (Gazzetta, 1932, **62**, 901—905; cf. A., 1889, 990).—The oily benzylidenepyruvic acid obtained by condensing PhCHO with $AcCO_2H$ in presence of gaseous HCl becomes, when dried in vac. at 25—30°, an amorphous solid which cannot be freed from a trace of the acid $C_{27}H_{20}O_6$ (*loc. cit.*). It softens at 80° and on further heating decomposes; mol. wt. determination in AcOH indicates the formula $(C_{10}H_8O_3)_2$. The solid benzylidenepyruvic acid, m.p. 62—63°, obtained from PhCHO and $AcCO_2H$ in alkali is $C_{10}H_8O_3$. The theory that the two acids are stereoisomerides is not supported. E. E. J. M.

Stereoisomerism of 2 : 2′-disubstituted derivatives of diphenyl. II. A. Corbellini and M. Angeletti (Atti R. Accad. Lincei, 1932, [vi], **15**, 968—973; cf. A., 1932, 849).—Crystallisation of the *brucine* salt of *2-α-hydroxy-α-methylethyldiphenyl-2′-carboxylic acid*, m.p. 137° (*lactone*, m.p. 123°), from EtOH yields (1) a fraction, m.p. 217°, $[\alpha]_D^{24}$ —35·35° in $CHCl_3$, and (2) a residue, m.p. 214°, $[\alpha]_D^{24}$ —33·49°. In $CHCl_3$ solution both salts are unstable, $[\alpha]_D$ gradually falling to that of the racemic salt, —1·87°. In the crystallisation of the racemic salt, the equilibrium dextro salt lævo salt is displaced towards the right, owing to the lower solubility of the lævo salt. *2-α-Hydroxy-α-ethyl-n-propyldiphenyl-2′-carboxylic acid*, obtained from Et H diphenate and MgEtI, has m.p. 140—141° (*lactone*, m.p. 137°; *Na* salt). T. H. P.

Oxidation products of 1 : 2 : 5-trimethylnaphthalene. I. M. Heilbron and D. G. Wilkinson (J.C.S., 1932, 2809—2810).—The Me ester (I), m.p. 71—72°, obtained by action of MeOH–HCl on 3-methylacetophenone-2-carboxylic acid (II) (cf. A., 1931, 484) is the ψ-ester, C_6H_3Me  , and does not react with semicarbazide. (II) or its normal Me ester with NH_2OH gives the *oxime anhydride*, m.p. 174°. "Me 4-methylacetophenone-2-carboxylate" (A., 1931, 80) proves to be identical with (I); the ester, m.p. 78—79°, described at the same time is Me 3 : 4-dimethylacetophenone-2-carboxylate, and the neutral substance, $(C_4H_4O)_n$, m.p. 70—71°, is the lactone of α-hydroxy-α-*o*-carboxyphenylethyl Me ketone (cf. A., 1931, 484). H. A. P.

Lichen substances. XV. Divaricatic acid. Y. Asahina and T. Hirakata (Ber., 1932, **65**, [*B*], 1665—1668).—Concentration of the ethereal extract of *Evernia mesomorpha f. esoredioso*, Mull. Arg., leads to the isolation of a little *d*-usnic acid and divaricatic acid (I), m.p. 137° (*Ac*$_2$ derivative, m.p. 145—146°, prepared with Ac_2O containing a trace of H_2SO_4; *Me* ester, m.p. 76°). (I) with excess of CH_2N_2 gives the corresponding *Me*$_2$ *ether* of the *Me* ester, m.p. 85°, hydrolysed by KOH–MeOH to 2 : 4-*dimethoxy-6-propylbenzoic acid*, m.p. 64°, and *Me* 4-*hydroxy-2-methoxy-6-propylbenzoate*, m.p. 121° [corresponding *acid*, m.p. 93° (also +0·5H_2O)]. H. W.



Constitution of the bile acids. XLIV. 6-(formerly 13)-hydroxy*allo*cholanic acid. H. Wieland and E. Dane (Z. physiol. Chem., 1932, **212**, 41—49; cf. A., 1932, 1131).—Oxidation of hyodeoxycholic acid with CrO_3 in AcOH gives 3-*hydroxy-6-ketocholanic acid* (I), m.p. 159—160° (from EtOAc), 160—162° (from dil. MeOH), 170—173° (needle clusters from EtOAc). Thermal decomp. of (I) gives *6-keto-3-cholenic acid* (II), m.p. 128°.

Catalytic hydrogenation (PtO_2) of (II) affords 6-*hydroxy*allo*cholanic acid* (II), m.p. 228° (*Me* ester, m.p. 95°), which with CrO_3 in AcOH gives 6-*ketocholanic acid*, m.p. 151°, and on distillation 6-*cholenic acid*, m.p. 148—149°. Oxidation of (III) with HNO_3 yields a *tricarboxylic acid*, m.p. 258°, probably *allo*thilobilianic acid, since its anhydride, m.p. 196—199°, gives no depression in m.p. with thilobilianic anhydride. With Na in EtOH the semicarbazone of (I) gives a 3-OH-acid (IV), m.p. 175° (*Me* ester, m.p. 115—117°, 162° after recryst.), apparently a mixture of isomeric lithocholic acids. The free acid (3-*hydroxy*allo*cholanic acid*) from the ester with m.p. 162° has m.p. 207—209°. This acid appears identical with a degradation product of chlorocholestane. If identity is established, the OH group of cholesterol in ring A must have the same position as in the bile acids, namely, C_3 not C_4. (IV) with CrO_3 in AcOH gives 3-ketocholanic acid; distillation yields 3-cholenic acid. By Wieland and Weyland's method, (IV) gives lithobilianic acid. On boiling with aq. KOH, (I) gives an inversion *product*, m.p. 185—187°. J. H. B.

Hydrogen cyanide. IV. Gattermann's hydrogen cyanide aldehyde synthesis. L. E. Hinkel, E. E. Ayling, and W. H. Morgan (J.C.S., 1932, 2793—2798).—At its b.p., but not at 40° or below, C_6H_6 interacts with HCN, HCl, and $AlCl_3$ to give PhCHO (14% of theory calc. on HCN). Apparently the compound $AlCl_3,2HCN$ is stable $< 40°$ (cf. A., 1898, i, 476). Yields of 85—100% of aldehyde are obtained from the simple homologues (PhMe, *o*-, *m*-, and *p*-$C_6H_4Me_2$, and mesitylene), the highest yields being obtained at 100°, and with $AlCl_3$ in excess of that needed to form the compound $AlCl_3,2HCN$. In no case does the yield exceed 100% calc. on the assumption that 2HCN enter into reaction, even with PhOMe or resorcinol, in which case $AlCl_3$ is unnecessary. This is in accordance with the hypothesis that chloromethyleneformamidine and not iminoformyl chloride is the active agent (cf. A., 1930, 1421); the reaction therefore follows the course:

$NH{:}CH{\cdot}N{:}CHCl + C_6H_6 \longrightarrow NH{:}CH{\cdot}N{:}CHPh \longrightarrow PhCHO + 2NH_3 + HCO_2H$. H. A. P.

Action of metallic oxides on benzotrichloride and benzylidene chloride. W. Davies and J. H. Dick (J.C.S., 1932, 2808—2809).—Interaction of pure ZnO with $CPhCl_3$ at 100° gives BzCl in 58% yield; technical $ZnCl_2$ (which contains ZnO), but not pure, also gives BzCl, although this is formed with pure $ZnCl_2$ in presence of H_2O. A little BzCl is also obtained with CdO or PbO, but not with Fe_2O_3; Al_2O_3 reacts only slightly, and P_2O_5 not at all. ZnF_2 (containing ZnO) gives BzF (65% of theory). With ZnO in C_6H_6 $CHPhCl_2$ gives PhCHO in 30% yield, but in absence of a diluent tarry products only are formed. H. A. P.

Action of bromine and iodine monochloride on some Schiff's bases. F. B. Dains and G. A. Lehmann (Trans. Kansas Acad. Sci., 1931, **34**, 297—302).—*N*-Halogenation is effected in CCl_4, $CHCl_3$, or glacial AcOH. ICl is a good iodinating agent, but contaminates the product with I. Ch. Abs.

Colour reaction of thiocarbonyl compounds. H. W. Schwechten (Ber., 1932, **65**, [*B*], 1734—1737).—Thiocarbonyl compounds which are themselves coloured in some degree and are to some extent sol. in H_2O or MeOH give colorations with $[Fe^{II}(CN)_5(NH_3)]Na_3$. Examples cited are $CS(NHAc)_2$, $CSCl_2$, Ph·CS·NH_2, Ph·CS·NHPh, CO_2H·CS·NHPh, $(CS{\cdot}NHPh)_2$, $(CS{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H)_2$, $MeCS_2H$, $PhCS_2H$, 4-thio-2 : 6-dimethylpyrone, and CSPhMe. Colorations are darker in MeOH than in H_2O. The compounds pass by autoxidation into coloured Fe^{III} derivatives. Dark blue colours are given when H_2S is passed into solutions or suspensions of the following aldehydes in $[Fe(CN)_5(NH_3)]Na_3$, reaction being attributed to the monomeric thioaldehyde: PhCHO, *m*- and *p*-C_6H_4Me·CHO, *p*-C_6H_4Ph·CHO, *p*-C_6H_4I·CHO, *p*-C_6H_4Br·CHO, *o*-, *m*-, and *p*-OH·C_6H_4·CHO, *p*-$C_6H_3Me(OH)$·CHO, *p*-OMe·C_6H_4·CHO, *p*-OEt·C_6H_4·CHO, vanillin, piperonal, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4$·CHO, *p*-CN·C_6H_4·CHO, *p*-$C_6H_4(CHO)_2$, *p*-$NMe_2{\cdot}C_6H_4$·CHO, CHPh:CH·CHO, CClPh:CH·CHO, furfuraldehyde, CHMe:CH·CHO, citral. Lower fatty aldehydes yield no or pale pink colours; heptaldehyde and citronellal give pink and violet-red solutions in H_2O and MeOH, respectively. CH_2Ph·CHO and $CH_2Ph{\cdot}CH_2$·CHO yield solutions which ultimately become blue. Ketones do not react. Incidence of the reaction appears to be conditioned by the presence of an ethylenic linking or an aromatic system vicinal to CHO. H. W.

Carbon rings. XX. Unsaturated 16- and 18-membered carbon rings of the type of civetone. L. Ruzicka, M. Stoll, W. Scherrer, H. Schinz, and C. F. Seidel (Helv. Chim. Acta, 1932, **15**, 1459—1467; cf. A., 1932, 1134).—Electrolysis of a mixture of Me H adipate and undecenoic acid in MeOH–NaOMe gives Me_2 sebacate, $\Delta^{\alpha\tau}$-eicosadiene, m.p. 30—32°, and Δ^{τ}-*pentadecenoic acid*; the *Me* ester, b.p. 135—140°/0·5 mm., of the last-named acid gives in AcOH the ozonide, decomposed by Zn dust and H_2O to *Me* μ-*aldehydododecane*-α-*carboxylate*, m.p. 101—103°, b.p. 130—150°/0·1 mm., which with $CH_2(CO_2H)_2$ and C_5H_5N at 80° gives Δ^{α}-*tetradecene*-α*ξ*-*dicarboxylic acid* (I), m.p. 122—125°, also obtained in very poor yield from α-bromohexadecane-α*π*-dicarboxylic acid and $NPhMe_2$. The *Ce* salt of (I) at 450° in vac. gives no cyclic ketone, but, amongst other products, Me dodecyl ketone; the acid is assumed to decompose to AcOH and dodecane-α*μ*-dicarboxylic acid, which further decomposes to give CO_2 and tridecoic acid; the latter with AcOH then gives the ketone. Me_2 θ-ketopentadecane-α*ο*-dicarboxylate, when hydrogenated (PtO_2) in AcOH at room temp., gives the θ-*OH*-ester, m.p. 55—56°, which with 2-$C_{10}H_7{\cdot}SO_3H$ (II) at 220° in CO_2 gives *Me*$_2$ Δ^{η}-*pentadecene*-α*ο*-*dicarboxylate*, m.p. 172—174°/0·3 mm. The *Y* salt of the corresponding *acid*, m.p. 86—87°, at 350—400° gives, amongst other products, Δ^{8}-cyclo*hexadecen*-1-*one*, m.p. 23°, b.p. 193—195°/19 mm. (*semicarbazone*, m.p. 180—181°). Δ^{ι}-Undecenoic acid and Fe at 240—300° give *di*-Δ^{ι}-*decenyl ketone*, b.p. 160°/0·2 mm., m.p. 41—42°, yielding with O_3 in CCl_4 ι-*ketoheptadecane*-α*τ*-*dicarboxylic acid* (20% yield), the *Me*$_2$ ester, m.p. 50—52°, of which is

hydrogenated (PtO_2) in AcOH to *Me*$_2$ *ι-hydroxyheptadecene-ατ-dicarboxylate*, m.p. 51—53°, b.p. 212—215°/0·05 mm. This with (II) at 210—220° in vac. gives Me$_2$ Δ^9-*heptadecene-ατ-dicarboxylate*, b.p. 180—190°/0·1 mm. The *Y* salt of the corresponding acid at 450° in vac. affords, amongst other products, Δ^9-*cyclooctadecen-1-one*, m.p. 37·5—38° (*semicarbazone*, m.p 178—180°). R. S. C.

Haloform reaction. VII. Effect of *ortho* chlorine atoms. R. C. Fuson, J. W. Bertetti, and W. E. Ross (J. Amer. Chem. Soc., 1932, **54**, 4380—4383).—2 : 4 : 6-*Trichloroacetophenone* (I), m.p. 156—157°, from MgMeI and 2 : 4 : 6-$C_6H_2Cl_3$·COCl, and aq. NaOBr give 2 : 4 : 6-*trichloro-ααα-tribromoacetophenone*, m.p. 126—127°, converted by 50% NaOH at 90° into 2 : 4 : 6-$C_6H_2Cl_3$·CO_2H. (I) and aq. NaOCl afford α : 2 : 4 : 6-*tetrachloroacetophenone*, m.p. 106·5—107·5°, converted by further treatment with aq. NaOCl–C_5H_5N into 2 : 4 : 6-$C_6H_2Cl_3$·CO_2H [also produced by prolonged action of NaOCl on (I)]. H. B.

Synthetical experiments in the tetraphenylallene series. E. Bergmann, H. Hoffmann, and H. Meyer (J. pr. Chem., 1932, [ii], **135**, 245—266).—*p*-Bromophenyl styryl ketone and MgPhBr give p-*bromophenyl* ββ-*diphenylethyl ketone*, m.p. 137—139°. Definite products are not obtained from this or *p*-bromophenyl β-phenyl-β-*p*-bromophenylethyl ketone and MgPhBr or from p-*bromophenyl* p-*bromostyryl ketone*, m.p. 185—186°, and *p*-C_6H_4Br·MgBr. Mg ββ-diphenylvinyl bromide (I) and di-*p*-tolyl ketone give *γγ-diphenyl-αα-di*-p-*tolylallyl alcohol*, m.p. 149—150°, and ααδδ-tetraphenyl-$\Delta^{\alpha\gamma}$-butadiene (II). Fluorenone and (I) afford (II) and 9-*hydroxy*-9-ββ-*diphenylvinylfluorene*, m.p. 118—121° (decomp.), which is dehydrated by AcCl or hot AcOH to αα-*diphenyl-γγ-diphenyleneallene*, m.p. 139—140°. 4 : 4′-Dibromobenzophenone and (I) yield (II) and *γγ-diphenyl-αα-di*-p-*bromophenylallyl alcohol*, m.p. 91—92° (meniscus formation), 110° (clear), dehydrated at 130° to αα-*diphenyl-γγ-di*-p-*bromophenylallene*, m.p. 112—114°. αα-*Diphenyl-γγ-di*-p-*chlorophenylallene*, m.p. 93—95°, is similarly prepared from *γγ-diphenyl-αα-di*-p-*chlorophenylallyl alcohol*, m.p. 85°. β-Phenyl-β-*p*-bromophenylvinyl bromide does not react with Mg, whilst Mg β-phenyl-β-*p*-chlorophenylvinyl bromide [from Mg activated with EtBr and the less fusible -vinyl bromide (A., 1932, 506)] and *p*-chlorobenzophenone give αδ-*diphenyl-αδ-di*-p-*chlorophenyl-*$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 230°, and an oil containing some allene derivative (since treatment with AcOH–HCl affords 6-*chloro*-1 : 3-*diphenyl*-1-p-*chlorophenyl*- or 1-*phenyl*-1 : 3-*di*-p-*chlorophenyl-indene*, m.p. 139°). PhF, BzCl, and $AlCl_3$ give p-*fluorobenzophenone* (III), b.p. 159—161°/13 mm., m.p. 45—47° [*phenylhydrazone*, m.p. 105°; *oxime*, m.p. 135°, converted by PCl_5 in Et_2O into *benz*-p-*fluoroanilide*, m.p. 187° (when prepared from *p*-C_6H_4F·NH_2 and BzCl)], whilst PhF, CCl_4, and $AlCl_3$ in CS_2 afford (after hydrolysis with conc. H_2SO_4) 4 : 4′-*difluorobenzophenone*, m.p. 109° (*phenylhydrazone*, m.p. 146—147°). CH_2Br·CO_2Et, (III), and Zn in C_6H_6 yield *Et* β-*hydroxy*-β-*phenyl*-β-p-*fluorophenylpropionate* (IV), m.p. 86°, dehydrated by 85% HCO_2H at 150° to *Et* β-p-*fluorophenylcinnamate*, b.p. 193—194°/11 mm., m.p. 61°, which with MgPhBr affords 6-*fluoro*-3 : 3-*diphenyl*- or 3-*phenyl*-3-p-*fluorophenyl-hydrindone*, m.p. 120—122° (the Cl-*analogue*, m.p. 111—112°, is similarly obtained by way of *Et* β-*hydroxy*-β-*phenyl*-β-p-*chlorophenylpropionate*, m.p. 69°, and *Et* β-*p-chlorophenylcinnamate*, b.p. 210—212°/13 mm.). The following are prepared as (IV): *Et* β-*hydroxy*-ββ-*di*-p-*chlorophenyl*-, m.p. 102°, -β-*phenyl*-β-p-*bromophenyl*-, m.p. 93°, -ββ-*di*-p-*bromophenyl*-, m.p. 111°, -β-*phenyl*-β-p-*iodophenyl*-, m.p. 75°, and -ββ-*di*-p-*tolyl*,- m.p. 81—82° [free *acid*, m.p. 163—164° (decomp.)], -*propionates*. These are dehydrated by HCO_2H (unless stated otherwise) to *Et* p-*chloro*-β-p-*chlorophenyl*-, m.p. 65°, *Et* β-p-*bromophenyl*-, b.p. 220—222 /12 mm., *Et* p-*bromo*-β-p-*bromophenyl*-, m.p. 80—81°, *Et* β-p-*iodophenyl*-, m.p. 100—102°, and *Et* β-p-*tolyl*-p-*methyl*-, b.p. 213°/71 mm. (free *acid*, m.p. 168—170°), -*cinnamates*, respectively; the last-named ester is best prepared by dehydration with HCl in EtOH–C_6H_6 in presence of Na_2SO_4. *Et* β-*hydroxy*-β*γ*-*diphenylbutyrate*, m.p. 60—62° (from deoxybenzoin, CH_2Br·CO_2Et, and Zn in C_6H_6), is dehydrated (HCO_2H) to the *Et* ester, b.p. 211°/15 mm., of β*γ*-diphenyl-Δ^{β}-butenoic acid. H. B.

Ease of substitution of aromatically bound hydrogen atoms. II. J. von Braun and A. Friedsam (Ber., 1932, **65**, [*B*], 1680—1686; cf. A., 1929, 562).—Experiments on the mode of ring-closure of dibenzylacetyl chlorides differently substituted in the two Ph groups show that the readiness of substitution of the H atom diminishes in the sequence *p*-Me·C_6H_4H, C_6H_5H, *p*-F·C_6H_4H, *m*-Me·C_6H_4H, *p*-Cl·C_6H_4H, *p*-Br·C_6H_4H. α-*m*-Chlorobenzyl-β-phenylpropionyl chloride is converted by $AlCl_3$ in CS_2 into a mixture of the two possible benzylhydrindones, $C_{16}H_{13}OCl$, b.p. 178—185°/0·2 mm. (semicarbazone, m.p. 175—192°; oxime, m.p. 80—102°), oxidised by CrO_3 in AcOH to phthalic acid containing a little 3-chlorophthalic acid and *m*-chlorobenzoic acid containing a little BzOH. *Et benzyl*-m-*bromobenzylmalonate*, b.p. 199—202°/0·3 mm., is transformed successively into the *acid*, m.p. 175°, and α-m-*bromobenzyl*-β-*phenylpropionic acid*, b.p. 215—218°/0·3 mm., m.p. 92°; the corresponding chloride gives a ketone mixture, b.p. 193—197°/0·5 mm. (semicarbazone, m.p. 170—182°; oxime, m.p. 99—120°), oxidised to monocarboxylic acids, mainly C_6H_4Br·CO_2H, and dicarboxylic acids, preponderatingly $C_6H_3Br(CO_2H)_2$. For comparison, 5-bromo-1-hydrindone is condensed with PhCHO to 5-*bromo*-2-*benzylidene*-1-*hydrindone*, m.p. 194°, hydrogenated in presence of Pd–C to 5-*bromo*-2-*benzyl*-1-*hydrindone*, m.p. 149° (*semicarbazone*, m.p. 184°). Similarly, 1-hydrindone and *m*-C_6H_4Br·CHO afford 2-m-*bromobenzylidene*-1-*hydrindone*, m.p. 149°, hydrogenated to 2-m-*bromobenzyl*-1-*hydrindone*, b.p. 180—181°/0·2 mm. (*semicarbazone*, m.p. 189°). *Et* m-*chlorobenzyl*-m-*bromobenzylmalonate*, b.p. 222—226°/0·7 mm., from C_6H_4Cl·CH_2·$CH(CO_2Et)_2$ and *m*-C_6H_4Br·CH_2Br, yields successively the corresponding *acid*, m.p. 175°, and α-m-*bromobenzyl*-β-m-*chlorophenylpropionic acid*, b.p. 235°/0·3 mm., m.p. 98—100°. Its chloride yields a ketone mixture, b.p. 237—245°/1 mm., m.p. 64—72° (semicarbazone, m.p. 134—160°; oxime, m.p. 92—

123°), the monocarboxylic acids from which contain about 70% of *m*-$C_6H_4Br\cdot CO_2H$ and the dicarboxylic acid about 70% of $C_6H_3Cl(CO_2H)_2$. *Et benzyl-m-fluorobenzylmalonate*, b.p. 214—216°/12 mm., from $CH_2Ph\cdot CH(CO_2Et)_2$ and *m*-$C_6H_4F\cdot CH_2Br$, gives the corresponding *acid*, m.p. 156—158°, and *m-fluorobenzyl-β-phenylpropionic acid*, b.p. 208—212°/12 mm., m.p. 83°. The mixture of ketones from the chloride has b.p. 200—206°/7 mm. (semicarbazone, m.p. 152—170°; oxime, m.p. 82—96°), and yields mixtures of mono- and di-carboxylic acids both containing about equal proportions of fluorinated and unsubstituted acids. Et *m*-chlorobenzylmalonate and *p*-$C_6H_4Me\cdot CH_2Br$ afford *Et* m-*chlorobenzyl*-p-*methylbenzylmalonate*, b.p. 199—203°/0·3 mm. (*acid*, m.p. 140—156°), whence α-m-*chlorobenzyl*-β-p-*tolylpropionic acid*, b.p. 190—192°/0·2 mm., m.p. 65°. The mixture of ketones, b.p. 174—178°/0·2 mm. (semicarbazone, m.p. 235—239°; oxime, m.p. 152—159°), is oxidised to a small amount of terephthalic acid, much *m*-$C_6H_4Cl\cdot CO_2H$, much trimellitic acid, and little $C_6H_3Cl(CO_2H)_2$. H. W.

2 : 3-Benzanthrone and 2 : 3-benzanthranyl acetate. E. DE B. BARNETT and R. A. LOWRY (Ber., 1932, **65**, [*B*], 1649—1650).—2 : 3-$C_{10}H_6(CO)_2O$ is converted by C_6H_6 and $AlCl_3$ at room temp. into 3-benzoyl-2-naphthoic acid, m.p. 210°, reduced by Zn dust, NH_3, aq. NaOH, and a little $CuSO_4$ to 3-*benzyl*-2-*naphthoic acid* (I), m.p. 204°. (I) is transformed by $ZnCl_2$ at 175° but not by H_2SO_4 into 2 : 3-benzanthrone, m.p. 184°, which, contrary to Fieser (A., 1931, 1064), is converted by Ac_2O and C_5H_5N at 100° into 2 : 3-*benzanthranyl acetate*, m.p. 213°. Tetrahydro-2 : 3-benzanthrone, best prepared by reduction of the quinone with Al and conc. H_2SO_4, similarly yields *tetrahydro*-2 : 3-*benzanthranyl acetate*, m.p. 175°. Tetrahydronaphthoylbenzoic acid is obtained in 97% yield by gradual addition of $AlCl_3$ to *o*-$C_6H_4(CO)_2O$ and tetrahydronaphthalene in $C_2H_2Cl_4$. H. W.

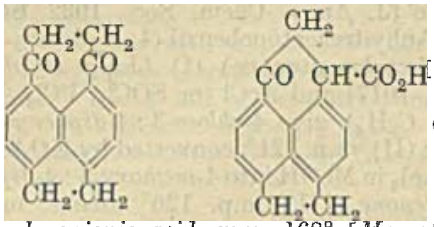
Anionotropic and prototropic changes in 4-hydroxy*cyclo*pentenones. H. BURTON and C. W. SHOPPEE (Chem. and Ind. 1932, 981).—Acetylation (Ac_2O–H_2SO_4) of 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (I) is considered to give 2-acetoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ³-*cyclo*pentenone (II), m.p. 137° [and not the acetate of (I) as stated by Gray (J.C.S., 1909, **95**, 2131, 2138)], as the result of an anionotropic change. The conversion of (II) into 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (III) by EtOH–KOH (Gray, *loc. cit.*) would then involve a prototropic change (concurrent with hydrolysis). Conclusive evidence for these tautomeric changes is furnished by the observation that (II) and 2 : 4-dinitrophenylhydrazine in EtOH–H_2SO_4 give 2-ethoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ³-*cyclo*pentenone-2 : 4-dinitrophenylhydrazone, m.p. 182° (decomp.), which differs from the 2 : 4-dinitrophenylhydrazone, m.p. 205°, of the Et ether of (III) and the 2 : 4-dinitrophenylhydrazone, m.p. 204° (decomp.), of the Et ether of (I) [obtained by ethylating (I) with EtI and "activated" Ag_2O]. The results of Allen and Spanagel (following abstract) are considered to be (partly) inconclusive. H. B.

Reactions of anhydroacetonebenzils with halogen compounds. C. F. H. ALLEN and E. W. SPANAGEL (J. Amer. Chem. Soc., 1932, **54**, 4338—4347).—Anhydroacetonebenzil (4-hydroxy-3 : 4-diphenyl-Δ²-*cyclo*pentenone) (I) (Japp *et al.*, J.C.S., 1899, **75**, 1017) and AcCl (or $SOCl_2$, PCl_3, $POCl_3$, or $AlCl_3$ in C_6H_6) give 4-*chloro*-3 : 4-*diphenyl*-Δ²-cyclo*pentenone* (II), m.p. 121°, converted by KOAc, AgOAc, or $Pb(OAc)_4$ in MeOH into 4-*methoxy*-3 : 4-*diphenyl*-Δ²-cyclo*pentenone* (III), m.p. 126° (*oxime*, m.p. 173°; 5 : 5-*Br*$_2$-derivative, m.p. 175°), which affords two *benzylidene* derivatives, m.p. 124° and 160°, both of which are converted by Ac_2O–H_2SO_4 into 4-acetoxy-3 : 4-diphenyl-5-benzylidene-Δ²-*cyclo*pentenone (Gray, J.C.S., 1909, **95**, 2131). (III) is reduced by red P and HI to 3 : 4-diphenyl-Δ³-*cyclo*pentenone. The chloride obtained from (I) and HCl by Japp (J.C.S., 1887, **51**, 420) is considered to be 2-*chloro*-3 : 4-*diphenyl*-Δ⁴-cyclo*pentenone*, m.p. 128° (IV) (2 : 4-*dinitrophenylhydrazone*, m.p. 217°); the 2-*Br*-analogue has m.p. 113°. (II) and (IV) are both converted by EtOH–KOH into the compound, $C_{34}H_{24}O_2$ (Japp, *loc. cit.*), which is also obtained from (I) and PCl_3 in absence of solvent, by reduction of (III) with Sn and HCl, and from (II) and EtOH. (I) and SO_2Cl_2 give a mixture of 5-*chloro*-4-*hydroxy*-3 : 4-*diphenyl*-Δ²-cyclo*pentenone*, m.p. 194° [*acetate*, m.p. 159°, formed together with a *compound*, $C_{34}H_{22}O_2Cl_2$, m.p. 217° (decomp.), by the action of Ac_2O–H_2SO_4], and a *compound*, probably $\left(\begin{matrix}CCl{:}CPh\\CO{-}CCl_2\end{matrix}\right)>CPh\cdot$ m.p. 129°. (I) and Br give (cf. Japp) 5-*bromo*-4-*hydroxy*-3 : 4-*diphenyl*-Δ²-cyclo*pentenone*, m.p. 198° [*acetate*, m.p. 148°, formed together with a *compound*, $C_{34}H_{22}O_2Br_2$, m.p. 212° (decomp.), by Ac_2O–H_2SO_4].

ββ-Dimethylanhydroacetonebenzil (4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone) (V) and $SOCl_2$ give 4-*chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone*, m.p. 133°, which with KOH, KOAc, or AgOAc in EtOH regenerates (V), with AgOAc in AcOH affords the 4-OAc-derivative (Gray, *loc. cit.*), and with AgOAc in MeOH gives 4-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone*, m.p. 144°. H. B.

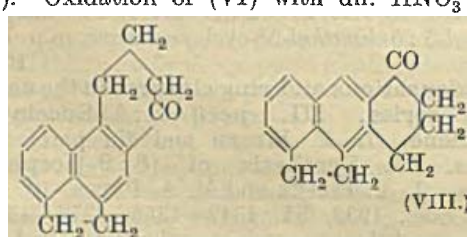
Condensations and ring closures in the naphthalene series. III. *peri*[—3 : 4]-Succinylacenaphthene. IV. Synthesis of [8 : 9-]acephenanthrene. L. F. FIESER and (in part) M. A. PETERS. L. F. FIESER and M. A. PETERS (J. Amer. Chem. Soc., 1932, **54**, 4347—4356, 4373—4379).—III. Acenaphthene, succinic anhydride, and $AlCl_3$ in $PhNO_2$ at 0° give 78% of β-3-*acenaphthoylpropionic acid* (I), m.p. 208° (decomp.) [*Me* ester (II), m.p. 89° (*oxime*, m.p. 146°)], and 15% of β-1-*acenaphthoylpropionic acid* (III), m.p. 181° (*Me* ester, m.p. 126°); at —15° the corresponding % are 87 and 5. Oxidation of (I) with $KMnO_4$ gives (according to the conditions used) naphthalene-1 : 4 : 5-tricarboxylic acid [anhydride (*Me* ester, m.p. 222°)] or an *acid*, $C_{15}H_{10}O_4$, m.p. 259°, or mellophanic acid [also formed by oxidation of (III)]. (II) heated with $AlCl_3$–NaCl at 150° affords 3 : 4-*succinylacenaphthene* (IV), m.p. 180° [*dioxime*, decomp. when heated (*diacetate*)], reduced (Wolff–Kishner) to 3 : 4-*tetramethyleneacenaphthene*, m.p. 138°, and oxidised ($Na_2Cr_2O_7$–AcOH) to naphth-

alene-1 : 4 : 5 : 8-tetracarboxylic acid. Compounds of type (IV) could not be obtained from β-2-*methyl*-1-

(IV.)  (V.)

naphthoylpropionic acid, m.p. 168° [*Me* ester, m.p. 85° (β-*Br*-derivative, m.p. 81°)], which appears to be identical with the β-6-methyl-2-naphthoylpropionic acid of Haworth *et al.* (A., 1932, 839), β-2 : 7-*dimethyl*-1-*naphthoylpropionic acid*, m.p. 130°, and β-2-*methoxy*-1-*naphthoylpropionic acid*, m.p. 152°, which are prepared from succinic anhydride and 2-$C_{10}H_7$·Me, 2 : 7-$C_{10}H_6Me_2$, and β-$C_{10}H_7$·OMe, respectively. β-2-*Hydroxy*-1-*naphthoylpropionic acid* has m.p. 232°. Acenaphthene and glutaric anhydride give a poor yield of γ-3-*acenaphthoylbutyric acid*, m.p. 201° (*Me* ester, m.p. 120°). *Me* β-*bromo*-β-3-*acenaphthoylpropionate*, m.p. 113°, from (II) and Br in $CHCl_3$, with NaOAc in AcOH at 100° gives *Me* β-3-*acenaphthoylacrylate*, m.p. 113° (free *acid*, m.p. 165°, also obtained in poor yield from acenaphthene and maleic anhydride), which with $AlCl_3$–NaCl at 140° affords about 5% of (probably) the *keto-acid* (V), m.p. 214° (decomp.). Maleic anhydride could not be condensed with $C_{10}H_8$. Anthracene, succinic anhydride, and $AlCl_3$ in $PhNO_2$ give (cf. G.P. 376,635) a complex mixture of substances including β-2-*anthroylpropionic acid*, m.p. 228° (*Me* ester, m.p. 148°; *quinone*, m.p. 207°). γ-2-*Anthrylbutyric acid* has m.p. 197°.

IV. Clemmensen reduction of Me β-3-acenaphthoylpropionate gives γ-3-*acenaphthylbutyric acid*, m.p. 148°, the *chloride*, m.p. 83°, of which with $AlCl_3$ in $PhNO_2$ at 0° affords 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-8 : 9-*acephenanthrene* (VI), m.p. 147° (*oxime*, m.p. 225°; *phenylhydrazone*, m.p. 206°; *semicarbazone*, m.p. 302°). Oxidation of (VI) with dil. HNO_3 at


(VIII.)

160° gives phenylglyoxyldicarboxylic acid (oxidised by $KMnO_4$ to hemimellitic acid), whilst reduction (Clemmensen or Wolff–Kishner) affords 1 : 2 : 3 : 4-*tetrahydro*-8 : 9-*acephenanthrene* (VII), m.p. 92·5° (*picrate*, m.p. 112°). Distillation of (VI) with Zn dust and subsequent dehydrogenation with S gives 8 : 9-*acephenanthrene*, m.p. 106° (*picrate*, m.p. 145°), oxidised by $Na_2Cr_2O_7$–AcOH to phenanthrene-8 : 9-dicarboxylic anhydride. (VI) and an excess of MgPhBr yield 1-*phenyl*-3 : 4-*dihydro*-8 : 9-*acephenanthrene*, m.p. 144°; with MgMeI, 1-*methyl*-, m.p. 159°, or 1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-, m.p. 133° (decomp.), -8 : 9-*acephenanthrene* is obtained, according to the conditions used. Succinic anhydride, (VII), and $AlCl_3$ in $PhNO_2$ give 5-β-*carboxypropionyl*-1 : 2 : 3 : 4-*tetrahydro*-8 : 9-*acephenanthrene*, m.p. 218° (*Me* ester, m.p. 146°), reduced (Clemmensen) to the 5-γ-*carboxypropyl* derivative, m.p. 158°, and cyclised (by way of the chloride) to 1-*keto*-5 : 6-*tetramethylene*-1 : 2 : 3 : 4-*tetrahydro*-8 : 9-*acephenanthrene*, m.p. 172°.

β-1-Acenaphthoylpropionic acid is reduced (Clemmensen) to γ-1-*acenaphthylbutyric acid*, m.p. 155°, which is cyclised (by way of the chloride) to 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-5 : 10-*aceanthrene* (VIII), m.p. 145°, convertible by distillation with Zn dust into *aceanthrene*, m.p. 113° (*picrate*, m.p. 120°) (cf. Liebermann and Zsuffa, A., 1911, i, 387). H. B.

Synthesis of 2 : 3-dimethoxyfluorenone. B. Reichert (Arch. Pharm., 1932, 9, 551—553).—3 : 4-Dimethoxybenzophenone and 65% HNO_3 at room temp. give the 6-NO_2-derivative, m.p. 137°, the constitution of which is proved by conversion into the 6-carboxylic acid, which yields 2 : 3-dimethoxyanthraquinone. Reduction (H_2, PtO_2) gives the 6-NH_2-compound, m.p. 201° (decomp.) (*Ac* derivative, m.p. 188°), which by diazotisation and boiling yields 2 : 3-dimethoxyfluorenone, m.p. 164° (cf. A., 1907, i, 142). R. S. C.

Mixed benzoins. IX. *meso*-Chloro-derivatives. J. S. Buck and W. S. Ide (J. Amer. Chem. Soc., 1932, 54, 4359—4365).—Benzoin, 4′-methoxy-, 2-chloro-4′-methoxy-, and 2-chloro-3′ : 4′-dimethoxybenzoins (for nomenclature see A., 1932, 1034) are converted by PCl_5 in C_6H_6 into Ph αα-dichlorobenzyl ketone, *anisyl* αα-*dichlorobenzyl ketone*, m.p. 81° (accompanied by a little p-*methoxytolane tetrachloride*, m.p. 153°), *anisyl* αα : 2-*trichlorobenzyl ketone*, m.p. 109°, and 3 : 4-*dimethoxyphenyl* αα : 2-*trichlorobenzyl ketone*, m.p. 120°, respectively; the corresponding benzils are intermediates. These ketones are reduced (H_2, PtO_2, EtOH) to *Ph* α-*chlorobenzyl*, m.p. 68°, impure anisyl α-chlorobenzyl, *anisyl* α : 2-*dichlorobenzyl*, m.p. 75°, and 3 : 4-*dimethoxyphenyl* α : 2-*dichlorobenzyl*, m.p. 99°, *ketones*, respectively (and then to the aryl benzyl ketones), which with EtOH–NaOEt regenerate the original benzoins. Ph αα-dichlorobenzyl ketone and EtOH–NaOEt give BzOEt and PhCHO (from $CHPhCl_2$): $PhCO{\cdot}CPhCl_2+EtOH \longrightarrow BzOEt+CHPhCl_2$; a side reaction is $PhCO{\cdot}CPhCl_2+EtOH+2NaOEt \longrightarrow CHPh(OEt)_2+BzOEt+2NaCl$. The other dichlorobenzyl compounds behave similarly. H. B.

Molecular rearrangements of α-glycols. IV. Influence of substituents on the reactivity of a pinacone. Reduction of 4 : 4′-dimethoxybenzophenone. V. Relative electronegativities of *p*-methoxy- and *p*-ethoxy-phenyl radicals. M. Migita (Bull. Chem. Soc. Japan, 1932, 7, 334—340, 341—345).—IV. Reduction of 4 : 4′-dimethoxybenzophenone (I) with Zn dust and hot or cold AcOH gives *anisyl trianisylmethyl ketone* (II), m.p. 140—141° (decomp.), the rearrangement product of *s*-tetra-anisylethylene glycol (III), decomp. 176° (slow), 181° (rapid heating) (cf. Bouvet, A., 1915, i, 766), which is prepared by reduction of (I) with EtOH in sunlight. The ready conversion of (III) into (II) by AcCl or warm AcOH is in accordance with the mechanism previously proposed (A., 1929, 448).

Dianisylcarbinol and (I) are produced when (III) is heated.

V. Reduction of *4-methoxy-4'-ethoxybenzophenone*, m.p. 106—107° (from PhOEt, *p*-OMe·C_6H_4·COCl, and $AlCl_3$ in CS_2), with Zn dust and hot AcOH gives *anisyl anisyldi*-p-*ethoxyphenylmethyl ketone*, m.p. 160°, also formed by reduction with EtOH in sunlight, thus showing that *p*-OEt·C_6H_4· is more negative than *p*-OMe·C_6H_4·. H. B.

Constitution and reactivity. I. Sulphonation of anthraquinone. II. Replacement of the sulphonic acid group in anthraquinone by hydrogen or chlorine. K. Lauer (J. pr. Chem., 1932, [ii], **135**, 164—181, 182—192).—I. A kinetic study of the sulphonation of anthraquinone in the β- and, under the influence of Hg salts, in the α-position. From the val. of the velocity coeffs. (k_1, k_2) at different temp. (T_1, T_2), the vals. of q and α are calc. by the equations $q=RT_1T_2/(T_1-T_2)$. $\log_e k_1/k_2$, and $\log_e k_1-\log_e \alpha-q/RT_1$. Further evidence is offered of the absence of α-sulphonation in complete absence of Hg and its repression by NaCl; it occurred to a slight extent in the β-monosulphonation studied, the ratio of α : β-SO_3H being unaltered by wide variations in temp. and concn. of SO_3. The extent of 2-sulphonation was determined by measuring the unreacted anthraquinone; the reaction is approx. bimol. Further sulphonation of the 2-SO_3H gave only 2 : 6- and 2 : 7-disulphonic acids, which were not interconvertible under the conditions used; the proportions formed were measured by mixed-m.p. determinations of the derived dichloroanthraquinones, and the vals. of q calc. on the assumption that α is equal in the two cases.

α-Sulphonation is approx. bimol., the val. of k depending on the concn. of Hg in the reaction medium; this is higher the less is the SO_3 content, and β-sulphonation is almost completely inhibited by $HgSO_4$ in 5% oleum. The Hg added is effective only as $HgSO_4$, and if added as metal or as another salt much β-sulphonation occurs in the early stages of the reaction. Further sulphonation in presence of Hg is essentially similar in these respects, and was studied in a similar manner to the β-disulphonation. Marked differences were found in the reaction consts. in the α- and β-series, corresponding with the differences in reaction mechanism.

II. The hydrolysis of anthraquinone-1- and -2-sulphonic acids, and -1 : 5-, -1 : 6-, -1 : 7-, and -1 : 8-disulphonic acids by means of aq. H_2SO_4 in presence of $HgSO_4$, and the conversion of these, and also of the -2-mono- and -2 : 6- and -2 : 7-disulphonic acids, into the corresponding chloroanthraquinones by the action of Cl_2 on a boiling aq. solution, are studied kinetically. The former reaction leads in the case of the 1-monosulphonic acid to anthraquinone, and with the αβ-disulphonic acid to anthraquinone-2-sulphonic acid. In both reactions similar vals. of α (but varying vals. of q) are observed for the α- and β-derivatives, respectively, but in the latter reaction where the β-SO_3H groups are displaced, although much slower than are the α-groups, there is a considerable difference in the vals. of α for the two series. H. A. P.

Constitution and reactivity. III. Replacement of sulpho-groups in anthraquinones by the amino-group. K. Lauer (J. pr. Chem., 1932, [ii], **135**, 204—208).—Vals. of $k\times10^4$, activation energies, and reaction coeffs. (cf. preceding abstract) for the reactions (involving replacement of one SO_3H by NH_2) between 1 mol. of 0·1*N*-solutions of anthraquinone-1- and -2-sulphonic, and -1 : 5-, -1 : 8-, -2 : 6-, and -2 : 7-disulphonic acids and 20% aq. NH_3 (100 mols.) in presence of $BaCl_2$ (1·5 mols.) and NH_4Cl (10 mols.) at 160—200°, are given. A similar reaction coeff. is found for all the acids containing the 1-SO_3H group; this is much smaller than the coeff. (also similar) for the 2-substituted acids. H. B.

Nitration of 3-methoxyacenaphthenequinone and 2-methoxynaphthalic anhydride. R. I. Davies, I. M. Heilbron, and F. Irving (J.C.S., 1932, 2715—2717).—3-Methoxyacenaphthenequinone (I) is converted by HNO_3 in H_2SO_4 at 10—30° into its 7-*NO*$_2$-derivative, m.p. 264—265°, the orientation of which follows from its oxidation by CrO_3–AcOH to *6-nitro-2-methoxynaphthalic anhydride* (II), m.p. 297—298°, which gives 6-nitro-2-naphthyl Me ether (Chem. News, 1896, **74**, II, 302) with Cu-bronze and quinoline at the b.p. CrO_3–AcOH oxidises (I) to 2-methoxynaphthalic anhydride (III), which with $Hg(OAc)_2$ gives *8-hydroxymercuri-7-methoxy-1-naphthoic anhydride*. This with Br in AcOH gives *8-bromo-7-methoxy-1-naphthoic acid*, m.p. 195° (decomp.), and with 3*N*-HCl at 100° gives 7-methoxy-1-naphthoic acid, which is readily demethylated by conc. HCl. Nitration of (II) in H_2SO_4 gives (II), converted by mercuration and hydrolysis into *3-nitro-7-methoxy-1-naphthoic acid*, m.p. 240—241°. H. A. P.

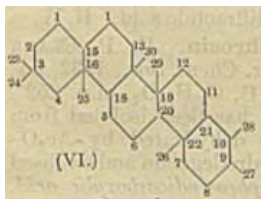
Identity of diffractaic acid with the dirhizonic acid of Hess. Y. Asahina and F. Fuzikawa (Ber., 1932, **65**, [*B*], 1668; cf. A., 1932, 396, 613).—Direct comparison of the acids, their Me esters, and the Me esters of the Me ethers establishes identity. It is proposed to retain the name diffractaic acid. H. W.

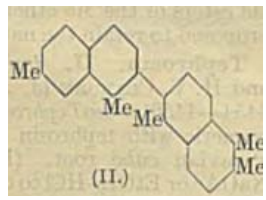
Tephrosin. II. *iso*Tephrosin. E. P. Clark and H. V. Claborn (J. Amer. Chem. Soc., 1932, **54**, 4454—4456).—iso*Tephrosin* (I), $C_{23}H_{22}O_7$, m.p. 252°, isomeric with tephrosin (II), has been isolated from Peruvian cube root. (I) is dehydrated by Ac_2O–NaOAc or EtOH–HCl to dehydrodeguelin and oxidised ($KMnO_4$ in $COMe_2$) to *isotephrosindicarboxylic acid*, $C_{23}H_{22}O_{11}$ (+0·5H_2O), m.p. 187°, which when heated with boiling Ph_2O for 30 sec. gives tephrosinmonocarboxylic acid (A., 1932, 950). (I) and (II) probably differ in the orientation of the OH group. H. B.

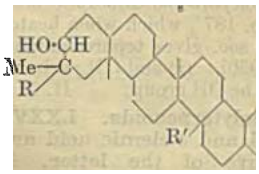
Polyterpenes and polyterpenoids. LXXVI. Dihydro-α-elemolic acid and δ-elemic acid and the tetrahydro-derivative of the latter. L. Ruzicka, R. L. Wakeman, M. Furter, and M. W. Goldberg. **LXXVII. Dehydration of betulin, gypsogenin, and siaresinolic acid. Hydroxysapotalin.** L. Ruzicka, H. Brungger, R. Egli, L. Ehmann, and M. W. Goldberg (Helv. Chim. Acta, 1932, **15**, 1454—1459, 1496—1506; cf. A., 1932, 1254).—LXXVI. Pure α-elemolic acid (I), m.p. 217—219°, $[\alpha]_D$ −27° in MeOH, yields, when hydrogenated (PtO_2) in EtOAc at 50—60°, dihydro-α-elemolic acid, dimorphic, m.p. about 232°, $[\alpha]_D$ −18·7°

in MeOH, −14·5° in $CHCl_3$ [*Me* ester, a mixture, m.p. 119—121° after sintering at 100°, $[\alpha]_D$ −6° in $CHCl_3$, contains one ethylenic linking (*R*)], low- and high-(about 258—263°) -melting mixtures. Crude (I) gives dihydro-acids, m.p. 284—287°, $[\alpha]_D$ −53° in MeOH–$CHCl_3$, and m.p. 239—241°, $[\alpha]_D$ +39° in $CHCl_3$. All these acids are $C_{30}H_{50}O_3$. Previous results (A., 1931, 1067) are thus confirmed and the contentions of Mladenović (A., 1932, 397) refuted. δ-Elemic acid (II), $[\alpha]_D$ +28·6° in MeOH, is hydrogenated (PtO_2) in EtOAc (1 mol. of H_2 is absorbed at room temp. and 1 at 50°) to *tetrahydro-δ-elemic acid*, $C_{30}H_{50}O_3$, m.p. 236—237°, $[\alpha]_D$ about +37° in MeOH, +55° in $CHCl_3$ [*oxime*, m.p. 233—234°; *Me* ester, m.p. 110—111° after sintering at 98°, saturated (*R*) (*oxime*, m.p. 191—192°)]. (II) is thus a diethylenic, tetracyclic keto-acid.

LXXVII. The low-boiling fraction of the Se-dehydrogenation products from betulin (I) contains 1 : 2 : 3 : 4-$C_6H_2Me_4$ (II). Gypsogenin and Se at 350° give 2 : 7-$C_{10}H_6Me_2$, sapotalin, an oily (possibly impure) *hydrocarbon*, $C_{14}H_{16}$ (*picrate*, m.p. 139—140°; *styphnate*, m.p. 135—136°), hydroxysapotalin (III), a *hydrocarbon*, probably $C_{27}H_{28}$ (possibly a dinaphthylethane), m.p. 117—118° (corr.) (*styphnate*, m.p. 223—224°; *picrate*, m.p. 207—209°), and a *hydrocarbon* (IV), $C_{25}H_{20}$, m.p. 304° (corr.), 294—295° (uncorr.). Sia-resinolic acid gives (II), (III), (IV), and a hydrocarbon (V), $C_{25}H_{24}$ (lit. $C_{27}H_{28}$), m.p. 141—141·5° (uncorr.), 143° (corr.) (lit. 138°) [dipicrate, new m.p. 212° (corr.), 206·5—207·5° (uncorr.); distyphnate, m.p. 226° (corr.); *compound* with $2C_6H_3(NO_2)_3$, m.p. 227° (corr.), 221—222° (uncorr.)]. (III) [*Me ether* (by Me_2SO_4), m.p. 89·5—90° (*compound* with $C_6H_3(NO_2)_3$, m.p. 145—146°)] with Zn dust at 400° in N_2 gives 1 : 2 : 7-$C_{10}H_5Me_3$. It is contended that the OH group of (III) is in position 2 or 13 of the general triterpene formula (VI). The formulæ shown are suggested for (I), (V), and hederagenin (VII). (IV) is possibly a trimethylpicene.


(VI.)


(II.)

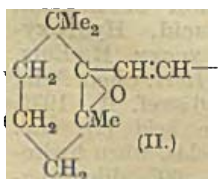


(I; R=Me; R′=CH_2·OH)

(VII: R=CH_2·OH; R′=CO_2H)

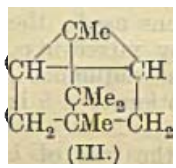
R. S. C.

Oxide of carotene. H. VON EULER, P. KARRER, and O. WALKER (Helv. Chim. Acta, 1932, **15**, 1507—1510).—β-Carotene (I) and BzO_2H (1 mol.) in $CHCl_3$ give a small amount of a substance, m.p. (impure) 180° (possibly *iso*carotene), and a 20% yield of *carotene oxide*, m.p. 161°, believed to be (II), since its absorption (max. at 486, 456, and 427 mμ in CS_2, and 465, 437, 410, 390, 364, and 320 mμ in $CHCl_3$) closely resembles that of (I). R. S. C.


(II.)

Neutral products of oxidation of pinene. II. K. SŁAWIŃSKI and W. ZACHAREWICZ (Rocz. Chem., 1932, **12**, 854—861).—The fraction, b.p. 88—97°/2 mm., of the neutral oxidation products of pinene yields norpinic acid, originating from pinononaldehyde, and a *dibromide*, $C_{10}H_{14}O_2Br_2$ (*A*), m.p. 116°, on treatment with NaOBr; with NaOEt the products are pinononic acid and a *keto-alcohol*, $C_{10}H_{16}O_2$ (*B*), m.p. 35°, b.p. 98—99°/2 mm. (*semicarbazone*, m.p. 204°, l- and i-*benzylidene* derivatives, m.p. 78—79° and 98°), which is also obtained by eliminating Br from (*A*). Since pinene glycol yields *l*-pinononaldehyde on oxidation with $K_2Cr_2O_7$ it is concluded that the original neutral fraction consists of pinene glycol, *l*-pinononaldehyde, and (*B*). R. T.

Derivatives of 4-methylcamphor in relation to its structure. S. NAMETKIN and L. BRUSSOF (J. pr. Chem., 1932, [ii], **135**, 155—163).—4-Methylcamphor (I) is converted by $NaNH_2$ and amyl nitrite in C_6H_6 into its *oximino*-derivative, m.p. 174—175°, which is hydrolysed by HCl and CH_2O to 4-*methylcamphorquinone*, m.p. 199—200°, the *hydrazone*, m.p. 108—109°, of which is oxidised by yellow HgO in light petroleum to *diazo-4-methylcamphor* (II), m.p. 87—90°. Distillation of (II) in presence of Cu-bronze gives *methylisotricyclenone*, m.p. 150—150·6° (*semicarbazone*, m.p. 251—253°; *hydrazone*, m.p. 89—92°), which is reduced by the Wolff–Kishner method to 4-*methylisotricyclene* (III), m.p. 113—114°; this is identical with the product of oxidation of 4-methylcamphorhydrazone with HgO (" methylcyclene," cf. A., 1924, i, 1176), thus affording further proof of the position of the Me group in (I).

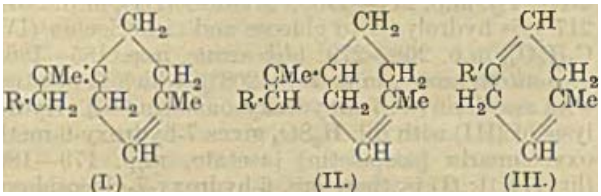

(III.)

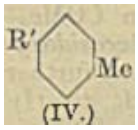
Attempts to dehalogenate the α-*Br*-derivative, m.p. 126—128°, of (I) to (III) failed; alcoholic alkali, NaOPh, and semicarbazide in EtOH regenerated (I), and NHPhEt at 150—160° gave an *isomeride*, m.p. 114—116°. H. A. P.

Syntheses in the santene series. G. KOMPPA (Ber., 1932, **65**, [*B*], 1708—1710).—Me_2 β-methylglutarate and $Me_2C_2O_4$ afford *Me*$_2$ 4 : 5-*diketo*-2-*methyl*cyclo*pentane*-1 : 3-*dicarboxylate*, m.p. 103—104° (corresponding *Et*$_2$ ester, m.p. 107—108°), transformed by MeI and NaOMe into *Me*$_2$ 4 : ɔ-*diketo*-2 : 3-*dimethyl*cyclo*pentane*-1 : 3-*dicarboxylate* (I), m.p. 54—55° [corresponding *Et*$_2$ ester, m.p. 53—54°, and its phenylosazone, m.p. 123° (decomp.)], and *Me*$_2$ (*Et*$_2$) 4-*keto*-ɔ-*methoxy*-2 : 3-*dimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylate*. Treatment of (I) with Na–Hg leads to non-cryst. 4 : ɔ-*dihydroxy*-2 : 3-*dimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid*, transformed by P and HI into 2 : 3-*dimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* (II), m.p. 195—196°. (II) and HBr yield a *Br*-acid reduced by Zn dust and AcOH to 2 : 3-*dimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* (π-apo*camphoric acid*), which with Ac_2O affords an *anhydride* of m.p. (93°) identical with that of *cis-iso*santenic anhydride. The prep. of a second *dehydro*---apo*camphoric acid*, m.p. 196—198°, is announced; the mixed m.p. with (II) is 164—170°. Santenic anhydride has been

catalytically reduced to *santenecampholide*, m.p. 50—51°, and *cis*- has been converted into *trans*-santenic acid. H. W.

Sesquiterpene ketones. A. PFAU (Helv. Chim. Acta, 1932, **15**, 1481—1483).—Atlas and Himalayan cedar oils contain, as chief constituent, *atlantone*, $C_{15}H_{22}O$, probably a mixture of (I) and (II). The chief constituent of turmeric oil is a mixture of *turmerone*, a monocyclic, hydroaromatic ketone, $C_{15}H_{22}O$, probably (III), and *dehydroturmerone*, a monocyclic, aromatic ketone, $C_{15}H_{20}O$, probably (IV). The natural occurrence of two dicyclic ketones, $C_{15}H_{22}O$, similar to eremophilone (following abstract), is announced.





(R = $Me_2C{:}CH{\cdot}CO{\cdot}$)

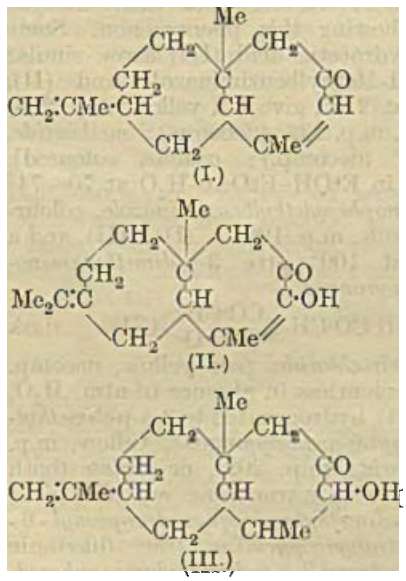
(R′ = $CMe_2{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}$)

R. S. C.

Constitution of eremophilone and of two related hydroxy-ketones from the wood oil of *Eremophila Mitchelli*. A. E. BRADFIELD, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1932, 2744—2759).—From the wood oil of *E. Mitchelli*, *eremophilone* (I), $C_{15}H_{22}O$, m.p. 41—42°, b.p. 111°/15 mm., $[\alpha]_{5461}$ −207°, 2-*hydroxy*- (II), m.p. 66—67°, $[\alpha]_{5461}$ +153°, and 2-*hydroxy*-1 : 2-*dihydro-eremophilone* (III), m.p. 102—103°, $[\alpha]_{5461}$ +94°, have been isolated. (I) forms a *semicarbazone*, m.p. 202—203° (decomp.), and *hydroxymethylene-eremophilone*, m.p. 105°, showing the presence of $\cdot CH_2{\cdot}CO{\cdot}CH{:}CH\cdot$. It is reduced catalytically to *tetrahydroeremophilone*, b.p. 165°/17 mm., d_{25}^{25} 0·9641, $[\alpha]_{5461}$ +12·5° [*semicarbazone*, m.p. 213—214° (decomp.); *oxime*, m.p. 126—127·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 178—179°], and by Na and EtOH to *dihydroeremophilol* (IV), b.p. 168—170°/14 mm., $[\alpha]_{5461}$ +68·8° (3 : 5-*dinitrobenzoate*, m.p. 119—121°), which is oxidised by CrO_3 to dihydroeremophilone [*semicarbazone*, m.p. 214—215° (decomp.)] and dehydrogenated by Se to eudalene. (IV) yields on ozonolysis CH_2O and 6-*acetyl*-4 : 9-*dimethyl*-2-*decalol* (2 : 4-*dinitrophenylhydrazone*, m.p. 146—149°), which is oxidised with NaOBr in MeOH to $CHBr_3$ and 4 : 9-*dimethyl*-2-*decalol*-6-*carboxylic acid*, m.p. 155°. Oxidation of (I) with H_2O_2 affords *eremophilone oxide*, m.p. 63—64°, $[\alpha]_{5461}$ −208° (reduced catalytically to *dihydroeremophilone oxide*, m.p. 53—54°, $[\alpha]_{5461}$ −205°), which is converted by AcOH and NaOAc into (II).

Oxidation of (II) (which is purified through the *Bz* derivative, m.p. 119—120°, $[\alpha]_{5461}$ +162°) with O_3 gives $COMe_2$, a trace of CH_2O, and a mixed *anhydride*, $C_{19}H_{18}O_5$, m.p. 186—188°, which on hydrolysis with KOH–EtOH affords BzOH and 9-methyl-Δ^2-decalene-4 : 6-dione-2-carboxylic acid, isolated as the *semicarbazone*, m.p. 215—216° (decomp.). (II) is oxidised by H_2O_2 to 2-*hydroxyeremophilone oxide*, m.p. 150—151°, $[\alpha]_{5461}$ +196° (*Ac* derivative, m.p. 122—123°), and a mixture of two stereoisomeric *forms* of 1-*methyl*-4-(α-*hydroxyisopropyl*)cyclo*hexane*-1-*acetic*-2-α-*lactic acid* (α-), m.p. 167—168° (decomp.) [which gives with AcCl the *Ac* derivative of the *lactonic acid*, m.p. 192—193 (decomp.)], and (β-), m.p. 198° (decomp.) [which forms with AcCl an anhydride or dilactone, m.p. about 172°)]. Benzoyl-2-hydroxyeremophilone is reduced catalytically to a hydroxy-ketone, isolated as 2-*hydroxytetrahydroeremophiloneoxime* (β-form), m.p. 146°.

(III) forms a 2 : 4-*dinitrophenylhydrazone*, m.p. 239—241° (decomp.), *diacetate*, m.p. 69—70°, and 3 : 5-*dinitrobenzoate*, m.p. 145—146°. Catalytic reduction of (III) yields 2-*hydroxytetrahydroeremophilone* (VI) (α-form), m.p. 84—85°, $[\alpha]_{5461}$ +84·2° (*oxime*, m.p. 158—160°; 2 : 4-*dinitrophenylhydrazone*, m.p. 210—220°), and with Na and EtOH, a glycol is obtained which is dehydrogenated with Se to eudalene. (III) is oxidised with O_3 to CH_2O and 6-acetyl-4 : 9-dimethyldecal-2-on-3-ol, obtained as the *semicarbazone*, m.p. 216—219° (decomp.), and with H_2O_2 to the α-form of (V). Reduction of (VI) with Na–Hg results in tetrahydroeremophilone, oxidation with H_2O_2 in an oil, and with CrO_3 in ketone forming 2-*hydroxy*-ω-*dihydroeremophilone*-2 : 4-*dinitrophenylhydrazone*, m.p. 158—160°. These results are in agreement with the formulæ (I), (II), and (III).



F. R. S.

Super-aromatic properties of furan. I. Scission of lead phenyl furyl compounds by hydrogen chloride. H. GILMAN and E. B. TOWNE (Rec. trav. chim., 1932, **51**, 1054—1064).—The reaction $PbR'_2R''_2 + 2HCl = PbR'_2Cl_2 + 2R''H$ is used as a criterion of aromatic character, the more aromatic groups being removed first. Furyl, thienyl, and Ph are thus decreasingly aromatic. $PbPh_2Cl_2$ and Mg furyl iodide [from purified 2-iodofuran (A., 1932, 399)] give *Pb Ph*$_2$ *di*-2-*furyl*, m.p. 118° (softens 116°), which in $CHCl_3$ with HCl gives $PbPh_2Cl_2$, and furan, isolated as 3 : 6-endoxytetrahydrophthalic anhydride. The following are similarly obtained, the scission products being given in parentheses: *Pb Ph*$_2$ *di*-2-*thienyl* (I), m.p. 185° (softens 184°) (yield 92%) ($PbPh_2Cl_2$ and thiophen, isolated as 2-chloromercurithiophen); *Pb Ph*$_3$ 2-*furyl*, m.p. 166—167° (softens 165°) (yield 82%) ($PbPh_2Cl_2$, $PbPh_3Cl$, and furan); *Pb Ph*$_3$ 2-*thienyl*, m.p. 206—207° (softens 204—205°) (yield 93·1%) [$PbPh_3Cl$ (64·8%), $PbPh_2Cl_2$ (32·1%), and

thiophen]. Pb tetra-2-thienyl in C_6H_6 with HCl gives Pb di-2-thienyl dichloride (II), decomp. 202° (sinters 200°) (yield 96%), which with Mg furyl iodide give *Pb di-2-furyl di-2-thienyl*, m.p. 117—119° (yield 62%). This with HCl gives (II) [converted by MgPhBr into (I)] and furan, but no thiophen. *Pb tetra-2-furyl* has m.p. 52—53° (softens 50°).

A. A. L.

p-Dimethylaminobenzylidene [derivatives of] ketones. III. Auxochromic groups. H. Rupe, F. Pedrini, and A. Collin (Helv. Chim. Acta, 1932, **15**, 1321—1329; cf. A., 1932, 60).—1-p-*Dimethylaminostyrylbenziminazole* (I) and its derivatives containing quinquevalent N are dyes for cotton, wool, and silk mordanted with tannin. 2-Methylquinoline and p-NMe_2·C_6H_4·CHO (II) give a coloured product, which gives coloured and colourless salts and a colourless methiodide. Ketones are thus not the only substances showing this phenomenon. Some derivatives of dehydracetic acid (III) show similar colour changes. 1-Methylbenziminazole and (II), best with H_3BO_3 at 215°, give (I), yellow, m.p. 256° [*perchlorate*, yellow, m.p. 232° (decomp.); *methiodide*, yellow, m.p. 234° (decomp.); *oxalate*, coloured], hydrogenated (Ni) in EtOH–EtOAc–H_2O at 70—74° to β-p-*dimethylaminophenylethylbenziminazole*, colourless, m.p. 187° (*picrate*, m.p. 198°). (II), (III), and a little piperidine at 100° give 3-p-*dimethylaminocinnamoyl*-6-*methylpyronone*, p-NMe_2·C_6H_4·CH:CH·CO·CH<CO·CH / CO—O>CMe, dark red, m.p. 215° [*hydrochloride*, pale yellow, decomp. 110°; *perchlorate*, colourless in absence of atm. H_2O, m.p. 150° (decomp.)], hydrogenated to 3-β-p-*dimethylaminophenylpropionyl*-6-*methylpyronone*, yellow, m.p. 115°, the *hydrochloride*, m.p. 202°, or *oxalate* (both colourless) of which with warm, conc. aq. NH_3 gives 2 : 4-*diketo*-3-β-p-*dimethylaminophenylpropionyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyridine* (the diketonic form of 2 : 4-*dihydroxy*-3-β-p-*dimethylaminophenylpropionyl*-6-*methylpyridine*), colourless, m.p. 191° [*oxalate*, m.p. 150° (decomp.)]. The Na salt of (III) in presence of a little acid in H_2O is hydrogenated (Ni) at room temp. to 3-*acetyl*-6-*methyldihydropyronone* (IV), solid (*semicarbazone*), and βδ-*dihydroxy*-n-*heptane* (formed in larger amount at 40—50°), b.p. 113°/11 mm. (*dibenzoate*, b.p. 218—219°/11 mm.). (IV) and (II) with a little piperidine at 100° give 3-p-*dimethylaminocinnamoyl*-6-*methyldihydropyronone*, red, m.p. 210° (*hydrochloride*, colourless, m.p. 168° (decomp.)], hydrogenated (Ni) to 3-β-p-*dimethylaminophenylpropionyl*-6-*methyldihydropyronone*, yellow, m.p. 81° (*hydrochloride*, colourless, m.p. 160°). (III) and MgPhBr (5 mols.) in C_6H_6 give a poor yield of the *substance*, OH·CPhMe·CH<CPh(OH)—CO·O·CMe>CH, m.p. 201°, and a small amount of a *substance*, m.p. 184°.

R. S. C.

Hydrogenation of heterocyclic compounds. G. M. Mach and V. N. Chadshinov (Ukrain. Chem. J., 1932, **7**, [Tech.], 32—40).—The products of hydrogenation of diphenylene oxide a 400—470° in presence of MoO_3 are unchanged substrate (45%), C_2H_6, methyl*cyclo*pentane, *cyclo*hexane, di*cyclo*hexyl, CH_4, C_6H_6, H_2O, phenols, and higher aromatic hydrocarbons.

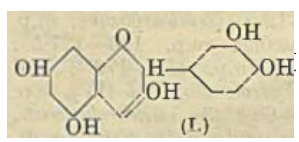
R. T.

Synthesis of anthocyanins. Synthesis of cyanenin chloride and an indication of the synthesis of cyanin chloride. R. Robinson and A. Leon. **Synthesis of malvenin chloride.** R. Robinson, A. Leon, and D. Sanroma (Anal. Fís. Quím., 1932, **30**, 840—845, 846—848).—Cf. A., 1932, 1038.

Cichoriin and constitution of æsculin and scopolin. K. W. Merz (Arch. Pharm., 1932, **270**, 476—494).—Cichoriin (I), $C_{15}H_{16}O_9,2H_2O$ (cf. Nietzki, A., 1877, i, 477, who gives $C_{32}H_{34}O_{19},4{\cdot}5H_2O$), m.p. 213—215°, $[\alpha]_D^{18}$ −104·5° in 50% dioxan [Ac_5 derivative (II), m.p. 217—218°; *Me ether* (III), m.p. 215—217°], is hydrolysed to glucose and cichorigenin (IV), $C_9H_6O_4$, m.p. 268—270° (*dibenzoate*, m.p. 185—186°; *di-p-nitrobenzoate*, m.p. 207—208°), which is identical with æsculetin [6 : 7-dihydroxycoumarin (V)]. Hydrolysis of (III) with dil. H_2SO_4 gives 7-hydroxy-6-methoxycoumarin [scopoletin] [acetate, m.p. 179—180° (lit. 177°)]; (I) is, therefore, 6-hydroxy-7-glucosidoxycoumarin. Acetobromoglucose and (V) in $COMe_2$–10% KOH give 6-*hydroxy*-7-*tetra-acetylglucosidoxycoumarin*, m.p. 194—195°, which is acetylated further to (II) and deacetylated by EtOH–NH_3 to (I). Æsculin [Ac_5 derivative, m.p. 166° (lit. 130°)] is 7-hydroxy-6-glucosidoxycoumarin; its *Me ether* (+$2H_2O$) (VI), m.p. 231—232°, is hydrolysed to 6-hydroxy-7-methoxycoumarin [formed together with 6 : 7-dimethoxycoumarin when (IV) is methylated (CH_2N_2)], which with acetobromoglucose gives 7-*methoxy*-6-*tetra-acetylglucosidoxycoumarin*, m.p. 176—177°, deacetylated to (VI). 6-*Methoxy*-7-*tetra-acetylglucosidoxycoumarin*, m.p. 168—169°, is similarly deacetylated to 6-methoxy-7-glucosidoxycoumarin [scopolin], which is identical with (III).

H. B.

Reductions with zinc dust in pyridine. II. Cyanidin. R. Kuhn and A. Winterstein (Ber., 1932, **65**, [*B*], 1742—1743).—The analogy between the cyanidin and $CHPh_3$ dyes is completed by the observation that cyanidin chloride is reduced by Zn dust and a few drops of AcOH in C_5H_5N to *leucocyanidin* (I), readily autoxidised to cyanidin.



(I.)

H. W.

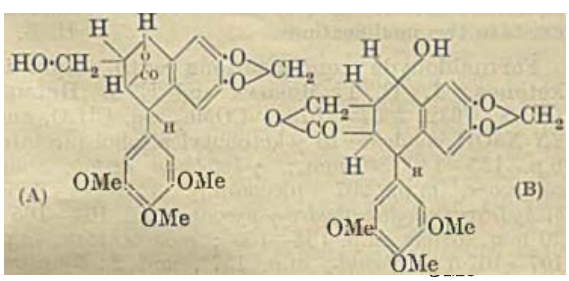
Constitution of the dye of *Robinia pseudacacia*. L. Schmid and F. Tadros (Ber., 1932, **65**, [*B*], 1689—1691; cf. A., 1931, 738).—The air-dried dye, $C_{15}H_{10}O_7,H_2O$, loses 1 H_2O at 70°/high vac. Reducing action towards Fehling's solution is proper to the dye and not caused by admixed sugars. Cautious alkaline degradation leads only to resorcinol. Treatment in MeOH with Et_2O–CH_2N_2 gives the Me_5 derivative, m.p. 149°, converted by KOH–EtOH into fisetol, m.p. 67°, and 3 : 4 : 5-trimethoxybenzoic acid, m.p. 172° (Me ester, m.p. 82°). The dye is therefore 3 : 3′ : 4′ : 5′-tetrahydroxyflavonol. Oxidation with HNO_3 (*d* 1·4) at 100° affords styphnic acid, m.p. 177°.

H. W.

Condensation of aldehydes with β-hydroxynaphthoic acid or its anilide and fission of di-

naphthylmethanes. K. BRASS and J. FIEDLER (Ber., 1932, **65**, [*B*], 1654—1660).—Gradual addition of CCl_3·$CH(OH)_2$ to 2-hydroxy-3-naphthoic acid (I) in conc. H_2SO_4 at room temp. affords *4-trichloromethyl-2 : 3 : 5 : 6-di-1′ : 2′ : 1″ : 2″-naphthapyran-3′ : 3″-dicarboxylic acid*, decomp. above 315° (*Et*$_2$ ester, m.p. 193°), in small yield. Condensation of (I) with PhCHO in AcOH containing conc. HCl gives *benzylidenedi-2-hydroxy-3-naphthoic acid* (II), decomp. above 253° [*Ac*$_2$ derivative (III), decomp. 285°], converted by Zn dust and NaOH into (I) and hydrobenzoin. The process is therefore essentially hydrolysis instead of reductive fission, leading through 2-hydroxy-1-hydroxybenzyl-3-naphthoic acid to (I) and PhCHO, whence benzoin and hydrobenzoin. Heating of (II) or (III) in AcOH containing H_2SO_4 or in $PhNO_2$ leads to *4-phenyl-2 : 3 : 5 : 6-di-1′ : 2′ : 1″ : 2″-naphthapyran-3′ : 3″-dicarboxylic acid*, decomp. 337° (*Et*$_2$ ester, m.p. 182·5—183°), also obtained directly from (I) in conc. H_2SO_4 and PhCHO in AcOH. 2-Hydroxy-3-naphthanilide does not condense with PhCHO under the conditions which lead to (II), whereas in presence of H_2SO_4 and AcOH, *4-phenyl-2 : 3 : 5 : 6-di-1′ : 2′ : 1″ : 2″-naphthapyran-3′ : 3″-dicarboxylanilide*, decomp. 365°, is obtained. H. W.

Constitution of podophyllotoxin and picropodophyllin. E. SPATH, F. WESSELY, and E. NADLER (Ber., 1932, **65**, [*B*], 1773—1777; cf. A., 1932, 1137).—Podophyllotoxin with alkaline $KMnO_4$ at 60—70° yields a small amount of 4 : 5-methylenedioxyphthalic acid (identified as the anhydride and ethylimide) in addition to 3 : 4 : 5-trimethoxybenzoic acid. Podophyllomeronic acid with KOH–NaOH at 230° affords 6 : 7-*dihydroxy-3-methylnaphthalene-2-carboxylic acid*, m.p. 250° (slight decomp.), transformed by CH_2N_2 into *Me* 6 : 7-*dimethoxy-3-methylnaphthalene-2-carboxylate*, dimorphous, m.p. 129° or m.p. 109—110° and 129° after re-solidification, whence 6 : 7-*dimethoxy-3-methylnaphthalene-2-carboxylic acid* (I), m.p. 228°. (I) in conc. H_2SO_4 is transformed by N_3H in $CHCl_3$ into 6 : 7-*dimethoxy-3-methyl-β-naphthylamine*, m.p. 204—205° (vac.), oxidised to 4 : 5-dimethoxyphthalic acid (anhydride, m.p. 178—179°). The constitutions A and B are therefore ascribed to podophyllotoxin and picropodophyllin, respectively.

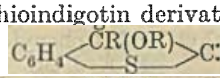


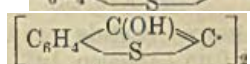
H. W.

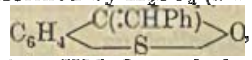
Derivatives of dioxan. J. BOESEKEN, F. TELLEGEN, and P. C. HENRIQUEZ (J. Amer. Chem. Soc., 1932, **54**, 4461—4462).—Chlorination of 2 : 3-dichlorodioxan gives a liquid *as*-tetrachlorodioxan (cf. Butler and Cretcher, A., 1932, 949), a cryst. hexachlorodioxan, and higher chlorinated derivatives. The naphthodioxans (A., 1931, 1162) and related compounds are being investigated. H. B.

Thiophen derivatives. I. J. RINKES (Rec. trav. chim., 1932, **51**, 1134—1142).—Thiophen-2-carboxylic acid in Ac_2O with HNO_3 (*d* 1·51) gives 5- (I), m.p. 158° (*Me* ester, m.p. 76°; gives 2-nitrothiophen when heated > 200°), and *4-nitrothiophen-2-carboxylic acid*, m.p. 154° (*Me* ester, m.p. 99°; gives 3-nitrothiophen, m.p. 68—69°, when heated > 200°), and 2-nitrothiophen by replacement of CO_2H by NO_2. 2-Methylthiophen similarly gives *5-nitro-2-methylthiophen* (II), setting point 27·4°, oxidised to (I). More intense nitration gives (?) 3 : *5-dinitro-2-methylthiophen* (III), m.p. 99—100°. 2-Methyl-5-acetothienone, new m.p. 23·8° (from 2-methylthiophen and AcCl), with $KMnO_4$ in KOH followed by H_2O_2 gives 2-methylthiophen-5-carboxylic acid, new m.p. 138—139° (and a little thiophen-2 : 5-dicarboxylic acid). Nitration of this at −10° to −5° gives (II), a little (III), and (?)*3-nitro-2-methylthiophen-5-carboxylic acid*, m.p. 180—181°, which gives *3-nitro-2-methylthiophen*, m.p. 44—45°, when decarboxylated. The last-named product gives (III) on further nitration. Orientation in the thiophen series is discussed. A. A. L.

Indigoid dyes. Ethers of leucothioindigotin. M. M. TSCHILIKIN (Ber., 1932, **65**, [*B*], 1651—1653).—Confirmation of the hypothesis that dissolved leucothioindigotin derivatives are an equilibrium mixture,





(R=H), is found in the conversion of the compound by CH_2PhCl at 100° into a *compound*, (I) $C_{30}H_{22}O_2S_2$, m.p. 213—214°, which is unchanged by HNO_2, by Mg in acid solution, and does not yield a hydrazone; it therefore has the structure A (R=CH_2Ph). (I) is transformed by H_2SO_4 (*d* 1·84) at 100° into the *substance*  , m.p. 129—130°, which decolorises $KMnO_4$ and does not yield a hydrazone. H. W.

Action of aromatic nitro-derivatives on magnesium pyrryl and indolyl compounds. M. GIUA and G. RACCIU (Atti R. Accad. Sci. Torino, 1932, **67**, 121—124; Chem. Zentr., 1932, ii, 875).—The oxidation of Mg pyrryl compounds affords black dyes (pyrrole-blacks). Mg indolyl compounds are less readily oxidised. Mg indolyl iodide and picryl chloride afford a red, amorphous substance and the additive *compound*, C_8H_7N,$C_6H_2Cl(NO_2)_3$, m.p. 126—127°; 1-chloro-2 : 4 : 5-trinitrobenzene similarly affords two *substances*, the latter having m.p. 113°. A. A. E.

Unsaturated diketones of the indole series. G. SANNA (Rend. Sem. Fac. Sci. Cagliari, 1931, **1**, 29—30; Chem. Zentr., 1932, i, 1784).—Aq. NH_3 at 100° (bomb tube) converts 3-chloroacetyl-2-methylindole (α-methylindacyl chloride) into a yellow powder containing the *compounds* $C_{22}H_{18}O_2N_2$, m.p. 162°, $C_{22}H_{18}O_2N_2$, m.p. 220°, probably the *cis–trans*-isomeride (*Br*$_2$-derivative, m.p. 241°), and $C_{33}H_{27}O_3N_3$, unchanged by Br. The first two compounds yield only one additive product, m.p. 220°, with aniline. L. S. T.

Pyridine boron trifluoride. P. A. VAN DER MEULEN and H. A. HELLER (J. Amer. Chem. Soc., 1932, **54**, 4404—4406).—Details are given for the prep. of C_5H_5N,BF_3, b.p. 300±5°, m.p. 45±1°, which is converted by 95% EtOH into C_5H_5N fluoborate. The heat of dissociation in the range 313—356° is 50,600 g.-cal. H. B.

Cleavage of phenacylpyridinium halides by alkali. S. H. BABCOCK, jun., F. I. NAKAMURA, and R. C. FUSON (J. Amer. Chem. Soc., 1932, **54**, 4407—4409).—αδ-Dibromo-αδ-dibenzoylbutane and C_5H_5N in BzOEt at 120° give the *dipyridinium dibromide* (+$2H_2O$), m.p. 212·5° (corr.), which with cold dil. NaOH affords BzOH. *Phenacylpyridinium chloride* (+H_2O), m.p. 109—110°, and dil. NaOH give BzOH; *p-bromophenacylpyridinium bromide* (+H_2O), m.p. 225—230°, similarly affords *p*-$C_6H_4Br\cdot CO_2H$. 2′ : 4′ : 6′-*Trimethylphenacylpyridinium chloride*, m.p. 245—246°, does not undergo cleavage to 2 : 4 : 6-$C_6H_2Me_3\cdot CO_2H$. H. B.

Catalytic synthesis of phenylpyridines. M. COLONNA and S. MUSAJO (Gazzetta, 1932, **62**, 894—901; cf. A., 1905, i, 609).—Attempts to prepare phenylethylpyridine from 4-ethylpyridine with MgPhBr or with PhN_2Cl with or without $AlCl_3$ were unsuccessful. Condensation of 1 mol. of COPhMe and 2 mols. of MeCHO with NH_3 at 400° in presence of Al_2O_3 pptd. on powdered pumice (A., 1931, 630) gives C_5H_5N and 2-phenyl-4-methyl- and 4-phenyl-2-methyl-pyridine. E. E. J. M.

Stereochemistry of platinum metals and nickel. H. REIHLEN and W. HUHN (Annalen, 1932, **499**, 144—157; cf. A., 1931, 1167).—The monoacetate of 3-methyl-4-ethyl-2-aminomethylquinoline (basic and neutral *chloropalladoates*; basic d-*bromocamphor-π-sulphonate*) and K_2PdCl_4 in aq. solution, give (first) *dichloro-3-methyl-4-ethyl-2-aminomethylquinolinepalladium*, $\left[\begin{matrix}C_{13}H_{14}N\\NH_2\end{matrix}\!\!>\!\!Pd\!<\!\!\begin{matrix}Cl\\Cl\end{matrix}\right]$ and then *di-3-methyl-4-ethyl-2-aminomethylquinolinepalladium chloride* (I), $\left[\begin{matrix}C_{13}H_{14}N\\NH_2\end{matrix}\!\!>\!\!Pd\!<\!\!\begin{matrix}N\\NC_{13}H_{14}\end{matrix}\right]Cl_2$(+$4H_2O$), convertible into the corresponding *nitrate* (II) (+H_2O), *chloropalladoate* (+$2H_2O$), and *tartrate* (+$3H_2O$), $[M]_D^{18}$ +123° in H_2O (readily racemised in warm aq. solution). (I) and NH_4 *d*-α-bromocamphor-π-sulphonate give about 70% of the corresponding d-α-*bromocamphor-π-sulphonate* (III) (+$3H_2O$), $[M]_D$ +524° in EtOH (whence $[M]_D$ −112° is obtained for the ion); the remainder of the material is not isolable in a pure state and probably consists of material formed by interaction of the complex with NH_4Cl. (II) [prepared from (I) and $NaNO_3$] and Na *d*-α-bromocamphor-π-sulphonate also give (III) in practically quant. yield, thus precluding the view that (I) may be a mixture of *cis*- and *trans*-forms. (III) is readily decomposed by aq. or EtOH–HCl: $[Pd(NC_{13}H_{14}\cdot NH_2)_2]X_2+2HCl \longrightarrow [Cl_2Pd\cdot NC_{13}H_{14}\cdot NH_2]+NC_{13}H_{14}\cdot NH_2,2HX$.

3-Methyl-4-ethyl-2-aminomethylquinoline hydrochloride and Ni hydroxide give *di-3-methyl-4-ethyl-2-aminoethylquinolinenickel chloride* (IV), $C_{26}H_{32}N_4Cl_2Ni$ (+$4H_2O$?), which with NH_4 *d*-α-bromocamphor-π-camphorsulphonate (V) affords the *l*-base *d*-acid *salt* (+$4H_2O$?), $[M]_{5463}$ +573° in EtOH (whence $[M]$ −221° for the ion). (IV) and Na tartrate give the neutral *tartrate*, $[M]_{5463}$ +484° in EtOH, which is a non-electrolyte; treatment of the mother-liquors with (V) affords the impure d-*base* d-*bromocamphor-π-sulphonate*, $[M]_{5463}$ +900° (whence $[M]$ +106° for the ion). H. B.

Preparation of 2-phenylquinoline from phenyl *o*-nitrostyryl ketone. R. J. W. LE FÈVRE and J. PEARSON (J.C.S., 1932, 2807—2808).—Ph *o*-nitrostyryl ketone is best prepared from *o*-$NO_2\cdot C_6H_4\cdot CHO$ and COPhMe in presence of HCl; under alkaline conditions indigotin is the principal product (cf. A., 1902, i, 379). It gives 2-phenylquinoline on reduction with Fe and EtOH–HCl. Ph *m*- and *p*-nitrostyryl ketones, m.p. 145—146° and 164°, respectively, may be prepared under both alkaline and acid conditions. H. A. P.

Reactivity of groups in substituted acridones. I. Replacement of nitro-groups by piperidyl and piperazyl. H. B. NISBET and (in part) A. B. GOODLET (J.C.S., 1932, 2772—2773).—2-*Chloro-*, m.p. 260—261°, and 2-*bromo-9-nitrodiphenylamine-6′-carboxylic acid*, m.p. 252°, prepared from 2-halogen-5-nitroaniline, K *o*-bromobenzoate, and Cu, give with H_2SO_4, 1-*chloro-*, m.p. 320°, and 1-*bromo-4-nitroacridone*, m.p. 305°. The NO_2 group in the acridones is replaced by $C_5H_{11}N$ or piperazine to form 1-*chloro-*, m.p. 110° (hydrochloride, m.p. 168—169°), and 1-*bromo-4-piperidino-*, m.p. 112° (decomp.) (hydrochloride, m.p. 164—165°), and 1-*chloro-4-piperazinoacridone*, m.p. 198°. The heterogeneous polarity caused by the *o*-position of CO and NO_2 is absent in 2-chloro- and Cl is replaced to yield 2-*piperidino-5-nitroaniline*, m.p. 79—81°. F. R. S.

Molecular compound in veramon. A. KOFLER and R. FISCHER (Arch. Pharm., 1932, **270**, 441—449).—Crystallographic data are given for the mol. (1 : 1) compound (I), m.p. 116—117° (micro-method; A., 1932, 713), of veronal (II) and pyramidone (III) present in veramon. (I) decomposes at or just above the m.p. and some (II) crystallises. Crystals of (I) and (III) are obtained when either veramon or a mixture of (II) (1 mol.) and (III) (2 mols.) is sublimed; (I) (mainly) is similarly obtained from an equimol. mixture of (II) and (III). Pyramidone exists in two modifications. H. B.

Formaldehyde condensations with aliphatic ketones. I. G. T. MORGAN and E. L. HOLMES (J.C.S., 1932, 2667—2673).—$COMe_2$, aq. CH_2O, and 2*N*-NaOH condense to γ-ketobutyl alcohol [acetate, b.p. 125—130°/30 mm.; *γ-ketobutyl acetate semicarbazone*, m.p. 207° (decomp.)], 3 : 3- or 3 : 5-*bishydroxymethyltetrahydro-γ-pyrone*, b.p. 164—165°/20 mm. (*oxime*, m.p. 134—135°; *monobenzoate*, m.p. 107—107·5°; *phenyl-*, m.p. 137°, and 2 : 4-*dinitrophenyl-hydrazone*, m.p 180°, of the benzoate), and much resin. Similar condensation of COMeEt gives little resin and a mixture of γ-keto-β-methylbutyl alcohol [*acetate*, b.p. 99—100°/20 mm., and its *semicarbazone*, m.p. 134·5°; p-*nitrobenzoate*, m.p. 54°; 1-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dimethyl*-4 : 5-*dihydropyrazole*, m.p. 191° (prepared from 2 : 4-dinitro-

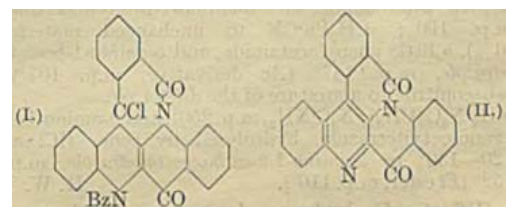
phenylhydrazine)], *γ-keto-β-hydroxymethyl-β-methylbutyl alcohol*, m.p. 60°, b.p. 138°/16 mm. [*dibenzoate*, m.p. 78—79°; *di*-p-*nitrobenzoate*, m.p. 177—178°; *diacetate*, b.p. 140—145°/10 mm., and its *semicarbazone*, m.p. 132·5°; 6-*phenyl*-3-*methyl*-3-*hydroxymethyltetrahydro-γ-pyrone*, m.p. 103° (prepared from PhCHO)], and numerous resin intermediates. $COEt_2$, aq. CH_2O, 2*N*-NaOH, and MeOH yield *γ-keto-β-methyl*-n-*amyl alcohol*, b.p. 191—192°/760 mm. [p-*nitrobenzoate*, m.p. 50—51°; 1-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-3-*ethyl*-4 : 5-*dihydropyrazole*, m.p. 149—150°], impure *γ-keto-β-methyl-β-hydroxymethyl-n-amyl alcohol* [*di*-p-*nitrobenzoate*, m.p. 147—148°; possibly 3-*acetyl*-1-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-4-*hydroxymethyl*-4 : 5-*dihydropyrazole*-2″ : 4″-*dinitrophenylhydrazone*, m.p. 123—124° (from 2 : 4-dinitrophenylhydrazine)], and *γ-keto-β-methyl-βδ-bishydroxymethyl-n-amyl alcohol*, m.p. 91° (*tribenzoate*, m.p. 79—80°; *tri*-p-*nitrobenzoate*, m.p. 147—148°). Resinification diminishes but the amount of NaOH required increases as the series is ascended. F. R. S.

Compounds of the type amino-acid-(2 : 5-diketopiperazine) and their behaviour towards acid, alkali, and enzymes. E. Abderhalden and E. Schwab (Z. physiol. Chim., 1932, **212**, 61—71).—The following anhydrides and precursors were obtained: l-*leucyl*(*glycyl*-l-*tyrosine anhydride*), decomp. at 275°, $[\alpha]^{20}$ +8·6° in aq. NH_3 (*Bz*$_2$ derivative, decomp. 155°), from d-α-*bromoisohexoylglycyl*-l-*tyrosine*, m.p. 92°, $[\alpha]^{20}$ +48·8° in EtOH, and the *tripeptide*, m.p. 185°, $[\alpha]^{20}$ +18·3° in H_2O; l-*leucyl*(*glycyl*-l-*leucine anhydride*), m.p. 250°, $[\alpha]^{20}$ +6·7° in MeOH; *leucyl*(*glycylserine anhydride*) (final product inactive), m.p. 248—249°, from d-α-*bromoisohexoylglycyl*-l-*serine*, m.p. 103°, $[\alpha]_D$ +36·8° in EtOH, and the *tripeptide*, m.p. 241°, $[\alpha]^{20}$ +14·3° in H_2O. The action of dil. NaOH and enzymes indicates that the 2 : 5-diketopiperazine ring in the anhydride is labile, the tripeptide being readily formed. J. H. B.

Complex compounds derived from diethylbarbituric acid. J. J. L. Zwikker (Pharm. Weekblad, 1932, **69**, 1178—1188).—The following *compounds* are described: $[(C_8H_{11}O_3N_2)_6Co(NH_3)_6]$ (red); $[Co(NH_3)_6](OH)(C_8H_{11}O_3N_2)_6$ (brown); $[Co(NH_3)_5OH](C_8H_{11}O_3N_2)_2$; $[CoCl_2(C_8H_{11}O_3N_2)_2]K_2$, and $[CoCl(OH)C_8H_{11}O_3N_2)_6]K_2$, (blue). The colour (blue or red) of the Co complexes formed under any given conditions is governed, not by the quantity of H_2O present in the reacting mixture, but by the quantity of NH_3; blue compounds result when only a limited amount of NH_3 is present. The *compound* $[Zn(C_5H_5N)$ barbital$_2]$, analogous to the corresponding Cu derivative, has been prepared, and the Cd derivative appears to exist also. The quinoline *derivative* $[Cu(C_9H_7N)_2$ barbital$_2]$ is described, but the analogous NH_2Ph and substituted quinoline derivatives could not be prepared. H. F. G.

Quinazolines. IV. Alcoholysis in the quinazoline series and preparation of mixed diethers of quinazoline. N. A. Lange and F. E. Sheibley (J. Amer. Chem. Soc., 1932, **54**, 4305—4310).—2-Chloro-4-methoxyquinazoline and EtOH–NaOEt give 2 : 4-diethoxyquinazoline, which with MeOH–NaOMe affords 4-*methoxy*-2-*ethoxyquinazoline*, m.p. 61—62°. Similarly, 2-chloro-4-ethoxyquinazoline (I) and MeOH–NaOMe give 2 : 4-dimethoxyquinazoline, converted by EtOH–NaOEt into 2-*methoxy*-4-*ethoxyquinazoline*, m.p. 57—58°. Alcoholysis of these mixed ethers can be accomplished; the 4-OAlk group is replaced. 2-Chloro-4-phenoxyquinazoline and EtOH–NaOEt give (I), whilst 2 : 4-*diphenoxyquinazoline*, m.p. 160—161° (from the 2 : 4-Cl$_2$-derivative and molten Na in PhOH), similarly affords 2-*phenoxy*-4-*ethoxyquinazoline* (II), m.p. 107—108°, also prepared by addition of (I) to molten Na in PhOH. 2-*Phenoxy*-4-*methoxyquinazoline* (III), m.p. 139·5°, is similarly prepared and is converted by EtOH–NaOEt into (II), whilst (II) and MeOH–NaOMe give (III). 2 : 4-Dichloroquinazoline and $(CH_2{\cdot}ONa)_2$ give 2 : 4-*di*-β-*hydroxyethoxyquinazoline*, m.p. 153—154° (*Ac*$_2$ derivative, m.p. 65—66°). H. B.

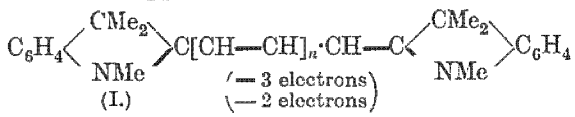
Benzoyl derivatives of indigotin. E. Hope and D. Richter (J.C.S., 1932, 2783—2787).—*NN′*-Dibenzoylindigotin, m.p. 238°, prepared by Schwartz (J. pr. Chem., 1863, **91**, 382) contains Cl and is identical with the " Dessoulavy compound " (I) (G.P. 247,154), $C_{30}H_{17}O_3N_2Cl$. The violet substance (cf. Posner and Hofmeister, A., 1926, 1156) is also converted into (I) by prolonged treatment with BzCl. Ciba-yellow 3G (II) (modified prep.; Cl-substituted compound, m.p. 306°, obtained from *m*-$C_6H_4Cl{\cdot}COCl$) with 15% aq. NaOH takes up 1 H_2O to give a carboxylic acid (co-ordination *compounds* with EtOH and MeOH) which is methylated to a *monomethyl-carboxylic acid* (III) or further to a *Me*$_2$ derivative (hydrolysed by aq. NaOH or aq. HI to the mono-acid). (III) loses CO_2 at 280° to form a *product*, m.p. 168°. (II) and 10% aq. NaOH at 220° afford 3-*hydroxy*-4-*phenylquinoline*-2′-*carboxylic acid* (?), m.p. 220—230°, which when heated gives a *lactone*, m.p. 215°, anthranihc acid, a pyridone *derivative*, m.p. above 360°, and a *substance*, m.p. 228°, isomeric with the lactone. With 15% NaOEt (II) forms a *base*, m.p. 197°. (I) is converted into (II) by heating alone or in presence of a catalyst. These results are not consistent with the formula of Posner and Hofmeister (*loc. cit.*) and (II) is suggested for ciba-yellow 3G, and (I) for the Dessoulavy compound.



F. R. S.

Reductions with zinc dust in pyridine. I. Reversible hydrogenation and dehydrogenation of cyanine dyes. R. Kuhn and A. Winterstein (Ber., 1932, **65**, [*B*], 1737—1742).—Anhyd. AcOH in dry C_5H_5N does not behave as an acid or react with Zn dust. In presence of a trace of H_2O the mixture develops very strong reducing properties, which appear to depend on the development of H_3O^+ ions and on the passage of Zn into complex Zn–C_5H_5N ions. Reduction can be moderated by substitution of

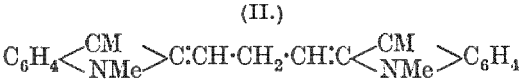
EtOH for H_2O. Indolenine-red (I; $n=1$) is rapidly and without apparent evolution of H reduced to the



(I.)



(II.)



(III.)

methine leuco-base (cf. II), m.p. 114—116° (decomp.), rapidly oxidised by $K_3Fe(CN)_6$ in acid solution to (I). It differs from the methylene base (III), m.p. 121—122° (decomp.), obtained by condensation of CH_2O with 1 : 3 : 3-trimethyl-2-methyleneindoline, which is not oxidised by $K_3Fe(CN)_6$. Indolenine-yellow (I; $n=0$) is reduced with difficulty by this method, reduction of the perchlorate with Zn dust and NH_3–EtOH being preferable. Indolenine-violet (I; $n=2$) is readily decolorised and the dye is partly re-formed by exposure of the solution to air. Indolenine-blue (I; $n=3$) is very easily reduced, but reduction appears to proceed beyond the stage of the leuco-base, since it has not been found possible to regenerate the dye. H. W.

Synthesis of tetrazole compounds from nitriles. J. VON BRAUN and W. KELLER (Ber., 1932, **65**, [*B*], 1677—1680).—Nitriles appear unable to add N_3H directly. In presence of conc. H_2SO_4 they add the NH: residue of N_3H, yielding carbodi-imides, $R{\cdot}C{:}B{+}NH{<}\longrightarrow R{\cdot}C(:NH)N{<}\longrightarrow NH{:}C{:}NR$, which readily add $1N_3H$, yielding products which form substituted tetrazoles by ring closure, $NH{:}C{:}NR + N_3H \longrightarrow NH_2{\cdot}C(N_3){:}NR \longrightarrow NH_2C{<}\begin{matrix}N{-}N\\ \|\ \ \|\\ NR{\cdot}N\end{matrix}$ The following examples are cited: heptonitrile with 2·5 mols. of N_3H in C_6H_6 and conc. H_2SO_4 at 35—40° to 5-*amino*-1-*hexyltetrazole*, m.p. 162° (*Ac* derivative, m.p. 106°), in about 60% yield; 5-amino-1-phenyltetrazole, m.p. 159° (*Ac* derivative, m.p. 211°), from PhCN; *p*-toluonitrile to unchanged material (5%), a little *p*-toluamide, and 5-amino-1-*p*-tolyltetrazole, m.p. 190°; $CH_2Ph{\cdot}CN$ to unchanged material (6%), a little phenylacetamide, and 5-*amino*-1-*benzyltetrazole*, m.p. 187° (*Ac* derivative, m.p. 107°); sebaconitrile to a mixture of the *ditetrazole*, $NH_2{\cdot}N_4C{\cdot}[CH_2]_8{\cdot}N_4C{\cdot}NH_2$, m.p. 250°, and 5-amino-1-ω-cyano-octyltetrazole, hydrolysed by conc. HCl at 120—130° to 5-*amino*-1-ω-*carboxyoctyltetrazole*, m.p. 152° (*Et* ester, m.p. 116°). H. W.

[Effect of] hydrogen-ion concentration on degradation of uric acid. F. ROSENTHAL.—See this vol., 33.

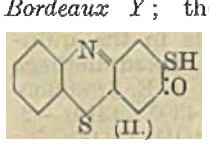
4-Nitro-5-(3-pyridyl)pyrazole, a new oxidation product of nicotine. II. Methylation products. H. KING (J.C.S., 1932, 2768—2770).—4-Nitro-5-(3-pyridyl)pyrazole (I) (A., 1932, 68) and MeI–MeOH give 4-*nitro*-5-(3-*pyridylmethiodide*)*pyrazole*, m.p. 257° (decomp.), from which the *base*, m.p. 287° (decomp.) [*methochloride*, m.p. 290° (decomp.); *picrate*, m.p. 212° (decomp.)], is liberated by NaOH. The *Ag* salt of (I) yields with MeI–MeOH a mixture of two monomethyl *methiodides*, m.p. 271—272° and m.p. 224—225°, unchanged by aq. NaOH and corresponding with the tautomeric forms of (I). F. R. S.

Constitution of bile pigment. IX. Synthesis of 5-hydroxy-2 : 4-dimethyl-3-ethylpyrrole and a new synthesis of xanthobilirubic acid or bilirubic acid. H. FISCHER, T. YOSHIOKA, and P. HARTMANN (Z. physiol. Chem., 1932, **212**, 146—156; cf. A., 1932, 1045).—Oxidation of cryptopyrrole (I) with H_2O_2 in C_5H_5N gives 5-*hydroxy*-2 : 4-*dimethyl*-3-*ethylpyrrole* (II), m.p. 84—84·5° [*phenylcarbimido*-derivative (obtained at 200°), m.p. 104°], and *di*-(2 : 4-*dimethyl*-3-*ethyl*-5)-*pyrryl peroxide*, m.p. 219°. A N-free by-product giving with picric acid a *compound*, $C_{18}H_{14}O_{13}N_6$, m.p. 181°, is formed. C_5H_5N by H_2O_2 oxidation gives 3-hydroxypyridine. Wolff–Kishner reduction of (II) gave no (I) but a small amount of a hydrazine reaction *product*, $C_8H_{13}N_3$, m.p. 179°. With (II) SO_2Cl_2 gives a *Cl*$_2$-compound (III), m.p. 150—151°, yielding with NH_2Ph a product $C_{20}H_{21}N_3$, m.p. 244—245°. (III) gave no methylethylmaleimide with HNO_3 or CrO_3. With Br in CCl_4 (II) gives a Br-compound (IV), which with excess of (II) then forms 5-hydroxy-4 : 3′ : 5′-trimethyl-3 : 4′-diethylpyrromethene, m.p. 244—245° (not 254° as previously stated). With the Me ester of the crypto-acid, (IV) affords Me xanthobilirubate. J. H. B.

Mechanism of the introduction of iron into porphyrins. A. TREIBS (Z. physiol. Chem., 1932, **212**, 26—32).—The Fe-porphyrin complex is reversibly decomposed by strong acids. In AcOH containing NaCl, $Fe(OAc)_2$ forms the complex on heating, but after cooling it is partly decomposed as shown by the colour change and spectrum. This effect is due, not to the production of HCl, but to the formation of a NaCl–AcOH complex, more strongly acid than AcOH (cf. the effect of salts on the dissociation of acids). Org. acids stronger than AcOH show a similar effect in proportion to their strength. J. H. B.

Ultra-violet absorption of the porphyrins. A. TREIBS (Z. physiol. Chem., 1932, **212**, 33—40).—All porphyrins examined show an intense band in the long-wave ultra-violet. Those of the ætioporphyrin group agree, but the uroporphyrins and rhodoporphyrins differ; uroporphyrin and *iso*uroporphyrin show a slight divergence in the position of the max. No gross differences are observed. J. H. B.

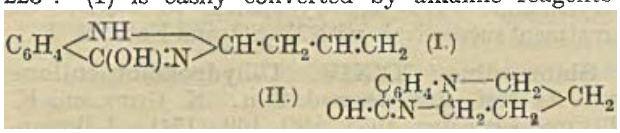
Composition and possible constitution of several sulphur dyes. W. N. JONES, jun., and E. E. REID (J. Amer. Chem. Soc., 1932, **54**, 4393—4402).—*p*-Hydroxydiphenylamine (25 g.), $Na_2S,9H_2O$ (90 g.), S (50 g.), and H_2O (70 c.c.) at 145—150°/34 hr. give (after dilution and oxidation with atm. O_2) a red *dye*, empirical formula, $C_{12}H_7ONS_3$, designated *Bordeaux Y*; the use of Na_2S_2 affords the keto-thiodiphenylimide (I) of Bernthsen (A., 1885, 259; 1886, 53), whilst Na_2S_3 gives (probably) a polymeric thiol compound (as II). 4-Hydroxy-4′-methyldiphenylamine (27 g.), $Na_2S,9H_2O$ (90 g.), S (50 g.), and H_2O (70 c.c.) at 120°/34 hr. afford a red *dye* (*Bordeaux X*),



(II.)

$C_{13}H_9ONS_4$, whilst 4-amino-4′-hydroxy-3-methyldiphenylamine similarly furnishes the dye Navy-blue RL, $C_{13}H_{10}ON_2S_3$; 4-amino-4′-hydroxydiphenylamine gives *dyes*, $C_{12}H_7ON_2S_7$ and $C_{12}H_7ON_2S_9$ (termed *Green Z* " B " and " A," respectively) under identical conditions. Reduction of the above dyes with $SnCl_2$ and conc. HCl in AcOH–H_3PO_4 causes elimination of 1, 2, 1, 4, and 6 atoms of S (as H_2S), respectively (for the above order); H_2S is not formed by similar reduction of (I) and (II). The dyes probably contain ·S:S·, ·S:S:S·, or ·S:S:S:S· groups (according to the no. of S atoms present); structural formulæ (units) are suggested. H. B.

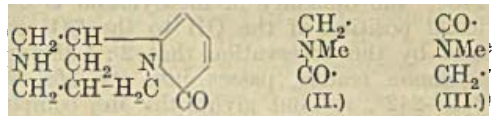
Vasicine. T. P. Ghose, S. Krishna, K. S. Narang, and J. N. Ray (J.C.S., 1932, 2740—2744; cf. A., 1925, i, 958).—Vasicine (I), m.p. 198°, is readily oxidised by aq. $KMnO_4$ at 0° and its hydrobromide decolorises aq. Br to give a *substance*, m.p. 225°. (I) is easily converted by alkaline reagents



into *iso*vasicine (II), m.p. 164° (decomp.) [which gives a methiodide, m.p. 191°, identical with that obtained from (I)], and with fused KOH forms anthranilic acid. Oxidation of (I) with $KMnO_4$ yields 4-quinazolone and with H_2O_2 gives two successive *substances*, $C_{11}H_{10}ON_2,\frac{1}{2}H_2O$, m.p. 168° (decomp.), and $C_{11}H_{10}O_2N_2$, m.p. 214°. Ac_2O and (I) form a *substance*, $C_{15}H_{11}ON_2$, m.p. 165°. The constitutions of (I) and (II) are suggested for vasicine and *iso*vasicine, respectively. F. R. S.

Alkaloids of *Picralima Klaineana*, Pierre. II. T. A. Henry (J.C.S., 1932, 2759—2768; cf. A., 1927, 982).—In addition to akuammine (I), the seeds contain akuammine hydrate (*methiodide*, m.p. above 300°), *akuammicine* (II), $C_{18}H_{17}ON_2(OMe)$, m.p. 177·5°, *pseudakuammicine*, $C_{18}H_{17}ON_2(OMe)$, m.p. 187·5° (*hydrochloride*, m.p. 216°), akuammenine, $C_{19}H_{19}O_3N_2(OMe)$ (*picrate*, m.p. 225°), *akuammidine* (III), $C_{20}H_{21}O_2N_2(OMe)$ $(+H_2O)$, m.p. 248·5°, $[\alpha]_D^{16}$ +21°, *akuammigine* (IV), $C_{21}H_{23}O_2N_2(OMe)$ $(+H_2O)$, m.p. 125°, $[\alpha]_D^{20}$ −44·4°, *pseudakuammigine* (V), $C_{20}H_{20}O_2N(OMe)(NMe)$, m.p. 165°, $[\alpha]_D^{19}$ −53·8°, *akuammiline* (VI), $C_{21}H_{21}O_3N_2(OMe)$, m.p. 160°, $[\alpha]_D^{20}$ +47·9°, NH_3, a trace of an alkylamine, a wax, oil, sucrose, and a substance resembling inulin. The alkaloids are isolated from the seeds in two groups by light petroleum and by EtOH. (I) forms with HNO_2–HCl *nitroakuammine hydrochloride* and a *Bz* derivative, m.p. 245°. (V) gives a *hydriodide*, m.p. 90° $(+H_2O)$, 238° (anhyd.), perchlorate, m.p. 70° and 110°, picrate, m.p. 215°, *methiodide*, m.p. 195° and 233°, $[\alpha]_D^{18}$ +16·3° (*Bz* derivative, m.p. 240°), *Ac*, m.p. 272°, and *Bz* derivatives, m.p. 219°. (VI) is converted into a *hydrochloride*, m.p. 196°, $[\alpha]_D^{20}$ −29·6°, *hydriodide*, m.p. 210°, *nitrate*, m.p. 204°, and *methiodide*, m.p. 233°, $[\alpha]_D^{20}$ −83·3°. (IV) yields a *nitrate*, m.p. 261°, picrate, m.p. 240°, and *hydrochloride*, m.p. 287°, $[\alpha]^{20}$ −37·8°. Derivatives of (V) are the *hydrochloride*, m.p. 183° $(+H_2O)$, 218° (anhyd.), $[\alpha]_D^{20}$ −15·4°, *hydriodide*, m.p. 215°, $[\alpha]^{20}$ −1·43°, *picrate*, m.p. 223°, and *methiodide*, m.p. 275°. (II) gives a *hydrochloride*, m.p. 171°, $[\alpha]_D^{16}$ −626·2°, sulphate $(+4H_2O)$, m.p. 161°, nitrate, m.p. 182·5°, and *methiodide*, m.p. 252°. F. R. S.

Cytisine. II. H. R. Ing (J.C.S., 1932, 2778—2780; cf. A., 1931, 1171; 1932, 1146).—Methylcytisine is oxidised by $Ba(MnO_4)_2$ to N-*methyl*-α-, m.p. 214—215°, and N-*methyl*-β-*cytisamide*, m.p. 179—180°, which are hydrolysed by KOH and converted by $PhSO_2Cl$, respectively, into N-*benzenesulphonyl*-N-*methyl*-α-, m.p. 152—153°, and -β-*cytis-*

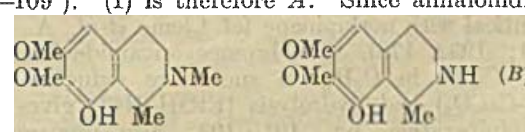


amic acid, m.p. 130—131° (decomp.). The β-acid loses CO_2 at its m.p. to give the *benzenesulphonyl base*, m.p. 141—142°. These results are explained by assigning formula (I) to cytisine, with (II) and (III) for α- and β-methylcytisamide, respectively. F. R. S.

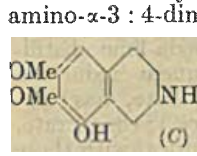
Reduction of 3 : 2′-nicotyrine to dihydronicotyrine and to inactive nicotine. Catalytic disproportioning of dihydronicotyrine into nicotine and nicotyrine. J. P. Wibaut and J. T. Hackmann (Rec. trav. chim., 1932, **51**, 1157—1165).—3 : 2′-Nicotyrine (I) with Zn and HCl gives nicotine (II) (picrate, m.p. 223—224°) (yield 12%), and a dihydronicotyrine (III), b.p. 244—246° (dipicrate, m.p. 163—164°), which is unaffected by further action of Zn and HCl. (III) with H_2 (Adams) gives (II), (I), and dihydrometanicotine [dipicrate, m.p. 161—162° (cf. A., 1909, i, 827)]. (III) in AcOH with the Pt catalyst in the absence of H_2 gives (II) and (I), yields being given under varying conditions. A. A. L.

Quinine hydrobromide with chloroform and bromoform of crystallisation. W. Schnellbach and J. Rosin (J. Amer. Pharm. Assoc., 1932, **21**, 1009—1012).—A description of cryst. *compounds* of quinine hydrobromide with $CHCl_3$ (2·5 mols) and $CHBr_3$ (2 mols). E. H. S.

Constitution of pellotine and anhalonidine. E. Späth [with, in part, J. Passl] (Ber., 1932, **65**, [*B*], 1778—1785; cf. A., 1922, i, 163, 567, 852).—Pellotine (I) is transformed by diazoethane in anhyd. EtOH at room temp. into the O-*Et ether*, b.p. 130—140° (bath)/1 mm., oxidised by $KMnO_4$ to 4 : 5-dimethoxy-3-ethoxyphthalic acid (II) (*anhydride*, m.p. 108—109°). (I) is therefore *A*. Since anhalonidine



is obtained by *iso*quinoline ring closure from β-amino-α-3 : 4-dimethoxy-5-acetoxyphenylethane, is a sec. base, and gives the same quaternary compound as pellotine when methylated under conditions which do not affect the phenolic OH, it must be *B*, whilst anhalamine is probably *C*. The structure of (II)

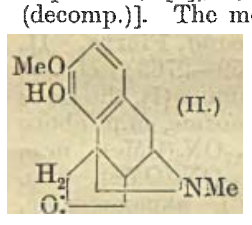


is elucidated as follows. 1 : 2 : 3 : 5 : 6 : 7-Hexahydroxyanthraquinone (III) is converted by short treatment with CH_2N_2 in Et_2O–MeOH into 1 : 5-*dihydroxy*-2 : 3 : 6 : 7-*tetramethoxyanthraquinone* (IV), m.p. 252—253°, which must have the free OH groups in the position indicated, since it does not give trimethoxyphthalic acid when oxidised and consumes the same relative amount of $KMnO_4$ as does 5-hydroxy-3 : 4-dimethoxybenzoic acid. Prolonged treatment of (III) with CH_2N_2 affords a single Me_5 ether (II), m.p. 189—190°, and a Me_6 ether, m.p. 239—240°; the difficulty of methylation is due to the vicinal position of the OH to the CO groups, confirmed by the observation that 2 : 3-dihydroxyanthraquinone readily passes into its Me_2 ether, m.p. 241—242°, without giving the Me_1 compound, whereas alizarin gives almost exclusively 1-hydroxy-2-methoxyanthraquinone. Oxidation of (V) with $KMnO_4$ affords 3 : 4 : 5-trimethoxyphthalic acid (anhydride, m.p. 144°), identical with the acid obtained from colchicine. Treatment of (IV) with KOH and EtI in EtOH yields 5-*hydroxy*-2 : 3 : 6 : 7-*tetramethoxy*-1-*ethoxy*- (VI), m.p. 175—176°, and 2 : 3 : 6 : 7-*tetramethoxy*-1 : 5-*diethoxy*-, m.p. 237—238°, -*anthraquinone*. Oxidation of (VI) affords 4 : 5-dimethoxy-3-ethoxyphthalic acid identical with that derived from pellotine. H. W.

Lupin alkaloids. VII. Synthesis of norlupinane. K. Winterfeld and F. Holschneider (Annalen, 1932, **499**, 109—122).—1-Methyl-2-pyrrolidone, Et pyridine-2-carboxylate, and NaOEt in C_6H_6 give 2-*pyridyl* 3-1-*methyl*-2-*pyrrolidonyl ketone*, m.p. 82—84° (slight previous sintering) [*picrate*, m.p. 137—138°; *mercurichloride*, $C_{11}H_{12}O_2N_2,HgCl_2,2HCl$, m.p. 212—213° (decomp.)], converted by fuming HCl into 2-γ-methylaminobutyrylpyridine (dihydrochloride, decomp. 183—184°; *phenylhydrazone hydrochloride*, decomp. 221—222°). The Bz derivative of this is reduced (H_2, PtO_2, AcOH) to the oily *N*-Bz derivative (I) of 2-δ-methylamino-α-hydroxybutylpiperidine. (I) and PBr_5 at 150—160°/vac. give PhCN, MeBr, and 2-αδ-dibromobutylpiperidine (admixed with a little unsaturated material); the latter is converted by EtOH–NaOEt into 9-bromo-octahydropyridocoline, which is reduced (H_2, Pd–$CaCO_3$, EtOH–KOH) to (mainly) octahydropyridocoline (II), b.p. 92—93°/14·5 mm. [picrate, m.p. 193°; chloroaurate, m.p. 168°; methiodide, m.p. 333—335° (decomp.); *hydrobromide*, m.p. 265—266°], and a small fraction, b.p. 110°/14·5 mm. (picrate, m.p. 192—193°). (II) is considered to be identical with norlupinane (cf. Clemo *et al.*, A., 1931, 499; 1932, 178). The bromocyanoamide from (II) and CNBr in C_6H_6 on successive reduction (H_2, Pd–$CaCO_3$) and hydrolysis (EtOH–HCl) gives 2-*n*-butylpiperidine, b.p. 191—193°, also prepared by reduction (Adams) of 2-*n*-butylpyridine, which is obtained by Ziegler and Zeiser's method (A., 1930, 1191). Norlupinane, obtained by soda-lime distillation of lupininic acid and subsequent reduction (H_2, Pd–$CaCO_3$, EtOH) of the distillate, has b.p. 70—72°/13 mm. (cf. Clemo *et al.*, *loc. cit.*); the picrate, chloroaurate, and methiodide are identical with those of (II). H. B.

Structure of strychnine and brucine. O. Achmatowicz (Rocz. Chem., 1932, **12**, 862—868).—*Neostrychnidine dimethiodide*, $C_{23}H_{30}ON_2I_2,H_2O$, m.p. 295°, prepared from neostrychnidine dimethosulphate and NaI, yields with AgCl the corresponding dimethochloride, identical with Clemo, Perkin, and Robinson's (A., 1927, 888) " methoxymethyldihydrostrychnidine dimethochloride (*A*), $C_{25}H_{36}O_2N_2Cl_2$," prepared by the successive action of Me_2SO_4, NaI, and AgCl on methoxymethyldihydroneostrychnidine. The (*A*) salt undergoes Emde's reaction during methylation, involving the stages of methylation, elimination of MeOH, and reconstruction of the strychnidine ring; the same applies to the (*A*) salts of methoxymethyltetrahydrostrychnidine, which are in reality dimethosalts of dihydrostrychnidine, and have the composition $C_{23}H_{32}ON_2X_2$, and not, as stated by Clemo *et al.*, $C_{25}H_{38}O_2N_2X_2$; in this case Emde's reaction is catalysed by H_2O. Methoxymethyldihydroneostrychnidine yields neostrychnidine methiodide on treatment successively with Me_2SO_4 and NaI. R. T.

Sinomenine. XXXIV. Dihydrosinomenilone and its Hofmann degradation. K. Goto and K. Takubo (Annalen, 1932, **499**, 169—174).—1-Bromosinomenilone (I) (A., 1932, 760) is debrominated (H_2, Pd–$BaSO_4$–$PdCl_2$, 5% AcOH) to *sinomenilone*, m.p. 176° (softens at 155°), $[\alpha]_D^{24}$ +442·14° (all rotations are in $CHCl_3$) (*oxime*, m.p. 238°). Reduction of (I) with Na–Hg and EtOH gives 1-*bromodihydrosinomenilone*, m.p. 224° [*oxime*, m.p. 222° (decomp.); *Bz* derivative, m.p. 180°; *methiodide*, m.p. 220° (decomp.)], debrominated (as above) to *dihydrosinomenilone* (II), m.p. 132°, $[\alpha]_D^{24}$ +207·75° [*oxime*, m.p. 155—156° (decomp.)]. The methiodide, decomp. 220—240°, of



(II) and boiling 16·6% KOH give *de*-N-*methyldihydrosinomenilone* (III), m.p. 220° (decomp.), the methiodide of which is similarly degraded to *anhydrobis-sinomelone* (IV), $C_{32}H_{30}O_5$, m.p. 266° (softens at 262°), $[\alpha]_D^{24}$ −522·71°, instead of the expected sinomelone [(IV) probably arises from this by condensation between a CH_2 of one mol. and a CO group of a second mol.]. Reduction (H_2, Pd–$BaSO_4$–$PdCl_2$, 5% AcOH) of (III) affords *dihydrode*-N-*methyldihydrosinomenilone*, m.p. 175° (softens at 170°), $[\alpha]_D^{24}$ −24·56°, the methiodide of which is degraded to *anhydrobisdihydrosinomelone*, m.p. 247° (softens at 244°), also prepared by catalytic reduction of (IV). H. B.

***p*-Arsanilic acid derivatives of *N*-substituted malonamides.** J. Kennedy (J.C.S., 1932, 2781—2782).—Condensation of the appropriate bromomalonamide with *p*-arsanilic acid has given the following: *p*-arsonoanilinomalon-amide (I), m.p. 226° (decomp.) (lit. m.p. >260°); -*bismethyl*-, m.p. >295°; -*bisethyl*- (II), m.p. >300°; -*bis*-n-*propyl*-, m.p. >265°; -*bis*-n-*butyl*-, m.p. 293° (decomp.); -*bisisobutyl*-, m.p. >260°; -*bis*-n-*amyl*-, m.p. 297° (decomp.) (*malonbis*-n-*amylamide*, m.p. 128°; *Br*-derivative, m.p. 98°); and -*bisisoamyl-amide*, m.p. >260° (*malonbisisoamylamide*, m.p. 74°; *Br*-derivative, m.p. 110°); and *Et* p-*arsonoanilinomalonate*, m.p. 230° (decomp.). *Methyl*-, m.p. 165°, and

ethyl-bromomalonamide, m.p. 160°; *ethyl-*, m.p. 177°, and *ethylbromo-malonbismethylamide*, m.p. 130°, are also described. Only (I) and (II) show therapeutic effect. F. R. S.

Aminomethylene derivatives containing arsenic and antimony from hydroxymethylene compounds. E. BENARY (Ber., 1932, **65**, [*B*], 1669—1677).—The following *N*-substituted *p*-aminophenylarsinic acids are obtained by addition of a conc. aq. solution of the Na salt of the requisite hydroxymethylene compound to a solution of the arsinic acid (I) containing an equiv. amount of HCl at room temp.: *γ-keto-*Δ^{α}*-butenyl-*, decomp. 172—175° after darkening at 165°, from hydroxymethyleneacetone; *γ-keto-β-methyl-*Δ^{α}*-butenyl-*, decomp. about 220°; *γ-keto-β-ethyl-*Δ^{α}*-butenyl-*, decomp. 225—230° after darkening at 215°; *γ-keto-γ-phenyl-*Δ^{α}*-propenyl-*, decomp. about 330°; *γ-keto-γ-1-naphthyl-*Δ^{α}*-propenyl-*, decomp. about 280°; *methylene*cyclo*hexanone-*, decomp. about 217—218°; methylenecamphor- (cf. Rupe, A., 1920, i, 241); *methylenementhone-*, decomp. 176—178°; *β-carbethoxyethenyl-*, m.p. about 168° (decomp.) [the corresponding *derivative* from 2-amino-4-hydroxyphenylarsinic acid (II) is described; the *Pr*$^{\alpha}$ and *amyl* esters are analogously prepared]; *β-cyanoethenyl-*, decomp. 210—230°; *methylene-5-acetyl-2-methylpyridine-*, decomp. about 220° after softening at 175°; *methylene-6-methoxy-4-acetylquinoline-*, decomp. about 265—266° [corresponding *derivative* from (II), decomp. about 205°]; *methylene-4-acetyl-2-phenylquinoline-*, decomp. about 185°; *di-ββ-carbethoxyethenyl-*, decomp. about 270° [from Et ethoxymethylenemalonate and (I) in boiling MeOH]; *γ-keto-β-carbethoxy-*Δ^{α}*-butenyl-*, decomp. 270—280° after darkening at 260°; *γ-keto-β-acetyl-*Δ^{α}*-butenyl-*, decomp. 245—250° after darkening at 235°; *δ-chloro-γ-keto-β-carbethoxy-*Δ^{α}*-butenyl-*, decomp. 235—240° after darkening at 210°. The *methyleneacetophenone-*, decomp. about 240° after darkening at 235°, and *methylene*cyclo*hexanone-*, decomp. 230—235° after darkening at 220°, derivatives of (II) are described. Pyrone and (I) yield the *compound* $CO(CH{:}CH{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2)_2$, decomp. 225—230° after darkening at 200°, whereas δ-hydroxy-$\Delta^{\alpha\gamma}$-butadiene-α-aldehyde yields the *substance* $AsO_3H_2{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$, decomp. about 180°; analogous *products* from (II) are described. 3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene with hydroxymethyleneacetone, hydroxymethylenemethyl Et ketone, and Et sodioformylacetate, respectively, gives the *compounds* $C_{20}H_{20}O_4As_2$, decomp. 225—235° after darkening at 180°, $C_{21}H_{22}O_4N_2As_2$, m.p. about 223° (decomp.) after softening at 180°, and $C_{22}H_{24}O_6N_2As_2$, m.p. about 175°. *p-γ-Keto-*Δ^{α}*-butenylaminophenylstibinic acid* and the corresponding *compound* with Et sodioformylacetate are described. Some of the simpler compounds show marked physiological activity, which diminishes with increase in size of the mol. of the hydroxymethylene compound. H. W.

Derivatives of phenylboric acid, their preparation, and action on bacteria. II. Hydroxyphenylboric acids. F. R. BEAN and J. R. JOHNSON (J. Amer. Chem. Soc., 1932, **54**, 4415—4425).—Arylboric acids are best prepared from Mg aryl bromides and Bu$^{\alpha}$ borate at −75° to −70°; phenyl-, *p*-tolyl-(I), anisyl- (II), and *p*-bromophenyl- (III), m.p. 286—289° (corr.) (decomp.), m.p. (block) 301—302°, -boric acids are thus obtained. m-*Hydroxyphenylboric acid* (IV), m.p. 225° (decomp.) (softens at 219°), m.p. (block) >380°, converted by aq. $HgCl_2$ into m-*hydroxyphenylmercuric chloride*, m.p. 240·5—241·5° (corr.), is prepared by the usual method from *m*-$NH_2{\cdot}C_6H_4{\cdot}B(OH)_2$, which is best obtained by reduction (H_2, PtO_2, aq. MeOH) of the NO_2-acid. *o*-Aminophenylboric acid, m.p. 179—180° (corr.) (cf. A., 1931, 502), is prepared by similar reduction of the *o*-NO_2-acid. (I) and HNO_2-free HNO_3 (*d* 1·5) at −30° to −28° give 2-*nitro*-p-*tolylboric acid*, m.p. 260—264° (corr.) (darkens at 250°), m.p. (block) 264°, reduced (as above) to the 2-*NH*$_2$-acid, m.p. 209—212° (corr.) (softens at 200°), m.p. (block) 267—270° (slowly), 285° (instantly) [*Ac*, m.p. 244—246°, and *Bz*, m.p. 95—100°, re-solidifying with m.p. 315° (corr.), derivatives], which is converted into 2-*hydroxy*-p-*tolylboric acid* (V), m.p. 266—268° (corr.) (decomp.), m.p. (block) >380°. (V) and aq. $HgCl_2$ give 2-*hydroxy*-p-*tolymercuric chloride*, m.p. 143·6—144·6° (corr.) with darkening. Nitration of (III) affords 4-*bromo*-3-*nitrophenylboric acid*, m.p. 300—301° (corr.), m.p. (block) 320°; (II) similarly gives 2 : 4-dinitroanisole. (IV) and (V) have practically no bactericidal action towards *S. aureus*. The bacteriostatic effects of the above and the nitrophenylboric acids are determined; (III) has the highest action. H. B.

Germanium. XI. Organic compounds of germanium. R. SCHWARZ and W. REINHARDT (Ber., 1932, **65**, [*B*], 1743—1746).—$GeCl_4$ in Et_2O is converted by the Mg derivative of αε-dibromopentane into *Ge* cyclo*pentamethylene dichloride*, $CH_2<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>GeCl_2$, b.p. 95—60°/12 mm., transformed by MgEtBr into 1 : 1-*diethylgermanium*cyclo*pentamethylene*, b.p. 52°/13 mm. $GeCl_4$ and K pyrrole in light petroleum, b.p. 60°, afford *Ge tetra*-1-*pyrrolyl*, m.p. 202°. NaOPh suspended in boiling C_6H_6 and $GeCl_4$ yield *Ge tetraphenoxide*, b.p. 210—220°/0·3 mm. Analogously, or by successive addition of PhSH and $GeCl_4$ to MgPhBr, *Ge tetrathiophenoxide*, m.p. 104°, is derived. $SnPhCl_3$ and Na in $C_6H_4Me_2$ yield $SnPh_4$ and Sn. H. W.

Globin. K. FELIX and O. KAHLERT (Z. physiol. Chem., 1932, **212**, 157—160).—Natural and denatured globin were esterified with MeOH. The analyses of the ester hydrochlorides of the two forms were identical. From the OMe and Cl content, the CO_2H and basic groups amount to 12·8 and 13·2, respectively, per 100 atoms of N. J. H. B.

Extractives of muscle. XXX. Determination of carnosine. II. Deamination of β-alanine by nitrous acid. XXXI. Determination of carnosine. III. L. BROUDE (Z. physiol. Chem., 1932, **212**, 196—204, 205—206; cf. A., 1928, 665).—XXX. A total error of 14% in the determination of carnosine by hydrolysis, deamination of the β-alanine to hydracrylic acid by HNO_2, conversion into acrylic acid, and measurement of the Br absorption is probably due in part to production of some acrylic

acid in deamination, which then forms β-nitropropionic acid with excess of HNO_2.

XXXI. The error is avoided by removal of excess of HNO_2 with $NH_2{\cdot}SO_3H$. There is an error of 4% inherent in the Br absorption; when this is corrected for the method gives exact results. J. H. B.

Basic amino-acids of livetin. T. H. JUKES and H. D. KAY (J. Biol. Chem., 1932, **98**, 783—788).—The arginine-N figure for livetin, determined by the arginase method, is 11·7% as compared with 14·7% for vitellin. The cystine content of livetin by the Sullivan method (cf. A., 1930, 1604) is 2·3%; that of vitellin is 1·1%. Isolation of the basic NH_2-acids of livetin gave a basic N distribution of 10·3% arginine-N, 2·11% histidine-N, and 5·92% lysine-N. R. N. C.

Clupein. VI. K. FELIX, K. DIRR, and A. HOFF (Z. physiol. Chem., 1932, **212**, 50—52; cf. A., 1932, 1269).—Arginase acts on arginine substituted in the NH_2 group by a peptide or protein group as in clupein Me ester hydrochloride, the optimum p_H varying with the substituent. This fact may be used to determine whether in a protein a free CO_2H group belongs to arginine. J. H. B.

Sources of error in organic elementary analysis. IX. Metallic copper as substitute for lead peroxide in micro-elementary analysis. J. LINDNER (Ber., 1932, **65**, [*B*], 1696—1706).—Increased accuracy in the determination of H, already attained by the volumetric method and refinement of apparatus in the case of N-free substances, cannot be secured with compounds containing N if PbO_2 is retained. The use of Cu is advocated, N_2 being employed as transport gas and O_2 or air used in the actual combustion. MeOH or HCO_2H is unsuitable for reduction of CuO, which should be effected with H_2. H. W.

Determination of halogens in organic compounds. F. GOVAERT (Compt. rend., 1932, **195**, 797—798).—A modification of the method of Vaughn and Nieuwland (A., 1931, 1393) is described. J. L. D.

Determination of chlorine and bromine in organic compounds. M. OESTERLIN (Angew. Chem., 1932, **45**, 673—674).—Viebock's method is inapplicable to such compounds as alkaloid salts which evolve acid vapours on decomp. In the method described, which is suitable for micro-determinations, the sample (5 mg.) is decomposed with H_2SO_4–$K_2Cr_2O_7$, and the gas evolved is passed through 0·2—0·3 c.c. N_2H_4,H_2O and then through H_2O. The solution is acidified (Congo-red) with HNO_3, and after addition of 0·2 c.c. of 10% Na nitroprusside solution is titrated with 0·01*N*-$Hg(NO_3)_2$. The method is very rapid, and is not influenced by large amounts of NO_3' or NO_2'. H. F. G.

Comparison of the methods of determining salicylic and benzoic acids in presence of each other. B. BRODSKY and J. PERELMANN (Pharm. Zentr., 1932, **73**, 721—725, 741—745).—Tests of the various methods of determining NaOBz and Na salicylate (I) show that the most trustworthy is to determine (*a*) the total Na and (*b*) (I) bromometrically (A., 1911, ii, 546) in $<0{\cdot}008N$ solution. R. S. C.

Determination of phenols by bromination. I. M. KOLTHOFF (Pharm. Weekblad, 1932, **69**, 1147—1158).—The method of Autenrieth and Beuttel for the determination of PhOH as tribromophenol yields results 7—8% low, whilst with Walton and O'Brien's iodometric method (A., 1932, 72) even greater errors occur. In one method recommended, 1 g. NaOAc and 20—40 c.c. saturated Br-H_2O are added to 5—10 c.c. of *M*-PhOH solution; the ppt. is separated after 5—10 min., washed with H_2O, and added to 5—10 c.c. *N*-KI, and after 10 min. the suspension is titrated with 0·1*N*-$Na_2S_2O_3$. Alternatively, the tribromophenol bromide may be dried over H_2SO_4 and weighed. The error of both these methods is ±2%. In a third method the ppt. is removed, 2 g. Hg_2Cl_2 are added to the filtrate to remove excess Br, and the HBr present is titrated with 0·1*N*-NaOH (bromocresol-green); if the ppt. filters with difficulty it may be removed with CCl_4 or $CHCl_3$. The error is about 1%. H. F. G.

Bromination of salicylic acid. I. M. KOLTHOFF (Pharm. Weekblad, 1932, **69**, 1159—1161).—Addition of Br-H_2O to a solution of salicylic acid yields first dibromosalicylic acid and then CO_2 and tribromophenol (I). The reaction may be employed for the determination of salicylic acid, by determining either the (I) formed or the CO_2 evolved; the error in either case is about 2%. H. F. G.

Detection of carbon dioxide during autoxidation of carotenoids. H. H. ESCHER (Helv. Chim. Acta, 1932, **15**, 1421—1424).—Carotene and xanthophyll in O_2 or air give CO_2 (0·827—0·848 and 0·642—0·679 mol., respectively) and a volatile substance (possibly glyoxal) which gives a Ag mirror in the cold. Carotene is thereby changed into an acid. Pure linseed oil gives no CO_2. Possibly glyoxal is the primary and CO_2 a secondary oxidation product. R. S. C.

Microscopical identification of ephedrine with nitrous acid. F. GRILL (J. Amer. Pharm. Assoc., 1932, **21**, 1012—1014).—Ephedrine hydrochloride and HNO_2 give characteristic crystals (NO-compounds ?). E. H. S.

Microchemical identification of alkaloids. F. AMELINK (Pharm. Weekblad, 1932, **69**, 1270—1272, 1289—1296). — Pantocaine (butylaminobenzoyldimethylaminoethanol hydrochloride) yields an ill-defined ppt. with $AuCl_3$, but by adding NaBr characteristic brown crystals are formed; the sensitivity is 0·1%. $K_4Fe(CN)_6$, preferably in neutral solution, and $K_3Fe(CN)_6$ (in neutral solution only) yield characteristic ppts. from 0·2% solutions. $PtCl_4$, $HgCl_2$, KOH, and Dragendorff's reagent do not yield cryst. derivatives. With $K_2Cr_2O_7$ a cryst. ppt. is formed from 0·1% solutions.

α-Eucaine yields a characteristic cryst. ppt. with $PtCl_4$, $AuCl_3$, $HgCl_2$, and KI in neutral solution, and with $K_4Fe(CN)_6$ in acid solution; the limiting concn. of alkaloid is about 0·1% in each case. Psicaine may be identified by the cryst. ppts. obtained with $PtCl_4$ in neutral solution, after addition of EtOH (limit 0·1%), and with $K_4Fe(CN)_6$ in acid solution (limit 0·2%). With eucodal the $PtCl_4$ reaction is of little use, but on addition of NaI characteristic crystals separate (limit 0·1%); the ppts. obtained

with $AuCl_3$ in neutral solution and with KOH are characteristic also (limits 0·5% and 0·1%). Various other reactions of the three alkaloids are described. H. F. G.

Microchemical detection of atropine. E. Iliescu (Rev. farm., 1931, **51**, No. 3, 34—39; Chem. Zentr., 1932, ii, 577).—Saturated aq. picric acid detects 0·04 mg.; glycerol+saturated picric acid in 96% EtOH detects 0·02 mg., whilst 5% aq. picric acid rendered alkaline with Na_2CO_3, treated with glucose, and boiled until reddish-brown, detects 0·01 mg. A. A. E.

Biochemistry.

Spectrophotometric studies. I. Spectrophotometric constants for common hæmoglobin derivatives in human, dog, and rabbit blood. D. L. Drabkin and J. H. Austin (J. Biol. Chem., 1932, **98**, 719—733).—The use of solutions of $CuSO_4$ in 2*N*-aq. NH_3 is suggested as a simple, reproducible, inorg. standard for spectrophotometric technique. Vals. of the mol. extinction coeff. at λ 510—600 mμ for 0·05*M*- and 0·025*M*-$CuSO_4$ solutions did not deviate by > 1·7%; at 610—700 mμ by > 4·1%. Vals. of the absorption const. of various hæmoglobin derivatives from blood of man, dog, and rabbit are presented. Under the same conditions, the absorption consts. do not vary with the species. The components of a mixture of two pigments can be determined by measurement of the absorption consts. of the pure components and of the mixture. The rate of conversion of oxyhæmoglobin into a hæmoglobin derivative on keeping after dilution also can be measured by observing the change in absorption const., but the solution must not be more dil. than 1/100, since oxyhæmoglobin is unstable in very dil. solutions. R. N. C.

Dissociation curve of oxyhæmoerythrin in the cœlomic liquid of *Sipunculus*. M. Florkin (Compt. rend., 1932, **195**, 832—833).—The dissociation curve of the respiratory pigment of *S. nudus* is practically independent of the CO_2 tension, and, as compared with that of human hæmoglobin, indicates greater combination with O_2 at the same O_2 tension. W. O. K.

Comparison of different stimulants of blood-cell regeneration. A. Ranson (Bull. Soc. Chim. biol., 1932, **14**, 1218—1221).—Rapid regeneration of hæmoglobin is caused by feeding anæmic rabbits with the following daily doses per animal for 9 days, respectively: (*A*) Fe peptonate 0·01 g. (128), (*B*) chlorophyll 0·004 g. and 5 units of carotene (132), (*C*) liver and spleen extracts 0·02 g. each (117), and (*D*) a mixture of the above quantities (132), the figures in parentheses indicating their val. by comparison of the hæmoglobin vals. at the end of treatment with untreated controls. Treatments (*A*) and (*C*) cause only slight, and (*B*) a marked, increase in the blood count. The mixture is superior in all respects to any of the single substances. A. C.

Factors in food influencing hæmoglobin regeneration. II. Liver in comparison with whole wheat and prepared bran. M. S. Rose and L. Kung (J. Biol. Chem., 1932, **98**, 417—437).—Rats, rendered anæmic by restriction to a milk diet, were fed with diets of milk supplemented by whole wheat (I), bran (II), dried liver (III), or a modified Osborne–Mendel diet (IV). During the period of return to a normal blood condition no differences occurred in the production of hæmoglobin expressed in terms of blood vol. Rats on (II) attained a normal level most rapidly, whereas greatest growth occurred with (III) and (IV). The gain in hæmoglobin per g. body-wt. was 20—60% greater in females than in males, a phenomenon also occurring after extensive bleeding, a process which reduced the Fe content of the body (minus digestive tract) to 0·0021±0·00003% for both sexes. F. O. H.

Differences in chemical behaviour of blood of various animal species. K. Bingold (Z. klin. Med., 1932, **120**, 503—509; Chem. Zentr., 1932, ii, 395).—Hæmatin, present in human blood only in pernicious anæmia and yellow atrophy of the liver, is frequently present in dog's, and always present in avian, blood. *Pneumococcus* and Fraenkel's bacillus convert hæmoglobin into hæmatin. At various high temp. decomp. of H_2O_2 by the blood is prevented by chemical decomp. of the pigment. Certain bacteria cause profound decomp. of hæmoglobin, such that porphyrins, urobilin, or bilirubin cannot be detected. A. A. E.

Glass electrode for testing the p_H of blood. D. DuBois (Science, 1932, **76**, 441—443).—An apparatus requiring 0·25 c.c. or less of blood and eliminating serious drift is described. L. S. T.

Applicability of Winterstein's microelectrode for the determination of blood-p_H. H. Winterstein (Arch. exp. Path. Pharm., 1932, **168**, 305—306).—A reply to Laubender (A., 1932, 635). W. O. K.

Determination of potassium in blood-plasma. A. D. Marenzi and R. Gerschmann (Bull. Biol. Pharm., 1932, **18**, 315—316).—K is pptd. as cobaltinitrite, and the Co determined colorimetrically. The method is accurate to 2%. The K content of dog plasma is 19·07 mg. per 100 c.c. A. L.

Ether-soluble acids of the blood. S. L. Ørskov (Skand. Arch. Physiol., 1932, **63**, 255—276; Chem. Zentr., 1932, ii, 554—555).—The acids (0—3·3, average 1·22, $\times 10^{-3}N$) extracted, like lactic acid, with Et_2O are largely sol. in PhMe. The volatile acids ($0{\cdot}1\times10^{-3}N$) include HCO_2H (<0·25 mg. per 100 c.c.) and AcOH (<0·5 mg. per 100 c.c.). Minute quantities of coupled glycuronic and bile acids are also present. A. A. E.

Lactic and total ether-soluble acids in the blood of dogs on various diets. S. L. Ørskov (Skand. Arch. Physiol., 1932, **63**, 213—239; Chem. Zentr., 1932, ii, 555).—Glucose, galactose, sucrose, and particularly fructose increase the blood-lactic acid. Fat following meat, but not following carbo-

hydrate, also causes an increase. Lean meat following carbohydrate diminishes the blood-lactic acid. The other Et_2O-sol. acids are unaffected. A. A. E.

Determination of blood-sugar A. J. L. TERWEN (Med. Tijdschr. Geneesk., 1932, **76**, 2487—2492; Chem. Zentr., 1932, ii, 577).—$K_3Fe(CN)_6$ is reduced to $K_4Fe(CN)_6$, which reacts with Fe^{III}, the Prussian-blue being retained in solution with $H_4P_2O_7$ and compared colorimetrically with that obtained using 0·1% glucose solution. A. A. E.

[Determination of] blood-sugar. R. RAZAFIMAHERY (Ann. Chim. Analyt., 1932, [ii], **14**, 488—493).—A discussion of the merits of the Hagedorn–Jensen method of determination and a modification in which $CCl_3{\cdot}CO_2H$ replaces $Zn(OH)_2$ as protein precipitant. P. G. M.

Relation of sugar to cholesterol in the blood. H. O. MOSENTHAL (Arch. Int. Med., 1932, **50**, 684—689).—After administration of 100 g. of glucose to adults, the plasma-cholesterol may rise, fall, or remain const. W. O. K.

Nature and stability of protein–lipin linkings in blood-serum. Extraction of lipins by ether in presence of alcohol. M. A. MACHEBŒUF and G. SANDOR (Bull. Soc. Chim. biol., 1932, **14**, 1168—1190).—The amount of lipin extracted from horse-serum in 6 hr. by an equal vol. of Et_2O rises sharply to a max. of 50% of the lipin content as the added EtOH is increased to 10% of the serum-vol., and falls rapidly as the EtOH is increased further to 20%. Moderate variation of the vol. of, or renewing, the Et_2O has little influence on the amount of lipin extracted. Following an initial period of slow extraction, which increases as the added EtOH is reduced, and is 1 hr. in the case of optimum concn. of EtOH, extraction of lipin proceeds rapidly. After extraction, the globulin and albumin can be isolated in the native state, and the latter is associated with the lipin fraction which resists extraction. Similar results are obtained with human, rabbit, and sheep sera. The hydrophilic groups of protein, and its possible linking with lipin through common groups, are considered in explaining the results. A. C.

Modifications of serum-proteins and myxoprotein isolated by the acetone method. A. BONOT (Compt. rend., 1932, **195**, 1046—1048).—Protein is pptd. from dog-serum by $COMe_2$ and dried in vac. from filter (I), or centrifuge (II). Aq. solutions of (I) and (II) give with 0·1*N*-HCl or CO_2 to p_H 5·5 protein fractions incompletely sol. in 0·1*M*-NaCl. The denaturation is partly reversed by storage at 0°. The serum, and a protein solution prepared from it as (II), but under anhyd. conditions, give ppts. of native globulin at p_H 5·5 and do not change with age at 0°. Myxoprotein is a mixture of almost native globulins rich in pseudoglobulins and denatured protein. A. C.

Factors involved in the use of organic solvents as precipitating and drying agents of immune sera. M. H. MERRILL and M. S. FLEISHER (J. Gen. Physiol., 1932, **16**, 243—256).—Concns. of 70—75% of MeOH, EtOH, PrOH, and $COMe_2$ completely ppt. serum-proteins and produce max. loss of solubility. With agglutinating sera the loss of agglutinin is approx. parallel to the loss of solubility. Concns. >75% produce complete pptn., but a decreased loss of solubility; at concns. >87% the ppts. are completely sol. in saline. Rise of temp. or prolonged exposure to the solvent increases the degree of denaturation. At 5° no denaturation occurs. A max. ppt. is obtained at p_H 6·0, whilst a greater proportion of protein is pptd. from a more conc. serum. Dry immune sera are prepared by pptn. with abs. EtOH or $COMe_2$. F. O. H.

Immunisation with lecithin from human urine. F. PLANT and H. RUDY (Z. Immunität., 1932, **73**, 385—391; Chem. Zentr., 1932, ii, 555—556).—The lecithin (C 65·79, H 10·55, P 3·80, N 1·73%; NH_2-N 0·8%) did not give a Molisch reaction for cerebroside. Lecithin antisera (rabbit) could not be prepared by combination of this lecithin with pig serum or by addition of pure cholesterol. The antigenic activity of commercial lecithin is due to the presence of egg-yolk. A. A. E.

Serological reactions with simple chemical compounds (precipitin reactions). K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1932, **56**, 399—409).—Azo-dyes are pptd. by immune sera prepared by injection of azoproteins containing the same azo-component. Hence antibodies combine specifically with substances of small mol. wt. The colloidal state of the solution and the composition of the substance determine the tendency to separate from the liquid on combination with antibody. The following were prepared: *p*-nitro-malon-, m.p. 157° (decomp.); -succin-, m.p. 194—195°; -glutar-, m.p. 170—171°; -adip-, m.p. 174—175°; -pimel-, m.p. 147—148°; -suber-, m.p. 158—159°, -anilic acids; *p*-NH_2-derivatives, m.p. 175—176° (decomp.), 183—184°, 186—187°, 165—166°, 178—179°, and 162—163°, respectively. CH. ABS.

Preparation of hæmolytic and precipitating sera. H. J. STAFSETH (Science, 1932, **76**, 444).—An immune serum prepared by using clear serum as antigen can function as a hæmolytic serum, and a hæmolytic serum prepared by washing red blood-cells as antigen can act as a precipitating serum. Hæmolytic and precipitating sera have been obtained, using the clear saline solution in which blood-cells have been washed as antigen. L. S. T.

Hæmolytic action of fatty acids. M. BODANSKY (J. Cell. Comp. Physiol., 1932, **1**, 429—434).—The hæmolytic action of fatty acids is discussed in relation to permeability, lipin solubility, and Traube's rule of attraction pressure. A. G. P.

Extractives of the embryo of *Acanthias vulgaris*. F. KUTSCHER, E. MÜLLER, and W. SPAHR (Z. Biol., 1932, **93**, 239—240).—Betaine and choline were isolated, but no $NMe_3{\cdot}O$ was detected. P. G. M.

Physiology of plant and animal membranes. E. WERTHEIMER (Kolloid-Z., 1932, **61**, 181—198).—A review. E. S. H.

Digestive enzymes of the Colorado potato beetle and the influence of arsenicals on their activity. D. E. FINK (J. Agric. Res., 1932, **45**,

471—482).—Amylase, lactase, invertase, lipase, and proteolytic enzymes exist only in the mid-gut of the beetle and in regurgitated liquids. As fed on sprayed foliage did not appreciably affect the activity of the digestive enzymes. Direct injection of As into the mouth inhibited the action of proteolytic enzymes. A. G. P.

[Composition of] ovaries of various animals and of commercial ovary powders. J. VINTILESCO and J. BIBESCO (J. Pharm. Chim., 1932, [viii], **16**, 369—375).—Detailed analyses are given of fresh dried (105°) ovaries of the ewe, cow, and sow, and of four commercial ovary powders. These powders, if unadulterated, should contain H_2O 8, Et_2O-sol. material 8—12, non-saponifiable material 2—3·5, cholesterol (total) 3·5—3·2, and glycogen 16—20%, and have sap. val. 180—205, and I val. 80—90. Fresh, but not dried, ovaries contain 0·21—0·33% of glutathione. Dried ovaries have only peroxidase action, probably due to traces of hæmoglobin. R. S. C.

Intracellular fatty substances in various tissues cultivated *in vitro*. Z. SZANTROCH (Atti R. Accad. Lincei, 1932, [vi], **15**, 904—907).—The fats appearing in embryonic tissue (hen) cultures are examined. T. H. P.

Surface resistance of human enamel to acid decalcification. E. C. DOBBS (J. Dental Res., 1932, **12**, 581—584).—The org. protective membrane is lost on tryptic digestion. CH. ABS.

Detection of elements in tissues. I. Lead. WALTHER GERLACH and WERNER GERLACH (Arch. Gewerbepath. Gewerbehyg., 1931, **2**, 7—10; Chem. Zentr., 1932, i, 2871).—Cu and Pb are detected spectroscopically (cf. A., 1931, 328). A. A. E.

Determination of oxygen and hydrogen potential in the muscle tissue of the frog. J. W. LANGELAAN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 440—441).—Two characteristic potentials at +0·37 to +0·32 and at −0·32 to −0·28 volt were observed, the exact val. depending on the p_H of the phosphate solution in which the tissue was placed. H. J. E.

Demonstration of organic phosphorus compounds and of a phosphatase in the mammary gland. W. BORST (Z. physiol. Chem., 1932, **212**, 126—134).—Mammary gland tissue contains org. P compounds. The amount is highest in the virginal gland and successively lower in the gravid organism, during lactation, and in the senile gland. Between lactation periods org. P is stored. From inactive tissue adenosinephosphoric acid was isolated. In mammary tissue and in many other organs an enzyme is present capable of eliminating P from adenylic acid. J. H. B.

Decomposition and synthesis of organic phosphate in the mammary gland. W. BRENNER (Z. physiol. Chem., 1932, **212**, 135—145).—In surviving mammary gland tissue, inorg. P increases by autolysis faster than lactacidogen is destroyed. The decomp. of lactacidogen is complete in 2 hr.; the production of inorg. P lasts 6 hr. F′ and citrate ions do not cause synthesis of H_3PO_4 esters, but they inhibit hydrolysis. Oxalate and lactate ions accelerate the hydrolysis. Ageing of the tissue changes the inhibition by fluoride only in respect of concn.; hexosediphosphatase is not injured by ageing. Ca strongly accelerates hydrolysis. From the acid hydrolysis curve it is concluded that the mammary gland contains no $H_4P_2O_7$. J. H. B.

Milk from amputated cow udders. I. Quantity. II. Composition. W. W. SWETT, F. W. MILLER, and R. R. GRAVES (J. Agric. Res., 1932, **45**, 385—400, 401—419).—I. The average yield *post mortem* from cows killed by a blow was 61·1% of that obtained during life, the udders being allowed to get cold, whilst in a group killed by shooting the yield was 75·32% when the udders were kept at blood-temp.

II. The butter-fat content in the first *post-mortem* milking was only 50% of that in *ante-mortem*, the % of total solids being also lower. The ash content of a second sample of *post-mortem* milk was > that of the first. The fat : protein ratio in *post-mortem* was < in *ante-mortem* milk. P. G. M.

Transference of drugs to mother's milk. O. TONN (Pharm. Zentr., 1932, **73**, 727).—Nicotine (I) in human milk can be detected by acidification, removal of the fat, addition of excess of NaOH, steam-distillation, and extraction of the distillate with Et_2O. The residue from the Et_2O gives ppts. characteristic of (I). Milk from a mother who smoked heavily contained (I) and caused nicotine-poisoning in her child. R. S. C.

Flavour in milk. I. R. H. LEITCH (Scot. J. Agric., 1932, **15**, 167—173).—Effects of physiological and pathological conditions and of food materials on milk flavour are recorded. A. G. P.

Variations in fat content of milk following the change from stall to pasturage. K. L. CHRZASZCZ (Milchwirts. Forsch., 1932, **13**, 339—362).—Transition from stall feeding to pasturage decreased the milk secretion, but increased the % of fat in the milk. The extent of the change was influenced by temp. and the composition of the herbage. A. G. P.

Influence of the marsh horsetail (*Equisetum palustre*) on the composition of milk and butter-fat. A. MEETZ (Milchwirts. Forsch., 1932, **13**, 405—430).—The feeding to milch cows of silage containing horsetail caused a reduction in the acidity and the sp. gr. of the milk. Effects on the fat, fat-free dry matter, and protein contents varied considerably in individual cows. The proportion of lactose was slightly, and that of Cl′ more markedly, increased. In general ash contents were slightly increased, there being a tendency towards lower P and higher Ca contents. The Ca and P of the blood increased. A. G. P.

Effect of work in harness on the secretion and composition of cow's milk. J. TAUFER, A. KARAKOZ, and S. KOLACEK (Vestn. Ceskoslov. Akad. Zem., 1932, **8**, 194—198; Chem. Zentr., 1932, ii, 459).—The lactose and protein fall correspondingly with the fall in milk production, but the fat production is increased, so that the fall in total solids

is smaller. The yield of good milkers is specially affected, but is usually normal after 32 hr. A. A. E.

Iodine content of the colostrum of cows. M. Miethke and H. Courth (Milchwirts. Forsch., 1932, 13, 394—404).—The colostrum contains high proportions of I for a few milkings after calving, but vals. return to normal after 2 days. The max. I content attained increases with the length of the preceding dry period, during which there is an apparent accumulation of I in the milk glands. A. G. P.

Thread-forming property of physiological liquids and the methods of measurement. J. Jochims (Kolloid-Z., 1932, 61, 250—256).—A review. E. S. H.

Thread-forming property of the vitreous humour of animal and human eyes. F. P. Fischer (Kolloid-Z., 1932, 61, 265—268).—Photo-ultramicrographs reveal the existence of thread-like particles in the vitreous humour. E. S. H.

Glucose and phosphate concentrations in blood-plasma, glomerular fluid, aqueous humour, cerebrospinal fluid, and lymph. A. M. Walker, E. H. Ellinwood, and J. A. Reisinger (Amer. J. Med. Sci., 1932, 184, 145—146).—In 61 experiments the mean glomerular urine of the frog and necturus contained 97% as much sugar and 100% as much PO_4 as the plasma. In 12 experiments the sugar and PO_4 of the lymph obtained from the frog's web were nearly identical with plasma vals. Cerebrospinal fluid of the frog contained 66% as much sugar and 39% as much PO_4 as the plasma. Aqueous humour contained 63% as much sugar and 42% as much PO_4 as the plasma. Ch. Abs.

Influence of plasma-protein on chloride content of cerebrospinal fluid. H. J. Coombs and K. W. Thompson (J. Exp. Med., 1932, 56, 449—453).—When the plasma-protein of dogs is lowered by plasmaphoresis the concns. of Cl' and $Na^{\cdot}$ in the plasma and cerebrospinal fluids tend to become equal. This accords with the theory that the cerebrospinal fluid is a dialysate, with the choroid plexus acting as a simple dialysing membrane. Ch. Abs.

Ammonia and urea content of human saliva. J. Maupetit (Bull. Biol. Pharm., 1932, 18, 303—304).—In normal and in several pathological salivas collected in aq. $CCl_3{\cdot}CO_2H$ to prevent fermentation, the sum of NH_3-N and urea-N is almost equal to the N evolved by NaOBr. Normally the last-named val. varies from 150 to 200 mg. per litre. A. L.

Relationship between internal secretions and sodium chloride content of bile. K. Sasaki (J. Chosen Med. Assoc., 1931, 21, 41—66).—Continuous feeding of thyroid increases the NaCl content of the fistula bile in a rabbit. Intravenous injection of thyroxine produces a less pronounced change. When adrenaline is given, biliary NaCl is decreased. Insulin also increases NaCl excretion by stimulation of bile flow. Ch. Abs.

Synthesis of bile acids. V. *Cortinellus shiitake* and the secretion of bile acids. S. Higashi (Arb. Med. Okayama, 1932, 3, 22—30).—*C. shiitake* fed to dogs increases the production of bile acids; the effect is due to the presence of ergosterol. Ch. Abs.

Stomach. I. Normal secretion of the Pavlov stomach. I. Sugishima (Japan. J. Exp. Med., 1932, 10, 177—201).—Changes in acidity, [Cl'], and peptic strength were followed. Ch. Abs.

Significance and origin of lactic acid in the gastric contents. I. Murray and A. B. Robertson (Brit. Med. J., 1932, I, 607—609).—Test meals from 37 out of 50 cases, pathological and normal, showed the presence of lactic acid (I), which is more frequent in hyposecretion than in hypersecretion, but is of no clinical significance. The formation of (I) is probably due to *B. acidi lactici*, which was identified in the normal stomach. L. S. T.

Natural pigments of raw silk fibre. III. M.p. of cocoon xanthophyll. M. Oku (J. Agric. Chem. Soc. Japan, 1932, 8, 655—658).—The purified xanthophyll has m.p. 193° (corr.), which is that of Kuhn's lutein. Ch. Abs.

Purification of snake venoms. A. Hansen (Compt. rend. Soc. Biol., 1932, 106, 322—324; Chem. Zentr., 1932, ii, 555).—Adsorption on Al_2O_3 is being tried. Proteolysis is not thereby affected. A. A. E.

Nitrogen and carbon of organic acids of human urine. Distribution of urinary carbon. M. Lafargue (Bull. Soc. Chim. biol., 1932, 14, 1191—1201, and Bull. Biol. Pharm., 1932, 18, 297—299).—The micro-method of determining urinary org. acids (A., 1931, 1082) has been modified to remove phenols and pigments before Et_2O-extraction of the acids. The N and C contents of the org. acids represent 2·5 and 16·8—19·8%, respectively, of the total urinary N and C. Urinary C is distributed as (*a*) N compounds 64·87%, (*b*) org. acids 18·45%, and (*c*) undetermined C 16·68%. A. C.

Organic acids of human urine. Index of acidosis. Index of acido-carbonuria. M. Lafargue (Bull. Soc. Chim. biol., 1932, 14, 1202—1209).—The normal urinary excretion of carboxylic acids as determined by the author's micro-method (A., 1931, 1082) is closely parallel to that of the combined N of NH_3 and urea. The ratio of the former (in c.c. 0·1*N*-acid) to the latter (in g.) is termed the index of acidosis, which has a normal val. of 20—25. This index may be artificially increased, without true acidosis, by low excretion of urea caused by a protein-poor diet. The "index of acido-carbonuria," the ratio org.-acid-C : total urinary C, offers a more trustworthy guide to acidosis. The normal val. is 15—20%. A. C.

Excretion of inorganic sulphates. J. M. Hayman, jun., and S. M. Johnston (J. Clin. Invest., 1932, 11, 607—619).—Inorg. SO_4 is less conc. than creatinine or urea by the human kidney. After intravenous injection of SO_4 its concn. ratio approaches that of creatinine. Ch. Abs.

Determination of enzymes in duodenal juice and fæces. L. Racz (Deut. med. Woch., 1932, 58, 814—815; Chem. Zentr., 1932, ii, 577).—Diastase

is extracted from fæces by means of Willstätter's PO_4–NH_3 solution of p_H 8. For the determination of trypsin in fæces 1 c.c. of the emulsion is allowed to act on 25 c.c. of 2% gelatin, the fission being measured by CH_2O titration. A. A. E.

Constituents of the blood in health and disease. J. S. Hepburn (Hahnemannian Monthly, 1932, **67**, 618—626).—A summary. Ch. Abs.

Copper and non-hæmoglobinous iron contents of the blood-serum in disease. A. Locke, E. R. Main, and D. O. Rosbash (J. Clin. Invest., 1932, **11**, 527—542).—Vals. ($\times 10^{-6}$ g. per c.c.) for Fe in hæmoglobin-free serum were: young men 1·0, young women 0·77, infants, adults with mild bilirubinæmia and cirrhosis of the liver, 1·4. Carcinoma, pregnancy, hypo- and hyper-thyroidism, and lues had no effect; barbital poisoning, nephritis, pituitary and ovarian dysfunction, leucæmia, tuberculosis, and diabetes gave low vals. Serum-Cu vals. were: young men 0·8, young women 0·92; vals. above 2·0 were found in pregnancy and advanced carcinoma. Ch. Abs.

Chemical changes in the blood in Addison's disease. R. F. Loeb (Science, 1932, **76**, 420—421).—Data for three cases are recorded. Loss of inorg. base appears to be an important factor. The Na content of blood-serum decreases, whilst that of K tends to increase. Administration of NaCl results in marked clinical improvement. L. S. T.

Phosphatase test in cases of arthritis and osteitis. J. Race (Arch. Med. Hydrology, 1932, **10**, 1798; Chem. Zentr., 1932, i, 1798).—A modification of Kay's process is described. L. S. T.

Fœtal blood. III. Chemical nature of asphyxia neonatorum. N. J. Eastman (Bull. Johns Hopkins Hosp., 1932, **50**, 39—50).—The primary change is an extreme fall in the fœtal blood-O_2. Ch. Abs.

Effects of excessive intake of magnesium by the rat. Production of renal calculi. E. Watchorn (J. Hyg., 1932, **32**, 156—170).—Excess of $MgCO_3$ in the diet caused the development of urinary calculi in rats; addition of excess of $CaCO_3$ prevented calculus formation. The blood-Ca, -Mg, and -P were not significantly altered. Extra Mg or Ca, or Na_2CO_3 lowered urinary PO_4. Mg and Ca had little mutual effect on the amount excreted in the urine. Ch. Abs.

Cancer problem from the physico-chemical viewpoint. V. Cofman (Bull. Biol. Pharm., 1932, **3**, 281—292).—A discussion.

Lubricating oils and cancer. H. R. Hirst and A. T. King (Nature, 1932, **130**, 810; cf. A., 1932, 1277).—Crude shale oils give rise to insol. compounds which are removed from wool fibres only with difficulty by solvents and not at all by soaps. The ionisation process of Hayes-Gratze gives products of reduced surface tension and high H_2O-emulsifiable nature when applied to oils, especially those of a vegetable origin. Ionised oil also has marked curative properties in cases of dermatitis. L. S. T.

Coal-tar constituents and cancer. J. W. Cook, C. Hewett, and I. Hieger (Nature, 1932, **130**, 926).—An active carcinogenic hydrocarbon possessing a typical fluorescence spectrum has been isolated from active fractions of coal-tar pitch. It is probably identical with 1 : 2-benzpyrene, which has now been synthesised. The synthetic and natural materials are equally active in producing cancer of the skin in mice, and much more active than 1 : 2 : 5 : 6-dibenzanthracene. Perylene and 4 : 5-benzpyrene have also been isolated from coal-tar pitch, and 1 : 2-benzanthracene from the chrysene fraction of coal tar. L. S. T.

Physico-chemical change of the blood in gynæcological diseases. I. Uterine cancer. A. Colloid stability of the blood-plasma and serum-protein. B. Cholesterol in the blood-serum. M. Ikeda (Japan. J. Obstet., 1931, **14**, 296—301, 302—306).—In uterine cancer the total protein is unchanged, but the colloidal stability much reduced except during menstruation. Pathological and normal vals. were, respectively: serum-albumin : globulin 0·51—1·82, 1·58—3·50; euglobulin, 0·30—1·10, 0·12—0·41; plasma-fibrinogen 0·31—0·89, 0·11—0·13; total cholesterol 105—201, 106—201; directly extractable cholesterol 33·0—68·5, 49·5—85·4 mg. per 100 c.c. Ch. Abs.

Glutathione in organs in presence of experimental tumours. N. B. Medvedev (Zhur. Med. Tsiklu, 1932, **2**, 93—103).—The glutathione content of the thyroid, adrenals, kidneys, brain, spleen, lungs, heart, muscles, submaxillary glands, pancreas, liver, testes, and ovaries is greater in normal rats and mice than in those infected with experimental sarcoma and carcinoma. During the growth of the tumour the tissue-glutathione decreases, particularly in the thyroid. Ch. Abs.

Glutathione in normal blood and in cancer. F. F. Ulibarri (An. vías digest. sangre nutrit., 1930, **2**, 242).—Blood-glutathione is normally 40 mg. per 100 c.c.; in cancer it is less. Ch. Abs.

Cholesterol in dermatoses. S. Rosner (Rev. Argentine dermat., 1931, **15**, 11).—Hypercholesterolæmia accompanies syphilitic, cancerous, or infectious skin affections. Ch. Abs.

Distribution of sugar in the blood of diabetic and non-diabetic Indians. J. P. Bose (Indian Med. Gaz., 1932, **67**, 415—435).—In normal persons the plasma-sugar (I) is slightly < the whole blood-sugar (II) and slightly > the corpuscular sugar (III), whereas in diabetes (I) is significantly > (II) and (III) to an extent depending on the severity of the disease. Hence the ratio (III) : (I) is a criterion of the gravity of diabetes. Administration of glucose and of insulin gives vals. for (I), (II), and (III) which indicate that the hormone increases the permeability of the corpuscles to sugar and facilitates its storage and utilisation. F. O. H.

Glycæmia in diphtheria. H. D. Gonzalez (Semana Med., 1932, I, 1949—1961).—No relation between the gravity of the case and the blood-sugar could be found. Ch. Abs.

Parathyroid physiology. III. Effect of phosphate ingestion in clinical hyperparathyroidism. F. Albright, W. Bauer, D. Claflin, and J. R.

COCKRILL (J. Clin. Invest., 1932, **11**, 411—435).—The serum-P and -Ca×P were increased and the serum-Ca and urinary Ca were decreased; the threshold for P excretion was lowered. CH. ABS.

Liver function in hyperthyroidism. S. S. LICHTMAN (Arch. Int. Med., 1932, **50**, 721—729).—In 16 out of 20 cases of uncomplicated hyperthyroidism there was an impairment in the ability to oxidise cinchophen, indicating diminished liver function, but little or no sign of impaired hepatic function was obtained from the galactose tolerance test, or from studies on the icteric index, bilirubinæmia, urobilinuria, and urobilinogenuria. W. O. K.

Metabolism of sodium *dl*-lactate. I. Response of normal human subjects to the intravenous injection of sodium *dl*-lactate. II. Subjects with acidosis. III. Subjects with liver damage, disturbed water and mineral balance, and renal insufficiency. A. F. HARTMANN and M. J. E. SENN (J. Clin. Invest., 1932, **11**, 327—335, 337—344, 345—355).—I. The lactate was apparently converted into glucose; Na appeared in body-fluids as $NaHCO_3$.

II. The Na lactate was metabolised normally.

III. In acute catarrhal jaundice there was slight delay. CH. ABS.

Modifications in the changes of blood-sugar produced by pharmacodynamic substances as a proof of altered equilibrium of the vegetative nervous system in experimental nephritis. R. MESSINA (Arch. Farm. sperim., 1932, **54**, 262—284).—The blood-sugar level of normal rabbits is raised by morphine and pilocarpine and lowered by ergotamine, probably by stimulation or depression, respectively, of the sympathetic nervous system. In nephritis produced by subcutaneous injection of $UO_2(NO_3)_2$, the blood-sugar level is lowered; morphine then lowers it slightly, pilocarpine produces a rise less marked than before, and the hypoglycæmic action of ergotamine is intensified. In nephritis there is vagotonia due to renal insufficiency, and the alteration in the effects of the alkaloids is due to this disturbance of the sympathetic–vagus equilibrium. R. K. C.

Excretion of xylose as an index of damaged renal function. E. H. FISHBERG and L. FRIEDFELD (J. Clin. Invest., 1932, **11**, 501—512).—After ingestion of xylose (50 g.) the intact kidney excretes 25% in 24 hr. Blood-vol. can be determined by the use of xylose. CH. ABS.

Blood in high intestinal obstruction. I. Distribution of phosphorus and intracellular changes. G. M. GUEST and W. DEW. ANDRUS. **II. Relation between "toxæmia" and chemical changes.** W. DEW. ANDRUS, G. M. GUEST, R. F. GATES, and A. ASHLEY (J. Clin. Invest., 1932, **11**, 455—473, 475—488).—I. In experimental pyloric and mid-duodenal obstruction in dogs the ester-P increased; the increase was prevented by parenteral administration of NaCl.

II. Repeated small injections of histamine into dogs with pyloric obstruction hastened blood changes usually regarded as the cause of death. CH. ABS.

Blood in normal pregnancy and eclamptogenic toxæmia. S. KAPLAN (Amer. J. Obstet. Gyn., 1932, **23**, 673—678).—Non-protein-N increased and sugar decreased from the third to the ninth month; uric acid increased slightly during the ninth month. In pre-eclamptic toxæmia the non-protein-N, urea-N, and uric acid increased slightly; eclampsia and, particularly, nephritic toxæmia were accompanied by larger increases. CH. ABS.

Blood and urinary amylase in pregnancy and its late toxæmias. A. N. ARNESON and K. C. MORRIN (Amer. J. Obstet. Gyn., 1932, **23**, 664—672).—In long and difficult parturition blood-amylase rises slightly above the normal (and pregnancy) val. (4—7 units per c.c.). Subnormal vals. were found in 35% of cases of toxæmia of pregnancy with hypertension. Urinary vals. show wide variations. CH. ABS.

Biochemical pregnancy test. Hormonal hypercholesterolæmia. R. L. MASCIOTTRA and R. M. DE HOZ (Semana Med., 1932, II, 53—55).—Urine of pregnancy or the anterior pituitary hormone, but not normal female urine, when injected into guinea-pigs, increases the blood-cholesterol (*e.g.*, by 30—50% within 24 hr.). CH. ABS.

Calcium and inorganic phosphorus content of prenatal and *post-partum* serum. J. W. MULL and A. H. BILL (Amer. J. Obstet. Gyn., 1932, **23**, 807—814).—The cord-serum contained 11·7 mg. Ca per 100 c.c. In women the normal val. is 10·4; at onset of labour it was 9·8, and on the 7th and 12th—14th day *post partum* it was respectively 10·3 and 10·5. The inorg. P was max. (5·1 mg.) at delivery; the val. declined slightly and then recovered to a slightly higher level. Six weeks *post partum* the val. was 3·7—3·9. The val. for cord-blood was 5·8. CH. ABS.

Relation of calcium and phosphorus to growth and rachitic leg weakness in chickens. R. T. PARKHURST and M. R. MCMURRAY (J. Agric. Sci., 1932, **22**, 874—882).—Low-Ca rations (0·26% Ca and Ca : P=0·44 : 1) and also a high-Ca ration (3% Ca and Ca : P=4·4 : 1) resulted in retarded growth and poor bone development. A. G. P.

Fixation of strontium in experimental rickets. G. MOURIQUAND, A. LEULIER, and NOGIER (Compt. rend. Soc. Biol., 1931, **106**, 18—19; Chem. Zentr., 1932, ii, 240).—Administration of Sr appears to intensify the rickets. Only then is Sr present (detected spectroscopically) in the ash of the epiphysis, and this ash is smaller in wt. in animals so treated than in normal animals. A. A. E.

Calcium and phosphorus content of the brain in experimental rickets and tetany. A. F. HESS, J. GOSS, M. WEINSTOCK, and F. S. BERLINER (J. Biol. Chem., 1932, **98**, 625—635).—Total Ca and inorg. P of the brain are decreased in the rachitic rat in spite of high-Ca diets. There is no relation between the concn. of Ca in blood and in brain. In rickets the total Ca is unchanged in blood and diminished in brain; in parathyroid tetany it is low in the blood and undiminished in the brain. H. G. R.

Metabolism in tetany. S. MORRIS (Biochem. J., 1932, **26**, 1606—1608).—A reply to Greenwald (A., 1932, 1159).

Intravenous injections. Composition of the blood during continuous intestinal trauma when no fluid is injected and when fluid is injected continuously. J. W. BEARD and A. BLALOCK (J. Clin. Invest., 1932, **11**, 249—265). CH. ABS.

Intravenous injections. Effects on composition of blood of injection of various fluids into dogs with normal and with low blood-pressure. A. BLALOCK, J. W. BEARD, and C. THUSS (J. Clin. Invest., 1932, **11**, 267—290). CH. ABS.

Effects of hæmorrhage, trauma, histamine, and spinal anæsthesia on composition of blood when no fluids are injected and when fluids are introduced intravenously. J. W. BEARD, H. WILSON, B. M. WEINSTEIN, and A. BLALOCK (J. Clin. Invest., 1932, **11**, 291—309). CH. ABS.

Effects on composition of blood of subcutaneous injection of normal salt solution into normal dogs and into dogs subjected to intestinal trauma, graded hæmorrhages, and histamine injection. A. BLALOCK and J. W. BEARD (J. Clin. Invest., 1932, **11**, 311—325). CH. ABS.

Cholesterol in tuberculosis. G. SAYAGO and I. DEL VILLAR (Prensa med. Arg., 1932, **18**, No. 27). —Subnormal vals. (*i.e.*, <0·1456%) are observed only in malignant cases. CH. ABS.

Oxygen tension–oxygen consumption curves of fertilised arbacia eggs. P. TANG and R. W. GERARD (J. Cell. Comp. Physiol., 1932, **1**, 503—513). —Earlier work (Biol. Bull., 1931, **60**, 242) is extended. A. G. P.

Manometric analysis of the metabolism in avian ontogenesis. I. Normal respiratory quotient of blastoderm, embryo, and yolk-sac during the first week of development. II. Effects of fluoride, iodoacetate, and other reagents on the respiration of blastoderm, embryo, and yolk-sac. J. NEEDHAM (Proc. Roy. Soc., 1932, **B**, **112**, 98—113, 114—138; cf. A., 1930, 1312).—I. Embryos (I) of 2½—6 days' development have a R.Q. of nearly 1. That of the yolk-sac (II) falls from 0·9 at 2½ days to approx. 0·6 at 8 days. Absence of the *area pellucida* (IV) from the blastoderm (III) results in low vals. of R.Q. Up to 2½ days of development (III) has a R.Q. varying between 0·85 and a little above 1.

II. Iodoacetate inhibits the respiration of (I), (II), and (III), the action with (I) being reversible (by addition of lactate) and with (II) irreversible. F′ inhibits the respiration of (I), (II), and (III), high concns. being necessary for total inhibition of that of (I), whilst only with (III) is there a lowering of the R.Q. Phenylurethane partly inhibits the respiration of (III) without affecting the R.Q. Malachite-green inhibits the respiration and considerably lowers the R.Q. of (I) and (III). KCN strongly inhibits the respiration of (III). F. O. H.

Excretion and re-absorption in the small intestine, with special reference to sterols. R. SCHONHEIMER and L. HRDINA (Z. physiol. Chem., 1932, **212**, 161—172).—By means of a sterile intestinal cyst in a dog, endogenous metabolic products not capable of resorption were allowed to accumulate for several months. Dihydrocholesterol was obtained in quantity. The secretions of the stomach and pancreas contained practically no sterols. J. H. B.

Heart function. II. Influence on the function of extirpated toad heart of the skeletal muscle extract and potassium exposed to ultra-violet rays, Röntgen rays, and radium emanation, and the characteristics of the active substance contained in the alcohol extract of the skeletal muscle. III. Controls. M. OANA (Japan. J. Exp. Med., 1932, **10**, 123—155, 157—175).—Skeletal muscle extract contains a thermostable substance (neither sensitised nor destroyed by irradiation), neither fat nor lipin, which stimulates the function of the extirpated heart of the toad. The ash of the extract also produced stimulation, the min. stimulating concn. being approx. the same as that of K. The active substance is present chiefly in heart-muscle. CH. ABS.

Anaerobic fatigue of cardiac muscle and the effect of temperature, cyanide, and adrenaline on its development. J. T. EDSDALL, H. B. HUNT, W. P. READ, and A. C. REDFIELD (J. Cell. Comp. Physiol., 1932, **1**, 475—501).—Relationships between stresses developed in successive beats, the duration of activity, and the lactic acid accumulation in muscle are discussed mathematically, and the different effects of cyanide and adrenaline on these factors are examined. A. G. P.

Growth-stimulating substance in fatigued muscle. H. M. FOX and G. P. SMITH (Nature, 1932, **130**, 774).—Blow-fly larvæ fed on fatigued frog muscle grow larger than those fed on resting muscle. L. S. T.

Metabolic changes involving phosphorus and carbohydrate in the autolysing gastrocnemius and cardiac muscles of normal, thyroxinised, and adrenalectomised animals. M. V. BUELL, M. B. STRAUSS, and E. C. ANDRUS (J. Biol. Chem., 1932, **98**, 645—669).—In gastrocnemius decomp. of phosphocreatine (I) and adenylpyrophosphate takes place rapidly and soon ceases, whereas lactic acid (II) production continues at its initial rate throughout the experimental period. Formation of equimol. quantities of (II) and inorg. P suggests that the precursor of most of the (II) is hexosediphosphate. In thyroxinised animals, formation of (II) is inhibited in gastrocnemius and the glycogen and total acid-sol. P decreased, but with no significant change in the relative distribution of P. Heart-muscle contains the normal acid-sol. P and lower glycogen, otherwise the autolysis curves are indistinguishable. In adrenalectomised animals, formation of (II) is inhibited, the total and inorg. P low, and the pyrophosphate > normal. It is suggested that characteristics of hyperthyroidism and Addison's disease may be associated with the inability of the muscles to produce (II) normally, limiting the resynthesis of (I). H. G. R.

Disappearance of lactic acid, arising from muscular activity, in the dehepatised animal. E. AUBEL, R. GAYET, and Y. KHOUVINE (Ann.

Physiol. Physicochim. biol., 1931, 7, 302—309; Chem. Zentr., 1932, ii, 399).—The blood-lactic acid (I) of dogs of which the liver was excluded from the circulation rose until death supervened; muscular contraction led to an immediate rise in (I), which then further rose until death occurred. Simultaneously the blood-sugar falls. Addition of glucose to the blood results in a fall in (I). A. A. E.

Exchange of materials between muscle, blood, and liver during work. L. WACKER (Biochem. Z., 1932, 255, 222—229).—In so far as it is not oxidised the lactic acid (I) produced in muscle during work passes out as alkali lactate, causing an average increase of 658·8% in the resting lactate content of the blood-serum. In the liver that lactate combines with CO_2 from the blood, carbohydrate and $NaHCO_3$ being regenerated. Since the amount of alkali in muscle is insufficient for neutralisation of the (I) liberated, it follows that $NaHCO_3$ from the blood passes into the muscle and a corresponding amount of Na lactate passes in the opposite direction. An explanation is thus provided for biochemical changes which occur during muscular contraction. W. McC.

Lactic acid transformability of muscle and liver. S. L. ØRSKOV (Skand. Arch. Physiol., 1932, 63, 240—254; Chem. Zentr., 1932, ii, 557).—Rabbit's liver and muscle can cause the transformation of large quantities (equal per unit wt.) of lactic acid. After exercise the cells of a living animal transform twice as much as those of perfused muscle or liver. The quantity of Et_2O-sol. acids is unaffected by perfusion. A. A. E.

Significance of bile acids in carbohydrate metabolism. XXI. Production of glycogen in liver and muscle by bile acid and adenylic acid. K. WATANABE (Biochem. Z., 1932, 255, 155—159).—In rabbits administration of adenylic acid (I) reinforces the action of cholic acid (II) in promoting the production of glycogen in the liver, but in muscle this effect of the (II) is diminished by giving (I). It follows that there is a close relation between the effect of (II) on glycogen production and its effect on nucleic acid metabolism. W. McC.

Influence of sex and age on liver- and muscle-glycogen, and alkali reserve in fasting rats. R. STOHR (Z. physiol. Chem., 1932, 212, 121—125).—The liver-glycogen of fasting rats varies with age and sex. In females the alkali reserve and muscle-glycogen are somewhat lower than in males. J. H. B.

Hypoglycæmia following glucose ingestion. W. S. MCCLELLAN and H. S. H. WARDLAW (J. Clin. Invest., 1932, 11, 513—526).—The causes of hypoglycæmia are reviewed. Hypoglycæmia following ingestion of glucose and due to excessive oxidation or excessive storage is recorded. CH. ABS.

Physiological behaviour of the trioses and related compounds. III. Muscle-glycogen and blood-sugar after feeding methylglyoxal and glyceraldehyde. IV. Alkali reserve after feeding methylglyoxal, glyceraldehyde, dihydroxyacetone, and glucose, and its relation to liver-glycogen. Alimentary hyperglycæmia. R. STÖHR (Z. physiol. Chem., 1932, 212, 85—98, 98—106; cf. A., 1932, 645).—III. AcCHO (I) and glyceraldehyde (II) fed to fasting rats do not increase the glycogen content of the muscle. They increase liver-glycogen, but to a smaller extent than dihydroxyacetone (III). In relation to the amount resorbed (II) is little inferior to (III) in glycogen-forming power. (I) causes a greater rise in blood-sugar than (II). The max. production of liver-glycogen by (II) is reached in 1 hr., by (I) not even in 3 hr.

IV. (I) and (II) decrease the alkali reserve of the blood, (I) more strongly; (III) has no effect. (I), (II), and glucose are probably transformed into glycogen by way of an acid intermediate product ($OH{\cdot}CHMe{\cdot}CO_2H$). J. H. B.

Behaviour of liver-glycogen, alkali reserve, and blood-sugar after acetol feeding. R. STOHR and R. MÜLLER (Z. physiol. Chem., 1932, 212, 107—110).—Acetol fed to fasting rats did not produce any marked change in liver-glycogen, alkali reserve, or blood-sugar. Acetol was present in the blood in high concn.; it does not appear to be converted into AcCHO. J. H. B.

Action of methylglyoxal on acetoacetic acid. IV. Muscle-glycogen, alkali reserve, and blood-sugar after ketol feeding. R. STÖHR and M. HENZE (Z. physiol. Chem., 1932, 212, 111—120; cf. A., 1932, 645).—The ketol does not affect muscle-glycogen, but depresses the alkali reserve; a transitory increase in blood-sugar is probably due to formation of AcCHO and can be almost suppressed by correct dosage. The increase of liver-glycogen by the ketol is confirmed. The behaviour shown strongly resembles that observed with AcCHO administration. J. H. B.

β-Oxidation. V. Effect of insulin and acetoacetic acid on the production of glycuronic acid. A. J. QUICK and M. A. COOPER (J. Biol. Chem., 1932, 98, 537—541).—By measuring the amount of glycuronic acid monobenzoate excreted after administration of BzOH as a measure of the glycuronic acid synthesised by dogs, insulin is shown to stimulate, and acetoacetic, lactic, and glycollic acids to decrease, the output. A. L.

Utilisation of melezitose by bees. E. F. PHILLIPS (Z. Unters. Lebensm., 1932, 64, 383—389).—Various methods are compared and criticised (cf. A., 1931, 1327). Bees or larvæ fed with melezitose survived the starved controls. J. G.

Digestibility of raw starch. E. POZERSKI (Ann. Physiol. Physicochem. biol., 1931, 7, 220—224; Chem. Zentr., 1932, ii, 398).—Starch of rye, buckwheat, or potato fed to fowls is almost completely digested, but when fed with caseinogen or gluten it is largely undigested. Starch of undamaged grain is digested better than that of milled grain. A. A. E.

Metamorphosis of insects. VIII. Rôle of the hæmolymph in the metabolism of butterfly pupæ. J. HELLER (Biochem. Z., 1932, 255, 205—221; cf. A., 1930, 809).—The compositions of the blood and of the remainder of the pupæ of *Deilephila euphorbiæ* which have hibernated and the changes in these compositions which occur during develop-

ment indicate that the blood, which also serves as a H_2O depot, supplies about 70% of the material needed for energy requirements. During the first half of the pupal period the rôles of the various constituents in the energy exchanges which occur resemble those assumed during pupation, whilst in the second half of the period they resemble those assumed in the butterfly. W. McC.

Yeast ingestion and the composition of the urine and fæces. H. B. PIERCE, D. D. POSSON, V. DU VIGNEAUD, C. A. MORRISON, Z. DU VIGNEAUD, and M. S. PEARCE (J. Biol. Chem., 1932, 98, 509—535).—Administration of live yeast has a laxative effect more marked on a carbohydrate-rich than on a protein-rich diet. With the ingestion of yeast elimination of inorg. SO_4 decreases, that of ethereal SO_4 increases. Total phenol, indican, and indole excretion rises, but the increase is not so great as would be expected were the yeast-tryptophan subject to the same degree of putrefaction as the protein in the control diet. Acidity of the urine falls, but urinary NH_3, and NH_3 and volatile acids in the fæces, increase. Most of the yeast-N is retained, and the excretion of uric acid decreases or remains unchanged. A. L.

Relation of the dicarboxylic amino-acids to nutrition. R. R. ST. JULIAN and W. C. ROSE (J. Biol. Chem., 1932, 98, 439—443).—Aspartic, glutamic, and hydroxyglutamic acids are not indispensable constituents of the diet of rats. F. O. H.

Proline and hydroxyproline in nutrition. R. R. ST. JULIAN and W. C. ROSE (J. Biol. Chem., 1932, 98, 445—455).—The mixtures of NH_2-acids obtained by acid hydrolysis of caseinogen, lactalbumin, and edestin were repeatedly extracted with abs. EtOH. The residues, used in diets as a source of N and supplemented by essential NH_2-acids not present in the original protein, promoted normal growth in rats. Hence proline and possibly hydroxyproline are not essential dietary constituents. F. O. H.

Possible interchangeability in nutrition of certain 5-carbon amino-acids. R. R. ST. JULIAN and W. C. ROSE (J. Biol. Chem., 1932, 98, 457—463).—The use of hydrolysed caseinogen, from which arginine, dibasic NH_2-acids, and the prolines have been removed, as a source of N in otherwise adequate diets results in deficient growth in rats even when tryptophan, cystine, and histidine are added. Subsequent addition of arginine, aspartic acid, glutamic acid, and proline does not improve growth. Hence ornithine, glutamic and hydroxyglutamic acids, proline, and hydroxyproline are not interchangeable from a nutritive point of view. F. O. H.

Metabolism of cystine and methionine. Availability of methionine in supplementing a diet deficient in cystine. R. W. JACKSON and R. J. BLOCK (J. Biol. Chem., 1932, 98, 465—477).—Experimental data and discussion of the replaceability of cystine by methionine in the diet of the rat are given (see A., 1932, 83). F. O. H.

Metabolism of sulphur. XIX. Distribution of urinary sulphur in the dog after oral administration of bromobenzene as influenced by the character of the dietary protein and by the feeding of *l*-cystine and *dl*-methionine. A. WHITE and H. B. LEWIS (J. Biol. Chem., 1932, 98, 607—624).—The org. S fraction of urine after oral administration of PhBr is higher when a protein rich in cystine is fed. On low-cystine diets the extra ethereal sulphate-S excretion is greater after PhBr is administered. The addition of either *l*-cystine or *dl*-methionine to the low-cystine diet prevents the increased excretion of N which occurs after the administration of PhBr; the S distribution is similar to that with high-cystine diet. No increase in org. S was observed after feeding *p*-$C_6H_4Br{\cdot}OH$ with a low-cystine diet. H. G. R.

Growth-promoting properties of *d*- and *l*-cystine. V. DU VIGNEAUD, R. DORFMANN, and H. S. LORING (J. Biol. Chem., 1932, 98, 577—589).—A method of resolving *dl*-cystine using the strychnine salt of the formyl derivative is described; *d*-, unlike *l*-cystine, is not active in producing growth. A. L.

Availability of *d*-tryptophan and acetyl-*d*-tryptophan to the animal body. V. DU VIGNEAUD, R. R. SEALOCK, and C. VAN ETTEN (J. Biol. Chem., 1932, 98, 565—575).—The growth resulting from the feeding of *d*- and *l*-tryptophan to rats is the same for both isomerides, whilst the feeding and subcutaneous injection of acetyl-*d*- and -*l*-tryptophan shows the former to be inactive and the latter quite active in producing growth. It is suggested that the oxidation of tryptophan, in contrast to the hydrolysis of the Ac derivative, is not an enzymic reaction, and that it takes place through the keto-acid, the next step in the case of the unnatural isomeride being the synthesis of the natural one. A. L.

Chemistry of mitogenetic radiation. III. Decomposition of creatinephosphoric acid as a source of the radiation. A. E. BRAUNSTEIN and B. A. SEVERIN (Biochem. Z., 1932, 255, 38—43; cf. A., 1932, 966).—Mitogenetic radiation (λ 2000—2150 Å.) is emitted by Ca creatinephosphate during hydrolysis (at room temp. and at 40°) with 0·5*N*-H_2SO_4. The spectrum of the reaction is very similar to that of the reaction which occurs during the metabolic changes in nerves following stimulation. W. McC.

Feeding tests with bran and linseed cake. J. A. CRICHTON and W. M. ALLCROFT (Scot. J. Agric., 1932, 15, 63—66).—The feeding val. of bran for cattle is probably nearer to the Scandinavian standard found in feeding trials than to Kellner's val. based on analysis. A. G. P.

Comparison between the reconstructive food values of certain vegetables and of grain. V. FAMIANI and V. ZAGAMI (Atti R. Accad. Lincei, 1932, [vi], 16, 57—61).—After fasting, pigeons gain wt. more rapidly on a diet of *Ervum lens*, *Lathyrus sativa*, and *L. cicera* than on one of *Triticum vulgare*; moreover, a certain loss in wt. is recovered on a smaller amount of the former diet. T. H. P.

Thyroid problem and iodine metabolism. A. SCHITTENHELM (Deut. med. Woch., 1932, 58, 803—806; Chem. Zentr., 1932, ii, 393).—Factors regulating the I metabolism are discussed. The

thyroid is not the centre of the total I metabolism. The central nervous system plays a leading part. A. A. E.

Inorganic salts in nutrition. IV. Changes induced in the blood by a ration deficient in inorganic constituents. V. Progressive changes in the blood of rats maintained on a ration poor in inorganic salts. P. P. SWANSON and A. H. SMITH (J. Biol. Chem., 1932, **98**, 479—498, 499—507).—A diet of low ash content (0·94% of the total diet) produced in rats a polycythæmia accompanied by a reduction in the size and abs. hæmoglobin content of the erythrocytes. F. O. H.

Minerals and vitamin in the nutrition of the hen. MÜLLER-LENHARTZ and VON WENDT (Z. Fleisch- Milch-hyg., 1932, **42**, 364—366; Chem. Zentr., 1932, ii, 890).

Calcium and phosphorus metabolism. XIV. Relation of acid–base balance to phosphate balance after ingestion of phosphates. W. T. SALTER, R. F. FARQUHARSON, and D. W. TIBBETTS (J. Clin. Invest., 1932, **11**, 391—410).—25% of the ingested PO_4 (NaH_2PO_4 and Na_2HPO_4) was stored. 25% of the excess PO_4 excretion was fæcal as Na_2HPO_4. Acid phosphate caused increased excretion of urinary inorg. base equiv. to the amount of base necessary to neutralise excess PO_4 excretion. CH. ABS.

Effect of the calcium–phosphorus relationship on growth, calcification, and blood composition of the rat. R. M. BETHKE, C. H. KICK, and W. WILDER (J. Biol. Chem., 1932, **98**, 389—403).—An increase of the Ca : P ratio from 1·0 to 5·0 produces a decrease in growth (I), bone-ash (II), and serum-inorg. P, that in (I) and (II) being most marked when vitamin-*D* is absent from the diet. High concns. of Ca and P favour increased vals. of (I) and (II), but the Ca : P ratio is of greater importance. The optimum ratio for (I) and (II) is between 2·0 and 1·0, at which val. vitamin-*D* requirements are at a min. F. O. H.

Strontium and the physiological function of calcium. O. LOEW (Münch. med. Woch., 1932, **79**, 718; Chem. Zentr., 1932, ii, 558).—Although Sr salts have a coagulating effect on milk and blood similar to that of Ca salts, Sr cannot replace Ca physiologically, *e.g.*, in bone formation. A. A. E.

Influence of sex on size and composition of tibiæ of growing chicks. A. D. HOLMES, M. G. PIGOTT, and W. B. MOORE (Poultry Sci., 1932, **11**, 243—249).—Variations in Ca and P are recorded. CH. ABS.

Induced and photochemical oxidations and their importance in biological phenomena. C. C. PALIT (J. Physical Chem., 1932, **36**, 2504—2514).—The oxidation of fats is retarded by carbohydrates and proteins, and that of proteins by fats and carbohydrates. Oxidation of insulin causes oxidation of glucose. Fe, preferably colloidal, accelerates food oxidation. Oxidation of foods is increased by alkali. ZnO, $U(NO_3)_2$, and $Fe(NO_3)_3$ act as sensitisers in org. photochemical oxidations. Org. substances are oxidised in sun and air to CO_2. Peroxides are formed in passing air through aq. suspensions of food oils and some carbohydrates. Irradiated and aerated olive oil is next to sunlight in its curative properties for deficiency diseases. I. J. P. (*c*)

[Therapeutical] adsorbing and neutralising substances. H. VOLLMER (Arch. exp. Path. Pharm., 1932, **168**, 379—399).—Experiments have been carried out to determine the power of charcoal, magnesia usta, and various commercial preps. used in dyspepsia, to adsorb colchicine salicylate, strychnine nitrate, and pepsin, as well as, in certain cases, their power to neutralise acids. Administration of Ca silicate to rabbits or man in sufficient quantity results in adsorption of Ca and increase of serum-Ca. W. O. K.

Excretion of thymol, carvacrol, eugenol, and guaiacol and the distribution of these substances in the organism. V. SCHRODER and H. VOLLMER (Arch. exp. Path. Pharm., 1932, **168**, 331—353).—The above substances administered to animals by mouth undergo 25—95% absorption from the intestinal tract in 24 hr. and soon appear in the urine. In the blood, lung, kidney, and liver significant amounts are found only during the first hr., whilst at most only traces are excreted through the lungs. Administration to guinea-pigs of thymol and K guaiacolsulphonate (I), but not of the other compounds, increases the H_2O content of the lungs, and thymol, carvacrol, eugenol, and (I) increase that of the liver. W. O. K.

Eye of the white mouse as pharmacological test object. I. Determination of very small quantities of atropine and other mydriatics. P. PULEWKA (Arch. exp. Path. Pharm., 1932, **168**, 307—318). W. O. K.

Leech preparations. Detection of acetylcholine in presence of other pharmacologically active substances of tissue origin. B. MINZ (Arch. exp. Path. Pharm., 1932, **168**, 292—304).—The leech-muscle eserine test (cf. A., 1932, 966) is not materially affected by the presence of choline, histamine, peptone, adrenaline, adenylic acid, or thyroxine. W. O. K.

Effect of histamine on the arterial oxygen-combining curve and on the arterial oxygen pressure. Action of histamine on the lung vessels. C. TANG (Arch. exp. Path. Pharm., 1932, **168**, 274—286).—The administration of histamine to man lowers the degree of saturation of the arterial blood as a result of inhibition of the attainment of equilibrium between the alveolar air and the lung-blood. The O_2-combining curve of the blood is usually modified in the sense that rather more complete saturation is obtained at any given O_2 pressure. Together these two effects result in a reduction of the O_2 pressure of the arterial blood. The clinical bearings are discussed. W. O. K.

Uric acid excretion through the intestine and the effect of drugs thereon. H. SCHROEDER and B. B. RAGINSKY (Arch. exp. Path. Pharm., 1932, **168**, 413—423).—Uric acid administered intravenously to cats in partly excreted into the intestinal tract, the rate being increased by substances which stimulate the normal intestinal secretions as well as

by heat. Atropine has an inhibiting, and atophan, histamine, and pilocarpine have no action. Colchicine increases the rate of secretion through the ileum. W. O. K.

Nicotine content of tobacco smoke. E. WASER and M. STAHLI (Z. Unters. Lebensm., 1932, **64**, 470—485).—Cigarettes were "smoked" artificially by the method of Pfyl and Schmitt (A., 1927, 955) and the degree of denicotinisation of the smoke was shown to increase with the H_2O content of the tobacco; the smoke from tobacco containing enough H_2O to render it almost unsmokable contained 15% < that from the same dry tobacco. Bonicot's fluid removed 12% of the nicotine and was the most effective of the denicotising agents tested. On shaking 500 c.c. of a 0·5% solution of nicotine with < 37·5 g. of active C, or re-activated C, or with < 50 g. of SiO_2 gel for 15 min., 80—94, 25—55, and 95% of the nicotine was removed, respectively. Pfyl and Schmitt's method of determination of nicotine (*loc. cit.*) gives results slightly > a modification of Rasmussen's method, the max. deviation being 0·03%. J. G.

Absorption of nicotine from cigarette smoke. C. PYRIKI (Z. Unters. Lebensm., 1932, **64**, 163—171).—Nicotine absorption in the mouth is very small, but considerable on inhalation. Tolerance to nicotine is developed in heavy smokers and absorption lessened. E. B. H.

Activity of *p*- and *m*-sympatol. H. FLECKEN (Arch. exp. Path. Pharm., 1932, **168**, 400—412).—*m*-Sympatol, *m*-OH·C_6H_4·CH(OH)·CH_2·NHMe, has a marked action on the blood-vessels, raises the blood-pressure, and decreases the heart-rate, whilst the *p*-isomeride has little effect on blood-pressure or pulse-rate but increases the heart-beat vol. W. O. K.

Local anæsthetics, pantocaine and larocaine, as compared with novocaine. O. GESSNER, J. KLENKE, and F. R. WURBS (Arch. exp. Path. Pharm., 1932, **168**, 447—472).—The toxicities and anæsthetic activities are in the order pantocaine>larocaine>novocaine. W. O. K.

Poisoning by veronal. E. LABORDE and P. DUQUENOIS (J. Pharm. Chim., 1932, [viii], **16**, 479—483).—The method of Fabre and Fredet (A., 1925, i, 1505) is recommended for the extraction of drugs of the barbituric acid series. Sublimation (330°) was employed as a confirmatory test. Veronal was found in the brain, but not in the liver, spleen, heart, or lungs. T. McL.

Salvarsan and blood-bilirubin. O. SATKE and K. THUMS (Z. klin. Med., 1932, **120**, 386—399; Chem. Zentr., 1932, ii, 395).—Injection of salvarsan affects (25% increases; 75% decreases) the serum-bilirubin independently of the amount present. Variation in the dose of salvarsan, or disturbance of liver function, was without influence. A. A. E.

Classification of different ions in natural chemical groups by their vasomotor action in trans-cerebral dielectrolysis. G. BOURGUIGNON and S. ELIOPOULOS (Compt. rend., 1932, **195**, 976—978).—Study of the trans-cerebral dielectrolysis (so-called "ionisation") of 24 different ions shows that in the production of change of the oscillometric index of the arm opposite to the hemisphere treated the inactive and active ions fall into groups identical with those in the periodic classification and that within an active group the activity increases with at. wt. R. K. C.

The Hofmeister series in muscle [irritation]. E. GELLHORN (Protoplasma, 1932, **16**, 369—377).—The effects of Na salts in maintaining and restoring irritability in muscle preps. were in the order citrate< SO_4''<$Cl' \leqq Br'$<SCN'. A. G. P.

Action of carbon dioxide on marine infusoria. M. A. GALADSHIEV and E. N. MALM (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 109—115).—CO_2 is toxic to oxybiotic infusoria; the tolerance of infusoria to CO_2 increases with their tolerance to H_2S and to deprivation of O_2. R. T.

Effect of heavy metals on ctenophores. O. V. HYKES (Compt. rend. Soc. Biol., 1932, **106**, 328—329; Chem. Zentr., 1932, ii, 558).—The order of decreasing toxicity is: Hg>Cu>Ag>Pb, Pt>Zn>U>Mn. A. A. E.

[Administration of] copper. II. C. G. SANTESSON (Skand. Arch. Physiol., 1931, **63**, 101—116, 117—118; Chem. Zentr., 1932, ii, 399).—Small (2·4 mg.) subcutaneous doses of $CuSO_4$ can be gradually increased beyond the toxic dose (7 mg.) for rabbits. Occasionally CuS is found in the intestines and large hepatic and renal veins. A. A. E.

Solubility of metallic sulphides in minced organs. C. G. SANTESSON (Skand. Arch. Physiol., 1931, **63**, 119—123; Chem. Zentr., 1932, ii, 558).—Injection of suspensions of insol. sulphides causes toxic symptoms in rabbits. HgS, Bi_2S_3, and CuS were dialysed with minced liver or serum at 37° in presence of 5% CO_2 for 1·5 weeks. The dialysate gave reactions for Cu>Hg>Bi. A. A. E.

Arsenic content of hair. L. VAN ITALLIE (Pharm. Weekblad, 1932, **69**, 1134—1145).—Existing data regarding the As content of human hair from cases of As poisoning are tabulated and discussed. In the method recommended for the determination, the sample is washed with EtOH and Et_2O, dried, and warmed with a mixture of H_2SO_4 (5 c.c.) and HNO_3 (5 c.c.) until carbonisation begins, and finally heated until free from HNO_3; As is then determined by Cribier's colorimetric method. The As content of the hair of normal persons rarely exceeds 0·03 mg. per 100 g. H. F. G.

Arsenic content of [finger and toe] nails. L. VAN ITALLIE (Pharm. Weekblad, 1932, **69**, 1145—1147).—The contents of As in finger and toe nails differ considerably, and vary between wide limits. H. F. G.

Poisoning by wine containing cadmium. P. FORTNER (Pharm. Zentr., 1932, **73**, 769—774).—The wine contained Cd, derived from the plating of filters through which it had passed. W. O. K.

Alteration of bones by experimental chronic sodium fluoride poisoning. W. DITTRICH (Arch. exp. Path. Pharm., 1932, **168**, 319—330).—The bones of guinea-pigs, rabbits, and young rats poisoned by the oral administration of small doses of NaF exhibit

macroscopic and microscopic abnormalities consisting in the inhibition of normal growth and marked resorption of the normal bone. Repair takes place if sufficient Ca is administered after ceasing the administration of NaF. W. O. K.

Poisoning by sodium fluosilicate. J. A. LABAT (Bull. Soc. Chim. biol., 1932, **14**, 1222—1227).—The deaths of four people were caused by ingestion of cake containing approx. 2·1% of Na_2SiF_6. F was found *post mortem* in the urine, blood, and several organs. A. C.

Hydrocyanic and thiocyanic acids in the living organism. J. A. KLAASEN (Pharm. Weekblad, 1932, **69**, 1311—1314).—In cases of HCN poisoning CN′ is converted into CNS′ in organs containing the highest concn. of labile S (glutathione etc.). Any dislocation of S metabolism (as in injury to liver) brings about decrease in CNS′ formation. Similar results are observed in P poisoning. S. C.

Mechanism of enzyme action. A. FODOR (Ergebn. Enzymforsch., 1932, **1**, 39—76; Chem. Zentr., 1932, i, 1793).—A summary of the author's views, which are opposed to Willstatter's. L. S. T.

Activation of plant enzymes. K. SUESSENGUTH (Ergebn. Enzymforsch., 1932, **1**, 364—369; Chem. Zentr., 1932, ii, 1796).—The question whether a certain effect is due to new enzymes or to the activation of enzymes is discussed. The saccharification of starch and the hydrolysis of maltose are considered. A. A. E.

Organic catalysts. VI. Preparation of and kinetics of [the catalytic decomposition of α-keto-acids by] derivatives of 3-amino-oxindole. W. LANGENBECK, R. JUTTEMANN, and F. HELBRUNO (Annalen, 1932, **499**, 201—212).—The following are prepared by reduction of the appropriate isatin-3-oxime with $SnCl_2$ and conc. HCl in AcOH except where stated otherwise: 5-bromo- (*hydrochloride*) and 5 : 7-dibromo- (*hydrochloride*) -3-amino-oxindoles; 3-amino-1-methyl- (*picrate*) and -1-phenyl- (*picrate*) -oxindoles; 3-amino-4 : 5-benzo-oxindole (*hydrochloride*); 3-amino-6 : 7-benzo-oxindole (I) (*hydrochloride*); 3-amino-oxindole-6-carboxylic acid [prepared by reduction (H_2, PtO_2, MeOH) of *isatin-3-oxime-6-carboxylic acid* (II), m.p. >290°]; 3-amino-6 : 7-2′ : 3′-pyridino-oxindole [obtained by reduction (H_2, Pd–C, AcOH) of 6 : 7-2′ : 3′-pyridinoisatin-3-oxime (*perchlorate*)]; 3-amino-7 : 6-2′ : 3′-pyridino-oxindole (*dihydrochloride*) [prepared by reduction (H_2, Pd–C, AcOH) of 6 : 7-2′ : 3′-*pyridinoisatin-3-oxime*, m.p. about 265° (decomp.) (darkens at about 250°)]. Oxindole-6-carboxylic acid and *p*-NO·C_6H_4·NMe_2 in EtOH give *isatin-3-p-dimethylaminoanil-6-carboxylic acid*, m.p. >290°, converted by an excess of NH_2OH into (II). 5-Aminoquinoline and $CO(CO_2Et)_2$ in AcOH afford *Et 3-hydroxy-6 : 7-2′ : 3′-pyridino-oxindole-3-carboxylate*, decomp. about 200° without melting, which when dissolved in 5% NaOH, oxidised with atm. O_2, and then neutralised (HCl) gives 6 : 7-2′ : 3′-pyridinoisatin (*hydrochloride*). 7 : 6-2′ : 3′-*Pyridinoisatin* is similarly prepared by way of *Et 3-hydroxy-7 : 6-2′ : 3′-pyridino-oxindole-3-carboxylate*, decomp. about 200° without melting, from 8-aminoquinoline. Of the above amino-oxindoles, (I) is the best catalyst for the decomp. of $BzCO_2H$ to PhCHO and CO_2 (cf. A., 1930, 714; 1931, 495). The kinetics of the catalytic decomp. of α-keto-acids are discussed briefly. H. B.

Organic catalysts. VII. Catalytic actions of iminazole-hæmins. W. LANGENBECK, R. HUTSCHENREUTER, and W. ROTTIG (Ber., 1932, 65, [*B*], 1750—1754).—Investigation has been made of the influence of 2-methyl-1-ethyl- (I), 2 : 4 : 5-trimethyl-, 2-methyl-, 4(5)-cyanomethyl-, 4(5)-methyl-iminazole, iminazole, 4(5)-*phenyliminazolesulphonic acid*, not molten below 300°, pilocarpine, and C_5H_5N on the catalase activity of hæmin, its peroxidase action towards pyrogallol, and its oxidising action towards cysteine. Na 4(5)-phenyliminazolesulphonate has no effect on the catalase action of hæmin, but increases the peroxidase action 14-fold. Iminazole increases catalase and peroxidase actions 4- and 12·5-fold. The oxidative actions of iminazole- and phenyliminazolesulphonic acid-hæmin show no characteristic differences. (I) strongly restricts catalase but enhances oxidase activity. H. W.

Catalase. IV. Optical behaviour. K. G. STERN (Z. physiol. Chem., 1932, **212**, 207—214; cf. A., 1932, 1062).—Purified catalase solutions were subjected to ultra-violet spectral analysis, luminescence analysis, and other optical tests. The colloidal carrier of the enzyme is probably responsible for the effects observed. J. H. B.

Tryptophanase. K. KURONO, H. KATSUME, and H. OKI (J. Agric. Chem. Soc. Japan, 1932, **8**, 82—94).—Koji and sake yeast contain tryptophanase, which is also present in commercial pepsin, trypsin, and papain. The optimum p_H is 6·2, and the optimum temp. 20°. Its action is arrested at 100°. It does not liberate NH_3 or produce melanin from tryptophan; the products give only weak reactions for indole-carboxylic and -acetic acid. CH. ABS.

Tyrosinase. II. Colloid-chemical behaviour of the tyrosinase reaction. D. OKUYAMA (Fukuoka-Ikwad. Zasshi, 1931, **24**, 29—32).—The conversion of the red dye into melanin is not accelerated by univalent cations, but is accelerated by Pb>Al, La, Ce >Ca>Ba>Mg. The transformation is electrolytic and is not due to the enzyme. In the action of tyrosinase on *p*-cresol the velocity does not increase parallel with the cresol concn.; the temp. coeff. is 1·2. The velocity is max. when *p*-cresol and glycine are present in equal quantities. The glycine reaction occurs only in an alkaline medium. CH. ABS.

Specificity and mechanism of action of carbohydrases. R. WEIDENHAGEN (Ergebn. Enzymforsch., 1932, **1**, 168—208; Chem. Zentr., 1932, i, 1793).—Views contrary to the theories of Kuhn and Leibowitz are based on the observation that the same α-glucosidase accomplishes the fission of sucrose and maltose. A new classification of carbohydrases is given. L. S. T.

Specificity of amylases. II. Enzymic analysis of starch and glycogen. G. A. VAN KLINKENBERG (Z. physiol. Chem., 1932, **212**, 173—195; cf. A., 1932, 1062).—On sol. potato-starch malt-β-amylase produces 64% of the possible amount of maltose. The initial velocity of hydrolysis is pro-

portional to enzyme concn.; at low concns. the velocity is const. With increasing amounts of α-amylase there is strong inhibition after 36% of the theoretical amount of maltose has been formed. The initial velocity is proportional to enzyme concn. The enzyme is activated by heating to 70°; it then rapidly produces 36% of maltose and more slowly up to 78%. Glutathione has no effect on the hydrolysis by either enzyme.

Starch (potato, wheat, buckwheat, arrowroot) is regarded as a mixture of two mutameric forms, α- and β-starch, present in the ratio 36 : 64. Only α-starch gives a colour with iodine. β-Amylase is associated only with green plants; in the animal body and colourless plants only α-amylases and hence α-starch occur. Glycogen consists almost exclusively of α-starch. J. H. B.

Influence of certain ions on the extraction of malt-amylase from alumina gel. M. L. Caldwell and S. E. Doebbeling (J. Biol. Chem., 1932, 98, 553—563).—The effectiveness of ions in the elution of malt-amylase from Al_2O_3 gel is $Cl' < AcO' <$ oxalate $< SO_4'' <$ tartrate $<$ citrate $< PO_4'''$. The close similarity of this series to that of the order of penetration of anions suggests that the mechanism involves an exchange of active enzyme from the Al ion complex for anions of the electrolyte. A. L.

Effects of certain variations in preparation of a starch substrate in amylase viscosimetry. C. H. Wies and S. M. McGarvey (J. Gen. Physiol., 1932, 16, 221—227).—The effect of dilution on the viscosity and amylase digestivity of a standard starch substrate (A., 1931, 1331) and the comparison of various commercial sol. starch preps. were investigated in order to establish a reproducible standard. F. O. H.

Reproducible standard substrate in starch-amylase viscosimetry. W. R. Thompson, S. M. McGarvey, and C. H. Wies (J. Gen. Physiol., 1932, 16, 229—231).—A fairly satisfactory reproduction of the standard (cf. preceding abstract) is prepared by admixture of two starches, which yield solutions of viscosity respectively $>$ and $<$ the standard, in proportions to give a relative viscosity comparable with that of the standard under certain definite conditions. F. O. H.

Similarity of the kinetics of invertase action *in vivo* and *in vitro*. II. B. G. Wilkes and E. T. Palmer (J. Gen. Physiol., 1932, 16, 233—242).—Under identical external conditions the p_H-activity curves for the hydrolysis of sucrose by the living cells of *Saccharomyces cerevisiæ* and by invertase preps. from this yeast are identical. Thus the intracellular site of invertase action changes its p_H to coincide with that of the surrounding medium and is therefore probably situated at the outer region of the cell. With living cells at p_H 6·9 no hydrolysis due to an α-glucosidase occurs. F. O. H.

Oxynitrilese of emulsin. I. Synthetic action of emulsin. H. Albers and K. Hamann (Biochem. Z., 1932, 255, 44—65; cf. Rosenthaler, A., 1909, i, 74).—The non-enzymic synthesis of mandelonitrile from PhCHO and HCN in aq. EtOH is a two-stage bimol. reaction (cf. Lapworth, J.C.S., 1904, 85, 1206) consisting of a slow addition of CN ions to the aldehyde mols. followed by a rapid addition of H to the hydroxynitrile ions thus produced. The velocity of the reaction is determined by the first stage and the velocity coeff. is independent of the [H·]. The asymmetric synthesis induced by the "oxynitrilese" of emulsin proceeds independently of the accompanying non-enzymic synthesis, the production of the *d*-hydroxynitrile being accelerated by the enzyme which likewise accelerates the hydrolysis to the same extent. W. McC.

Biochemical synthesis of αγ-butylene glycol-β-glucoside. J. Vintilesco and N. Ioanid (Bull. Soc. Chim. biol., 1932, 14, 1228—1234).—In the presence of emulsin, glucose reacts with 10—95% aq. solutions of αγ-butylene glycol. The optimal concn. of the latter is 70%, when 69% of glucose is converted in several weeks. A mixture of 450 g. of optically inactive glycol, 193 g. H_2O, 190 g. glucose, and 5 g. emulsin yielded in 2·5 months 135 g. of non-cryst. αγ-butylene glycol-β-glucoside, $[\alpha]_D$ −33·96°. The synthesis is not asymmetrical, since both the unchanged glycol and that produced by hydrolysis of the glucoside are inactive. A. C.

Production of lactic acid by tissues. W. Haarmann (Biochem. Z., 1932, 255, 103—124).—The anaerobic production of lactic acid from preformed and added carbohydrate (glycogen, hexosediphosphate, glucose, fructose) by tissues (muscle, heart, liver, kidney, spleen, pancreas, brain, lung, thyroid, and suprarenal glands of rabbit, dog, cat, frog) and the factors which influence this production have been measured and examined. In the dog the power of the thyroid gland to decompose glycogen varies greatly with the time of year, there being max. production of lactic acid in March and October. W. McC.

Production of lactic acid from methylglyoxal; influence of carbohydrates. W. Haarmann (Biochem. Z., 1932, 255, 125—135).—AcCHO is converted (to the extent of 80—90%) into lactic acid by muscle, liver, kidney, or brain (rabbit, dog), but some of it is otherwise changed. When carbohydrate (glucose, fructose, glycogen, hexosediphosphate) is added the amount of lactic acid obtained is sometimes $<$ the sum of the amounts to be expected from the substances together. W. McC.

Production of lactic acid from pyruvic acid. W. Haarmann (Biochem. Z., 1932, 255, 136—137).—Surviving tissue from liver, heart, muscle, brain, kidney (dog, rabbit, cat, pigeon, goose) produces lactic acid from $AcCO_2H$ anaerobically. The same organ from different animals varies greatly in activity. W. McC.

Combined action of carbohydrates in production of lactic acid. W. Haarmann (Biochem. Z., 1932, 255, 138—141).—The production of lactic acid by tissues from muscle, heart, or kidney (rabbit, dog, pigeon, goose) is in some cases unaffected, in some increased, and in others decreased by addition of single carbohydrates or pairs of carbohydrates (glucose, fructose, hexosediphosphate, glycogen). W. McC.

Degradation of glycogen and glucose in tissues. W. HAARMANN (Biochem. Z., 1932, **255**, 142—150).—Skeletal muscle (dog, rabbit, pigeon) converts glycogen approx. quantitatively into lactic acid, but with other organs (heart, spleen, tongue) the amount of the acid produced does not correspond with that of glycogen degraded. It follows that in these cases the reducing intermediate carbohydrates produced are not further degraded to lactic acid. W. McC.

Production of lactic acid from products of enzymic hydrolysis of glycogen. W. HAARMANN (Biochem. Z., 1932, **255**, 151—154).—The products of degradation (carbohydrates) obtained from glycogen by the action of organs (other than liver) are further degraded to lactic acid by such organs only as can also produce the acid from glycogen itself (*e.g.*, striped muscle). Liver converts glycogen into a carbohydrate the further degradation of which resembles that of added glucose. W. McC.

Proteolytic enzymes of the animal and vegetable kingdoms. W. GRASSMANN (Ergebn. Enzymforsch., 1932, **1**, 129—167; Chem. Zentr., 1932, i, 1795).—A summary. L. S. T.

Action of rennet. H. HOLTER (Biochem. Z., 1932, **255**, 160—188; cf. A., 1931, 766).—A viscosimetric method for the determination of the time of coagulation of caseinogen (I) solutions treated with rennet is described. The coagulation consists of a chemical change [(I) to casein] followed by a colloidal change (flocculation). Sometimes at least proteolytic hydrolysis accompanies the changes, but it may be caused by impurities. There is a close relation between coagulation and Ca content. The product of time of coagulation and concn. of enzyme is not const. and depends on experimental conditions, but a factor, calc. in a manner described, may be substituted for this product and used as a basis for a unit for measuring the action of rennet. On the assumption that (I) is an unstable complex consisting of at least three substances (cf. Linderstrøm-Lang, A., 1928, 1043), one, which is easily attacked by rennet, is supposed to act as a protective colloid for the others. The active agent of rennet is not identical with pepsin. W. McC.

Kinetics and structural chemistry of the enzymic hydrolysis of proteins. M. BERGMANN (Collegium, 1932, 751—761).—The rate of dissolution of gelatin by trypsin is proportional to the concn. of the latter. The degree of hydrolysis x is expressed by $x=kt\sqrt{F}$, where F is the concn. of the enzyme and t the time of reaction. Gelatin strips were treated with pancreatin solutions, then thoroughly washed, and placed in H_2O at 28°. The gelatin was decomposed in all the tests, so that some of the pancreatin must have combined with the gelatin in the preliminary treatment. The rate and amount of hydrolysis of the washed strips were independent of the time of exposure to, and the concn. of, the pancreatin employed in the pretreatment. The action of the combined enzyme gradually diminished. Putrefaction in raw skins cannot be checked by washing, owing to the formation of such protein–enzyme compounds. The effect of the structure of dipeptides on their hydrolysis by different enzymes is discussed. D. W.

Proteolytic enzymes. II. Mode of union of proline in gelatin. M. BERGMANN, L. ZERVAS, and H. SCHLEICH (Ber., 1932, **65**, [*B*], 1747—1750).—Hydrolysis of gelatin by trypsin containing mainly active proteinase and carboxypolypeptidase with little dipeptidase and scarcely any aminopolypeptidase proceeds with production of equiv. amounts of NH_2 and CO_2H groups, thus involving the exclusive fission of normal ·CO·NH· linkings. Further hydrolysis by erepsin occurs with preponderating liberation of CO_2H in comparison with NH_2 groups. It appears, therefore, that in gelatin the ·NH· group of proline (and also hydroxyproline) is concerned in the structure of the peptide chains and that the linking is ruptured by ereptic fermentation. H. W.

Proteolytic enzymes: behaviour of proline peptides. M. BERGMANN, L. ZERVAS, H. SCHLEICH, and F. LEINERT (Z. physiol. Chem., 1932, **212**, 72—84).—The following dipeptides were synthesised by condensation of carbobenzyloxy-glycine or -alanine with the appropriate NH_2-acid and catalytic hydrogenation of the product, whereby the carbobenzyloxy-group is eliminated as PhMe and CO_2: *glycyl*-l-*proline* (I), m.p. 185° (corr.), $[\alpha]^{20}$ −113·8° in H_2O, from the N-*carbobenzyloxy*-derivative, m.p. 156° (corr.); d-*alanyl*-l-*proline* (II), m.p. 178° (corr.), $[\alpha]^{25}$ −114·4°, from *carbobenzyloxy*-d-*alanyl chloride*, m.p. about 35°, *glycylsarcosine* (III), m.p. 220° (corr.), from the *carbobenzyloxy*-derivative, m.p. 102° (corr.). (I) is not hydrolysed by pancreatic proteinase or polypeptidase. (I) and (II) are attacked by aminopolypeptidase or a similar enzyme, but not by dipeptidase of yeast. The latter also fails to hydrolyse (III). For the action of dipeptidase, NH at the peptide linking appears to be essential. J. H. B.

Crystalline trypsin. I. Isolation and tests of purity. II. Properties. III. Methods of measuring activity. IV. Reversibility of inactivation and denaturation by heat. V. Kinetics of digestion of proteins with crude and crystalline trypsin. J. H. NORTHROP (J. Gen. Physiol., 1932, **16**, 267—294, 295—311, 313—321, 323—337, 339—348).—I. Cryst. trypsin (A., 1931, 655) is not a pure protein, but probably a solid solution. It is stable in dil. HCl, its behaviour in this medium indicating the presence of an inactive protein denatured by heat and an active protein not denatured by heat. This leads to an improved method of prep. using a preliminary pptn. with acid and yielding a P-free cryst. material of twice the activity of the original cryst. prep. Fractionation is accompanied by a considerable loss of milk-clotting activity and the final material is free from amylase and resembles trypsin-kinase in not hydrolysing dipeptides (A., 1929, 1338). Fractionation and solubility data indicate that the recryst. product is neither a mixture nor an adsorption complex. In hot acid solution the degree of denaturation is parallel to the loss of activity. Loss of activity accompanies peptic digestion or keeping in slightly alkaline media.

II. The enzyme hydrolyses caseinogen (I), gelatin

(II), edestin (III), denatured (but not native) hæmoglobin (IV), and peptones prepared by peptic digestion of (I), (II), and (III). It accelerates the coagulation of blood but not the clotting of milk. The extent of the digestion of (II) by cryst. trypsin equals that due to pepsin. Enterokinase does not increase the activity. The following data were obtained: mol. wt., 34,000; mol. radius, $2{\cdot}6\times10^{-7}$ cm.; isoelectric point, p_H 7·0—8·0; optimum for hydrolysis of (I), 8·0—9·0; optimum stability at p_H 1·8.

III. Evaluation was determined by changes in the viscosity of (I) and (II), in the sol. N of (I), and in the formol titre of (I) and (II).

IV. The degrees of protein denaturation and of tryptic activity for various temp. and salt concns. indicate that between native and denatured trypsin there is an equilibrium the extent of which is determined by the temp. Evidence for the proteolytic activity being an intrinsic property of the native protein mol. is also forthcoming.

V. The rate of hydrolysis of (I), (II), and (IV) increases approx. in proportion to the concn. of protein. Hydrolysis of (I) by crude trypsin is a unimol. reaction, whilst with purified trypsin the velocity coeff. decreases as the reaction proceeds. With (IV) the unimol. velocity coeff. decreases with both purified and crude enzyme. The effect of various substrate concns. disappears in viscosity determinations and a unimol. reaction is indicated. The abnormalities are probably due to the occurrence of several consecutive reactions and not to the formation of a substrate–enzyme complex.

F. O. H.

Digestion and inactivation of crystalline urease by pepsin and papain. J. B. Sumner, J. S. Kirk, and S. F. Howell (J. Biol. Chem., 1932, 98, 543—552).—The rapid inactivation of cryst. urease by pepsin and papain–H_2S corresponds with the proteolysis. Below p_H 4·3 the rate of inactivation is increased, whilst above p_H 4·3 and at 0° it is much slower. The inactivation of urease by acid follows the unimol. law. The evidence in support of the identity of the enzyme proper and cryst. urease questioned by other workers is discussed. A. L.

Activation of urease. W. A. Perlzweig (Science, 1932, 76, 435—436).—The SH group is partly responsible for urease activity. L. S. T.

Alcoholic fermentation. Initial stages of fermentation. Fermentation in the yeast cell. A. Harden (Ergebn. Enzymforsch., 1932, 1, 113—128; Chem. Zentr., 1932, i, 1799). L. S. T.

Lactic acid dehydrogenase in yeast. A. Hahn, E. Fischbach, and H. Niemer (Z. Biol., 1932, 93, 121—122).—An extract of fresh yeast will decolorise methylene-blue in a vac. in presence of lactic, but not of succinic, malic, citric, or hexosediphosphoric, acid. Lactic acid is oxidised to $AcCO_2H$.

P. G. M.

Yeast co-zymase. K. Myrback, H. von Euler, and H. Hellstrom (Z. physiol. Chem., 1932, 212, 7—25).—Yeast adenylic acid (I) is chemically closely related to muscle adenylic acid (II). The ultra-violet adsorption of co-zymase was compared with that of other adenylic acids, inosic acid, and guanosine. Co-zymase and other adenine derivatives show an ultra-violet adsorption max. at 258—260 mμ, indicating that the adenylic acid group is responsible and similar in (I) and (II). Phosphatase has no action on co-zymase. Co-zymase is inactivated after 1 hr. at 100° at p_H 3, but only 4·5% of the P is eliminated. The diffusion coeffs. of the active and inactivated solutions are similar, but the optical rotations differ. The titration curve of (II) also differs from that of co-zymase. The inactivation of co-zymase by heating is closely paralleled by the increase in NaOH required during neutralisation. The final val., however, is practically the same in both active and inactive material, indicating that no new acidic groups are unmasked. J. H. B.

Cytochrome and yeast-iron. T. B. Coolidge (J. Biol. Chem., 1932, 98, 755—764).—The oxidation–reduction potential of cytochrome has been determined in artificially prepared solutions and in the yeast cell; in each case E_h=0·260 volt. Yeast extracts contain, besides cytochrome, a colourless Fe compound the apparent mid-point potential of which in presence of protein is about 0·020 volt. This compound is an Fe–protein complex, and its potential is the same as that of any similar Fe–protein complex artificially prepared. A P compound is associated with the complex. The potential of the Fe compound is lowered considerably by deproteinisation of the yeast extract. The purest preps. of cytochrome so far obtained contain at least 2/3 of their Fe in the form of this compound, and the cytochrome-Fe forms 0·3% or less of the total yeast-Fe. R. N. C.

Sensitisation of yeasts to *X*-rays by dyes. A. A. Imschenetski (Bull. Acad. Sci. U.S.S.R., 1932, No. 2, 225—240).—The toxicity of dyes to yeasts increases in the order trypan-blue<Congo-red<eosin<cresol-blue<Bismarck-brown<neutral-red; the toxic action of *X*-rays in the presence of dyes is > that of the sum of these factors taken separately. R. T.

Influence of nitrogenous nutrition on spore formation in six yeasts. W. Ochmann (Zentr. Bakt. Par., 1932, II, 86, 458—465).—Combined N is not always essential to spore formation. Sporulation is favoured by the presence of nitrates and by K salts to a greater extent than by Ca salts. NH_4 salts accelerate spore formation, the effect varying with the salt used and with the nature of the yeast. Amides have a favourable effect on *Saccharomyces* (I), but an inhibitory action on *Schizomyces* (II). NH_2-acids accelerate sporing of (I). NH_2-monocarboxylic acids favour and NH_2-dicarboxylic acids repress sporulation of (II). Cyanates had a favourable effect on (I) and retarding action on (II), whereas thiocyanates were less favourable to the former and less injurious to the latter type of organism. A. G. P.

Staining of the spores of the *Schizosaccharomyces*. W. Ochmann (Woch. Brau., 1932, 49, 381—382).—The spores may be identified by treatment with methylene-blue followed by Bismarck-brown. The spores are stained grey to bluish-green and the vegetative cells brown. C. R.

Thermodynamics of cell reactions. E. I. FULMER (Ergebn. Enzymforsch., 1932, **1**, 1—20; Chem. Zentr., 1932, i, 1792).—Theoretical. A thermodynamic treatment of cell reactions with special consideration of the decrease in free energy in the chemical action of micro-organisms. L. S. T.

Effect of temperature, salts, and [H·] on the rupture of the plasma-gel sheet, rate of locomotion, and gel/sol ratio in *Amœba proteus*. S. O. MAST and C. L. PROSSER (J. Cell. Comp. Physiol., 1932, **1**, 333—354).—Frequency of rupture is increased by a rise in temp. and by lowered concn. of salts and H·, which reduce the thickness of the gel layer. Relationships between the gel/sol ratio and salt concn. are of a similar nature for the chlorides of Na, Mg, and Ca, but a higher concn. of NaCl than of $MgCl_2$ or $CaCl_2$ is necessary to produce a given ratio. The rate of locomotion of the organism increases with salt concn. to a max. val. and subsequently declines to zero. Each salt possesses a sp. concn. giving max. locomotion. A. G. P.

Energy of growth of *Aspergillus niger*. E. F. TERROINE and R. WURMSER (Bull. Soc. Chim. biol., 1932, **14**, 1163—1167).—Polemical against Algera (Rec. Trav. bot. néerland., 1932, **29**, 48). The energy yield is reduced by half by the increased respiration caused by the growth of the culture. The energy content of the mycelium arises from incomplete oxidation of glucose. A. C.

Assimilation of molecular nitrogen by *Aspergillus*. M. ROBERG (Zentr. Bakt. Par., 1932, II, **86**, 466—479).—*Aspergillus* failed to utilise free N_2. A. G. P.

Production of fructose from steamed glutinous rice by moulds. N. YAMAZAKI and K. NOGUCHI (J. Agric. Chem. Soc. Japan, 1931, **7**, 539—546).—*Rhizopus*, *Aspergillus*, and *Mucor* were employed with a 50% aq. solution at 30° for 90 hr. CH. ABS.

Preparation of citric acid by moulds. II. *Penicillium*. K. SAKAGUCHI (J. Agric. Chem. Soc. Japan, 1932, **8**, 172—176).—The production of citric acid from a solution containing glucose 10, peptone 0·3, NH_4NO_3 0·2, K_2HPO_4 0·015, KH_2PO_4 0·015, $MgSO_4,7H_2O$ 0·01 g., NaCl and $FeCl_3$ trace, in 100 c.c. H_2O, by 17 species of *Citromyces*, 4 species of " bridge forms," and 4 species of *Penicillium* has been compared. CH. ABS.

Energy and chemical mechanism of nitrogen fixation by *Azotobacter*. D. BURK (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 67—71).—A supply of Ca considerably in excess of that required for metabolic processes is essential for N fixation by *Azotobacter*. Sr, but no other element, may replace Ca for this purpose (cf. A., 1930, 1068). A. G. P.

Utilisation of various hemicelluloses as sources of energy for nitrogen-fixing bacteria. R. A. DIEHM (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 151—157).—Mannan, galactan, and xylan act as energy sources for *Azotobacter vinelandii*. Hemicellulose cannot be utilised (cf. A., 1931, 1192). A. G. P.

Production of phthalic acid by *Azotobacter*. K. ASO, M. MIGITA, and M. TOMODA (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 40—41).—In culture solutions *Azotobacter* produced HCO_2H, AcOH, and *o*-phthalic acid. A. G. P.

Injury and recovery of respiration and catalase activity in *Azotobacter*. D. BURK, C. K. HORNER, and H. LINEWEAVER (J. Cell. Comp. Physiol., 1932, 435—449).—Respiratory activity of *Azotobacter* is a reversible function of p_H, with an optimum val. at p_H 7·2 and range limits of p_H 5—9. Respiration permanently ceases at p_H 4·6. Catalase activity of *Azotobacter* reaches an optimum at neutrality, but is still apparent at p_H 3—4. Complete lack of O_2 or carbohydrate does not destroy permanently the capacity for growth or N fixation by the organism. A. G. P.

Physiological characteristics of *B. fluorescens* as a denitrifier. E. V. RUNOV (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 160—163).—The denitrification process under aerobic conditions differs considerably from that under anaerobic conditions. Considerable reaction changes in the medium are involved. At the same p_H, temp. has little effect on the quantity of N lost. The extent of the denitrification increases with the amount of NO_3' present. A. G. P.

Growth of *B. radicicola* under reduced oxygen pressure. C. BARTHEL (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 72—73).—Growth in an atm. containing 0·5% O_2 (in N_2 or H_2) was approx. 25% of that under normal aerobic conditions. A. G. P.

Micro-organisms in oil waters and rocks and their biochemical processes. T. GINSBURG-KARAGICHEV (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 297—298).—Micro-organisms from depth samples of oilfields are able to reduce SO_4'', yielding H_2S and FeS, and also to decompose S-containing proteins with the production of H_2S and NH_3. Nitrates are reduced and cellulose is decomposed to yield CH_4, H_2, CO_2, and lactic and acetic acids. Organisms develop in media containing 18% NaCl, but max. H_2S formation occurs with 1—7% NaCl. A. G. P.

Acetic fermentation. A. BERTHO (Ergebn. Enzymforsch., 1932, **1**, 231—269; Chem. Zentr., 1932, i, 1798—1799).—In both the stages EtOH⟶MeCHO⟶AcOH the same dehydrase is active. The AcOH bacteria also show a mutase, apparently different from the dehydrase, catalase, cytochrome, and indophenoloxidase, as well as a complete zymase system. L. S. T.

Biological decomposition of *n*-butyric acid. I. Formation and transition of butyric acid in natural fermentative processes. G. BREDEMANN (Zentr. Bakt. Par., 1932, II, **86**, 353—381).—Pr^nCO_2H is produced from sugars by soil bacteria, but is subsequently decomposed by other organisms for which its salts serve as sources of C. In artificial culture the fermentation of $(PrCO_2)_2Ca$ without gas production results in the separation of crystals of $CaCO_3$. The production of volatile acids of lower mol. wt. as intermediate products is indicated. A. G. P.

Effects of hormones and certain other substances on cell (luminous bacteria) respiration. G. W. TAYLOR (J. Cell. Comp. Physiol., 1932, **1**, 297—331).—Among numerous hormones examined, only adrenaline (I) showed a definite effect on

luminescence, which it invariably decreased. This action is attributable to the ability of (I) to act as a H acceptor in cell oxidative processes. The intensity of luminescence is to some extent influenced by respiratory activity. Luminous bacteria are able to detoxicate cresol. A. G. P.

Pigments of *Sarcina lutea*. E. CHARGAFF and J. DIERYCK (Naturwiss., 1932, **20**, 872—873).—The organism contains two carotenoids: (1) a hydrocarbon *sarcinin*, with two strong absorption bands in C_6H_6 solution at 469 and 440 mμ and a weaker band at 415 mμ; (2) a xanthophyll-like compound, with absorption bands at 469 and 440 mμ. W. O. K.

Reversible reduction in two stages of pyocyanine and α-hydroxyphenazine. L. MICHAELIS, E. S. HILL, and M. P. SCHUBERT (Biochem. Z., 1932, **255**, 66—81; cf. A., 1932, 809).—The theory of oxido-reduction in two stages is applied experimentally to pyocyanine and α-hydroxyphenazine. It is shown how the three partial normal potentials which can be distinguished in the two-stage system are related to each other and to the p_H and to what extent the ordinary one-stage reduction of quinonoid dyes is a limiting case of the two-stage process. W. McC.

Decomposition of fats by micro-organisms. G. SELIBER (Proc. 2nd Internat. Cong. Soil Sci., 1932, **3**, 142—150).—A review. A. G. P.

Lipins of tubercle bacilli. XXVIII. Phthioic acid. Isolation of a lævorotatory acid from the phthioic fraction of the human tubercle bacillus. R. J. ANDERSON (J. Biol. Chem., 1932, **97**, 639—650).—Fractionation of Me phthioate (A., 1930, 252) at < 0·0001 mm., followed by freezing of the $COMe_2$ solution, gave Me phthioate, hydrolysed to the acid, $C_{26}H_{52}O_2$, $[\alpha]_D^0$ +11·96°, and the *Me* ester of an *acid*, $C_{30}H_{60}O_2$, m.p. 48—60°, $[\alpha]_D^0$ −6·16°. A. A. L.

Specific agglutination and precipitation. II. Velocity of reactions. H. EAGLE (J. Immunol., 1932, **23**, 153—186). CH. ABS.

***B. pestis* antigens. I. Antigens and immunity reactions of *B. pestis*. II. Antigenic relationship of *B. pestis* and *B. pseudotuberculosis rodentium*. III. Prophylactic value of the envelope and somatic antigens of *B. pestis*.** H. SCHÜTZE (Brit. J. Exp. Path., 1932, **13**, 284—288, 289—293, 293—298). CH. ABS.

Production of toxin by *C. diphtheriæ*. I. Energy sources. II. Effects produced by additions of iron and copper to the medium. C. G. POPE (Brit. J. Exp. Path., 1932, **13**, 207—217, 218—223). CH. ABS.

Loss of immune substances from the body. III. Diphtheria antitoxin in human sweat. J. M. NEILL, E. L. GASPARI, R. A. MOSLEY, and J. Y. SUGG (J. Immunol., 1931, **21**, 101—102).—Diphtheria antitoxin was found in the sweat of men having large amounts in the blood. CH. ABS.

Purification and concentration of the virus of poliomyelitis. A. B. SABIN (J. Exp. Med., 1932, **56**, 307—317).—Adsorption and inactivation of the virus on Al_2O_3 gel *C* is reversible by changing the p_H, whereby the virus also undergoes considerable purification. The purified virus gave negative biuret, xanthoproteic, and ninhydrin reactions. CH. ABS.

Intestinal antisepsis: observations on mice. J. G. GRAHAM (J. Pharm. Exp. Ther., 1932, **46**, 273—283).—The administration to mice, by mouth, of various antiseptic compounds, including anil and styryl derivatives of quinoline, Na argentothioglycerolsulphonate, hexylresorcinol, and certain dyes, failed to sterilise the intestinal tract. At most only some reduction of bacterial content was effected. W. O. K.

Is calcium a necessary element for micro-organisms? A. RIPPEL and U. STOESS (Arch. Mikrobiol., 1932, **3**, 492—506).—Apart from the neutralising action of $CaCO_3$, the presence of Ca accelerated the growth of a no. of fungi and bacteria. In some cases (*e.g.*, *Aspergillus niger*) no definite effect was observed except in media abnormally high in Mg. The function of Ca depends partly on the phenomenon of ion antagonism and partly on ecological and physiological factors. Ca may be partly replaced by Sr or by tannin. A. G. P.

Colorimetric determination of peptones in nutrient media. E. GUBAREV and E. SERGEJEVA (Biochem. Z., 1932, **255**, 88—91).—After removal of proteins (if necessary) peptones are determined colorimetrically in the media by means of the biuret reaction. A const. ratio must be maintained between the amounts of $CuSO_4$ and peptone. The average error is −3·85%. W. McC.

Determination of hormones. (MISS) K. CULHANE and S. W. F. UNDERHILL (Analyst, 1932, **57**, 684—698).—Physiological tests are described. Adrenaline, especially synthetic, may show an $[\alpha]_D$ of −49° to −53° and yet display only 64—88% of activity. Thyroxine is best determined by chemical methods. T. McL.

Influence of adrenaline on nitrogen metabolism and blood-sugar in hypophysial insufficiency. B. BRAIER (Rev. soc. argentina biol., 1931, **7**, 283—301).—Intravenous injection of adrenaline (I) reduces urinary N in normal and hypophysectomised fasting dogs; creatinine falls and blood-urea rises. Blood-sugar rises less in operated than in control animals. In non-fasting animals (I) produces greater hyperglycæmia in operated dogs than in the controls. CH. ABS.

Relation of creatinuria to muscle-glycogen in man. C. BRENTANO (Z. klin. Med., 1932, **120**, 249—271; Chem. Zentr., 1932, ii, 557).—Injection of adrenaline (I) is followed by increase in blood-lactic acid (II) (10—36·5 mg. per 100 c.c.), but in creatinuria the increase is zero or much < 10 mg. The behaviour of (II) after injection of (I) is apparently related to the muscle-glycogen; hence creatinuria probably indicates a disappearance of glycogen from skeletal muscle. A. A. E.

Blood-coagulating influence of parathyroid injections. G. F. BUME and E. WERBER (Klin. Woch., 1932, **11**, 988—989; Chem. Zentr., 1932, ii, 554).—The decrease in blood-coagulation time follow-

ing injection of parathormone is due to increase in thrombokinase and not to the increase in blood-Ca. A. A. E.

Effect of parathyroid extract on blood-magnesium. D. M. GREENBERG and M. A. MACKEY (J. Biol. Chem., 1932, 98, 765—768).—Subcutaneous injection of parathormone in the dog produced a small increase in blood-Mg, which appeared between the 2nd and 6th hr. after injection, and fell quickly to the normal val. The average rise was 0·6 mg. Mg per 100 c.c. plasma. The Mg increase appeared to be independent of the extent of the subsequent increase in blood-Ca. R. N. C.

Activation of insulin. H. P. HIMSWORTH (Lancet, 1932, 223, 935—936).—Variation in the efficiency of insulin (I) in diabetes is discussed. Experiments with normal subjects showed that by altering the composition of the diet the efficiency of (I) in depressing blood-sugar could be varied at will, and that there is a definite latent period after injection during which (I) exerted no measurable action. (I) as known and as secreted by the pancreas is an inactive material which requires activation by an unknown substance, called insulin-kinase, which is probably produced in the liver. L. S. T.

Effect of lecithin on the action of insulin. E. SKOUGE and A. SCHRUMPF (Z. klin. Med., 1932, 120, 754—767; Chem. Zentr., 1932, ii, 890).—Lecithin alone has no action on the blood-sugar, but when given with insulin it delays the action. A. A. E.

Hypoglycæmic action of callicrein (padutin). E. K. FREY, H. KRAUT, and E. WERLE (Klin. Woch., 1932, 11, 846—849; Chem. Zentr., 1932, ii, 394).—In diabetes, or in the depancreatised dog, but not in normal man or animals, the blood-sugar is markedly lowered, but the effect gradually diminished on repeated dosage. The activity is partly regained after administration of insulin. The hypoglycæmic and pressor components are destroyed by boiling. The prep. contains only a small quantity of P, chiefly inorg.; the amount of adenylphosphoric acid is too minute to have pharmacological action. A. A. E.

Hormone of the pituitary pars intermedia. II. Intermedin in the organism. B. ZONDEK and H. KROHN (Klin. Woch., 1932, 11, 849—853; Chem. Zentr., 1932, ii, 392; cf. A., 1932, 432).—The intermedin (I) contents of the pituitary of various animals are: minnow 7, frog 10, hen 75, rabbit 200—300, ox 5000—6000, man 4000—7000 phoxin units; the content per g. is: ox 3300, man 10,000. (I) is produced in the pars intermedia and diffuses into the other portions of the gland. Low vals. were obtained in pernicious anæmia and high vals. in uræmia, carcinoma of the liver, and eunuchoid adiposity. In the brain, (I) exists only in the wall of the third ventricle. A. A. E.

Effect of the growth-promoting hormone on the mouse. F. WADEHN (Biochem. Z., 1932, 255, 189—199).—A method for obtaining from the anterior lobe of the pituitary gland stable preps. containing growth-promoting hormone and for testing them on the mouse is described. Greatly increased growth, only partly due to accumulation of H_2O and accompanied by decrease in fat content and in ash content of the skeleton, follows injection of the preps. The ash content of the rest of the mouse and Ca and PO_4 remain unchanged, but in the skeletal ash Ca is reduced. Apart from the spleen, the wt. of which is increased by about 50%, there is no increase in the relative wt. of the organs. W. McC.

Effects of combinations of potassium iodide with anterior pituitary and with thyroid on basal metabolism in guinea-pigs. W. J. SIEBERT and E. W. THURSTON (J. Pharm. Exp. Ther., 1932, 46, 293—301).—The intraperitoneal administration to guinea-pigs of acid extracts of the anterior lobe of ox pituitary raised the basal metabolic rate and caused a decrease in wt., but these changes were inhibited when a daily dose of 0·05 g. KI was given. The administration by mouth of Armour's anterior pituitary tablets, or of thyroid gland, to guinea-pigs also caused a rise in basal metabolic rate and a loss of wt., but in both cases simultaneous administration of KI had no inhibitory effect. W. O. K.

Preparation of extracts of anterior pituitary-like substances of urine of pregnancy. P. A. KATZMAN and E. A. DOISY (J. Biol. Chem., 1932, 98, 739—754).—Active extracts of the anterior pituitary-like substance from urine of pregnancy have been obtained by the two following methods: (1) acidification of the urine to p_H 5 with AcOH, adsorption on norit, elution with 90% PhOH, pptn. with 95% EtOH, and extraction with H_2O; (2) acidification with AcOH, adsorption on BzOH, elution by dissolving BzOH in $COMe_2$, and extraction with H_2O. Extracts prepared by the BzOH method had a potency of 1250 mouse units per mg. By fractional pptn. with $COMe_2$ the extract was purified to a potency of more than 3000 mouse units per mg. The extract gave positive biuret and Millon reactions, and was shown by bio-assay to be free from œstrogenic hormones. The immature mouse and rat units are defined. R. N. C.

Mucification of the vaginal epithelium of mice as a test for pregnancy-maintaining potency of extract of corpora lutea. R. G. HARRIS (Science, 1932, 76, 408).—A reply to criticism (A., 1932, 423). L. S. T.

New crystalline sex hormone. A. GIRARD, G. SANDULESCO, A. FRIDENSON, and J. J. RUTGERS (Compt. rend., 1932, 195, 981—983; cf. A., 1932, 433, 547).—The mother-liquors of the hormone from urine from pregnant mares yield a substance of greater acidity, *equilenin*, $C_{18}H_{18}O_2$, m.p. 258—259° (decomp.), $[\alpha]_D^{20}$ +87° in dioxan (crystallographic description) (*Bz*, m.p. 222—223°, and *Ac*, m.p. 156—157°, derivatives; *oxime*, m.p. 249—250°). Bromination yields $C_{18}H_{17}O_2Br$, m.p. 225—227° (decomp.). (All m.p. are corr.) The œstrogenic activity is to $\frac{1}{20}$ that of œstrin. R. K. C.

Vitamins aid reduction of lost time in industry. A. D. HOLMES, M. G. PIGOTT, W. A. SAWYER, and L. COMSTOCK (Ind. Eng. Chem., 1932, 24, 1058—1060).—The beneficial effects of cod-liver oil are demonstrated. E. H. S.

Vitamin-*A*, *B*$_1$, *C*, and *B*$_2$ content of Concord grapes. E. P. DANIEL and H. E. MUNSELL (J. Agric. Res., 1932, 45, 445—448).—The pulp and juice are a poor source of vitamins-*A* and -*B*$_1$, whilst vitamins-*C* and -*B*$_2$ are entirely lacking. The vitamins may be conc. in the skins. P. G. M.

Halibut-liver oil. I. Vitamin potency, physical constants, and tolerance. A. D. EMMETT, O. D. BIRD, C. NIELSEN, and H. J. CANNON (Ind. Eng. Chem., 1932, 24, 1073—1077).—Halibut-liver oils (d^{25} 0·927—0·928, sap. val. 179—193, I val. 118—126, unsaponifiable matter 7·44—7·9%) were about 100 (75—125) times as vitamin-*A*-potent as was cod-liver oil. The colour in the Carr–Price test, however, is bluish-green, the dominant band being at λ 622. The vitamin-*D* potency of the oil is also very high. Massive doses produced no abnormality in the test-animals. E. L.

Quantitative variations in vitamin-*A* content of butter-fat. G. S. FRAPS and R. TREICHLER (Ind. Eng. Chem., 1932, 24, 1079—1081).—Cows fed on cottonseed meal and hulls yielded butter-fats containing about 2 units of vitamin-*A* per g. (modified Sherman–Munsell bio-assay; cf. Fraps, A., 1932, 433). Cows receiving in addition (*a*) sorghum silage and (*b*) silage and pasture grass gave a higher daily yield of butter-fat containing, respectively, 2—12 and about 33 units of vitamin-*A* per g. (cf. butter-fats from local farm animals reared on grain and pasture containing 17—50 units per g. according to season). Only a small proportion of the vitamin-*A* content of the food was accounted for by the vitamin in the butter-fat in cases (*a*) or (*b*). E. L.

Does vitamin-*A* possess vitamin-*D*-sparing properties when fed to growing chicks? J. E. HUNTER, R. A. DUTCHER, and H. C. KNANDEL (Poultry Sci., 1932, 11, 239—240).—No sparing effect, so far as the ossifying properties of vitamin-*D* are concerned, was observed. CH. ABS.

Vaginal smear method of determining vitamin-*A*. C. A. BAUMANN and H. STEENBOCK (Science, 1932, 76, 417—420).—The growth, ophthalmic, and vaginal smear methods have been compared in rats, using carotene as the source of vitamin-*A*. The smear method can be used to determine this vitamin. L. S. T.

Antimony trichloride test for vitamin-*A*. A. F. MCCARLEY (Analyst, 1932, 57, 709).—Certain oil-sol. aniline dyes give intense carmine to violet colours with $SbCl_3$ and the possibility of their presence must be considered. T. McL.

Ferrous iodide and linoleic acid in vitamin-*A* deficiency. F. E. CHIDESTER (Science, 1932, 76, 436—437).—A reply to criticism (A., 1932, 1293). L. S. T.

Do the *B*-vitamins influence the utilisation of lipins? R. LECOQ (Compt. rend., 1932, 195, 827—829).—The replacement, in a diet which produces polyneuritic symptoms in pigeons, of carbohydrate by lipins furnishing an equal quantity of energy, does not abolish its polyneuritic action. When yeast is also administered to pigeons on such a diet of high lipin content the polyneuritic symptoms disappear. W. O. K.

Antineuritic vitamin. IV. Preparation of a highly potent concentrate. R. J. BLOCK and G. R. COWGILL (J. Biol. Chem., 1932, 98, 637—643).—Assuming vitamin-*B*$_1$ to be an org. base, extraction from aq. alkaline solution by org. solvents should be possible. By this technique concentrates approximating in potency to those of Jansen and Donath (A., 1926, 644) can be obtained directly from rice polishings or yeast. H. G. R.

Potency of vitamin-*B*$_1$ preparations. H. W. KINNERSLEY, J. R. P. O'BRIEN, and R. A. PETERS (Nature, 1932, 130, 774).—Comparative tests on pigeons show that cryst. vitamin-*B*$_1$ from baker's yeast is more potent that the prep. of Windaus *et al.* (A., 1932, 310). L. S. T.

Ultra-violet absorption spectrum and chemical structure of vitamin-*B*$_1$. F. F. HEYROTH and J. R. LOOFBOUROW (Nature, 1932, 130, 773; cf. A., 1932, 1175).—Absorption curves for ten different vitamin-*B*$_1$ concentrates have been determined. Correlation of biological activity and absorption, which shows a max. at or near 2600 Å., indicates that vitamin-*B*$_1$ is characterised by a band at 2600 Å. This type of absorption resembles most closely that of compounds containing a pyrimidine ring or of the type of ergothioneine. The curve of Windaus' prep. (*ibid.*, 310) is similar to that of uracil. L. S. T.

Ultra-violet absorption spectrum and chemical structure of vitamin-*B*$_1$. F. P. BOWDEN and C. P. SNOW (Nature, 1932, 130, 774).—A reply to criticism. L. S. T.

Effect of heat at varying hydrogen-ion concentrations on vitamin-*B*$_1$ in protein-free milk. N. HALLIDAY (J. Biol. Chem., 1932, 98, 707—717).—The vitamin-*B*$_1$ potency of protein-free milk has been studied at p_H 4·3, 7, and 10, the milk being supplied to rats on the Sherman–Chase diet. Storage in the cold of solutions at p_H 4·3 and 7 caused practically no loss of activity, but nearly complete loss at p_H 10. Heating for 1 hr. at 97° destroyed 10% at p_H 4·3, 30% at p_H 7, and 75—90% at p_H 10; heating for 4 hr. destroyed 15% at p_H 4·3, 40—50% at p_H 7, and 75—90% at p_H 10. The results show close similarity with those reported for vitamin-*B*$_2$ under the same conditions. Addition of whole wheat to the diet prevented cessation of growth after 5—6 weeks which normally occurs in rats on this diet. It is suggested that the wheat contains a third factor necessary for the growth of the rat, which is thought to be identical with vitamin-*B*$_4$. R. N. C.

Effects of parboiling and milling on the antineuritic vitamin (*B*$_1$) and phosphate content of rice. W. R. ARKROYD (J. Hyg., 1932, 32, 184—192).—Highly milled parboiled rice was rich in vitamin-*B*$_1$, whilst roughly milled raw rice was deficient. Polishings from raw rice contained less B_1 than those from parboiled rice. Parboiled rice contained more P_2O_5 than raw rice when milled to the same degree. Parboiling probably causes vitamin-*B*$_1$ and phosphate to diffuse through the endosperm. CH. ABS.

Vitamin-*C*. J. TILLMANS (Z. Unters. Lebensm., 1932, **64**, 11—20).—A review. E. B. H.

Hexuronic acid as the antiscorbutic factor. E. G. COX, E. L. HIRST, and R. J. W. REYNOLDS (Nature, 1932, **130**, 888).—The taking-up of 2 I by aq. solutions of hexuronic acid is due to oxidation at a double linking. H_2O is essential and the product (I), which is not a di-iodide, can be reduced to hexuronic acid by evaporation in presence of HI. The biological activity of the acid is probably due to this double function of oxidation and reduction. I is further oxidised by NaOI; O is absorbed, two new CO_2H groups are formed, and 1 mol. of $H_2C_2O_4$ is produced quantitatively. Acid $KMnO_4$ and hexuronic acid form a trihydroxybutyric acid (possibly *d*-threonic acid), whilst HCl gives furfuraldehyde quantitatively on heating. Hexuronic acid is monobasic and not a lactone; a suggested structure is $CO_2H{\cdot}[CO]_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$. It forms a diphenylhydrazone, a hydrated di-(*p*-bromophenylhydrazone), and yields a condensation product with *o*-tolylenediamine at 15°. The Na or Ca salt gives a violet colour with $FeCl_3$, and the Na salt a deep blue colour with Na nitroprusside. Acid and salts show an intense absorption band with a head at approx. 265 mμ. At 175° the acid loses CO_2 without darkening or melting, but when heated rapidly the pure acid melts at 192°. In H_2O $[\alpha]_{5780}$ +24° and the slow change $[\alpha]_{5780}$ +24° to +31° is due to partial neutralisation by the alkali from the glass. Mutarotation does not occur. The Na salt has $[\alpha]_{5780}$ +105° in H_2O, +135° in 0·1*N*-alkali. Alkaline solutions of the acid are stable in the absence of O_2. The absorption spectrum of decitrated lemon juice shows the hexuronic acid content to correspond with the recorded antiscorbutic activity of the isolated acid. L. S. T.

Vitamin-*C*, adrenaline, and adrenals. A. VON SZENT-GYORGYI (Deut. med. Woch., 1932, **58**, 852—854; Chem. Zentr., 1932, ii, 392—393).—Animals receiving 1 mg. daily of hexuronic acid (from adrenals) showed normal growth and were not scorbutic. Hexuronic acid is probably related to Swingle's cortin. "Novadrenin" from the adrenal medulla is 15 times as active as adrenaline and is probably the true hormone of the adrenal medulla. It appears to be readily convertible into adrenaline. A. A. E.

Reducing value of plant-juices containing vitamin-*C* as determined by 2 : 6-dichlorophenolindophenol. H. H. MOTTERN, E. M. NELSON, and R. WALKER (J. Assoc. Off. Agric. Chem., 1932, **15**, 614—616).—This indicator is more sp. than I for vitamin-*C*, although it is reduced by many compounds having no vitamin-*C* activity. The titration val. of cabbage-juice decreases by almost 50% after 5 min. in air, owing to the presence of active hexoxidase, but if this is destroyed by steaming the original cabbage, the results are more consistent with the biological response (cf. A., 1932, 658). J. G.

Indirect determination of the vitamin-*C* state of students in Upsala in autumn and spring by measurement of the strength of skin capillaries. K. O. GEDDA (Skand. Arch. Physiol., 1932, **63**, 306—311; Chem. Zentr., 1932, ii, 556).—Lack of vitamin-*C* during the winter was indicated; normal conditions were re-established very slowly. A. A. E.

Determination of vitamin-*D*. L. L. LACHAT, H. A. HALVORSON, and L. S. PALMER (J. Assoc. Off. Agric. Chem., 1932, **15**, 660—675).—The use of chickens enables results to be obtained in a short time, and since the vitamin-*D* requirement of the chick is high, the results are correspondingly trustworthy. Of 13 rickets-producing rations a mixture of 59 parts of yellow maize, 25 of wheat-flour middlings, 12 of crude casein, and 1 each of pptd. $CaCO_3$, $Ca_3(PO_4)_2$, NaCl, and dry baker's yeast gives the best growth rate and uniformly low bone-ash vals. at 4—5 weeks of age (viz., 30—34% for negative control groups, and 45—48% for a satisfactory supply of vitamin-*D*). J. G.

Plasticity of calcified tissues. II. Results of minor variations in the calcium–phosphorus–vitamin-*D* complex. W. G. DOWNS, jun. (J. Dental Res., 1932, **12**, 363—373).—Marked alterations in dietary Ca : P produced decalcification of the teeth and jaws of rats. Addition of vitamin-*D* emphasised the histological changes when the P content of the diet was low, but aided the tissues to prevent the changes when Ca was low. CH. ABS.

Growth and calcification catalysts in animals. F. BILEK (Vestn. Československ. Akad. Zem., 1932, **8**, 363—367; Chem. Zentr., 1932, ii, 397).—Vitamin-*D* promotes calcification, but growth only to a small extent, whilst carotene in large doses markedly accelerates growth. A. A. E.

Photochemical reaction in photosynthesis. R. EMERSON and W. ARNOLD (J. Gen. Physiol., 1932, **16**, 191—205; cf. A., 1932, 548).—Cells of *Chlorella pyrenoidosa* of varying chlorophyll content were exposed to continuous and intermittent light of high intensity. With an intensity approaching that necessary for max. photosynthesis, 2480 mols. of chlorophyll are present for each mol. of CO_2 reduced for a single flash of light. The duration of a complete cycle of photochemical and Blackman (recovery) reactions is 0·02 sec. at 25°. The rate of photochemical reaction is given by $R=AIN$, where R=velocity coeff., I=light intensity, and N=no. of units available for photochemical reaction, a unit being the mechanism capable of reducing 1 mol. of CO_2. F. O. H.

Mol. wt. of phycocyan and of phycoerythrin. III. T. SVEDBERG and I. ERIKSSON (J. Amer. Chem. Soc., 1932, **54**, 3998—4010; cf. A., 1930, 233).—The sedimentation const. of *c*-phycocyan (I) determined in fresh extracts of *Aphanizomenon flos aquæ* is identical with the val. for (I) purified by crystallisation with $(NH_4)_2SO_4$. (I) therefore probably exists in the cells of the algæ with the same mol. wt., 208,000, as in the purified product. The sedimentation const. of *r*-phycoerythrin (II) in fresh extracts of *Ceramium rubrum* is identical with the val. for (II) purified with $(NH_4)_2SO_4$; native (II) is therefore probably identical with the purified product with regard to mol. wt. Phycoerythrin (III) (from *Polysiphonia urceolata*) is not quite homogeneous

but the sedimentation const., $12{\cdot}4\times10^{-13}$, mol. wt., 196,000, and p_H stability range are of the same order of magnitude as for normal (II). The sedimentation const. of the modifications of (III) from the algæ *Bornetia secundiflora* (IV), *Griffithsia furcellata* (V), and *Sebdenia monardiana* (VI) are determined; that from (VI) shows the same val. as (II) ($11{\cdot}3\times10^{-13}$), whilst the consts. for (IV) and (V) are slightly higher ($12{\cdot}1\times10^{-13}$). This deviation is probably due to inhomogeneity. The p_H stability range is the same as for (II). The light absorption of the modification from (IV) is identical with that of (II), that of (V) resembles closely (III), but that of (VI) differs considerably from that of the other modifications. A semi-quant. study of the fluorescence of the modifications did not reveal any marked difference in the wave-length of the fluorescence light but showed that the intensity is considerably lower for that from (V). From p_H 2·5 to 5·0 the sedimentation const. of (II) is $11{\cdot}3\times10^{-13}$, and the mol. wt. is 209,000. On both the alkaline and acid sides of this normal region, which includes the isoelectric point (p_H 4·85), there is a region where the sedimentation const. is $5{\cdot}8$—$5{\cdot}9\times10^{-13}$ and the mol. wt. half the normal val. These regions are connected to the normal by transition regions where the solution contains mols. of the normal and of half the normal wt. at the same time. In solutions of $p_H < 1{\cdot}5$ or $> 8{\cdot}0$, the phycocyan mol. begins to decompose and form systems heterogeneous with regard to mol. wt.

C. J. W. (*b*)

Energy transformations at surfaces. VI. Carbon dioxide assimilation. I. H. KAUTSKY, A. HIRSCH, and F. DAVIDSHOFER (Ber., 1932, **65**, [*B*], 1762—1770).—Irradiation of a green leaf which has been kept in the dark with ultra-violet or visible light causes (i) a rapid increase of fluorescence to a max., (ii) a steady decline reaching within a few min. (iii) a level which remains const. under fixed conditions. The course of alteration in the intensity of fluorescence can be repeated at will if the leaf is kept in the dark for a period corresponding with that of its irradiation. The initial, almost extinguished fluorescence of chlorophyll in (i) is ascribed to the transference of the absorbed light energy to a particular type of mol. of the assimilation system. The rapid decline is due to the rapid decrease of possibility of transference of energy, since the already excited mols. pass into a condition in which for the time being they cannot absorb energy from the fluorescing pigment. This phase is not appreciably influenced by lowering of temp. or by the presence of HCN. The phase (ii) is characterised by the gradual incidence of a catalytic–chemical reaction of assimilation which is restricted or abolished by lowering of temp. or the presence of HCN. Two changes are therefore involved, the chemical process coupled with the liberation of O and the increasing transference of absorbed light energy from the chlorophyll to a definite mol. type of the assimilation system which becomes increasingly available. Phase (iii) represents the steady state of normal assimilation under the given conditions. On the assumption that the total light energy necessary for assimilation is absorbed by the chlorophyll and transferred to the system and that this transference involves a more or less pronounced diminution of the fluorescence of chlorophyll, it is shown that O is the only type of mol. of the system to which the energy is transferred. O is therefore the collector and carrier of the energy of assimilation. H. W.

Life of plants in a closed atmosphere. J. BEAUVERIE and S. MONCHAL (Compt. rend., 1932, **195**, 897—899).—Various plants sealed in glass jars with H_2O and soil survive sometimes for 4 years. Gas pressure may rise at night by atm. and fall $\frac{1}{10}$ atm. in the day. H. D.

Effect of amino-acids on the oxygen consumption of submerged plants. G. SCHWABE (Protoplasma, 1932, **16**, 397—451).—Natural, optically active NH_2-acids increase O_2 consumption, but no relationship between this effect and the constitution of the acid was observed. The action of NH_2-acids (I) is more marked in plants of high physiological activity and having adequate nutrients. The effect of (I) is sp. and does not depend on p_H changes. Treatment of plants with (I) does not alter the R.Q. The inhibitory action of HCN on the activity of (I) resembles that on normal respiration. (I) do not affect peroxidase activity. The respiratory changes examined are ascribed partly to the actual oxidation of the (I) and partly to the action of the latter as O_2 carriers. A. G. P.

New aspects of plant nutrition. R. W. THATCHER (Science, 1932, **76**, 281—285).—Evidence is discussed for the view that in plant nutrition there is a series of phenomena (the action of small amounts of elements such as Cu, Mn, B, and Zn) and principles which are comparable with the vitamin function in animal nutrition. L. S. T.

Plant nutrition. B. V. NATH (Soc. Biol. Chem. India. Reprint, 1932, 39 pp.).—The nutritive processes in plants are discussed and their general similarity to the corresponding processes in animals is emphasised. A. G. P.

Relation of mineral nutrition to transpiration in plants. A. H. K. PETRIE (J. Counc. Sci. Ind. Res. Australia, 1932, **5**, 177—180).—The effect of NO_3' treatment in reducing the transpiration ratio of *Atriplex semibaccatum* cannot be explained in terms of reduction of the osmotic pressure of the cell sap. Other possible interpretations are discussed.

W. G. E.

Relationship between transpiration and resorption of ions [in plants]. M. GRACANIN (Compt. rend., 1932, **195**, 899—901).—Comparison of the quantities of HPO_4'' resorbed and the intensity of transpiration of plants maintained in pure solutions of $CaHPO_4$ and subjected to varying degrees of illumination shows no correlation between the two processes. H. D.

Amounts and distribution of some phosphorus and nitrogen compounds in wheat during growth. F. KNOWLES and J. E. WATKIN (J. Agric. Sci., 1932, **22**, 755—766).—The phytin- (I), lipin- (II), and inorg. P, and the protein- (III) and non-protein-N contents of the root straw and ear of wheat throughout the growing season are recorded and discussed.

Variations in the (II) and (III) constituents were similar. (I) and (III) rose and fell concurrently. A. G. P.

Growth and differentiation. III. Distribution of calcium and phosphate in tissues of *Kleinia articulata* and some other plants. D. THODAY and H. EVANS (Ann. Bot., 1932, **46**, 781—806).—Ca occurs in the stems of *K. articulata* in solution in the sap, in pith, and in patches in the inner cortex in areas sharply defined from adjoining Ca-free tissue. PO_4''' accumulation is mainly in the bundle zone. Acidity is low in the pith and high in the bundle zone. Complementary localisation of Ca and P was observed in several plants and in *Mesembryanthemum* sol. Ca and sol. oxalate occurred in separate cells. A. G. P.

Effect of [H·] on growth and geotropism. S. STRUGGER (Ber. deut. bot. Ges., 1932, **50**, 77—92).—The rate of growth of both the intact and decapitate germinal roots of *Helianthus annuus* is increased on acidification within the limits p_H 7—3. By immersion in suitable buffers curvature of the hypocotyls, indicating active membrane growth and of non-osmotic nature, can be produced. This phenomenon is reversible only in the early stages. P. G. M.

Potash requirements of the tobacco crop. P. J. ANDERSON, T. R. SWANBACK, and O. E. STREET (Connecticut [New Haven] Agric. Exp. Sta. Bull., 1932, No. 334, 137—217).—The K content of tobacco leaves is inversely related to the proportions of Ca and Mg, is increased in proportion to the amount of K applied, and is usually higher in dry than in wet seasons. Liberation of relatively unavailable K in soils is accelerated to some extent by treatment with $CaSO_4$, S, $NaNO_3$, acid fertilisers, and by the ploughing-in of cover crops. In lysimeter tests losses of K in drainage were considerable. These were increased by applications of $(NH_4)_2SO_4$ and decreased by $NaNO_3$. Org. manures had no action in this respect. The period of max. rate of intake of K by plants corresponded with the max. intake of N and max. increase in dry wt. produced. Reduced applications of K affect the quality of the leaf more than the actual yield. A. G. P.

Test on plant material for diagnosing phosphorus deficiencies. S. F. THORNTON (Indiana Agric. Exp. Sta. Bull., 1932, No. 355, 20 pp.).—Samples of stems or leaf petioles are taken from or near actively growing points of plants. 1—1·5 g. of the crushed material are treated with 10 c.c. of a reagent containing 4 g. of NH_4 molybdate dissolved in 500 c.c. of H_2O, to which are added 63 c.c. of conc. HCl and 437 c.c. of H_2O. After vigorous shaking with the reagent a small crystal of $SnCl_2$ is added. The blue coloration indicates the inorg. P in the stems. A. G. P.

Determination of the atomic weight of potassium separated from peas. V. G. CHLOPIN and M. A. PASVIK-CHLOPIN (Bull. Acad. Sci. U.S.S.R., 1932, 381—390).—Determinations of the KCl : AgCl ratio with K from peas give for the at. wt. of K 39·09+0·018, so that no accumulation of the heavy, radioactive isotope of K occurs in peas. That separation of the isotopes in living organisms does not occur is not, however, considered to be finally proved (cf. Loring and Druce, Chem. News, 1930, **140**, 34; Druce, *ibid.*, 1931, **142**, 33; Lowry, A., 1931, 141). T. H. P.

Effect of plane-polarised light on the formation of carbohydrate in leaves. R. H. DASTUR and R. D. ASANA (Ann. Bot., 1932, **46**, 879—891).—In the plants examined no significant differences were apparent in the carbohydrate content of leaves grown in polarised and in non-polarised light. A. G. P.

Role of reserve substances of the vine in the setting of fruit and in the ripening of the grapes. L. MOREAU and E. VINET (Ann. Agron., 1932, **3**, 363—374).—The development of fruit buds is largely influenced by the accumulation of sugars in the sap. Ripening is associated with a rapid initial rise in the sugar content of the grapes, followed by a further but slower increase to the period of full maturity. The rapid accumulation of sugars is derived to a large extent from the carbohydrate reserves of the main stem. A. G. P.

Seasonal changes in the composition of Stayman apple trees. I. Carbohydrates. H. R. KRAYBILL, J. T. SULLIVAN, and L. P. MILLER (Proc. Amer. Soc. Hort. Sci., 1931, **27**, 206).—Starch is max. in November; subsequently it is hydrolysed, synthesised between February and April, and again hydrolysed in April and May. CH. ABS.

Nitrogen and carbohydrate metabolism of young apple trees as affected by excessive applications of sodium nitrate. N. W. STUART (New Hampshire Agric. Exp. Sta. Tech. Bull., 1932, No. 50, 26 pp.).—In leaves from trees receiving heavy dressings of nitrates the general level of N metabolism was much higher than in those from unfertilised controls. Differences were associated with the lipin- and residual N fractions. The carbohydrate content of leaves was lower in unfertilised trees. Differences in carbohydrate metabolism were shown in the nature of the insol. reserve produced. The carbohydrate : N ratio was narrower in fertilised trees. A relationship between leaf injury and the presence of NO_3' in the leaves is suggested. A. G. P.

Æsculin changes during the breaking of buds of *Æsculus hippocastanum*. G. KLEIN and H. LINSER (Planta [Z. wiss. Biol.], 1932, **17**, 641—643; cf. A., 1932, 436).—Earlier work is confirmed in older trees and further details of variations in æsculin content of buds and bud scales are recorded. A. G. P.

Biosynthesis. IX. Plant materials. H. EMDE (Ber. Sachs. Ges. Wiss., math.-physikal. Kl., 1931, **83**, 219—237; Chem. Zentr., 1932, i, 2963).—The biochemical synthesis of cinchonine and the *Coca* alkaloids, and the plant physiological role of quinic, shikimic, protocatechuic, gallic, salicylic, and benzoic acids, are discussed. It is postulated that these alkaloids are synthesised in the plant primarily from sugars or their transformation products, and only secondarily from NH_2-acids arising from hexoses. The relation between alkaloids and essential oils as plant products is also considered. A. A. E.

Effect of manuring with blood on the colour of flowers of *Primula auricula*. A. MUSSACK (Ber. Deut. bot. Ges., 1932, **50**, 391—392).—Addition of blood manures to soil provides a stimulant to the production of carotene in flowers. A. S. P.

Physiological processes causing the loss of winter cereals under the ice crust. A. A. RICHTER and A. I. GRETSCHUSCHNIKOV (Bull. Acad. Sci. U.S.S.R., 1932, 391—408).—The formation of an ice crust results in anaerobic conditions and increases the hot-bed effect, a rise in temp. occurring under the ice layer at the expense of the sunlight traversing it. Anaerobic processes, leading to development of CO_2 and accumulation of EtOH in the tissues, proceed to a greater or smaller extent in different cereals and in their different parts, and the plant undergoes alcoholic auto-poisoning. T. H. P.

Utilisation of atmospheric nitrogen by germinating seeds of leguminous plants. III. N. VITA and R. SANDRINELLI (Bioehem. Z., 1932, **255**, 82—87; cf. A., 1932, 1180).—The amount of N absorbed by germinating seeds (peas, lupin) is usually increased by addition of dil. solutions of salts (Fe, Mn, Mg, K sulphates), but the extent of the increases varies greatly with the concn. of salt and of O_2 in the atm., the duration of the action, and the degree of illumination. It is possible that the observations give the results of several concurrent processes of different kinds. W. McC.

Oxidising power of the chondriosome and cytoplasmic sexualisation of fungi. P. JOYET-LAVERGNE (Compt. rend., 1932, **195**, 894—896).—The oxidising power of the filaments of *Pythium* is manifested by the coloration of the leuco-derivatives of methylene-, Nile-, cresyl-, and methyl-blue. In the male gamete the mitochondria have a higher oxidising power than in the female, demonstrating the sexualisation of the cytoplasm. H. D.

Bioelectric potentials in *Valonia*. Effect of substituting potassium chloride for sodium chloride in artificial sea-water. E. B. DAMON (J. Gen. Physiol., 1932, **16**, 375—395; cf. A., 1930, 965).—The p.d. across the protoplasm of *V. macrophysa* is decreased by lowering and increased by raising the concn. of KCl in the external solution. Changes of p.d. with changes of p_H of the medium indicate that K enters the cell more rapidly from alkaline than from acidified KCl-rich sea-H_2O. F. O. H.

Biology of the potato. XIII. Water cultures of potato. W. SCHROPP. **XIV. Determination of the degree of decomposition of tubers by electrometric measurements.** A. HEY. **XV. Catalase of potato tubers.** M. KLINKOWSKI (Arb. biol. Reichsanst. Land- u. Forstwirts., 1932, **20**, 49—77, 79—90, 91—99).—XIII. The effects of various nutrient solutions on the growth and nutrient intake of potatoes are recorded. Nutrients containing high proportions of Cl′ produce plants of higher H_2O content than do those having a predominance of SO_4''. The sensitivity of plants in high Cl′ nutrients to the addition of $(NH_4)_2SO_4$ is associated with the markedly increased Cl intake produced.

XIV. Relations between the reduction–oxidation potential of tubers and the degenerative process are examined.

XV. Sound potatoes in storage show a smaller decrease in catalase activity than do those undergoing decomp. In the vegetative period no relationship exists between the health condition of the plant and its catalase activity. A. G. P.

Effect of carbon dioxide content of storage atmosphere on carbohydrate transformation in certain fruits and vegetables. E. V. MILLER and C. BROOKS (J. Agric. Res., 1932, **45**, 449—459).—Storage in an atm. containing 35—47% CO_2 at $>85°$ did not result in appreciable carbohydrate transformation in sour or sweet cherries or peaches. Under similar conditions the transition of sugars in peas and sweet corn was retarded. Limiting conditions of temp., $[CO_2]$, and period of exposure necessary to avoid changes in flavour of various materials are examined. A. G. P.

Hormone and growth-promoting substance of pollen. F. LAIBACH (Ber. Deut. bot. Ges., 1932, **50**, 383—390).—Pollen hormone present in H_2O extracts of pollen from certain orchids and *Hibiscus* and the growth-promoting substance are very similar if not identical substances. A. G. P.

Chlorophyll mutants of barley. H. VON EULER, D. BURSTRÖM, H. HELLSTRÖM, and B. VON KÖHLER (Z. physiol. Chem., 1932, **212**, 53—60; cf. A., 1932, 785).—Further chlorophyll-normal and -defective mutants of barley show similar absorption curves in the ultra-violet. The chlorophyll ratio in defective and normal shoots is not paralleled by their absorption. Tyrosine, tryptophan, and Mg were determined, but marked differences were not observed. J. H. B.

Constituents of the northern mistletoe, *Viscum album*, L. J. A. MÜLLER (Arch. Pharm., 1932, **270**, 449—476).—Details are given for the isolation of AcOH, Mg *dl*-lactate, *d*-mannitol, choline, propionylcholine (I) ("*reineckate*"), and acetylcholine (?) from the expressed juice. (I) is responsible for the depressor action of the juice. H. B.

Rhatany catechin. M. NIERENSTEIN (J.C.S., 1932, 2809).—The presence of *d*- and *dl*-gambircatechin in "rhatany root" is proved by extraction with $CHCl_3$, fractionation by Et_2O and aq. AcOH, and conversion into Ac_5 derivatives. H. A. P.

Colouring matter of acacia wood. K. BRASS and H. KRANZ (Annalen, 1932, **499**, 175—187).—Extraction of the wood of *Gleditschia monosperma* with $COMe_2$ gives *5′-hydroxyfisetin* [7 : 3′ : 4′ : 5′-*tetrahydroxyflavonol*] (I), which is obtained anhyd. (green) and +1 (bronze), 1·5 (brick-red), and $2H_2O$ (yellow); the *hydrochloride*, Ac_5 derivative, m.p. 224°, and *Me- ether* (II), m.p. 148°, are prepared. KOH fusion of (I) affords *m*-$C_6H_4(OH)_2$ and β-resorcylic acid, whilst (II) is degraded by MeOH–KOH in N_2 to 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}CO_2H$ and 2-hydroxy-ω : 4-dimethoxyacetophenone. 3-Oximino-7 : 3′ · 4′ : 5′-tetramethoxyflavanone (Dean and Nierenstein, A., 1925, i, 951) and 10% H_2SO_4 in AcOH give 7 : 3′ : 4′ : 5′-tetramethoxyflavonol, m.p. 194°, methylated (Me_2SO_4) to (II). The $COMe_2$ extract of the wood of *Robinia pseudacacia* contains (probably)

a glucoside of (I) (cf. Schmid and Pietsch, A., 1931, 738) (acetylation gives the above penta-acetate) and a substance, decomp. 230—240° (acetate, m.p. 141°). H. B.

Globulins of some *Cucurbitaceæ* seeds. R. Hirohata (Z. physiol. Chem., 1932, **212**, 1—6).—Cryst. globulins were isolated from species representing seven genera. The preps. showed great similarity in chemical properties, but by means of the precipitin reaction differences were observed. The genera *Benincasa, Citrullus, Cucumis, Lagenaria,* and *Cucurbita* are very similar. *Trichosanthes* and *Luffa* differ from these and from one another. *Momordica* gave no cryst. globulin. *Citrullus* globulin has a high feeding val. J. H. B.

Chemical examination of the seeds of *Abrus precatorius*, L. I. N. Ghatak and R. Kaul (J. Indian Chem. Soc., 1932, **9**, 383—387).—Extraction of the powdered kernels (scarlet variety of seeds) with light petroleum gives an oil, $[\alpha]_D^{35}$ +0·39°, d^{25} 0·9139, n^{25} 1·4662, acid val. 2·44, sap. val. 191·7, Hehner val. 88·06, Ac val. 0, I val. 95·1, unsaponifiable matter 1·68%. Further extraction with EtOH gives *abrine*, $C_{12}H_{14}O_2N_2$, m.p. 295°, and *abralin*, $C_{13}H_{14}O_7$, amorphous, m.p. 105°, $[\alpha]_D^{35}$ —27·37° in H_2O, in addition to a considerable amount of reducing sugars. H. B.

Presence of sucrose in the branches and leaves of *Euonymus europæus*. F. D. Baton (Compt. rend., 1932, **195**, 823—825).—The branches and leaves contain sucrose and dulcitol. W. O. K.

Alcohol and sugar contents of olive press-water. II. A. Mangini (Annali Chim. Appl., 1932, **22**, 658—662; cf. A., 1931, 1199).—Atm. pptn. and *Mosca olearia* have no influence on the sugar content of olives and hence on the sugar and EtOH contents of the H_2O expressed with the oil, but the presence of mannitol in the olives has some effect in this connexion. T. H. P.

Determination of sugar in plant extracts (including glucoside sugars). G. Kerstan (Planta [Z. wiss. Biol.], 1932, **17**, 491—492).—Glucosides (I) and maltose are removed from plant extracts by adsorption on charcoal, and hexoses are determined in the filtrate. In another portion of extract (I) are hydrolysed by emulsin and after treatment with charcoal glucoside sugars are recorded by the increased reducing power of the filtrate. If large proportions of charcoal are used, other sugars (glucose, sucrose) may be partly adsorbed. Adsorbed maltose, but not (I), can be removed from charcoal by washing with Et_2O (cf. Lehmann, B., 1931, 1038). A. G. P.

Determination of pentosans in vegetable materials by Tollens' method. A. P. Zakoshchikov, V. T. Ivanova, and A. Kurennova (J. Appl. Chem., Russia, 1932, **5**, 235—245).—The method is untrustworthy. Ch. Abs.

Simple sugars and polysaccharides in hemp stems. E. Parisi (Annali Chim. Appl., 1932, **22**, 555—560).—From the powdered material first extracted with warm H_2O, then treated with sulphite solution (4·35% SO_2 and 0·62% CaO), and finally boiled with 6% aq. NaOH, were obtained glucose, fructose, and hemicelluloses which on hydrolysis produce xylose, glucose, and a xylan. From the residue cellulose was obtained. O. F. L.

Nature and composition of the mucilage of the seed of white mustard (*Brassica alba*). K. Bailey and F. W. Norris (Biochem. J., 1932, **26**, 1609—1623).—The mucilage is a complex of cellulose and acid polysaccharides. The former can be readily separated by warming with dil. H_2SO_4. The addition of aq. $Ba(OH)_2$ to the mucilage solution forms a gel and also a sol. fraction composed of rhamnose, arabinose, galactose, and galacturonic acid. By the action of 4% NaOH the gel is further separated into cellulose and a fraction composed of arabinose, galactose, galacturonic acid, and glycuronic acid. The acid polysaccharides contain OMe groups in other linking. Aldobionic acids, probably rhamnose- and galactose-galacturonic acids are present in the mucilage. A peroxidase system is present in the cells close to the mucilage-secreting cells. S. S. Z.

Biochemical properties and difference in fermentation of various kinds of molasses. W. Braun and M. Kotschopoulos (Biochem. Z., 1932, **254**, 398—409).—The view that differences in fermentability of molasses are due to differences in protein content is not upheld, the inability to ferment being much more the result of the presence of inhibitors than lack of fermentable material. Pptn. by $Fe(OH)_3$ does not differentiate between proteins, but $CCl_3{\cdot}CO_2H$ ppts. only a particular protein group and this group is qualitatively very different for different samples of molasses. The greater the melanin-N, the poorer is the fermentation of the molasses. In a well-fermenting mash, the protein pptd. by $CCl_3{\cdot}CO_2H$ decreases and almost disappears, whereas in a feebly fermenting mash it tends to increase. P. W. C.

Analysis of *Cicer arietinum*, var. *album* and *fuscum*. A. Rius y Miró and F. de Bustinza (Anal. Fís. Quim., 1932, **30**, 673—678).—The results accord generally with those in the literature, but the phytin content is high (0·88% for *album*, 0·995% for *fuscum*). H. F. G.

Organic acids in the fruits of Ceylon olives (*Elæocarpus serratus*, Lin.). R. Yamamoto, Y. Osima, and T. Goma (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1932, **19**, 132—133).—The pulp of the Ceylon olive contains H_2O 85·73%, total acid (as citric acid) 4·37%, reducing sugar (as glucose) 1·93%, non-reducing sugar (as sucrose) 0·98%, ash 0·62%, crude fibre 1·8%, crude fat 0·23%, and N 0·05%. Citric, mucic, and tartaric (a trace) acids were identified. The fresh juice gives Bezssonoff's vitamin-*C* reaction and 4 c.c. are equiv. to 3 c.c. of lemon juice when fed to guinea-pigs. R. S. C.

Wax-like coating of apples. K. S. Markley, S. B. Hendricks, and C. E. Sando (J. Biol. Chem., 1932, **98**, 103—107).—The petroleum extract of apple cuticle does not contain a ketone in isolable amounts (cf. A., 1923, i, 990), the principal hydrocarbon being *n*-nonacosane, m.p. 65·1°, whilst the *sec.* alcohol present is nonacosan-κ-ol (A., 1932, 203) and not heptacosan-ξ-ol. F. O. H.

Determination of the sterol contents of cereals and legumes. E. KEDING (Biochem. Z., 1932, **254**, 374—380).—A table summarises the sterol contents of a no. of cereals before and after hydrolysis. Pre-treatment with alkali considerably increases the yield of sterol. P. W. C.

Alkaloid content of various organs of *Atropa belladonna*. A. TORRICELLI (Pharm. Acta Helv., 1932, **7**, 20—24; Chem. Zentr., 1932, i, 3452).—The leaves and unripe berries have the highest alkaloid content (0·97—0·89%), but the stem, even when completely lignified, contains noteworthy quantities. A. A. E.

Alkaloids of fumaraceous plants. I. *Dicentra canadensis*, Walp. II. *Dicentra cucullaria* (L.), Bernh. R. H. F. MANSKE (Canad. J. Res., 1932, **7**, 258—264, 265—268).—I. The tubers of *D. canadensis* contain protopine, bulbocapnine, corydine [methiodide, decomp. 228—230° (corr.) after sintering at 220°], *iso*corydine, at least one other alkaloid, and an orange *substance*, $C_{32}H_{29}O_5(OMe)_3(NCO)_2$, m.p. 237—238° (corr.). Dicentrine is absent. The separation of the phenolic bases is modified. The genetic significance of the results is discussed.

II. The tubers of *D. cucullaria* contain sucrose (34·8%), protopine, cryptopine, and two phenolic *alkaloids*, α-, $C_{20}H_{17}O_6N$ (OMe absent), m.p. 177° (corr.), and β-, $C_{20}H_{23}O_6N$, $C_{20}H_{23}O_7N$, or $C_{19}H_{19}O_5N$, m.p. 215° (corr.). R. S. C.

New active principle in *Bryonia dioica*. J. CHAZE (Compt. rend., 1932, **195**, 825—827).—An alkaloid-like principle has been detected in the superficial cells of various parts of *B. dioica*. It is located in the cell vacuoles. W. O. K.

Microchemical reactions in plant fibres. V. M. GLEZIN (Farm. Zhur., 1932, 65—67).—Colour reactions of colchicine, aconitine, hyoscyamine, strychnine, and certain glucosides with H_2SO_4, vanillin, HNO_3, and furfuraldehyde are tabulated. CH. ABS.

Feulgen's nucleal reaction with plants. F. BOAS and O. BIECHELE (Biochem. Z., 1932, **254**, 467—474).—The nucleal reaction with many plants proves very suitable for staining cell nuclei and chromosomes. P. W. C.

The carboxylase system in green plants. K. WETZEL (Planta [Z. wiss. Biol.], 1932, **17**, 1—14).—The reduced carboxylase activity of finely-powdered leaves is not due to carboxylase deficiency in the green tissue (Kobel and Scheuer, A., 1930, 258), but to the injurious effects of grinding on the co-zymase and co-carboxylase or on the carboxylase itself. Addition of yeast extract increases CO_2 production both from hexosediphosphate and K pyruvate, its action being to favour the normal alcoholic rather than the lactic fermentation. A. G. P.

Enzymes of the coffee plant. E. HERNDLHOFER (Biochem. Z., 1932, **255**, 230—246).—The enzyme (lipase, protease, amylase, catalase, peroxidase, oxygenase) content of the coffee plant and of its parts at various stages of development (seed to 30-years-old trees) has been examined. The enzymes are absent from or present only in small amounts in the resting seeds, but increase in amount, often greatly, during germination. In the young plants there are great variations in the presence (or absence) and distribution of the various enzymes throughout the various parts of the plant, the functions of both enzyme and part of plant being factors involved. At all stages the leaves have a low content of the enzymes, some of which are never found in them. In old plants the young branches have high enzyme content, but the young fruit is poor in enzymes. W. McC.

Localisation of tyrosinase in the sugar beet. E. W. SCHMIDT (Z. Ver. deut. Zucker-Ind., 1932, **82**, 564—569).—The method consists in treating the parts of the plant with a dil. solution of tyrosine (*e.g.*, 0·1%), and observing the colour change. J. P. O.

Isolation of glutamine from an enzymic digest of gliadin. M. DAMODARAN, G. JAABACK, and A. C. CHIBNALL (Biochem. J., 1932, **26**, 1704—1713).—Gliadin was digested in succession with pepsin, trypsin, and yeast-dipeptidase and glutamine obtained in successive crops of crystals from the decomposed phosphotungstic acid ppt. of the digest. Glutamine is unstable in aq. solution. S. S. Z.

Hydrocyanic acid in *Glyceria aquatica*, Wahlb. (*G. spectabilis*, M. and K.). P. GUERIN (Compt. rend., 1932, **195**, 1036—1037).—In April the leaves, creeping stem, and fine roots contain 1·053, >0·2, and 0·162 g. of glucosidic HCN per kg., respectively. The leaf figure falls to 0·6 in May and 0·348 in June, when the spikelets of the panicle contain 0·66 g. per kg. The HCN content of September shoots is 0·35 g. per kg. A. C.

Calcium content of cabbage. S. J. COWELL (Biochem. J., 1932, **26**, 1422—1423).—The Ca content of the outermost leaves in summer may be from 20 to 30 times as great as that of the inner leaves. S. S. Z.

Occurrence of calcium tartrate. J. GICKLHORN (Biochem. Z., 1932, **254**, 459—466).—The mucous sap obtained at old internodal cross-sections of the stem of *Tradescentia zebrina*, Lont., on drying yields crystals of Ca tartrate. The occurrence is sp., and of the types examined only the above and *T. purpurea* gave these crystals. The cell press-juices of the medullary, cortical, and epidermal cells do not give the crystals. P. W. C.

Silicic acid content of bread. R. BERG (Biochem. Z., 1932, **254**, 329—331).—Tables summarise the contents of sol. silicic acid in rye grain and meal and in various samples of rye bread. P. W. C.

Boron as a physiologically critical element. T. SCHMUCKER (Naturwiss., 1932, **20**, 839).—The development of the pollen grains of the tropical water-lily does not occur in artificial medium in the absence of small quantities of H_3BO_3. 0·01 mg. per 1 c.c. of medium was highly active, whilst 0·0005 mg. had a marked effect. W. O. K.

Twisted trees—real and mineral. M. COPISAROW (Nature, 1932, **130**, 541—542).—The genetic role of mineral matter and its substitution is discussed in relation to tree-twisting. This appears to be due primarily to local soil peculiarities which in the course of time modify the structural constituents of plants. L. S. T.

Zinc in fungi. M. Mousseron and P. Fauroux (Bull. Soc. Chim. biol., 1932, **14**, 1235—1239).—The Zn contents of several species of fungus determined by the micro-method (A., 1931, 1260) are recorded. These increase with the nucleolytic power as measured by determining the PO_4''' liberated from Na nucleinate by the fungus extract. With the exception of *Hygrophorus conicus*, which contains an agglutinin, fungi containing >100 mg. of Zn per kg. (dry) are hæmolytic. The fungus extracts also hydrolyse Na α-glycerophosphate and phytin. A. C.

Microcolorimetric determination of iron in small amounts of plant ash. W. Scholz (Z. Pflanz. Dung., 1932, **26A**, 212—216).—The NH_4CNS reaction is utilised for quantities of approx. 0·01 mg. Fe in 1 c.c. A. G. P.

Determination of the inorganic nitrogen in the maize plant by the expressed sap method. R. W. Gerdel (Plant Physiol., 1932, **7**, 517—526).—The total inorg. N in the sap can be determined satisfactorily by the method of Sessions and Shive (A., 1929, 960). Sap samples may be preserved for a time by addition of PhMe or by storage at −20°. A. G. P.

Antigen-antibody reactions in plants. O. Moritz (Ber. Deut. bot. Ges., 1932, **50**, 100—106).—*Vicia faba* plants grown in sand and watered with 2—3% ovalbumin solution for 2 days before an experiment are able to produce typical anaphylactic reactions with the isolated uterus of a guinea-pig previously sensitised to ovalbumin. The general principles of immunity reactions applied to plants are discussed. P. G. M.

Effect on the geotropic reaction of roots of *Zea mais* of pretreatment with fluorescein dyes and salts. D. Mildebrath (Bot. Archiv, 1932, **34**, 161—215).—The geotropic reaction period of seedling maize roots was increased and the extent of the reaction decreased by dipping in solutions of the dyes. Growth rates were not, however, retarded. Comparative effects of fluorescein, cosin, erythrosin, and their salts and of various inorg. salts indicate that cations, anions, and mol. compounds have each a sp. action. A. G. P.

Photodynamic action of eosin on the root tips of *Vicia faba*. W. Prescher (Planta [Z. wiss. Biol.], 1932, **17**, 461—488).—The inhibitory action of eosin on root elongation increases with the concn. of the dye used, with the period of action and light intensity. A. G. P.

Influence of narcotics, mechanical agents, and light on the permeability of protoplasm. W. W. Lepeschkin (Amer. J. Bot., 1932, **19**, 568—580).—Narcotics (*e.g.*, $CHCl_3$) increase or decrease the permeability of protoplasm to H_2O-sol. substances according to whether the solubility of these substances in the narcotic is > or < that in H_2O. A. G. P.

Toxic action. IV. Relative toxicities of isomeric alcohols of the aliphatic series. W. Stiles and M. L. L. Stirk. **V. Toxicity of aliphatic aldehydes towards potato tuber.** K. W. Dent (Protoplasma, 1932, **16**, 79—101, 357—368).—IV. The toxicity of isomeric alcohols, as determined by the rate of exosmosis of electrolytes from cells of potato tubers, was in the order: normal>other primary>*sec.*>*tert.* alcohols. In general the change in toxicity resulting from the substitution of Me for H in aliphatic alcohols depends on the relative positions of the substituted and the OH group; higher toxicity is associated with substitution furthest removed from the OH group and *vice versa*.

V. Using the exosmosis method (Stiles and Stirk, A., 1932, 206) the relative toxicity of aldehydes is shown to be: CH_2O, 1; MeCHO, 0·64; EtCHO, 1·28; PrCHO, 1·54; valeraldehyde, 7·37. Pr$^{\beta}$CHO and *iso*-valeraldehyde are more toxic than the corresponding normal isomerides. CH_2O is much more toxic than MeOH. A. G. P.

Plant tumours. I. Nitrogen balance. II. [H·]. G. Klein and E. Keyssner. III. Catalase content of normal and tumour tissue. G. Klein and W. Ziese (Biochem. Z., 1932, **254**, 251—255, 256—263, 264—285).—I. In all the plants investigated, the protein-N of the tumour tissue produced by *Bacterium tumefaciens* is many times that of normal tissue and the sol. inorg. and org. N in tumour tissue is higher in balsam, geranium, and tomato, but lower in beet, than in normal tissue.

II. The p_H, acid, and ash contents of normal and tumour tissues are recorded. The results show that tumour tissue is more alkaline than normal tissue.

III. The catalase content of the tumour tissue of various types of beetroot is much higher than of normal tissue. The increased activity is not due to the presence of a non-enzymic activator. The catalase content is not directly related to the particular strain of organisms used. P. W. C.

Use of an extract of the seeds of *Echinocystis lobata* for the detection of citric acid. T. Broman (Skand. Arch. Physiol., 1932, **64**, 171—176; Chem. Zentr., 1932, ii, 412).—The seeds can replace those of *Cucumis sativa*. The reaction is also given by hexosediphosphoric and adenosinetriphosphoric acids.

Diphenylbenzidine as a test for nitrates and nitrites. H. Stromberg.—See A., 1932, 1221.

Spectrographic microanalysis. Histological detection of certain elements. A. Morel and A. Policard (Bull. Soc. chim., 1932, [iv], **51**, 1125—1131).—A method is described for the direct spectrographic detection of elements in microscopic pieces of tissue, preliminary ignition of the material being unnecessary. D. R. D.

Determination of iodine according to Kuhn and Loeser. G. Barkan and G. Kingisepp (Arch. exp. Path. Pharm., 1932, **168**, 228—231).—The method of Kuhn and Loeser (cf. A., 1928, 1064) is not always trustworthy for the determination of organically combined I and the empirical factor introduced by them in calculating the results is unnecessary. W. O. K.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1933.

General, Physical, and Inorganic Chemistry.

Resonance spectrum of hydrogen. K. R. Rao and J. S. Badami (Proc. Roy. Soc., 1932, **A**, **138**, 540—549; cf. A., 1931, 1343).—The anomalous effect previously reported (*loc. cit.*) is considered to be caused by a transfer of energy by collisions of the second kind between As atoms in the metastable state $4p^{2}{}^{1}S_{0}$ of As II and atoms of H. A new type of impact is thus demonstrated, for the energies of ionisation and excitation of one atom are simultaneously transferred to another atom by a single act of collision. L. L. B.

Rotational uncoupling, with application to the singlet hydrogen bands. P. M. Davidson (Proc. Roy. Soc., 1932, **A**, **138**, 580—593).—Theoretical. The theory of rotational uncoupling is applied to the *nd'* bands of H_2, and found to give fairly good results for the levels and the intensities in the bands. L. L. B.

Photographic elementary process for lithium hydride. F. Bach and K. F. Bonhoeffer (Naturwiss., 1932, **20**, 940).—The absorption spectrum of LiH shows a sharp absorption max. at 2517 ± 2 Å., which corresponds with the photographic elementary process for this substance, the electron of the H^- ion being transferred to the Li^+ ion and giving rise to neutral atoms of H and Li. A. J. M.

Structure of β-nitrogen and the different phosphorescing powers of the two forms of nitrogen. L. Vegard (Z. Physik, 1932, **79**, 471—491).—In the low-temp. α-N_2 the mol. axes behave as if "frozen," whereas in the β-form they appear to precess or rotate; assuming phosphorescent bands due to a metastable state, this explains their absence from the β-modification. A. B. D. C.

Absorption measurements and transition probabilities for the *A* (0,0) and *B* (0,1) bands of oxygen. W. H. J. Childs (Phil. Mag., 1932, [vii], **14**, 1049—1060).—The ratio of the vibrational transition probabilities $0\longrightarrow0$, $0\longrightarrow1$, determined from the relative intensities of the *A* and *B* atm. O_2 bands, is 1 : 0·081. The total absorption is proportional to the square root of the no. of absorbing mols. H. J. E.

Continuous absorption of oxygen at 1450 A. E. C. G. Stueckelberg (Physical Rev., 1932, [ii], **42**, 518—524).—Mathematical. The explanation in the term diagram of the mol. of the measurements of Ladenburg is compared with the corresponding matrix elements. N. M. B.

Displacements and their significance in (*PP*)-combinations of the sodium arc spectrum. H. Bartels (Z. Physik, 1932, **79**, 345—369).—18 members of (*PP*)-combinations were observed in the Na arc. Displacements from calc. positions are explained as a quadratic Stark effect. A. B. D. C.

Spectra of Na IV, Mg V, Al VI, Mg III, and Al IV in the extreme ultra-violet. J. Soderqvist (Z. Physik, 1932, **79**, 634—641). A. B. D. C.

Hyperfine structure of the spectra of sodium, mercury, and lead. Origin of the intensity variation of hyperfine structure components. K. Murakawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **20**, 1—12).—Data are given for the lines λ 3302·34, 3302·94, 5889·96, and 5895·93 of Na, indicating a nuclear moment of 1/2 in opposition to that given by band spectra; for λ 5790·66, 3663·28, and 3131·84 of Hg, and for λ 4057·83, 3572·74, and 4340·43 of Pb. Intensity variation is due to uneven self-absorption of hyperfine structure components. N. M. B.

Calculation of the terms of the optical spectrum of an atom with one series electron. J. McDougall (Proc. Roy. Soc., 1932, **A**, **138**, 550—579).—Mathematical. Hartree's method for determining energies of optical terms (A., 1928, 216) gives good vals. for the *X*-ray levels, but not for the optical terms; the discrepancy is attributed to the polarisation of the core by the series electron. Slater's approximation to the many-body problem (A., 1930, 126) is used to obtain more accurate expressions for the terms, and calculations have been carried out for 12 optical terms of Si^{+3}. L. L. B.

Pole effect of iron. (Frl.) M. Adam (Ann. Physik, 1932, [v], **15**, 568—612).—The Stark and pole effects of Fe have been studied. The relationships between the pole effect and pressure, inner quantum no., Stark effect, and the dependence of pole effect on the series character of individual multiplets are discussed. W. R. A.

First spark spectrum of tellurium. S. C. Deb and H. B. Mohanti (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 26—32).—About 90 lines of the first spark spectrum of Te in the wave-length range 2600—7200 Å. have been measured and classified. J. W. S.

Hyperfine structure and isotopes. B. Venkatesachar (Current Sci., 1932, **1**, 10).—Unexplained lines in the fine structure of CdI lines excited by pass-

age through a Hg arc were observed. The line 5086 Å. has a satellite at −0·026 Å., which is a doublet of separation 0·012 Å., indicating the presence of isotopes in small quantities. CH. ABS.

Isotope effect in the spectrum of cadmium hydride. E. SVENSSON (Nature, 1933, **131**, 28).—Components belonging to Cd^{118} and Cd^{108} have been detected in addition to those for Cd^{114}, Cd^{112}, Cd^{110}, and Cd^{116}. Indications of Cd^{111} may have been obtained. Peculiarities of intensity distribution among the isotope components are discussed. L. S. T.

Zeeman effect of " forced " dipole lines. C. J. BAKKER and E. SEGRÈ (Z. Physik, 1932, **79**, 655—660).—An investigation of the Zeeman effect in the forbidden Hg line at 3680 Å. confirms the theory of forced dipole radiation. A. B. D. C.

Hyperfine structure of arc lines in vacuum of bismuth in the visible and ultra-violet regions. W. MOHAMMAD and P. N. SHARMA (Phil. Mag., 1932, [vii], **14**, 1143—1149; cf. this vol., 2).—Term schemes for levels in Bi are given. H. J. E.

Pressure broadening and displacement of spectral lines. M. KULP (Z. Physik, 1932, **79**, 495—510).—Line displacement in absorption and emission is associated with a const. density of gas, and line width with fluctuations in density. Stark effect and multiplet lines are discussed. A. B. D. C.

Spectrum of cosmic radiation. A. S. SKAPSKI (Nature, 1932, **130**, 893).—A correction (cf. A., 1932, 1187). L. S. T.

Spectral light zones in front of glow discharge cathodes. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, **79**, 563—565).—The light zones previously reported have been photographed (cf. A., 1932, 552). A. B. D. C.

Process of space quantisation. R. FRISCH, T. E. PHIPPS, E. SEGRÈ, and O. STERN (Nature, 1932, **130**, 892—893).—Results for K are described. L. S. T.

Optical investigations of discharge by condensed spark in low-pressure gases. N. RYDE (Z. Physik, 1932, **79**, 626—633).—Intensity distribution and displacement of spectral lines were used to determine the field at various points of the discharge. A. B. D. C.

Black-body radiator of electrically heated carbon. T. N. PANAY (Compt. rend., 1932, **195**, 1256—1258).—An arrangement is described whereby the radiation issuing through a hole from the interior of a hollow C cylinder heated electrically to about 2400° can be observed. C. A. S.

Inversion measurements with spectral lines for estimation of total absorption and relative numbers in excited atomic states. H. KOHN (Physikal. Z., 1932, **33**, 957—963).—When a continuous spectrum is passed through a gas which absorbs and emits selectively, certain lines are removed from the continuous spectrum and in the limit they disappear. This " inversion " can be made use of to calculate total absorption and other data of various energy levels. A. J. M.

Fine structure of $K\alpha$ of carbon. W. MORAND and A. HAUTOT (Compt. rend., 1932, **195**, 1070—1071).—$K\alpha$ of C consists of two lines 0·6 Å. apart, as required by theory, that of longer λ being the stronger (cf. A., 1929, 366). C. A. S.

$K\alpha_1\alpha_2$ doublet of chlorine in different compounds. O. LUNDQUIST (Naturwiss., 1932, **20**, 905—906; cf. A., 1932, 1072).—The displacement of the $K\alpha_1\alpha_2$ lines of Cl_2 by combination in NaCl, $NaClO_3$, and $NaClO_4$ has been investigated. There is displacement towards the shorter waves, greatest for $NaClO_4$. A. J. M.

***K*-Absorption edges of nickel, copper, zinc, and their compounds.** M. ISHINO and K. KOJIMA (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 293—300).—The structures of the absorption edges for the pure metals differ from those of their respective compounds, and appear to be more closely related to the crystal forms of the substances. J. W. S.

Modification of *X*-rays by passage through matter. S. BHARGAVA and J. B. MUKHERJEE (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 48—53; cf. A., 1931, 277).—With Cu *K* radiation through six sheets of black paper 1 mm. thick a satellite is observed corresponding with the modification by C expected, analogous to the Raman effect for visible radiation. A similar modified line has been observed using Ag *K* radiation and a Ni film 0·04 mm. thick. J. W. S.

Diffraction of cathode rays by single crystals. III. Simultaneous reflexion. K. SHINOHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **20**, 40—51; cf. A., 1932, 979).—Theoretical. Additional lines, due to the simultaneous reflexion of cathode rays from two net-planes, in the diffraction patterns of electrons are investigated. N. M. B.

Multiple Compton effect. H. HULUBEI (Compt. rend., 1932, **195**, 1249—1251).—Theory requires that in addition to the line caused by the normal (single) Compton effect there should be bands resulting from multiple application thereof. This has been confirmed by means of Mo *K* radiation on paraffin and of Rh *K* radiation on Li, when bands with max. at 785 and 700·68 X, respectively, are produced, the lines resulting from the ordinary effect due to $K\beta$ being at 656·5 and 570 X, respectively ($\theta=92°$). C. A. S.

Intensity measurement of *X*-radiation by means of enumeration of light quanta. V. LOECK (Ann. Physik, 1932, [v], **15**, 527—544). W. R. A.

Corrections for *X*-ray spectrometers. H. SEEMANN (Z. Physik, 1932, **79**, 661—667).—Corrections are given for calculations of the zero point, the inclination of the crystal surface to the photographic plate, and interpolation of a line between two known lines. A. B. D. C.

Absorption of short electric waves in ionised gases; an attempt to detect the long-wave radiation of hydrogen atoms. O. BETZ (Ann. Physik, 1932, [v], **15**, 321—344).—The absorption of electric waves (3—30 cm.) by ionised H, O, and N has been studied. H shows 3 regions of absorption at 3, 9, and 28 cm. corresponding, respectively, with the transitions

$2p_1-2s$, $3d_2-3p_2$ or $2p_1-2s$, and $3d_1-3p_1$. O and N show no characteristic absorption. W. R. A.

Photo-electric quantum counters for visible and ultra-violet light. I. G. L. LOCHER (Physical Rev., 1932, [ii], **42**, 525—546).—The principles of the photo-electric cell and Geiger–Müller tube counter are combined to give a means of measuring faint light in the range 900—7500 Å., and sensitive to photo-currents of 0·05 electron per sec., by direct electron counting. For ultra-violet light the most sensitive photo-electric surface was I on Sc. Surfaces sensitive to visible light were made by coating Cu cathodes with fused NaCN, and with amalgams of Na, K, Cs, Sr, and Na–K, and forming by reduction thin films of the respective hydrides by intense H^+ bombardment. The most sensitive were KH–Hg. Very thin films of 30 org. dyes and photographic sensitisers coated on the Zn cathode of a counter shifted the photo-electric threshold towards the ultra-violet and increased the sensitivity of the surface. By introducing $NPhEt_2$ in the vicinity of the W cathode and reversing the field direction the sensitivity was increased 25 times; gases with high min. ionisation potentials gave the best results. Results are illustrated for various light sources. N. M. B.

Electronic ionisation at low and high pressures. K. MASCH (Z. Physik, 1932, **79**, 672—675).—The ionisation coeff. is determined for N_2, O_2, and air at pressures between 20 and 1077 mm. Hg, and at different field intensities. A. B. D. C.

Unifying relation for intensity of ionisation in gases. W. KOLHORSTER (Z. Physik, 1932, **79**, 682—683).—Earlier work (Naturwiss., 1919, **7**, 412) is extended to intensity of ionisation at various temp. and pressures, and with different gases. A. B. D. C.

Transfer of energy between molecules during collisions: quenching of mercury resonance radiation by admixed thallium vapour. O. S. DUFFENDACK (Physical Rev., 1931, [ii], **37**, 107).—At 0·8 mm. and 750° the radius of the excited Hg atom has an apparent val. 30 times the normal kinetic theory radius. He added to the Hg–Tl mixture gives a radius little greater than normal at 0·001 mm. and 750°. N_2 instead of He gives a slightly larger radius. The differences are attributed to differences in the concn. of excited Hg atoms in the $^3P_1$ and $^3P_0$ states. L. S. T.

Fraction of the current traversing a low-potential arc carried by positive ions. A. GEHRTS and H. VATTER (Z. Physik, 1932, **79**, 421—435).—At low currents only 0·5% is carried by positive ions from a glowing cathode. Increase of the current lowers the temp. of the cathode until a limiting current is reached, when the cathode temp. rises with increasing current; 5% is then carried by positive ions. A. B. D. C.

Method for the production of slow canal rays. W. REUSSE (Ann. Physik, 1932, [v], **15**, 252—255). W. R. A.

Energy loss of slow canal rays by passage through a solid body. W. REUSSE (Ann. Physik, 1932, [v], **15**, 256—258).—The method of measuring energy loss and the dependence of energy loss on the linear velocity are discussed. W. R. A.

Emission of positive ions from heated metals. LEE. L. BARNES (Physical Rev., 1932, [ii], **42**, 487—491).—In addition to the emission of singly-charged atoms of the alkali metals by Fe, Ni, Cu, Rh, Nb, Pt, U, and Th, the five first named emit singly-charged atoms of their own metals. N. M. B.

Temperature variation of the positive-ion emission from molybdenum. LEE. L. BARNES (Physical Rev., 1932, [ii], **42**, 492—497).—Vals. for the positive-ion work function and the reflexion coeff. for Mo ions were in better agreement than those of Smith (cf. A., 1930, 514) with the latter's theory of positive-ion emission. N. M. B.

Non-existence of ion mobility spectrum in air. R. N. VARNEY (Physical Rev., 1932, [ii], **42**, 547—555; cf. Loeb, A., 1932, 4).—New experimental methods indicate the absence of a spectrum in relatively clean air, and its appearance after prolonged radiation, or in presence of impurities. N. M. B.

Accommodation coefficient of gaseous ions at cathodes. K. T. COMPTON (Proc. Nat. Acad. Sci., 1932, **18**, 705—711; cf. A., 1931, 780).—Available data are reviewed and interpreted. The theory of pressures on a cathode is confirmed by measurements on a Mo cathode in ionised He. N. M. B.

Influence of the angular distribution of scattered electrons on the measurement of effective cross-sections. R. KOLLATH (Ann. Physik, 1932, [v], **15**, 485—515).—Theoretical. W. R. A.

Inelastic collisions of fast electrons. O. KLEMPERER (Ann. Physik, 1932, [v], **15**, 361—394). W. R. A.

Polarisation of electrons after two scatterings through 90°. E. RUPP (Z. Physik, 1932, **79**, 642—654).—Electrons of 130 kv. showed unsymmetrical reflexion of 3—4%, and those of 250 kv. showed 9—10%. A. B. D. C.

Electron microscope. M. KNOLL and E. RUSKA (Z. Physik, 1932, **79**, 699).—An acknowledgment (cf. A., 1932, 1184). A. B. D. C.

Behaviour of electrons in nitrous oxide. V. A. BAILEY and J. B. RUDD (Phil. Mag., 1932, [vii], **14**, 1033—1046; cf. A., 1930, 1081; 1932, 559).—A peak occurs in the λ (fractional energy loss on collision of an electron with N_2O)–u (electron velocity) curve at $u=3\times10^7$ cm. per sec. This energy corresponds with the strongest infra-red absorption band of N_2O. There is a smaller peak at $u=7\times10^7$ cm. per sec. H. J. E.

Determination of energy states of metal electrons from optical constants. H. FROHLICH (Naturwiss., 1932, **20**, 906).—The dependence of the optical consts. of a metal on frequency provides a method of finding the energy states of the electrons. The quantity $nk\nu^2$, where n is refractive index, k absorption coeff., and ν frequency, can be obtained from a study of the absorption spectrum. This determination of the intensity of absorption bands indicates that the behaviour of the electrons of Cu, Ag, and Au differs considerably from that of free electrons. A. J. M.

At. wt. of lead from cyrtolite. G. P. BAXTER and C. M. ALTER (Science, 1932, **76**, 524—525).—Four determinations of the at. wt. of Pb from cyrtolite (Bedford, N.Y.) gave an average val. of 205·924 from the ratio $PbCl_2$: 2Ag (Ag 107·88, Cl 35·457). Comparative determinations with common Pb and Pb from Swedish kolm gave 207·211 and 206·012, respectively. Cyrtolite lead is thus nearly, if not quite, free from common Pb, and the Pb–U ratio found by Muenen can be used to estimate the age of this mineral. The low val. is difficult to reconcile with Aston's isotopic wt. of Ra-Pb (205·98±0·02) and ratio of Pb^{206} to Pb^{207} in pure U-Pb from Katanga. L. S. T.

Chemical elements and atomic types from the viewpoint of investigation of isotopes. (Report on work from end of 1931 to end of 1932.) O. HAHN (Ber., 1933, **66**, [*A*], 1—14).—A discussion and tabular presentation of the present knowledge of individual and chemical (practical) at. wts. calc. therefrom. H. W.

Rare earths. W. KLEMM (Z. anorg. Chem., 1932, **209**, 321—324).—The classification of rare earths proposed by Endres (A., 1932, 696) is regarded as unsatisfactory. E. S. H.

Recalculation of mass defects. D. IWANENKO (Nature, 1932, **130**, 892).—New mass defect vals. are plotted from the point of view that only neutrons and protons are present in the nucleus. New vals. for Sn^{124} and Pb^{208} are given. L. S. T.

Vapour pressure of hydrogen rich in the heavier isotope. W. MEISSNER and K. STEINER (Z. Physik, 1932, **79**, 601—612).—The difference in v.p. of normal H_2 and H_2 rich in H^2 increases with time, and this increase gives 26% of the richer mixture as *iso*hydrogen (H_2 with one H of mass 1 and the other of mass 2), whereas density determinations give 0·9%: the larger percentage given by v.p. is explained by the presence of two modifications of the *iso*hydrogen, the heavier having nuclear moment 0 or 1. A. B. D. C.

Cosmic occurrence of the H^2 isotope. A. UNSOLD (Naturwiss., 1932, **20**, 936—937).—By studying the H lines in the solar spectrum it is found that the relative cosmic occurrence of H^2 is <1 in 100,000. A. J. M.

Mass ratio of the boron isotopes from the spectrum of BO. F. A. JENKINS and A. MCKELLAR (Physical Rev., 1932, [ii], **42**, 464—486).—New wave-no. data of the rotational structure of bands of the $B^{11}O$ and $B^{10}O$ systems are tabulated. Vibrational, rotational, and electronic isotope effect data are deduced. N. M. B.

Method of separating gaseous isotope mixtures and its application to the isotopes of neon. G. HERTZ (Z. Physik, 1932, **79**, 700).—A correction (cf. this vol., 4). A. B. D. C.

Neutronic equilibrium of isotopes. W. SWIENTOSLAWSKI (Nature, 1932, **130**, 964).—The existence of every kind of atom and of all isotopes can be explained by assuming that the atoms of different elements can emit or incorporate neutrons (Nr) even under astronomical conditions, thus $O^{18} \rightleftharpoons Nr + O^{17}$ and $O^{17} — Nr + O^{16}$. The concn. of each isotope then depends on the velocity of formation or decomp. of the heavier isotope. The neutronic equilibrium among all the isotopes of one element was probably established under astronomical conditions of formation of the elements and exists at the present time, although the non-radioactive elements are decomposed with extremely small velocity. L. S. T.

Ionisation produced in a spherical vessel by radon. COLMANT (Bull. Soc. chim. Belg., 1932, **141**, 464—476).—Tables based on Mund's equations are given for calculating the no. of ion pairs formed; their use does not involve the range of the α-particles concerned nor the total ionisation, and they are independent of the distribution of the Ra-*A* and Ra-*C*. H. F. G.

Internal conversion coefficient for radium-*C*. H. R. HULME (Proc. Roy. Soc., 1932, **A**, **138**, 643—664).—Mathematical. Assuming the radiation field to be represented by an oscillating dipole at the nucleus, the internal conversion coeff. has been calc. for Ra-*C*. Actual wave functions were used, instead of the asymptotic expansion (cf. Casimir, A., 1931, 139). The process may be explained as an ordinary photo-electric effect, provided the ray $h\nu = 14{\cdot}26 \times 10^5$ e.v., which is almost completely converted, be excluded. In some cases the γ-rays are due to transitions where the angular momentum of the nucleus changes by one unit, whilst Taylor and Mott (this vol., 111) have shown that the assumption of quadripole radiation explains the remaining lines. L. L. B.

Origin of the actinium series of radioactive elements. A. VON GROSSE (Physical Rev., 1932, [ii], **42**, 565—570).—It is concluded from the correlation of data on selected material that the Ac series is independent of, and the decay much more rapid than in, the U–Ra series. The geological significance of this result is discussed. N. M. B.

Velocities of emission of α-particles. G. H. BRIGGS (Nature, 1932, **130**, 1000).—Vals. for the relative velocities of Ra-*C'*, Th-*X*, thoron, Th-*A*, -*C*, and -*C'*, and Ra-*A* and radon are recorded. L. S. T.

Absorption of β-rays by matter. G. FOURNIER and M. GUILLOT (Compt. rend., 1932, **195**, 1264—1265; cf. A., 1930, 130).—Using a source of Ra-*E* the mass absorption coeffs., μ/ρ, of Pt and Pb are respectively 25·8 and 26·4, compared with 26·08 and 26·64 deduced from the author's formula $\mu/\rho = 15 + 0{\cdot}142Z$. C. A. S.

Measurement of radium in minerals of small uranium content by the method of γ-rays. F. BEHOUNEK (Z. Physik, 1932, **79**, 583—594).—An electrometer method for measurement of small Ra content in pitchblende is described. A. B. D. C.

Number of electrons expelled by the action of hard γ-rays. H. HERSZFINKIEL (Acta phys. Polon., 1932, **1**, 237—248; Chem. Zentr., 1932, ii, 1885).—For γ-rays of wave-length 6·6 X, the absorption coeff. and the relative no. of electrons expelled were for Al, Fe, Ag, and Pb, respectively, 245, 283, 352, 473, and 0·85, 1·0, 1·33, 1·67. A. A. E.

Theory of the internal conversion of γ-rays. H. M. TAYLOR and N. F. MOTT (Proc. Roy. Soc., 1932, **A**, **138**, 665—695).—Mathematical. Hulme's calculations (this vol., 110) have been repeated, assuming the field of a quadripole, instead of that of a dipole, for the nucleus. L. L. B.

Disintegration of light elements by fast protons. J. D. COCKCROFT and E. T. S. WALTON (Nature, 1933, **131**, 23; cf. A., 1932, 556, 893).—A more sensitive method shows that the disintegration of Li gives a second group of particles of max. range approx. 2 cm. in addition to the α-particle group of 8·4 cm. range. The no. of particles in the second group is approx. equal to that of the first. The group appears to be composed of α-particles. By decreasing the absorption between target and ionisation chamber the no. of particles from B greatly increases and approx. 25 times as many are obtained from B as from Li. One particle per 2×10^6 incident protons at 500 kv. is emitted. The ionisation produced indicates that they are α-particles, and the energy of the main group supports the assumption that a proton enters the B^{11} nucleus to form a nucleus which breaks up into 3 α-particles. A few particles with a range up to approx. 5 cm. also appear to be present. L. S. T.

Neutron and neuton, the new element of at. no. zero. W. D. HARKINS (Nature, 1933, **131**, 23).—Theoretical. Neutrons of unit mass may be considered to constitute an element of at. no. 0, for which the name "neuton" is suggested. L. S. T.

Interaction between neutrons and atomic nuclei. L. MEITNER and K. PHILIPP (Naturwiss., 1932, **20**, 929—932).—To find whether there is any connexion between neutrons and the accompanying γ-rays, the Wilson method was used to compare the intensities of H-rays liberated from paraffin and an air–H_2O mixture by neutrons from Be, B, and Li. The results agreed with those of Becker and Bothe (A., 1932, 671, 1187) with γ-rays. It is therefore probable that neutrons and γ-rays are emitted simultaneously. The neutron emission from Be is not homogeneous. Some examples of breakdown experiments with Be neutrons are given. It is possible to carry out these nuclear processes in both directions. By bombarding B with α-rays, N_2 is obtained, and a neutron is split off; when N_2 is bombarded with neutrons, the B nucleus is formed, and an α-particle is split off. A. J. M.

Binding energy of nuclear constituents. H. R. VON TRAUBENBERG (Naturwiss., 1932, **20**, 934—936).—The nucleus may be regarded as made up of free electrons, α-particles, neutrons (N), duotons (H^2, D), and triotons (H^3, T). It is possible to make up the at. nuclei of elements, including isotopes, of α-particles, N, D, and T, and without free electrons up to O^{18}. Above this it is necessary to include free electrons. The curve connecting binding energy with the no. of α-particles is characteristic of each type of nucleus, and by extrapolation the binding energy of H^2 and H^3 can be determined. That of H^2 is approx. 5 microergs, and of H^3, 15 microergs. The binding energy of two α-particles is $<$ that between an α-particle and D, or an α-particle and T. A. J. M.

Theory of atomic nuclei. E. N. GAPON (Z. Physik, 1932, **79**, 676—681).—Mass defect and isotope formation can be explained between He and A by assuming nuclei of α-particles and protons. A. B. D. C.

Evaporation phenomena of mercury droplets and their influence on the elementary electric charge. A. LUSTIG and M. REISS (Z. Physik, 1932, **79**, 696—699).—Polemical, against Nestle (A., 1932, 981) and Schafer (*ibid.*, 198). A. B. D. C.

Can the eye distinguish a "schrot" effect for photons? R. B. BARNES and M. CZERNY (Z. Physik, 1932, **79**, 436—449).—The human eye accommodated to darkness is sufficiently sensitive to observe inherent fluctuations in the no. of photons emitted by a weak light source; experiments that might reveal this effect are described. A. B. D. C.

Direction-quantised atoms in a variable magnetic field. E. MAJORANA (Nuovo Cim., 1932, **9**, 43—50; Chem. Zentr., 1932, ii, 970).

Atomic physics and vital activities. (SIR) F. G. HOPKINS (Nature, 1932, **130**, 869—871).—An address. L. S. T.

Value of e/m by deflexion experiments. G. E. UHLENBECK and L. A. YOUNG (Physical Rev., 1931, [ii], **37**, 99).—Quantum mechanical considerations predict no observable deviations for the val. of e/m from classical results for electrons possessing energies of the order of magnitude used in deflexion experiments. L. S. T.

Colours of inorganic salts. M. N. SAHA and S. C. DEB (Bull. Acad. Sci. Agra and Oudh, 1931–1932, **1**, 1—11; cf. A., 1931, 545).—A detailed discussion of results described previously. J. W. S.

Rotational analysis of ultra-violet bands of silicon monoxide. P. G. SAPER (Physical Rev., 1932, [ii], **42**, 498—508).—From measurements on Si arc spectrograms a rotational analysis of the (0,1), (0,2), (0,3), (0,4), and (1,4) ultra-violet band system of SiO is made. An equation for the band origins of the Q branch system is obtained. N. M. B.

Influence of temperature on absorption of aqueous hydrochloric acid in the far ultra-violet. R. TREHIN (Compt. rend., 1932, **195**, 1269—1270; cf. A., 1931, 19).—The absorption of H_2O is independent of temp. between −6° and 95°; that of aq. HCl between 25° and 90° increases continuously as λ decreases from 2816 to 2170. For each temp. a max. absorption occurs for some definite concn. and wavelength. Beer's law is not obeyed. C. A. S.

Absorption spectra of some alkali fluorides and the heat of dissociation of fluorine. M. S. DESAI (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 116—118).—See A., 1931, 912; 1932, 698. J. W. S.

Absorption spectrum of calcium chloride vapour. S. C. DEB and B. MUKERJEE (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 110—115).—From measurements made at 900—1300° two band systems have been observed in the absorption spectrum of $CaCl_2$, a system of 6 bands with heads at 3920—

3850 Å. and 9 bands in the region 2850—2730 Å. Beyond 2640 Å. continuous absorption begins and extends to 2530 Å., where absorption is completely cut off. The distance between the two absorption bands is of the same order of magnitude as the distance of the metastable state of Ca^+ from the normal state. J. W. S.

Absorption spectra of saturated halides. S. C. DEB (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 92—99).—The intensity of absorption and the absorption limits of $MgCl_2$, $MgBr_2$, $AlCl_3$, $AlBr_3$, AlI_3, $SiCl_4$, $SiBr_4$, and SiI_4 vapours have been measured. J. W. S.

Absorption spectra of saturated halides of multivalent elements. A. K. DATTA and M. N. SAHA (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 19—25; cf. A., 1931, 667).—Details of results reported previously are given. J. W. S.

Absorption spectrum of sulphur dioxide. A. K. DUTTA (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 88—91).—27 bands of SO_2 have been observed and measured in the region 3400—2800 Å., and the assignment agrees with infra-red and Raman spectra data. J. W. S.

Band spectra produced by certain explosion mixtures. H. A. WILHELM (Iowa State Coll. J. Sci., 1932, **6**, 475—478).—Spectra of explosions such as those of flash-light powders were examined. Spectra of MgS, PbS, and CuS have been identified. CH. ABS.

Zeeman effect of perturbed terms in the CO Angstrom bands. W. W. WATSON (Physical Rev., 1932, [ii], **42**, 509—517).—Perturbed line data and quantum assignments are recorded; the Zeeman patterns are described and explained. N. M. B.

Ultra-violet absorption spectra of azoxybenzenes. III. E. MÜLLER and E. HORY (Z. physikal. Chem., 1932, **162**, 281—285; cf. A., 1932, 734).—Determination of the absorption curves of various symmetrical azoxybenzenes and their isomerides has shown that the *iso*-form always exhibits, in addition to the characteristic azo-absorption band at 3200—3600 Å., a second max. at about 2400 Å. These observations, together with other data, show the occurrence of *cis–trans* isomerism. The spectra of the *iso*-forms markedly resemble those of Angeli's α-isomerides. R. C.

Absorption spectra of metallic colloidal solutions, and emission and absorption of metallic films. A. T. WILLIAMS (Nature, 1932, **130**, 963—964).—The absorption curves of colloidal solutions and films of Ag are practically coincident. L. S. T.

Absorption and dispersion of celluloid between 300 and 1000 Å. H. M. O'BRYAN (J. Opt. Soc. Amer., 1932, **22**, 739—748).—The absorption max. is $1{\cdot}1\times10^6$ per cm. at 800 Å., when a film 100 Å. thick transmits 30%. Reflecting power, extinction coeffs., and refractive indices are obtained for various wave-lengths. The dispersion min. is at 550 Å. Electron dispositions are calc. and discussed. N. M. B.

Rigidity and type of binding from continuous absorption spectra. J. FRANCK and H. KUHN (Naturwiss., 1932, **20**, 923—925).—It is possible to determine whether a mol. possesses ionic or at. binding from a study of continuous absorption spectra, and results of various authors are quoted. The usual definitions of ionic and at. mols. based on following the oscillation term from its ground state to convergence and noting whether an atom or an ion is formed are ambiguous. Ionic mols. are always heteropolar, whilst at. mols. may have electric moment, or may be non-polar. The use of the potential curve may give misleading results. Conclusions on the dissociation work and type of binding of polyat. mols. cannot at present be reached from observations of the long-wave limit of the continuous absorption spectrum. A. J. M.

Energy of the ground state of methane. H. J. WOODS (Trans. Faraday Soc., 1932, **28**, 877—885).—Mathematical. The calc. val. lies between −5·3 and −4·9 volts, in agreement with experiment. F. L. U.

Band system of CaO in the near infra-red. P. H. BRODERSEN (Z. Physik, 1932, **79**, 613—625).—20 band edges and rotational lines were measured between 6000 and 9000 Å.; the upper state has a Ca–O separation of 1·82 Å. and the lower 1·74 Å. A. B. D. C.

Absorption bands of hydrogen halides in the liquid state. E. O. SALANT and W. WEST (Physical Rev., 1931, [ii], **37**, 108—109).—The (0,2) bands of liquid HCl, HBr, and HI and the (0,3) band of liquid HI show no rotational structure, the centres of the HCl and HBr bands being displaced to longer waves as compared with the corresponding gas bands. Frequencies and gas-liquid displacements are HCl 5543 (125), HBr 4850 (180), and HI 4262 and 6262 cm.$^{-1}$ HI absorption, in particular, is strongly intensified in the liquid. The vibration frequencies and anharmonic coeffs. of the vibrational terms are calc. L. S. T.

Quantum theory of rotational dissociation of diatomic molecules. G. MULLER (Z. Physik, 1932, **79**, 595—600).—An expression is deduced for the width of rotational lines near rotational dissociation; the expression differs by a factor of 4 from that of Kronig (A., 1930, 981). A. B. D. C.

New infra-red band system of the CO molecule. B. K. VAIDYA (Nature, 1932, **130**, 963).—A discussion. L. S. T.

Infra-red spectra of ammonium salts in the region of anomalous specific heats. R. POHLMAN (Z. Physik, 1932, **79**, 394—420).—The sublimation method was used to give thin layers of NH_4Cl, NH_4Br, $(NH_4)_2SO_4$, and NH_4NO_3, and their spectra were investigated between 2·5 and 9 μ at temp. between −80° and room temp. Isochromates, or curves of transparency at a given wave-length plotted against temp., for the NH_4 and SO_4 radicals show discontinuities at the temp. of anomalous sp. heat. Fine structure of the bands indicates that the NH_4 group occupies rotation states in NH_4 salts. A. B. D. C.

Infra-red region of the spectrum. VII. Infra-red grating spectrometer as a double monochromator. A. B. D. CASSIE and C. R. BAILEY (Proc. Roy. Soc., 1932, **A**, **138**, 531—539).—Details are given of the construction and method of working

of an infra-red grating spectrometer for use as a double monochromator. The experimental errors and resolving power are calc. L. L. B.

Infra-red absorption of quartz. D. G. DRUMMOND (Nature, 1932, **130**, 928—929). L. S. T.

The OH band of phenol in the near infra-red. A. A. NAHERNIAC (Compt. rend., 1932, **195**, 1254—1255).—The OH band in PhOH increases in intensity as temp. rises from 63° to 140°, whilst the max. moves from λ 9852 to 9776. In CCl_4 solution the band is double, max. at λ 9728 and 9892, the former moving to 9684 on dilution, the latter decreasing in intensity and disappearing in solutions containing < 10% PhOH; rise in temp. acts as dilution. Addition of a compound containing double linkings, *e.g.*, C_6H_6 or $C_{10}H_8$, but not C_6H_{12} or $C_{10}H_{18}$, to the dil. CCl_4 solution brings out the λ 9892 band. C. A. S.

Rotation-vibration spectrum of acetylene. W. LOCHTE-HOLTGREVEN and E. EASTWOOD (Z. Physik, 1932, **79**, 450—454).—Experimental results agree with those of Leug and Hedfeld (A., 1932, 982), but a different allocation of frequencies is given. A. B. D. C.

Infra-red absorption spectra of aliphatic and aromatic hydrocarbons. P. LAMBERT and J. LECOMTE (Ann. Physique, 1932, [x], **18**, 329—390; cf. A., 1932, 212, 445).—For the range 6—16 μ absorption curves and diagrams of position and intensity max. are given for 16 aliphatic and 40 aromatic hydrocarbons. In each case the position of the absorption max. is directly related to the mol. structure, and allows isomerides and homologues to be distinguished. N. M. B.

Progressive relationships in the near infra-red absorption spectra of the halogen derivatives of benzene. F. S. BRACKETT and U. LIDDEL (Physical Rev., 1931, [ii], **37**, 108).—The spectra have been analysed with respect to the second overtone of the fundamental vibration of C_6H_6 occurring in the region 3·25 μ, which probably approximates to a linear oscillation of H with respect to C. In C_6H_6 (8772 cm.$^{-1}$), PhI (8780 cm.$^{-1}$), PhBr (8787 cm.$^{-1}$), and PhCl (8800 cm.$^{-1}$), a progressive shift to shorter wavelengths of this second overtone at 8772 cm.$^{-1}$ is observed. Further reduction of electron density about the C centres resulting from substitution by an increasingly electronegative halogen appears to be the explanation. Other predicted shifts are substantiated in a general way for the three dichloro-, 1 : 2 : 4- and 1 : 3 : 5-trichloro-, pentachloro-, and *p*-dibromobenzene. L. S. T.

Existence of a continuous Raman effect in liquids. R. BAR (Z. Physik, 1932, **79**, 455—470).—Investigation of continuous light scattered by many org. liquids in a direction parallel to the incident beam showed that it is due either to fluorescence or to Rayleigh scattering (cf. A., 1932, 675). A. B. D. C.

Raman effect in crystals. F. RASETTI (Nuovo Cim., 1932, **9**, 72—75; Chem. Zentr., 1932, ii, 976).—Gypsum, calcite, fluorspar, quartz, anhydrite, baryte, aragonite, rock-salt, and ice have been examined, and new lines have been observed. A. A. E.

Molecular diffusion of light. Cabannes-Daure effect and molecular field. A. ROUSSET (J. Phys. Radium, 1932, [vii], **3**, 555—563).—A more detailed account of work already noted (A., 1932, 792).

Molecular symmetry and diffusion spectra. J. CABANNES (Ann. Physique, 1932, [x], **18**, 285—328).—Theoretical. From the concept of the anisotropic mol. a simple theory of selection rules and rules for the polarisation of Raman lines of polyat. mols. is deduced and applied. N. M. B.

Critical opalescence. Y. ROCARD (Compt. rend., 1932, **195**, 771—773; cf. A., 1928 1310).—The theories of Ornstein and Zernicke and of Einstein relating to fluctuations of density err in applying to states far from equilibrium, relations which are valid only for the equilibrium state. In dealing with such fluctuations density must not be treated as const., and it is pointed out that even at the crit. point some work is required to produce such fluctuations, and hence that there will at that point be only a finite intensity of opalescence which should be proportional to $1/\lambda^4$ instead of $1/\lambda^2$, and also that similar diffusion should occur at angles θ and π—θ. A formula for the intensity of diffusion in binary mixtures is thus obtained which agrees with experimental results. C. A. S.

Raman effect in CO. E. AMALDI (Z. Physik, 1932, **79**, 492—494).—Up to 6 atm. pressure CO showed the single displacement 2145 cm.$^{-1}$ and rotation lines about the undisplaced lines. A. B. D. C.

Carbon-oxygen linking in the metal carbonyls. J. S. ANDERSON (Nature, 1932, **130**, 1002).—The Raman effect in Ni carbonyl shows that the CO is present in the mols. of the metal carbonyls as such and not as a :C:O group. L. S. T.

Raman spectra of C and Si compounds. M. DE HEMPTINNE (Ann. Soc. sci. Bruxelles, 1932, **B**, **52** 185—189).—Data for $CHCl_3$, $SiHCl_3$, PCl_3, and $SiCl_4$ are given, and compared with calc. vals. N. M. B.

Raman effect of some inorganic halides in the molten and gaseous states. H. BRAUNE and G. ENGELBRECHT (Z. physikal. Chem., 1932, **B**, **19**, 303—313).—In the vapour state the frequency of the inactive oscillation of the Hg halides is proportional to the heat of dissociation. The frequency is greater in the vapour than in the molten state, which is attributed to either coupling of the mols., *i.e.*, increase in the oscillating masses, or reduction of the binding forces under the influence of adjacent mols. For Hg, P, As, and Sb halides the graph of the % difference in frequency in the vapour and molten states against the linking dipole moment is approx. linear. R. C.

Raman effect of molecules of the types XY_6 and XY_5. O. REDLICH, T. KURZ, and P. ROSENFELD (Z. physikal. Chem., 1932, **B**, **19**, 231—241).—The Raman spectra of $HSbCl_6$, H_2SnCl_6, Li_2SnCl_6, and $MgSnCl_6$, all of which are due to the group XY_6, and of $SbCl_5$ have been determined. The corresponding mol. frequencies are deduced by means of Placzek's selection rules (A., 1931, 893) and Bjerrum's central force principle (Verh. Deut. physikal. Ges., 1914, **16**,

737). For the compounds XY_6 the results do not agree with those obtained by applying the valency force principle. R. C.

Circular polarisation of Raman lines. II. W. HANLE (Ann. Physik, 1932, [v], **15**, 345—360; cf. A., 1932, 108).—Measurements of the circular polarisations of the Raman lines of xylene, PhCl, PhCHO, trichloroethane, $(CHCl_2)_2$, AcOH, $COMe_2$, Et_2O, glycerol, CS_2, aq. NH_3, HNO_3, and H_2SO_4 have been made and are discussed. W. R. A.

Raman effect in organic nitrates. A. S. GANESAN and V. THATTE (Phil. Mag., 1932, [vii], **14**, 1070—1080).—Raman spectra for Me, Et, Pr^{α}, Pr^{β}, Bu^{β}, and *iso*amyl nitrates have been measured. The NO_3 ion frequency is missing, but appears for solutions of $MeNO_3$ in MeOH and for $C_5H_{11}\cdot NO_3$ in *iso*amyl alcohol. H. J. E.

New photo-electric experiment. Q. MAJORANA (Atti R. Accad. Lincei, 1932, [vi], **16**, 82—86, 173—179, and Compt. rend., 1932, **195**, 1358—1360).—A more detailed account of work already noted (A., 1932, 898). O. J. W.

Nature of the spontaneous current on illumination of various detector substances. E. RUPP (Z. Physik, 1932, **79**, 562).—Polemical, against Waibel (A., 1932, 1189). A. B. D. C.

Internal photo-electric effect in crystals. A. H. WILSON (Nature, 1932, **130**, 913—915). L. S. T.

Electrical conductivity of graphite powder. Z. SPECHT (Z. Elektrochem., 1932, **38**, 920—925).—The variation of conductivity with pressure has been measured in the case of graphite powders from various sources. Ryschkewitsch's results (B., 1922, 597) have been confirmed. D. R. D.

Dependence of electrical conductances and dielectric constant on frequency in mixtures of strong electrolytes. H. FALKENHAGEN and W. FISCHER (Nature, 1932, **130**, 928).—A discussion. L. S. T.

Utilisation of dipole moment data. H. M. SMALLWOOD (Z. physikal. Chem., 1932, **B**, **19**, 242—254).—In dipole moment measurements of solutions neither the at. polarisation nor the effect of the solvent on the solute is capable of exact theoretical treatment, and either may cause such serious errors in the val. deduced for the dipole moment that determinations made with a single solvent at a single temp. are of little more than qual. significance. Smyth and Dornte's observations with CPh·CPh (A., 1931, 669) may be explained by interaction of solvent and solute. By extrapolation the moment of the CH linking is found to be about $0{\cdot}5\times10^{-18}$ e.s.u. The methods of deriving group moments are critically examined. Group moments are closely related to the polarity of the linking as deduced from heats of formation. R. C.

Anisotropy of the forces of crystal growth. G. SOMMERFELD (Zentr. Min. Geol., 1932, **A**, 189—202; Chem. Zentr., 1932, ii, 969).

Optical activity. I. Valency theory. C. H. JOHNSON (Trans. Faraday Soc., 1932, **28**, 845—856).—Attempts to resolve $K_3M(C_2O_4)_3,3H_2O$ (M=Fe, Mn, Cr) and salts of $M\,en_3^{++}$ (M=Ni, Cu, Zn, Cd) have been unsuccessful. It is therefore considered that these compounds possess the ionic type of binding. Magnetic and optical-activity criteria of valency are in agreement where both can be applied. F. L. U.

Magnetic rotatory dispersion and absorption of the cerous ion in solution. R. W. ROBERTS and L. A. WALLACE (Nature, 1932, **130**, 890—891).—The magnetic rotations of 0·7, 2·7, and 4·4% aq. solutions of $Ce_2(SO_4)_3$ at room temp. indicate the existence of two paramagnetically active absorption bands, one weak near 300 mμ and the other strong near 240 mμ. The presence of other absorption bands of the $Ce^{\cdots}$ ion is discussed. L. S. T.

New empirical formula for refractive indices. A. BIOT (Ann. Soc. sci. Bruxelles, 1932, **B**, **52**, 177—185).—A convenient formula accurate to 5 decimal places is deduced, and illustrated for quartz. N. M. B.

Fundamental frequencies of the group SiO_4 in quartz crystals. J. WEILER (Nature, 1932, **130**, 893). L. S. T.

Calculation of characteristic frequencies of organic chain-molecules by means of models. E. BARTHOLOMÉ and E. TELLER (Z. physikal. Chem., 1932, **B**, **19**, 366—388).—Calculations are made for hydrocarbons and some derivatives on the basis of greatly simplified mol. models, in which the internal oscillations of the constituent groups are disregarded. The observation that in the Raman effect of halogeno-hydrocarbons the halogen frequency is independent of the length of the chain is accounted for. R. C.

Dimensions of complex anions and lattice dimensions of Werner's co-ordination compounds of the fluorite and yttrium fluoride type. O. HASSEL and H. KRINGSTAD (Z. anorg. Chem., 1932, **209**, 281—288).—Lattice consts. have been determined for compounds of $[Ni(NH_3)_6]^{\cdots}$ and $[Co(NH_3)_6]^{\cdots}$ with BF_4', ClO_4', and SO_3F'. The effective radii of the anions are ClO_4' 2·42, SO_3F 2·45, BF_4 2·36 Å. E. S. H.

Diamagnetism of thin films of bismuth. C. T. LANE (Nature, 1932, **130**, 999; cf. A., 1932, 449).—The magnetic susceptibility of Bi remains const. for films from 0·2 to 15 μ thick. L. S. T.

Gyromagnetic effect in some ferromagnetic powders. D. P. RAY-CHAUDHURI (Nature, 1932, **130**, 891).—For pptd. Fe_3O_4, ferromagnetic Fe_2O_3, and NiO,Fe_2O_3 the vals. determined for the ratio of angular momentum to magnetic moment of the elementary magnet are 1·008, 1·016, and 1·022 m/e, respectively. L. S. T.

Magnetic susceptibilities of some paramagnetic substances. W. SUCKSMITH (Phil. Mag., 1932, [vii], **14**, 1115—1126).—An apparatus for measuring susceptibilities between −183° and 470° is described. The temp. variation for Yb_2O_3, Nd_2O_3, Sm_2O_3, and Eu_2O_3 follows Van Vleck's theory (cf. A., 1928, 572). The paramagnetism of MoCl-, $MoCl_3$, $U(SO_4)_2$, and UCl_4 is probably due to spin moment only. H. J. E.

Magnetochemical researches. VII. Magnetism of rare-earth borides. W. KLEMM, W. SCHUTH, and M. VON STACKELBERG (Z. physikal. Chem., 1932, **B**, **19**, 321—327; cf. A., 1932, 985).—Susceptibility measurements show that in LaB_6, CeB_6, PrB_6, NdB_6, and SmB_6 the rare-earth metal is present as tervalent ions set in the electron gas responsible for the metallic characteristics of these borides. The nos. of effective Bohr magnetons are the same as for the metals themselves. R. C.

Volume chemistry of liquid carbon compounds. F. WRATSCHKO (Pharm. Presse, 1931, 157—163, 177—183; 1932, 1—6; Chem. Zentr., 1932, ii, 1113).—Theoretical. A. A. E.

Surface tension near the critical point. A. W. PORTER (Nature, 1932, **130**, 929—930).—A discussion. L. S. T.

Surface tension of mercury in silica apparatus. R. S. BURDON (Trans. Faraday Soc., 1932, **28**, 866—876).—The surface tension of Hg distilled and manipulated in vac. was found from measurements of the height of large sessile drops to be 488 dynes per cm. at 25°. The temp. coeff. of surface tension is −0·23 dyne per 1° up to 230°. The lowering of surface tension observed in presence of air is thought to be due to an adsorbable impurity. F. L. U.

Rotation goniometer diagram and the reciprocal lattice. E. SAUTER (Naturwiss., 1932, **20**, 889—890).—By rotating an oriented single crystal in a monochromatic beam of *X*-rays, the interference spots obtained in the ordinary rotation diagram are somewhat altered. A. J. M.

Interpretation of *X*-ray term values. M. N. SAHA and R. S. SHARMA (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 119—134).—Theoretical. J. W. S.

***X*-Ray spectrum and lattice binding force.** R. GLOCKER (Physikal. Z., 1932, **33**, 963—967).—Experiments with very soft *X*-rays on C and substances containing C give different intensity distributions in the spectra. The difference in form and width of the lines obtained for graphite, diamond, and carborundum are explained theoretically. A. J. M.

Rotation of crystals floating on liquid surfaces. P. GAUBERT (Compt. rend., 1932, **195**, 1088—1090).—Any solid, cryst. or amorphous, and lighter or not much heavier (*e.g.* aspirin, *d* 1·39, or NHAcPh, *d* 1·211, on H_2O) than the liquid, will rotate on the surface of such liquid provided that it is itself sol. or is saturated with a substance sol. therein. The phenomena as exhibited by crystals of *iso*valeramide (*d* 0·955, n_α 1·438, n_β 1·450, n_γ 1·457) and thymol (*d* 1·035) are described. The movements are recoil effects due to diffusion currents from the dissolving substance. C. A. S.

Scattering of *X*-rays by gases and crystals. G. E. M. JAUNCEY (Physical Rev., 1932, [ii], **42**, 453—463).—Theoretical. Woo's formulæ (cf. A., 1932, 892), the effect of temp. on electron distribution, and the classical relations for scattering are discussed. N. M. B.

Free electrons in a crystalline network. Wave equations and magnetic properties. L. BRILLOUIN (J. Phys. Radium, 1932, [vii], **3**, 565—581).

Theory of glass formation and the glassy state. E. BERGER (J. Amer. Ceram. Soc., 1932, **15**, 647—677).—Recent research leads to a theory, according to which the formation of glass from the liquid state, in contrast to crystallisation, is a continuous process from the liquid, through the viscous (supercooled) to the brittle state. A transformation point is recognised, which represents the boundary temp. between viscous and brittle glass, at which the property–temp. coeffs. change more or less suddenly. When a melt is cooled, a dynamic aggregation is assumed; this proceeds more slowly as the transformation point is approached and is checked completely at lower temp. Viscosity and electrical conductivity of the liquid or viscous state between 1300° and 300° follow a hyperbolic law, whilst the brittle state properties follow a different, more complicated course below the transformation point. Brittle glass is not identical, therefore, with a supercooled liquid. A thermodynamical interpretation of the transformation point cannot be given, but kinetic considerations suggest an analogy with the gelation of sols. E. S. H.

Vitreous state. R. O. HERZOG and H. C. KUDAR (Naturwiss., 1932, **20**, 951—952).—The kinetic theory is applied to the vitreous state. A. J. M.

Zwicky's theory of the structure of real crystals. E. OROWAN (Z. Physik, 1932, **79**, 573—582).—The polarisation energy deduced by Zwicky from the contraction of a lattice plane on formation of a crystal is three times too large, and the effect termed "self-perpetuating polarisation" is a well-known property of ferromagnetic substances; the hypothesis of a secondary structure is thus rendered unnecessary. A. B. D. C.

Ostwald's gradation rule. I. N. STRANSKI and D. TOTOMANOW (Naturwiss., 1932, **20**, 905).—Volmer's expression for the probability of nucleus formation in supersaturated media (A., 1926, 676) provides an explanation in support of Ostwald's gradation rule for the formation of polymorphous modifications from supersaturated gaseous or liquid phases. A. J. M.

Transformations in homogeneous substances. G. TAMMANN (Z. anorg. Chem., 1932, **209**, 204—212).—Recent work and theories on transformations without recrystallisation are reviewed with especial reference to the α–β transformations in Fe and Ni, the β–β′ change in brass, and the CuAu and Cu_3Au transformations in Au–Cu alloys. A. R. P.

Transformation of metal phases. IV. Kinetic curves for the process of precipitation. U. DEHLINGER (Z. Physik, 1932, **79**, 550—557).—Theoretical. A system of differential equations is established which gives all the characteristic resistance effects for Al_2Zn_3. A. B. D. C.

Grating constants of copper–palladium mixed crystals. J. O. LINDE (Ann. Physik, 1932, [v], **15**, 249—251).—Two types of crystal, Cu_3Pd and CuPd,

are discussed. The lattice is cubic, face-centred for the Cu_3Pd, and body-centred for the CuPd. W. R. A.

Crystal structure of ammonium iodate. J. GARRIDO (Anal. Fis. Quím., 1932, **30**, 811—814).—NH_4IO_3 has a 4·51 Å., and the structure is of the perowskite type. H. F. G.

Structure of tetra- and tri-phosphonitrilic chloride. F. M. JAEGER and J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 756—762).—The crystal structures of $(PNCl_2)_4$ and $(PNCl_2)_3$ have been investigated by X-ray diffraction methods. The structure found for $(PNCl_2)_3$ is not in agreement with the cyclic structure suggested by Schenck and Römer (A., 1924, ii, 752). Electronic structures for these compounds are suggested. J. W. S.

Crystal structure of borides of composition MB_6. M. VON STACKELBERG and F. NEUMANN (Z. physikal. Chem., 1932, **B**, **19**, 314—320).—The lattice of CaB_6 has the CsCl structure, the lattice points being occupied by Ca atoms and B_6 groups, and the atoms of a B_6 group occupy the corners of an octahedron. The lattices of SrB_6, BaB_6, LaB_6, CeB_6, PrB_6, NdB_6, ErB_6, and ThB_6 are probably of the same type. All these borides are metallic in their physical properties. R. C.

X-Ray study of borides. G. ALLARD (Bull. Soc. chim., 1932, [iv], **51**, 1213—1215).—A study of the following borides by the powder method indicates that they have the same structure as ThB_6 (A., 1929, 987; cf. A., 1931, 1218), the val. of a in Å. being: CaB_6 4·10, SrB_6 4·19, BaB_6 4·38. LaB_6 4·16, CeB_6 4·12, NdB_6 4·07, GdB_6 4·12, ErB_6 4·05, YbB_6 4·13, YB_6 4·07. D. R. D.

Crystal lattice of so-called orthosilicates. B. GOSSNER and C. REICHEL (Zentr. Min. Geol., 1932, **A**, 25—29; Chem. Zentr., 1932, ii, 2144—2145).—Zoisite and epidote have space-group V^{16} and C_{2h}^2, respectively. Lievrite has a 8·82, b 13·07, c 5·86 Å., with 4 mols. of $CaFe^{II}_2(Fe^{III}OH)(SiO_4)_2$ in the unit cell; possible space-groups Axinite has a 12·87, b 7·15, c 8·91 Å.; α 82° 26′, β 95° 20′, γ 135° 35′, with 2 mols. of $Ca_2MgHAl_2B(SiO_4)_4$ in the triclinic unit cell. A. A. E.

X-Ray investigation of normal paraffins near their m.p. A. MÜLLER (Proc. Roy. Soc., 1932, **A**, **138**, 514—530).—X-Ray photographic measurements have been made of the lattice dimensions of 15 normal paraffins ranging from $C_{18}H_{38}$ to $C_{44}H_{90}$ at temp. between 20° and the m.p. The substances tend to become hexagonal at the m.p., and in the range of C_{21} to C_{29} this state of high symmetry is actually reached; substances outside this range melt before becoming hexagonal. C_{21} and C_{23} show a continuous change of the a and b axes with rise of temp. up to the m.p. C_{24}, C_{25}, C_{26}, C_{27}, C_{29}, C_{30}, C_{31}, C_{34}, and C_{44} show abrupt transitions between room temp. and the individual m.p. Combining the present measurements with Garner's data on the heat of crystallisation and transition (A., 1931, 899), it is found that the internal energy decreases rapidly with increasing mol. distance. L. L. B.

Structural changes in crystalline salts of long-chain fatty acids at m.p. of parent substances. P. A. THIESSEN and E. EHRLICH (Z. physikal. Chem., 1932, **B**, **19**, 299—302; cf. A., 1931, 1367).—For Na salts of higher fatty acids the cooling curve exhibits a halt near the m.p. of the corresponding acid, and at the same time the coeff. of cubical expansion changes discontinuously and there is a reversible change in the lattice. Similar changes occur at the m.p. of the hydrocarbon with the corresponding C–H chain. These "genotypic" effects are ascribed to dualism of the lattice linkings, sets of lattice planes acting on each other almost entirely through the presence of polar ionic linkings of the CO_2H groups together with sets of planes in which the linking is determined by the cohesive forces of the long chains. R. C.

X-Ray investigation of a case of chromo-isomerism. E. HERTEL and G. H. ROMER (Z. physikal. Chem., 1932, **B**, **19**, 228—230).—The yellow form of 1 : 2 : 4-$C_6H_3Me(NHMe)\cdot NO_2$ has a monoclinic lattice, space-group C_{2h}^5, and a continuous succession of identically placed mols. occurs along the c axis, the planes of the rings coinciding with the (001) planes. In the triclinic lattice of the red form mols. are spaced along the c axis at a distance equal to half the period of identity, and are not identically placed. The red colour is ascribed to the formation of a unimol. mol. compound. R. C.

Change of properties of non-metallic substances by working. G. TAMMANN (Naturwiss., 1932, **20**, 958—960).—The change of hardness and density of AgCl after heating to temp. up to 250° is investigated. Changes of colour with other substances when subjected to heat treatment are noted. Phosphors show phosphorescence when rubbed. Grinding affects solubility; this may be due not only to the decreases in particle size, but also to change of solubility owing to cold working. A. J. M.

Theory of metals. I. A. H. WILSON (Proc. Roy. Soc., 1932, **A**, **138**, 594—606).—Mathematical. A method, analogous to that used for diat. mols., is developed for examining the interaction between the electronic motions and the nuclear vibrations in a metal. The "mean free path" of the electrons is calc. by this method. Existing theories are discussed, and Peierl's criticisms of Bloch's theory (A., 1930, 281) are considered to be unfounded. L. L. B.

Changes in the resistance of ferromagnetic crystals. R. GANS and J. VAN HARLEM (Ann. Physik, 1932, [v], **15**, 516—526).—Mathematical. W. R. A.

Change of electrical resistance on magnetisation. W. GERLACH (Physikal. Z., 1932, **33**, 953—957).—The anomalous resistance–temp. curve shown by ferromagnetic conductors below the Curie point is studied, and the change of resistance with magnetisation in the neighbourhood of and below the Curie point is investigated. Simple formulæ are given connecting the resistance change with temp. and magnetisation. A. J. M.

Resistance anomaly of pure bismuth. C. DRUCKER (Z. physikal. Chem., 1932, **162**, 305—317).—

The results reported previously (A., 1928, 10) have been confirmed. Just above 100° the negative temp. coeff. of Bi pressed into wire at or rather below 100° abruptly becomes much more negative, then with further rise in temp. quickly becomes more positive again. After heating at 130° the discontinuity has disappeared. With wires pressed out at 100° and 225° the anomaly is less marked after annealing at a temp. above the temp. of formation, whereas if the wires are not annealed they give reproducible results at low temp. only. The observed effects seem to arise from the simultaneous operation of several factors considered. R. C.

Magnetisation of paramagnetic crystals in alternating fields. I. WALLER (Z. Physik, 1932, **79**, 370—388).—Theoretical. Two cases are considered: (i) where the applied field is small compared with the field due to interaction of the magnetic particles; (ii) where the applied field is large. The crit. frequency is deduced. A. B. D. C.

Permeability of iron at ultra-radio frequencies. J. B. HOAG and H. JONES (Physical Rev., 1932, [ii], **42**, 571—576). N. M. B.

Triboelectricity and friction. VII. Quantitative results for metals and other solid elements, with silica. P. E. SHAW and E. W. L. LEAVEY (Proc. Roy. Soc., 1932, **A**, **138**, 502—514; cf. A., 1928, 467).—A metal or other rod is rubbed on a Si tube, using an apparatus maintaining const. pressure and length of rub. The volta and triboelectric effects are found to be somewhat similar, but there are disparities. At least ten factors are concerned in the process of rubbing two solids. These are discussed. L. L. B.

Influence of cold-working on the temperature of the beginning of grey glow heat. G. TAMMANN, F. NEUBERT, and W. BOEHME (Ann. Physik, 1932, [v], **15**, 317—320).—Cold-working lowers the temp. of the grey glow of metals. The corresponding temp. in salts is lowered by pulverisation. W. R. A.

Change in conductivity of metal [tungsten] foil by the action of an electric discharge. M. PIERUCCI (Nuovo Cim., 1932, **9**, 33—42; Chem. Zentr., 1932, ii, 1032).

Change in electrical conductivity of a metal foil dependent on its electric charge. G. POLVANI (Nuovo Cim., 1932, **9**, 69—71; Chem. Zentr., 1932, ii, 1032).

Electric superconduction in metals. J. C. MCLENNAN (Nature, 1932, **130**, 879—886).—A British Association discussion. L. S. T.

Theory of the thermo-electric effect at low temperatures. W. KROLL (Z. Physik, 1933, **80**, 50—56).

Quantum theory of latent heat of fusion. H. C. KUDAR (Z. Physik, 1932, **79**, 529—531).—Preliminary. Application of Boltzmann's law to excited electronic levels gives a solid finite energy near 0° abs.; if Boltzmann's law applies to electronic levels only at temp. above that at which the energy content of the solid body becomes equal to that of the mean electronic energy (according to Boltzmann's law), a definite m.p. is defined, and Richardson's law explained; the essential property of liquids, diffusion into one another, is explained as an exchange effect. A. B. D. C.

Fusion under pressure. II. E. JANECKE (Z. physikal. Chem., 1932, **162**, 286—288).—With the derivation by van Laar (this vol., 16) of an equation for the fusion curve which indicates that there is no max. fusion temp. at high pressure the interpolation formulæ previously suggested for the fusion curves of pure substances (A., 1931, 1222) are shown to be inapplicable at high pressures. R. C.

Molecular heat of gaseous nitric oxide at low temperatures. A. EUCKEN and L. D'OR (Nachr. Ges. Wiss. Gottingen, 1932, 107—112; Chem. Zentr., 1932, ii, 682).—The mol. heat increases below room temp. (max. at about 70° abs.) owing to the existence of para- and dia-magnetic modifications with energy difference 354 cal.; cooling increases the proportion of the latter, of lower energy. The theoretical course of C_p is calc., and vals. have been obtained by Lummer and Pringsheim's method from 127° to 288° abs. A thermostat for low temp. is described. Equilibrium between the two mol. species is attained about 0·001 sec. after change of temp. A. A. E.

Calorimetric investigations at liquid helium temperatures. K. MENDELSSOHN and J. O. CLOSS (Z. physikal. Chem., 1932, **B**, **19**, 291—298).—The at. heat of Cu has been determined at 4·5—15° and that of Ag at 2—20° abs. For Cu the results can be represented by a Debye function, but with Ag the vals. at very low temp. show slight positive deviations. R. C.

Graphical method for the calculation of boiling points at various pressures. E. SCHLENKER (Chem.-Ztg., 1932, **56**, 1001—1002).—The method suggested by Cox and by Davis (B., 1923, 699; 1925, 690; A., 1926, 142) of plotting $\log_e p$ against t is shown to give straight lines for glycerol–H_2O mixtures. It is suggested that this facilitates the measurement of the concn. of such mixtures. J. W. S.

Thermal state of superheated steam at high pressures. W. KOCH (Z. tech. Physik, 1932, **13**, 263—266; Chem. Zentr., 1932, ii, 1275).—A discussion of measurements at 120—200 atm. from saturation temp. to 450°. A. A. E.

New equation of state for water vapour. H. HAUSEN (Forsch. Gebiet Ingenieurw., 1931, **A**, 2, 319—326; Chem. Zentr., 1932, i, 1763).

Van der Waals' equation. I. K. JABŁCZYŃSKI (Rocz. Chem., 1932, **12**, 773—781).—It follows from van der Waals' equation that $b=2w$, and $a-2wRT-pw^2$, where w is the vol. of 1 mol. at the pressure p for which pw^2 has a min. val. The val. of b is const., and is 0·0320 for CO_2 over the range 37—198°, and 0·0454 for C_2H_4 over the range 10—198·5°. In the liquid phase the val. of b is slightly $<$ in the gaseous phase, for both gases. The val. of a varies with temp. and pressure, at first diminishing to a min. with the mol. vol., and then rising; with rise of temp. it increases from 2·58 at 21° to 2·86 at 107°, and then falls to 2·28 at 198° for CO_2, whilst for C_2H_4 it falls irregularly from

3·94 at 0° to 3·15 at 198·5°. Substitution of the vals. of a and b into the ordinary formulæ for calculating crit. consts. gives variable results differing widely from experimental vals., due to the formulæ in question being based on the erroneous assumption that a and b are const. R. T.

Empirical control of a simple equation for real gases. E. J. M. Honigmann (Forsch. Gebiet Ingenieurw., 1931, 2, 261—266; Chem. Zentr., 1932, i, 1762; cf. A., 1931, 31).—For various gases and vapours $d(PV)/dJ=(n-1)/An$ and $C_p=g(TP^{(n-1)/n})$, where A is the mechanical equiv. of heat, J the heat content, n a sp. const., and g is a no. to be determined. L. S. T.

Entropy, heat content, and free energy of iron. J. B. Austin (Ind. Eng. Chem., 1932, 24, 1388—1391).—The entropy, heat content, and free energy of both α- and γ-Fe have been calc. for the temp. range —250° to 1600°. The heat of transition changes sign between the transition points, in accordance with theory. J. W. S.

Vapour-pressure constant of methane. T. E. Sterne (Physical Rev., 1932, [ii], 42, 556—564; cf. A., 1932, 566).—The consts. of the statistical quantum mechanical formula are evaluated. The v.-p. const. is —1·94, in close agreement with experiment. N. M. B.

Study of association by the fluidity method. E. C. Bingham and H. L. de Turk (J. Rheology, 1932, 3, 479—493).—Fluidities and vals. of d are recorded over the temp. range 0—100° for CEt_3·OH, phenylethyl alcohol, cetyl alcohol, MeCNS, PhSCN, COPhPr, Bu$^{\alpha}$ formate, acetate, propionate, n-butyrate, n-valerate, Et n-valerate, n-heptoate, n-amyl n-butyrate, and n-heptyl acetate. E. S. H.

Flow of viscous liquids. C. Camichel and collaborators (J. Rheology, 1932, 3, 413—436).—Applications of theory are considered. E. S. H.

[Stability of] liquid sodium amalgams. G. R. Paranjpe and R. M. Joshi (J. Univ. Bombay, 1932, 1, 17—24).—Sodium amalgams are said to represent colloidal suspensions of sodium in mercury. A. S. C. L.

Thermal and electrical conductivities of magnesium alloys. R. Kikuchi (Kinzoku-no-Kenk., 1932, 9, No. 6, 239—243).—When Mg is alloyed with another element the thermal and electrical conductivities generally decrease proportionally to the amount added. The effects are in the order Al, Sn, Zn, Ag, Ni, Cu. The ratio of the changes in the two vals. is not const. Ch. Abs.

Transformation of β-mixed crystals in brass. R. Ruer (Z. anorg. Chem., 1932, 209, 364—368; cf. A., 1930, 161).—Heating and cooling curves for Cu–Zn alloys with 44·7—65·6% Cu give no indication of a double transition of the β-mixed crystals. A simple transition occurs at 453° with alloys having 53—64% and at 465° with those having 42—52% Cu in the presence of the α- and γ-phases, respectively. F. L. U.

Mechanism of the transformations in β-brass and in β-silver-zinc alloys. J. Weerts (Z. Metallk., 1932, 24, 265—270).—Micrographic, X-ray, and kinetic observations show that both transformations are governed strictly by crystallographic lattice relations. After quenching β-brass the β–α transformation occurs by a lattice displacement similar to that in the formation of martensite from supercooled austenite; the displacement parallel to the (110) plane in the $(1\bar{1}0)$ direction amounts to 0·36 Å. and that parallel to the (112) plane in the (110) direction to 0·22 Å. The β′–ζ transformation in Ag–Zn alloys, on the other hand, shows all the characteristics of a growth from a const. no. of nuclei at a const. linear rate. A. R. P.

Nature of the β-transformation of copper–tin alloys. II. H. Imai and M. Hagiya (Mem. Ryojun Coll. Eng., 1932, 5, 77—89).—Dilatometric measurements confirm the results afforded by thermal and electrical resistance data (A., 1931, 33). The striated cryst. structure gives place to a closer texture, which appears to be characteristic of the β″ state. The martensitic needle-like structure, formed by chilling β-bronze poor in Sn from a high temp., is destroyed by annealing at 450—500°; it is apparently characteristic of the intermediate β′ form. E. S. H.

Alloys of gallium with zinc, cadmium, mercury, tin, lead, bismuth, and aluminium. N. A. Pushin, S. Stepanović, and V. Stajic (Z. anorg. Chem., 1932, 209, 329—334).—M.-p. data show that Ga forms two immiscible liquid layers with Cd, Hg, Bi, and Pb. With Zn and Sn eutectic mixtures and with Al the compounds Ga_6Al, GaAl, and $GaAl_2$ are formed, whilst with Na a compound of high m.p. and unknown composition is formed. Ga has a max. solubility of 5% in liquid Pb, about 11% in liquid Bi, 12—13% in liquid Cd, and is practically insol. in Hg at low temp. E. S. H.

Alloys of palladium with antimony. A. T. Grigoriev (Z. anorg. Chem., 1932, 209, 308—320).—Thermal analysis and observations on microstructure and electrical resistance confirm the existence of the compounds PdSb and Pd_3Sb, but not Pd_5Sb_3. The eutectic contains 58·17 at.-% Pd. E. S. H.

Alloys of gold with antimony. A. T. Grigoriev (Z. anorg. Chem., 1932, 209, 289—294).—Electrical conductivity measurements support the results of thermal analysis and confirm the existence of $AuSb_2$. It is probable that each metal is slightly sol. in the other in the solid state. E. S. H.

System tungsten–cobalt. C. Agte, K. Becker, and von Goler (Metall-Wirt., 1932, 11, 447—450; Chem. Zentr., 1932, ii, 1682).—Co is sol. in W up to 10 at.-%; W is sol. in Co up to 8 at.-%. There is an intermediate crystal form, containing 52—63 at.-% Co, which has m.p. 1710° and is an intermetallic compound. It decomposes on fission. A. A. E.

Rules of valency electron concentration in binary intermetallic alloys. H. Perlitz (Acta Comm. Univ. Tartu., 1932, No. 24, 3—16).—From a consideration of the rules governing the valency electron concn. in β-, γ-, and ε-lattices, it is shown that such lattices can be expected only in those binary intermetallic alloys in which one pure component contributes at the most one, and the other component at least two, valency electrons to the lattice structure;

β-, γ-, and ε-lattices will thus be expected in binary alloys containing a transition metal or Cu, Ag, or Au, together with a metal of a *B* sub-group or Be or Mg. The nos. of valency electrons which take part in the metallic binding are given for various metals. A. J. M.

System silver–copper–cadmium. M. KEINERT (Z. physikal. Chem., 1932, **162**, 289—304).—The equilibrium diagram has been established by micrographic methods. R. C.

Copper-rich alloys of the copper–nickel–tin system. J. T. EASH and C. UPTHEGROVE (Amer. Inst. Min. Met. Eng., Preprint, 1932).—For alloys containing 0—20% Ni, the α-phase boundary and the liquidus and solidus temp. have been determined. Alloys containing >31% Sn and 5% Ni were also investigated. Addition of Ni to Cu–Sn alloys decreases the solubility of Sn in the α-phase; fall of temp. produces the same effect. The α+δ eutectoid which occurs in Cu–Sn alloys is replaced by either the θ phase or the δ′ phase when >1% Ni is added. The θ phase is always homogeneous; the second new phase may be homogeneous or in the form of the α+δ′ eutectoid, depending on the rate of cooling. CH. ABS.

Polymorphic transformation of iron at points A3 and A4. V. N. SVECHNIKOV (Domez, 1932, No. 4—5, 29—32).—Sp. vol. changes are 1·94 and 6·67%, and the heat changes 0·9 and 3·4 g.-cal. per g., for A4 and A3, respectively. Different ratios obtained with another sample are attributed to the presence of gaseous impurities. CH. ABS.

Surface energy of iron carbide. Y. CHU-PHAY (Amer. Soc. Steel Treating, 13th Ann. Conv., 1931, 25 pp.).—The surface energy of Fe_3C is calc. to be 4900 and 3800 ergs per sq. cm. at 20° and 1136°, respectively. These vals. account for the hardness of martensite, in which the particle size of Fe_3C corresponds with a radius of $3—4\times10^{-7}$ cm. C. W. G.

Effect of carbon on the hardness and the transformation points of nickel–chromium steels. T. MURAKAMI and M. MIKAMI (Kinzoku-no-Kenk., 1932, **9**, No. 6, 225—238).—The steel contained Ni 3·21, Cr 0·96, C 0·31—1·11%. A3 gradually falls as the C content increases, although A1 is nearly const. As the max. heating temp. or the cooling rate increases, the transformation point is markedly lowered, resulting in self-hardening. The self-hardening ability increases as the C content increases up to 0·8%. The hardness of the Ni–Cr steels increases as the cooling rate increases and as the C content increases up to 0·8%. The micro-structure of the specimens is described. CH. ABS.

Transformations in the hardening of steel. F. WEVER (Z. Metallk., 1932, **24**, 270—275).—In the first stage of the transformation of austenite (650—500°) excess ferrite saturated with C separates above the pearlite point (590°), and below this point the austenite decomposes into a highly disperse mixture of ferrite and cementite owing to the sudden decrease in the rate of diffusion. In the second stage (500—120°) the austenite is converted into an intermediate stage characterised by needle-like crystals which slowly decompose by diffusion into cubic ferrite and cementite or an unknown C compound of Fe. In the third stage transformation of austenite proceeds directly to the intermediate state of tetragonal martensite without diffusion; on annealing this decomposes by diffusion into the more stable cubic form with the pptn. of C. A. R. P.

Martensite crystallisation followed cinematographically. H. J. WIESTER (Z. Metallk., 1932, **24**, 276—277).—Steel with 1·65% C was quenched in a metal bath at 100° to obtain homogeneous austenite; the specimen was then etched at 100°, allowed to cool slowly to room temp. or quenched in liquid air to −20°, and the formation of martensite followed by taking photographs with a cine-camera at 20 exposures per min. The film showed that the formation of a martensite needle takes place in <0·05 sec. A. R. P.

Refractive index of liquid mixtures having benzene as a component. N. A. PUSHIN and P. G. MATAVULJ (Z. physikal. Chem., 1932, **162**, 415—418).—The *n*–concn. (wt.-%) curves of various binary mixtures of C_6H_6 with phenols and aromatic amines are convex to the concn. axis, which is ascribed to dissociation in the mixtures of associated mols. of the second component. With C_6H_6–C_5H_5N mixtures the curve is slightly concave to the concn. axis. R. C.

Influence of cellulose nitrate of varying stability on the refraction of liquid mixtures. T. TOMONARI (J. Soc. Chem. Ind., Japan, 1932, **35**, 465—467B).—The val. of *n* for dispersions of cellulose nitrate in mixed solvents is shown to vary with the method of prep. and after-treatment of the cellulose nitrate and to be independent of the N content. The determination of *n* would seem to provide a rapid and sure means of assessing the stability of cellulose nitrate preps. V. E. Y.

Vapour–liquid equilibria of ethyl alcohol–water mixtures at temperatures from 120° to 180°. T. KLEINERT (Angew. Chem., 1933, **46**, 18—19).—The relation between the composition of the vapour and of the liquid at 120°, 140°, 160°, and 180° is expressed graphically. The compositions of the azeotropic mixtures at these temp. are given. E. S. H.

Heat content of liquid ethyl alcohol–water mixtures. F. BOSNAJAKOVIĆ and J. A. GRUMBT (Forsch. Gebiet Ingenieurw., 1931, **2**, 421—428; Chem. Zentr., 1932, i, 1763).—Heat contents, heats of mixing, and b.p. under pressures up to 3 atm. are recorded. L. S. T.

Mechanical properties of binary inorganic salt mixtures. K. LAYBOURN and W. M. MADGIN (Trans. Faraday Soc., 1932, **28**, 857—866).—Transverse breaking strength, compression strength, and Brinell hardness have been measured for the systems $NaNO_3$–KNO_3, $Ph(NO_3)_2$–$NaNO_3$, and $Pb(NO_3)_2$–KNO_3. Property–composition curves are of the same general form in all three. Such measurements therefore do not distinguish between solid solutions and eutectics. Reproducible results can be obtained

only when the effects of atm. moisture on the surface of the castings are removed by treatment with H_2O and subsequent protection with oil. F. L. U.

System water–phenol. II. Viscosities. O. R. HOWELL (Trans. Faraday Soc., 1932, 28, 912—928; cf. A., 1932, 990).—Viscosities of the homogeneous mixtures have been determined at intervals of 10° from 20° to 70°. The viscosity–composition curve at 70° is sagged in the neighbourhood of the crit. composition. The results are considered to indicate formation of an equimol. compound. The applicability of various formulæ to represent the relation between viscosity and composition or temp. is discussed. F. L. U.

Two liquid phases of minimum density in the system carbon disulphide–ethylene dichloride. D. L. HAMMICK and J. HOWARD (J.C.S., 1932, 2915—2916).—The temp. curve for the solid–liquid equilibrium in the system CS_2–$C_2H_4Cl_2$ shows a flat portion indicating a separation into two liquid layers at −50°. Mixtures corresponding with this part of the curve become turbid at various temp. below about −30°, with a max. temp. for an approx. equimol. mixture. For the equimol. mixture d^{20} is a min. M. S. B.

Systems of four immiscible layers. J. R. PARTINGTON (Nature, 1932, **130**, 967).—The system previously described (A., 1931, 159) is unstable and separates into two layers on long keeping. L. S. T.

Behaviour of sulphur dioxide towards water. D. S. DAVIS (Chem. and Met. Eng., 1932, **39**, 615—616).—Equations are given which express the variation of the dissociation const. of H_2SO_3 and the solubility of SO_2 between 0° and 40°. A solubility nomograph has also been derived. D. K. M.

Is ammonia evolved by the freezing of sea-water ? G. TAMMANN and H. J. ROCHA (Z. anorg. Chem., 1932, **209**, 257—263).—Partial pressures of NH_3 in aq. solutions of NaCl, $CaCl_2$, and $MgCl_2$ have been determined between 0° and −80°. The salts (especially $MgCl_2$) lower the partial pressure of NH_3. The question whether appreciable amounts of NH_3 can accumulate in the atm. in geological time by the continual transport of sea-water from the tropics to the polar regions is discussed. E. S. H.

Volatility of boric acid in steam. S. BEZZI (Annali Chim. Appl., 1932, **22**, 713—725).—Discordant results of previous authors are attributed to differences in the experimental conditions. The transformation of the *o*- into the *m*-acid is due to dehydration. At 100°, *m*-boric acid is stable and non-volatile and the *o*-acid is converted into the *m*-acid even at 50°. In solution the two acids co-exist, but the *o*-acid is alone volatile in steam at temp. up to slightly above 100°. T. H. P.

Equilibrium in binary systems under pressure. III. Influence of pressure on the solubility of ammonium nitrate in water at 25°. L. H. ADAMS and R. E. GIBSON (J. Amer. Chem. Soc., 1932, **54**, 4520—4537; cf. A., 1932, 810).—Sp. vols. of NH_4NO_3 solutions at atm. pressure are recorded. Measurements of the compressibility show that the partial vol. of NH_4NO_3 does not increase with pressure, except with 15% solutions at low pressures. Above 5000 bars the partial vol. of NH_4NO_3 is independent of the concn. when this is >15%. The solubility of NH_4NO_3, calc. thermodynamically, decreases continuously with increasing pressure, and the solubility curve intersects the freezing pressure curve of ice_{VI} at 12,100 bars and 25·3 wt.-% NH_4NO_3. The equilibrium diagram for pressures up to 12,000 bars is confirmed by experiment. J. G. A. G.

Partial pressures and distribution ratios of acetic acid over its aqueous solutions at 25°. K. FREDENHAGEN and H. LIEBSTER (Z. physikal. Chem., 1932, **162**, 449—453).—Partial pressure measurements show that the distribution ratio of single mols. between the liquid and gaseous phases varies from $8{\cdot}24\times10^4$ for $0{\cdot}018N$ to $14{\cdot}5\times10^4$ for $2{\cdot}54N$ solution. R. C.

Distribution ratios of hydrogen fluoride over the binary system water–hydrogen fluoride at 25°, and b.-p. curve of this system under atmospheric pressure. K. FREDENHAGEN and M. WELLMANN (Z. physikal. Chem., 1932, **162**, 454—466).—The conductivity of aq. HF has been measured at dilutions of 0·5—10,000 litres. The dilution law is not valid even at the highest dilution. The distribution ratio of single HF mols. between the liquid and gas phase, as deduced from partial pressure measurements with 0·090—63·7 mol.-% solutions, passes through a max. at about 0·9 mol.-%. The b.-p. curve, measured over the whole range of concns. under 1 atm., exhibits a max. at about 33 mol.-% HF. R. C.

Distribution ratios of hydrogen cyanide and water over the binary system water–hydrogen cyanide at 18°. K. FREDENHAGEN and M. WELLMANN (Z. physikal. Chem., 1932, **162**, 467—470).—The distribution ratio of HCN between the liquid and gaseous phase, calc. from partial pressure data (A., 1927, 819), passes through a max. at about 80 mol.-% HCN. R. C.

Distribution method for determining dissociation pressures of salt ammoniates. R. P. SEWARD (J. Amer. Chem. Soc., 1932, **54**, 4598—4605).—The solubility of NH_3 at pressures < 455 mm. in $CHCl_3$ at 25° has been determined. Dissociation pressures of salt ammoniates, in accord with vals. obtained statically, are determined more rapidly by shaking the solid ammoniates with $CHCl_3$. Experiments with $ZnCl_2,4NH_3,H_2O$ indicate that a dissociation pressure of NH_3 can be measured in the presence of H_2O by the distribution method with $CHCl_3$. J. G. A. G.

Adsorption of gases by active charcoal. H. REMY [with W. HENE] (Kolloid-Z., 1932, **61**, 313—322).—The adsorbability of a series of gases by active C at 15° bears a simple relation to the v.p. of the liquefied gases. The variation of adsorption with pressure has been determined for SO_2, MeCl, CO_2, N_2O, N_2, O_2, and H_2, and an empirical formula expressing the influence of temp. has been derived. The adsorption of gases from mixtures bears no relation to the partial pressures of the components. E. S. H.

Testing the adsorption formula by adsorption measurements with a highly active charcoal.

E. L. LEDERER (Kolloid-Z., 1932, **61**, 323—328).—Remy's data (cf. preceding abstract) agree with the Langmuir isotherm. The data suggest that the adsorbabilities of gases or vapours in corresponding states are equal. The application of the mixture rule to the adsorption of mixed gases is complicated by differences in the velocity and structure of the mols. E. S. H.

Adsorption of electrolytes by ash-free charcoal. VII. Evidence that negative adsorption of inorganic bases decreases with time of contact of charcoal with solution. E. J. MILLER (J. Physical Chem., 1932, **36**, 2967—2980; cf. A., 1928, 167).—C must be heated at or above 1000° to produce negative adsorption from solutions of NaOH. The degree of negative adsorption increases with time. It is impossible to remove completely even a feebly adsorbed acid (HCl) by repeated extraction with boiling H_2O, but complete removal may be effected by electrodialysis. E. S. H.

Adsorption displacement and molecular orientation on activated ash-free carbon. E. LANDT and W. KNOP (Z. physikal. Chem., 1932, **162**, 331—345).—When HCl is displaced by monobasic fatty acids and alcohols in the adsorption from aq. solution on sugar-C which does not adsorb alkali, the quotient, k, of the no. of HCl mols. displaced by the no. of adsorbed org. mols. is const. for a given org. compound, but is proportional to the no. of C atoms. It is therefore concluded that there is no sp. poisoning of the centres adsorbing HCl, but that the org. mols. act simply by the C atoms lying flat on the C surface and thus reducing the adsorbing area. For dibasic org. acids of low mol. wt. k varies considerably with the concn., which is attributed to the simultaneous occurrence of mol. adsorption and ionic exchange, but with the higher homologues the variation of k with the concn. is less marked and apparently the CH_2 groups lie on the surface. The ring of BzOH seems to lie on, and the CO_2H to stand at right angles to, the C surface. R. C.

Adsorption of electrolytes by carbon mixtures. J. ŠÁNA (Z. Zuckerind. Czechoslov., 1932, **57**, 121—125).—Electrolytes are adsorbed by mixtures of gas and chemically activated C in a selective manner. In general, such mixtures show a greater adsorption than would be expected according to the mixture rule, although the difference is not so great as that observed for their colour-adsorption val. J. P. O.

Adsorption. I. Adsorption of carbon dioxide, sulphur dioxide, and water. II. Adsorption of lower fatty acids. R. C. BOSWORTH (Trans. Faraday Soc., 1932, **28**, 896—902, 903—912).—I. Refractometric determination of the adsorption of CO_2 or SO_2 from air, both dry and moist, at a Hg surface, shows that CO_2, SO_2, and H_2O are selectively adsorbed as a unimol. layer in $<0{\cdot}25$ sec. When two active gases are present each is adsorbed in a proportion depending on the relative concns., but the total no. (n) of adsorbed mols. corresponds with a unimol. layer and is independent of the relative concns. For a layer not saturated, $n \propto c^{2/3}$.

II. Similar results have been obtained for unsaturated vapours of the first five fatty acids. At and near saturation multimol. layers are formed. $EtCO_2H$, $PrCO_2H$, and $BuCO_2H$ can form two types of adsorption layers, one at low and the other at high pressures. The behaviour is interpreted on the basis of two-dimensional packing. Gibbs' equation is valid for concns. $> 30\%$ saturation. F. L. U.

Adsorption of oxalic acid by alumina. P. H. DEWEY (J. Physical Chem., 1932, **36**, 3187—3188).—AcOH and $H_2C_2O_4$ are adsorbed by Al_2O_3; AcOH, but not $H_2C_2O_4$, can be washed out by H_2O. The adsorbed $H_2C_2O_4$ can be determined by titrating with hot, acid $KMnO_4$ solution. E. S. H.

Sorption of alcohol and ether vapour by silica gel. L. VON PUTNOKY and W. NERATH (Math. nat. Ber. Ungarn, 1931, **38**, 173—225; Chem. Zentr., 1932, ii, 514).—A period of adsorption is followed by one of capillary condensation. In the former the velocity depends on the internal surface of the gel, and in the latter on the size of the pores. A. A. E.

Hygroscopic moisture of cellulose. X. Velocity of sorption of water vapour on cellulose. S. OGURI (J. Soc. Chem. Ind., Japan, 1932, **35**, 507—515B).—The sorption velocity of H_2O vapour on cellulose of varying origin and on fibrous materials such as wool and silk is examined. The sorption of H_2O vapour on cotton and other celluloses at const. pressure and temp. proceeds in at least two stages, the velocity in each being represented fairly well by $dx/dt = k(x_\infty - x)$, where x and x_∞ denote the sorption at time t and at equilibrium, respectively. V. E. Y.

Sorption of vapours on wood and cellulose. N. H. GRACE and O. MAASS (J. Physical Chem., 1932, **36**, 3046—3063).—Apparatus and technique for measuring the sorption of vapours by cellulose by the use of a quartz spring balance in an evacuated glass system are described. Results are given for the sorption of H_2O vapour by various woods, and are compared with the vals. for cotton cellulose. Cellulose sorbs gaseous HCl appreciably, but equilibrium is attained very slowly; the process is more rapid with white spruce as sorbent. The form of the sorption curve is quite different from that of H_2O vapour and resembles the Freundlich isotherm. Equilibrium vals. are reached more quickly with wet wood than with dry wood, and the amount of HCl sorbed by the wet wood is greater (after allowing for the amount taken up by the H_2O present). It is probable that the sorption of HCl approximates to true surface adsorption, in which case the phenomena can be explained by supposing that the H_2O increases the active surface available for adsorption of HCl. Preliminary results are reported on the sorption of SO_2, NH_3, CO_2, Et_2O, amylene, and MeOH. Sorption of Et_2O and of amylene is very small, but large amounts of MeOH are taken up. E. S. H.

Sorption of sodium hydroxide on cellulose and wood. R. RICHARDSON and O. MAASS (J. Physical Chem., 1932, **36**, 3064—3073).—Data for the sorption of NaOH in aq. solution by cotton, spruce flake, and "celanese" are given. Theoretical treatment of the results is reserved. E. S. H.

Condensation of water vapour on dust nuclei. G. R. PARANJPE, H. D. MIRCHANDANI, and Y. G. NAIK (J. Univ. Bombay, 1932, **1**, 5—17).—The influence of the number of nuclei on the size of the drops in the formation of a cloud has been examined. A. S. C. L.

Adhesion tension. Receding contact angle, pressure of displacement method. F. E. BARTELL and C. E. WHITNEY (J. Physical Chem., 1932, **36**, 3115—3126).—A rapid method for measuring the receding contact angles formed in the pores of a membrane of compressed powder is described. The adhesion tensions of a no. of liquids against SiO_2 (including those which have zero contact angle), determined by this method, agree closely with those obtained by the single capillary method. The results furnish evidence that the free surface energy changes, which occur when org. liquids come into contact with polar solids, are of the same order as the corresponding energy changes for contact of the same liquids with H_2O. E. S. H.

Interfacial tension between asphaltic materials and solutions of alkaline inorganic salts. R. N. TRAXLER and C. U. PITTMAN (Ind. Eng. Chem., 1932, **24**, 1391—1393).—Solutions of Na_3PO_4 and Na_2SiO_3 give lower interfacial tensions in contact with asphaltic fluxes than do Na_2HPO_4 and $Na_2B_4O_7$, whilst Na_2CO_3 solutions give intermediate results. The occurrence of reaction at such interfaces may have considerable influence on the type and stability of a bituminous emulsion. Possible effects of varying p_H and of the nature of the anion are discussed. J. W. S.

Surface activity and surface tension as a method of investigation of flotation reagents. I. M. E. LIPETZ and M. M. RIMSKAYA (Tzvet. Met., 1931, 594—610).—Surface tension measurements have been used to determine: (1) the solubility of $C_{10}H_7{\cdot}NH_2,HCl$, *m*-xylidine, *m*- and *p*-cresol, *n*-hexoic and *n*-heptoic acids in H_2O, (2) the effect of p_H of the medium on the surface activity of *p*-$C_6H_4Me{\cdot}SO_3H$ and α-$C_{10}H_7{\cdot}NH_2$ distributed between H_2O and PhMe or H_2O and C_6H_6, (3) the flattening of the meniscus on the C_6H_6–H_2O surface caused by alkalis and hydrolysing salts, and (4) the partition of *p*-cresol between H_2O and C_6H_6 and its adsorption isotherm on the H_2O–C_6H_6 boundary. CH. ABS.

Spreading of oil on water. P. WOOG (Ann. Office Nat. Combust. liq., 1931, **6**, 617—655; Chem. Zentr., 1932, i, 1764).—A theoretical discussion of the spreading of oil on H_2O, of the difference between fatty, mineral, and activated mineral oils, and of the smoothing of waves by means of oil. L. S. T.

Boundary lubrication by soap solutions. R. C. WILLIAMS (J. Physical Chem., 1932, **36**, 3108—3114). —A dynamometer for the study of lubrication in wire-drawing is described. The effectiveness of solutions of Na or NH_4 soaps is due to the fatty acid or acid soap formed by hydrolysis; the solutions have no lubricating properties when hydrolysis is repressed. There is no close relation between lubrication and surface tension when the p_H is varied. E. S. H.

Transmission of surface changes in the interior of crystals. D. BALAREV and B. SREBOV (Kolloid-Z., 1932, **61**, 344—346).—The temp. of reaction of finely-divided BaO, CaO, and MoO_3 with various oxides and salts varies with the relative amounts of the reactants, but not in accordance with any simple rule. Surface changes are believed to be transmitted to the interior of crystals. E. S. H.

Electrokinetics. XII. Interfacial energy and molecular structure of organic compounds. II. Al_2O_3–organic liquid interfaces. O. G. JENSEN and R. A. GORTNER (J. Physical Chem., 1932, **36**, 3138—3151; cf. A., 1932, 804).—Streaming potentials of Al_2O_3–liquid interfaces for 15 org. liquids have been measured and the ζ potential, electric moment of the double layer, and degree of orientation calc. The streaming potential increases linearly with pressure. For a series of *n*-aliphatic esters, the ζ potential and electric moment of the double layer decrease with increasing no. of C atoms. In all the esters examined the immobile side of the double layer is negatively charged (except HCO_2Et), and is positively charged in the series of *n*-aliphatic acids. The ζ potential and electric moment also show the alternating effect of odd and even no. of C atoms. The symmetrical C_6H_6 and CCl_4 mols. give no streaming potential. The % of unbalanced mols. oriented in the interface decreases with increasing length of the C chain and is parallel with the electric moment per unit area of the double layer. This observation suggests that the electrokinetic forces at a solid–org. liquid interface are due to the electrical dissymmetry of oriented org. mols. E. S. H.

Fundamental assumptions and equations of electrokinetics. J. W. MCBAIN and M. E. LAING-MCBAIN (Z. physikal. Chem., 1932, **161**, 279—298).—The classical Helmholtz theory is inadequate because it does not take into account the existence or properties of ions. The authors' theory (A., 1924, i, 937; ii, 594; 1931, 1121), however, leads to a clearer picture of electrokinetic phenomena and also gives a comprehensive and quant. representation of the experimental data. R. C.

Application of the double-layer theory of Otto Stern. I. F. URBAN and H. L. WHITE (J. Physical Chem., 1932, **36**, 3157—3161).—Using Stern's equation, a relation between ζ potential and surface conductance is derived. All the ions of the double layer are believed to be mobile in an electric field. E. S. H.

Correlation of stream potentials and surface conductance. H. L. WHITE, F. URBAN, and E. A. VAN ATTA (J. Physical Chem., 1932, **36**, 3153—3156).—Streaming potentials measured with capillaries of 0·005 mm. diam. are 0—25% > those determined with large capillaries (cf. A., 1932, 699). This result cannot be accounted for by the classical stream-potential equation. E. S. H.

Liesegang rings. S. C. BRADFORD (Nature, 1932, **130**, 1002).—Polemical. L. S. T.

Osmotic systems in which non-diffusing substances may occur also. II. Equilibrium and change of permeability of the membrane. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1131—1139).—Mathematical. D. R. D.

Dispersion of salt solutions. Relation between dispersion and osmotic coefficients. G. KARAGUNIS (Praktika, 1931, **6**, 385—391; Chem. Zentr., 1932, ii, 2149).—The relative differences in dispersion of alkali halide solutions have been determined and related to the osmotic coeff. A. A. E.

Classical dissociation theory. G. TAMMIANN (Z. physikal. Chem., 1932, **163**, 17—32).—If the internal work due to the change in the internal pressure caused by ionisation is taken into account, the heat of ionisation calc. from the variation of the mass action const. with the temp., T, is positive and independent of T. The effect of pressure on the conductivity of solutions of salts and strong acids points to complete ionisation. Heats of neutralisation of strong acids and bases do not vary with T when the internal work is taken into account. The vol. changes in the neutralisation are to be attributed, not to the formation of H_2O from its ions, but to changes in internal pressure, and their variation with T corresponds with that of the compressibility of H_2O. In the formation of $NH_4^{\cdot}$ from NH_3 and $H^{\cdot}$, however, there is a considerable contraction. Corresponding solutions have equal internal pressures, and are not usually isohydric. R. C.

Association of strong electrolytes. J. ZIRKLER (Z. physikal. Chem., 1932, **163**, 1—7).—The degree of association of $Ba(NO_3)_2$ deduced from the temp. coeff. of the conductivity agrees approx. with the val. calc. from the temp. coeff. of the heat of dilution. Vals. have therefore been calc. for other electrolytes from conductivity data. Differences between the thermal and conductivity data are ascribed to heat of solvation of the ions. R. C.

Dusts, smokes, mists, and fogs. W. E. GIBBS (Chem. and Ind., 1932, 1042—1043).—An alternative classification of aerosols is proposed instead of that advocated by Blacktin (this vol., 23), emphasis being placed on the importance of particle size. D. R. D.

Dusts, smokes, mists, and fogs. S. C. BLACKTIN (Chem. and Ind., 1932, 1077—1078).—A reply (cf. preceding abstract). D. R. D.

Theory of emulsions. C. H. M. ROBERTS (J. Physical Chem., 1932, **36**, 3087—3107).—A general discussion, in which the properties and behaviour of emulsions are described in terms of those of ions and mols. in heterogeneous systems. E. S. H.

Dielectric constants of disperse systems. A. PIEKARA (Acta phys. Polon., 1932, **1**, 135—153; Chem. Zentr., 1932, ii, 1601).—For Hg–vaselin emulsions ε depends on the particle size; deviations from the theoretical val. increase as the size of the Hg particles diminishes. The deviation is attributed to the effect of boundary layers of oriented mols. about 100 mols. thick. A. A. E.

Dielectric constants of water and alcohol emulsions. A. PIEKARA (Acta phys. Polon., 1932, **1**, 155—163; Chem. Zentr., 1932, ii, 1602).—For the emulsions examined the deviations from the Clausius–Mosotti vals. are much $<$ for media of low ε; an orientation effect is not apparent. A. A. E.

Validity of the Clausius–Mosotti law for emulsions. W. S. URBANSKI (Acta. phys. Polon., 1932, **1**, 165—176; Chem. Zentr., 1932, ii, 1601).—Vals. of ε for suspensions of Wood's metal of const. particle size in vaselin–vaselin oil deviate considerably from calc. vals. The deviations are attributed to changes in the polarisation of the suspended particles. A. A. E.

[Validity of the Clausius–Mosotti law for emulsions.] A. PIEKARA (Acta phys. Polon., 1932, **1**, 285—287; Chem. Zentr., 1932, ii, 1602).—Polemical (cf. preceding abstract). A. A. E.

Colloidal boron. A. L. ELDER and N. D. GREEN (J. Physical Chem., 1932, **36**, 3085—3086).—Sols of pure B are prepared by fusing Mg and B_2O_3 (1 : 3), extracting with HCl, and refluxing 0·5—1·0 g. of the dried B with 100—250 c.c. distilled H_2O. The sol differs in properties from impure B sols formerly described. The particles are negatively charged and are extremely resistant to coagulation, even by multivalent ions. The sol cannot be conc. by evaporation. E. S. H.

Preparation and properties of highly concentrated sols. II. Sols of vanadium pentoxide, silicic acid, and molybdic acid. C. AHOBALACHARYA and N. R. DHAR. **III. Sols of zirconium hydroxide.** R. D. SHARMA and N. R. DHAR (J. Indian Chem. Soc., 1932, **9**, 441—453, 455—461).—II. The viscosities of sols prepared from NH_4 vanadate and HCl and from $SiCl_4$ and H_2O increase greatly during dialysis and the concn.–viscosity curves of the dialysed sols are very steep. The viscosity of a conc. sol prepared from NH_4 molybdate and HNO_3 is practically the same as that of H_2O. The ratio of the coagulating concns. of KCl and $BaCl_2$ decreases with increasing purity of the V_2O_5 and molybdic acid sols, but increases with increasing purity of the SiO_2 sol sensitised with aq. NH_3.

III. By dialysing hot solutions of $Zr(NO_3)_4$, sols containing 100 g. and 55 g. of ZrO_2 per litre were obtained, in which the ratios ZrO_2/NO_3 were 6·6 and 16·1, respectively. These sols are very viscous, and the purer is the sol the steeper is the concn.–viscosity curve. Addition of $Zr(NO_3)_4$ diminishes the viscosity and increases the ratio of the coagulating concns. of $KBrO_3$ and K_2SO_4. The surface tension may be as low as 70·2, and the electrical conductivity increases on ageing. When the sol is dried slowly in the dark the residue returns to the sol state on addition of H_2O. A. G.

Stable suspension of dibenzanthracene in water. I. BERENBLUM (Lancet, 1932, **223**, 1107—1108).—Stable suspensions are produced by adding C_5H_5N solutions of 1 : 2 : 5 : 6-dibenzanthracene drop by drop with stirring to H_2O or, for more conc. suspensions, to a 6% solution of gum acacia, and dialysing for 2 or 3 days until C_5H_5N is removed. L. S. T.

Colloidal solutions of 1 : 2 : 5 : 6-dibenzanthracene. E. BOYLAND (Lancet, 1932, **223**, 1108; cf. preceding abstract).—A $COMe_2$ solution of 1 : 2 : 5 : 6-dibenzanthracene is poured into excess of 0·5% aq. gelatin solution (40—50°) with rapid stirring and boiled until $COMe_2$ is removed. The colloidal solution is

stable for long periods. Colloidal solutions stable towards heat and electrolytes, but of lower concn., are produced when gelatin is omitted. The hydrocarbon is negatively charged. 1 : 2-Benzanthracene, dihydroanthracene, and chrysene, but not anthracene, naphthacene, acenaphthene, and 1 : 2 : 5 : 6-dibenzphenazine, form colloidal solutions in this way. L. S. T.

Kinetics of cupric oxide sol formation. N. Peskov and E. Preis (Kolloid-Z., 1932, **61**, 328—335).—The formation of CuO sols by hydrolysis of Cu succinimide is a typical autocatalytic reaction of the first order. Cu succinimide has properties intermediate between those of colloids and crystalloids, probably by reason of its high dispersity; it is coagulated to CuO by electrolytes, but coagulation is inhibited by protective colloids or by excess of succinimide. E. S. H.

Relation between charge and stability of colloidal solutions of gold and ferric hydroxide dialysed to different extents. B. N. Desai, G. M. Nabar, and P. M. Barve (J. Indian Chem. Soc., 1932, **9**, 463—469).—When Au sols are dialysed the coagulating concn. of KCl and the cataphoretic speed increase at first and then decrease; the two effects show a close correspondence. $Fe(OH)_3$ sols also give a max. cataphoretic speed, but the coagulating concn. of KCl falls continuously. A. G.

Specific conductivity of the intermicellar liquid in gold sols. R. Wintgen and W. Hacker (Kolloid-Z., 1932, **61**, 335—344).—The electrical conductivity of a Au sol prepared by reduction with CH_2O is very nearly the same as that of the intermicellar liquid remaining after centrifuging the solid phase. Unprotected sols of relatively high Au content (up to 0·27%) can be obtained with the aid of the centrifuge. E. S. H.

Filtration phenomena in colloids. M. Annetts (J. Physical Chem., 1932, **36**, 2936—2939).—By passing an As_2S_3 sol through filter-paper, the electrical conductivity is decreased by about 50%. Repetition of the process reduces the conductivity to a const. val. These and other effects observed are explained by combination of (*a*) an increase in conductivity due to impurities derived from the filter-paper and (*b*) a decrease due to adsorption of $H^{\cdot}$ by the filter. E. S. H.

Critical potential characteristic of coagulation of a colloid. B. N. Desai (J. Univ. Bombay, 1932, **1**, 25—27).—Theoretical. The coagulation of a colloid by an electrolyte will be affected by both the non-coagulating and the coagulating ion. The initial adsorption of the former may lead to an increase of potential and of cataphoretic velocity before the concn. of the latter is sufficient to cause coagulation. With multivalent ions, the activity of the coagulating ion is so much greater that the effect does not occur. A. S. C. L.

Gelation of sucrose with metal hydroxides. W. Coltof (Kolloid-Z., 1932, **61**, 347—363; cf. A., 1932, 1202).—Under certain conditions solutions of sucrose and $Ca(OH)_2$ give a gelatinous ppt. on warming, which redissolves on cooling. A ppt. is also formed by great dilution or by adding KOH. Equilibrium diagrams are shown. E. S. H.

Study of gels by physical methods. E. Hatschek (J. Physical Chem., 1932, **36**, 2994—3009).—Gelatin cylinders with plane ends have been used in the determination of Young's modulus by compression and the results compared with those obtained by tension. The modulus decreases with increasing compression, and increases with increasing elongation. The modulus of agar gel decreases with increasing compression and undergoes no change with time. The modulus of SiO_2 gel is const. under increasing compression, but rises rapidly with age. The increase with age is very marked in gelatin gels hardened with CH_2O. The optical anisotropy of strained gels and the lenticular form of bubbles produced therein are discussed. Observations on the orientation of the equatorial planes of the lenticular bubbles show that: (1) during reversible deformation the direction of min. tensile strength is that in which the linear dimension has been increased, and (2) after irreversible deformation it is that in which the linear dimension has been reduced. Diffusion from a point source in a gelatin gel under strain gives a perfectly spherical zone; gels remain isotropic for diffusion both during reversible and after irreversible deformation. These results are discussed in relation to the fibrillar structure of the gel. E. S. H.

Structure of gelatin sols and gels. V. Insolubilisation of gelatin by heat. S. E. Sheppard and R. C. Houck (J. Physical Chem., 1932, **36**, 2885—2900; cf. A., 1932, 995).—Measurements of the rate of diminution of the swelling power and solubility in warm H_2O of gelatin after prolonged heating show that this is a function of temp. The reaction is termol., and the crit. increment, calc. from the temp. coeff., is 23,160 g.-cal. With ultra-violet light the change follows the same course, but is more rapid. The product has the same H_2O absorption as collagen and is converted into gelatin by extraction with hot H_2O, but the *X*-ray diagram of collagen and optical birefringence are not shown. When gelatin jellies, containing much EtOH, are stretched greatly and dried at room temp., the product is anisotropic and gives the *X*-ray diagram of collagen, but the H_2O absorption is the same as for unstretched gelatin. These facts suggest that the conversion of collagen into gelatin involves more than the disorientation of long-chain mols. assembled in crystallites; hydrolytic disruption of chemical linkings between the chains is probably involved. These linkings involve 2- or 3-dimensional polymerisation and hence the insolubility and restricted intermicellar absorption of H_2O. The phenomenon is compared with the vulcanisation of rubber and the " permanent set " of steamed hair. E. S. H.

Active oxides. LV. Dehydration of hydrogels in presence of different gases. G. F. Huttig and K. Strial (Z. anorg. Chem., 1932, **209**, 249—256; cf. A., 1932, 988, 1008).—The rate of loss of H_2O by hydrogels of $Cr(OH)_3$, $Zr(OH)_4$, and $Th(OH)_4$ depends on the gas or vapour in contact with the gel; it is greatest with NH_3 and MeOH, smaller with O_2 and H_2, and least with N_2. The H_2O content of

the product dried at a given temp. has a characteristic val. for each gas. These phenomena are related to the affinity of the gas for H_2O. E. S. H.

Determination of jelly strength and the modulus of elasticity E_D of gelatin jellies, and the effect of additions on the viscosity and E_D. E. GOEBEL (Collegium, 1932, 830—838).—Apparatus is described for the determination of jelly strength and E_D for different concns. of the jelly. E_D diminishes rapidly with rise of temp. A curve is given showing the variation of viscosity with E_D. E_D is practically independent of p_H in the region 5·0—7·5. The viscosity of hide glues is increased and E_D unaffected by addition of alum or CH_2O. Neither viscosity nor E_D is altered by addition of $ZnSO_4$. D. W.

Crystallisation and the setting of gelatin jellies. J. C. DERKSEN (Collegium, 1932, 838—842).—*X*-Ray interference rings are shown by gelatin jellies below their setting point, but not above; the behaviour suggests the presence of crystals. Similar interference effects are shown by air-dried gelatins, but not by gelatin jellies dried by hot air. The setting of gelatin solutions is attributed to the conversion of an amorphous form gelatin-*A* into a cryst. form gelatin-*B*. D. W.

Influence of acidity on solubility of silver chromate in gelatin solution. B. N. DESAI and G. M. NABAR (J. Univ. Bombay, 1932, **1**, 28—30).—The stability of Ag_2CrO_4 in gelatin solution increases as the p_H decreases from 5·15 to 5·00 on addition of AcOH. As the p_H decreases, the amount of Ag_2CrO_4 in ionic dispersion increases. A. S. C. L.

Coagulation, viscosity, and thixotropy in colloidal systems. S. S. KISTLER (J. Physical Chem., 1932, **36**, 2948—2966).—Theoretical. Colloids are divided into two classes, corresponding with lyophobic and lyophilic, according as the formation of cybotactic complexes (evanescent lattice-like arrangements of liquid mols.) is favoured by the surfaces or not. The stability of a lyophilic sol depends mainly on a concn. gradient of cybotactic complexes decreasing with the distance from each colloid particle, whilst the tendency to coagulate is connected with a gradient in the opposite direction. Coagulation, viscosity, and thixotropy, and the phenomena of viscosity, dispersion, diffusion, and lyotropic series are discussed in the light of these views. E. S. H.

Swelling and dissolution of cellulose esters. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1932, **35**, 500—503B).—The electrostatic attraction between the dipoles of cellulose acetate and the liquid media is the main factor in the swelling and dissolution of this ester (cf. B., 1929, 713). This dipole attraction results in a mol. aggregation of cellulose esters and the solvents. Both $COMe_2$-sol. acetates (I) and cellulose triacetate (II) swell better in strongly polar media, as is shown by the swelling of (II) in 2*M*-C_6H_6 solutions of various substances. All active swelling media have a high dipole moment. (II) swells in weakly polar media more, and in strongly polar media less, than (I); this is shown more clearly in binary mixtures. Cellulose nitrate (III) behaves substantially the same. Dissolution and swelling are also functions of the degree of depolymerisation of the ester. The order of the esters as regards swelling and dissolution in org. media is: (II)>(I)>(III). V. E. Y.

Elastometric method of measuring swelling. A. V. HOCHLOV (Kolloid-Z., 1932, **61**, 364—365).—Swelling is measured by the loss of elasticity. E. S. H.

Elasticity of caoutchouc. K. H. MEYER, G. VON SUSICH, and E. VALKÓ (Kolloid-Z., 1932, **61**, 370—371).—Polemical (cf. A., 1932, 1089). E. S. H.

Physical structure of elastic colloids. W. F. BUSSE (J. Physical Chem., 1932, **36**, 2862—2879).—The following features are regarded as characteristic of elastic colloid systems: (1) long, fibrous mols., (2) weak or uniform cohesive forces, (3) interlocking of the fibres, (4) a means of storing free energy when the fibres are distorted. The sp. properties of rubber are discussed in the light of these views. Fibrous rubbers are obtained by stretching cured, soft rubber and further curing it with S_2Cl_2 while stretched. When this treatment is applied with simultaneous stretching in two directions, a non-fibrous, parchment-like material is obtained, in which the fibres are probably oriented at random. This product is strong and flexible, and is very resistant to org. liquids. E. S. H.

Dielectric constants of aqueous solutions of some amino-acids and polypeptides. M. FRANKENTHAL (Z. physikal. Chem., 1932, **B**, **19**, 328—343).—NH_2-acids and polypeptides increase the dielectric const., ε, of H_2O, and with increase in the concn., c, ε rises and apparently approaches a limiting val. This behaviour is attributed to increase in the proportion of zwitterions. Among the α-monoaminomonocarboxylic acids the tendency to zwitterion formation seems to diminish as the no. of C atoms increases. Glycine anhydride depresses the ε of H_2O. These results agree qualitatively with the accepted configuration of the solutes. R. C.

Union of biocolloids. XI. Union between two proteins. S. J. PRZYŁECKI. **XII. Aggregation of gelatin.** S. J. PRZYŁECKI and J. TARGONSKA (Biochem. Z., 1932, **255**, 393—405, 406—419; cf. A., 1932, 1274).—XI. The factors which influence the combination of two proteins are discussed.

XII. Changes in the state of aggregation of gelatin have been followed by observing the time required for an Fe sphere to fall a known distance in the gel, the changes being produced by variation of p_H and by the introduction of various electrolytes, glucose, starch, and albumin. P. W. C.

Equilibrium constant of the reaction between ethyl alcohol and acetic acid. A. L. CORSO and C. A. DURRUTY (Anal. Asoc. Quim. Argentina, 1932, **20**, 140—146).—The equilibrium const. at 100° increases approx. linearly from 2 to 5 as the initial AcOH concn. is raised from 20 to 80 mol.-%; for a 50 mol.-% mixture the val. of the const. is 3·80±0·03. H. F. G.

Dissociation constants of organic acids. VI. Acetic acid. G. H. JEFFERY and A. I. VOGEL (J.C.S., 1932, 2829—2838).—Conductivity measure-

ments have been made at 25° on AcOH in SiO_2 cells and on NaOAc and KOAc in Pyrex cells, over the range 0·0001—0·01*N*. The data obtained for the salts have been corr. for hydrolysis. The classical and thermodynamic dissociation consts. are 1·813 and $1·776 \times 10^{-5}$, respectively. The limiting vals. for OAc′, determined from the Na and K salts, are 39·7 and 40·0, respectively. The results are compared with those of Shedlovski and MacInnes (A., 1932, 695, 699) and reasons for the discrepancies suggested. M. S. B.

Ammines. VI. Nickelammine salts in aqueous solution. H. J. S. King, A. W. Cruse, and F. G. Angell (J.C.S., 1932, 2928—2931).—From f.-p. depressions of pentamminonickel sulphate and hexammino- and hexapyridino-nickel nitrate in H_2O solutions of various concn. vals. are deduced for the no. of mols. of NH_3 or C_5H_5N still combined with each atom of Ni by attributing the excess f.-p. depressions of the ammines over those of equiv. solutions of $NiSO_4$ or $Ni(NO_3)_2$ to free base. New *compounds* are $[Ni(NH_3)_5]SO_4,H_2O$ and $[Ni(C_5H_5N)_6](NO_3)_2$ (I). In the former the proportion of free NH_3 varies from 0·6 to 3 mols. for concns. 0·3—0·075*M* and in $[Ni(NH_3)_6](NO_3)_2$ (II) from 0·44 to 0·8 mol. for 0·3—0·2*M* solutions. Free base in the C_5H_5N compound varies from 1·5 to 3·3 mols. for concns. 0·25—0·05*M*. (II) is more stable and (I) less stable than the corresponding Cu compound (cf. A., 1930, 1536). M. S. B.

Properties of volatile hydrides. III. System H_2S–CO_2. A. Klemenc and O. Bankowski (Z. anorg. Chem., 1932, **209**, 225—235).—The partial pressures of H_2S and CO_2 in liquid mixtures have been measured at low temp. The equilibrium diagram is characterised by a eutectic at −95·2° and 90·21 mol.-% H_2S. E. S. H.

Equilibrium diagram of a ternary system containing a gaseous phase. H. Nishimura (Suiyokwai-Shi, 1932, **6**, 735—744).—The diagram is derived theoretically. The systems Fe–N_2–H_2 and Fe–O_2–H_2 are discussed. Ch. Abs.

System lead acetate, acetic acid, water. G. Tarbutton and W. C. Vosburgh (J. Amer. Chem. Soc., 1932, **54**, 4537—4544; cf. A., 1928, 131).—Solubilities in HOAc–H_2O mixtures at 25° and 30° are recorded. The *compounds* $Pb(OAc)_2$,0·5AcOH and $Pb(OAc)_2$,0·5H_2O exist as stable solid phases. Anhyd. $Pb(OAc)_2$ is metastable. J. G. A. G.

Equilibria in systems containing magnesium oxide, iron oxide, and magnesium aluminate. H. G. Fisk and W. J. McCaughey (Ohio State Univ. Eng. Exp. Sta. Bull., 1932, No. 70, 1—44).—Fe oxide passes into solid solution in periclase at high temp., probably as MgO,Fe_2O_3 with Fe_3O_4. Mg ferrite separates on slow cooling. A continuous series of solid solutions is formed with spinel, which retains up to 50% Fe_3O_4 in solid solution at room temp. Spinel and Mg ferrite are isomorphous. Ch. Abs.

System $2FeO,SiO_2$–FeS. B. P. Selivanov, A. S. Ginzberg, and S. I. Nikolski (Sovbshch. Vsesoy. Inst. Met., 1931, No. 3—4, 74—78).—The m.-p. diagram shows solid solutions of FeS in $2FeO,SiO_2$, and of the latter in the former, with an intermediate region characterised by distinct liquid layers. A eutectic at 940° corresponds with about 43% $2FeO,SiO_2$ and 57% FeS. Ch. Abs.

Equilibria between metals and slags in melts. III. Equilibrium $2MnO+Si \rightleftharpoons SiO_2+2Mn$. W. Krings and E. Kehren (Z. anorg. Chem., 1932, **209**, 385—408; cf. A., 1932, 811).—The law of mass action is followed only when the regulus contains < 20% Si, the const. $([MnO]^2[Si]/[SiO_2][Mn]^2)$ being $0·113 \pm 0·025$ at 1500°. The decrease in the val. of the const. when the Si content is > 20% is attributed to auto-complex formation in the SiO_2. The thermal val. of the reaction at 1500° is 14·3 kg.-cal. The influence of admixtures was studied. F. L. U.

Formulation of the second law of thermodynamics. H. Hansen (Forsch. Gebiet Ingenieurw., 1932, **3**, 206—208; Chem. Zentr., 1932, ii, 985—986).

Activity coefficients of potassium chloride. Application of the extended Debye–Hückel theory to interpretation of f.-p. measurements. H. M. Spencer (J. Amer. Chem. Soc., 1932, **54**, 4490—4497).—Vals. are calc. from recent f.-p. data for aq. solutions and corr. for heats of dilution. A method of extrapolating from the low concn. region, where observations become difficult, to infinite dilution is given. J. G. A. G.

Activity coefficients of hydrochloric acid in uni-univalent chloride solutions at constant total molality. J. E. Hawkins (J. Amer. Chem. Soc., 1932, **54**, 4480—4487).—The e.m.f. of the cells $H_2|HCl(m_1)|AgCl|Ag$ and $H_2|HCl(m_1)+MCl(m_2)|AgCl|Ag$, where M=Li, Na, and K, and $m_1+m_2=0·1-6·0M$, has been determined at 25°. The linear relation between $\log \gamma$ and concn. is valid for the high concn. used, and the activity coeff. of HCl in LiCl is greater than that of pure HCl at the same concn. The consts. of the Hückel equation, derived by a simplified method, are in satisfactory agreement with the experimental data. J. G. A. G.

Free energies and heats of formation of tetrahydrate and anhydrous forms of cadmium bromide and their transition temperatures. H. M. Spencer and R. F. Selden (J. Amer. Chem. Soc., 1932, **54**, 4504—4515).—The e.m.f. of the cells $Cd,Hg|CdBr_2,4H_2O(s)|$sat. $CdBr_2,4H_2O$ + AgBr|AgBr(*s*)|Ag(*s*) and $Cd,Hg|CdBr_2(s)|$sat. $CdBr_2$ + AgBr|AgBr(*s*)|Ag(*s*), set up in the absence of O_2, have been determined at 25—35° and 35—45°, respectively. The transition point $CdBr_2,4H_2O(s)$–$CdBr_2(s)$–saturated solution determined thermally is 35·82° and from e.m.f. data is 35·63°. The thermodynamic quantities computed are compared with existing vals. J. G. A. G.

Thermodynamic properties of solid solutions of gold and silver. A. Wachter (J. Amer. Chem. Soc., 1932, **54**, 4609—4617; cf. A., 1931, 1371; 1932, 573).—The e.m.f. of the cell Ag(*s*)|AgCl(*s*)|Ag+ 0·0—0·85 mol. fraction Au (*s. solution*) has been determined at temp. between 192° and 415°. The e.m.f. at const. temp. varies continuously with the composition

of the alloy, and the vals. are lower than previously reported. The energy changes in the dilution of Ag with Au show the solid solution containing 0·5 mol. fraction of Ag to be the most stable. The activities of both Au and Ag exhibit large negative deviations from Raoult's law; the results are, however, compatible with the existence of a regular arrangement of Au atoms in the Ag crystal lattice. J. G. A. G.

Free energies of formation of various forms of lead monoxide. H. M. SPENCER and J. H. MOTE (J. Amer. Chem. Soc., 1932, **54**, 4618—4624; cf. A., 1928, 841).—Free energies of formation at 25° of the several forms of PbO are computed from e.m.f. data for cells Pb,Hg|PbO|0·05—0·21*M*-$Ba(OH)_2$|HgO(red) +PbO|Hg(*l*). The free energy contents of PbO,$\frac{1}{3}H_2O$ (neglecting that of H_2O) and yellow PbO exceed that of red PbO by 233 and 145 g.-cal., respectively. J. G. A. G.

Exact thermodynamics of membrane equilibria. F. G. DONNAN and E. A. GUGGENHEIM (Z. physikal. Chem., 1932, **162**, 346—360; cf. A., 1925, ii, 528).—By using Gibbs' chemical potential method and the function electrochemical potential (A., 1929, 885) exact thermodynamic equations have been derived for the membrane equilibrium of electrolytes and non-electrolytes in ideal and non-ideal solution, assuming that all the solutions become ideal at infinite dilution and that their compressibility is independent of the pressure. The relations between these equations and the usual approx. equations are worked out. R. C.

Heat of dissolution of water vapour in various solvents. R. P. BELL (J.C.S., 1932, 2905—2911).—The concn. of dissolved H_2O in equilibrium with the system Na_2SO_4–$Na_2SO_4,10H_2O$ has been determined for a no. of org. solvents at 15°, 20°, and 25° by the method previously described (this vol., 135). The vals. of Q, the heat of dissolution of H_2O vapour at const. vol., calc. from these and other data, are used to test the equations previously developed (A., 1931, 901; 1932, 21) for the electrostatic energy of dipole mols. in different media. The agreement is satisfactory. The equation $A=RT\log_e c_1/c_2$ has no thermodynamic basis when c_1 and c_2 refer to different media. M. S. B.

Heats of dilution of solutions of strong electrolytes, and Nernst's association hypothesis. E. PLAKE (Z. physikal. Chem., 1932, **162**, 257—280; cf. A., 1928, 953, 1097).—The heat of dilution, V, for the 25- and 50-fold dilution of 0·01—0·5*M* aq. solutions of various salts has been determined at 20°, and measurements have been made at 0° and 10° to ascertain the variation of V with temp. The results indicate that at about 20° bi-bivalent salts at concns. $<0·25M$ are practically completely dissociated, and application of the Gronwall–La Mer–Sandved extension of the electrostatic theory (*ibid.*, 841) gives vals. for the mean ionic diameters which agree with activity coeff. data. $Ca(OAc)_2$, $CaCl_2$, and $NiCl_2$ approx. follow the Debye–Bjerrum law (A., 1926, 476; 1927, 1028), and at concns. $< 0·5M$ are completely dissociated at 20°. The true degree of association, $(1-\alpha)$, and heat of dissociation have been calc. from V for various uni-bi- and bi-uni-valent salts by Nernst's method. The vals. of V calc. by assuming the mass law to be valid for the variation with concn. of the true association agree with the measured vals. only when equilibria of the type $[Ca(NO_3)]^{\cdot} \rightleftharpoons Ca^{\cdot\cdot}+NO_3'$ are assumed to occur. The tendency to true association increases with decrease in the valencies of the ions. For uni-bi- and bi-uni-valent salts the vals. of $(1-\alpha)$ deduced from data for V agree, in order of magnitude at least, with vals. deduced from f.-p. depression and conductivity data. R. C.

Concentration at which heats of dilution are measured in the calorimetric method. Correction. V. K. LA MER and I. A. COWPERTHWAITE (J. Amer. Chem. Soc., 1932, **54**, 4754—4755; cf. A., 1932, 1206).—A criticism is withdrawn. J. G. A. G.

Heats of formation of halide phosphinates. III. R. HOLTJE (Z. anorg. Chem., 1932, **209**, 241—248; cf. A., 1930, 876; 1931, 583).—The heats of formation for solid phosphinates produced from the solid halide and gaseous PH_3 are: $AlCl_3,PH_3$ 9·9±0·2, $AlBr_3,PH_3$ 14·3±0·3, AlI_3,PH_3 14·7±0·1, $SnCl_4,1·5PH_3$ 15·9±0·2, $TiCl_4,PH_3$ 16·4±0·1, $TiCl_4,2PH_3$ 13·6, $TiBr_4,PH_3$ 16·0±0·2, $TiBr_4,2PH_3$ 13·9. The compounds are more stable than the corresponding compounds with H_2S. E. S. H.

Limiting mobilities of some univalent ions and the dissociation constant of acetic acid at 25°. A. I. VOGEL and G. H. JEFFERY (Nature, 1933, **131**, 27—28).—A reply to criticism (this vol., 28). L. S. T.

Conductivity of aluminium chloride in non-aqueous solution. E. WERTYPOROCH and T. FIRLA (Z. physikal. Chem., 1932, **162**, 398—414).—Results similar to those recorded for $AlBr_3$ (A., 1931, 913) have been obtained. At small concns. the mol. conductivity, μ, of $AlCl_3$ in EtCl scarcely varies with the concn., which indicates that the complexes formed by solvation of Al_2Cl_6 and Al_4Cl_{12} are completely ionised and that the ions are not dissociated on dilution. In Pr$^{\alpha}$Cl, Pr$^{\beta}$Cl, and chloro*cyclo*hexane μ is much larger than in EtCl, which is attributed to the formation of propylene or *cyclo*hexene and its incorporation in the complex. BzCl and AcCl as solvents form salt-like compounds with the $AlCl_3$ and become part of the cation. With all these solutions the addition of C_6H_6 causes an increase in μ. Transport measurements with EtCl solutions containing hydrocarbons show that 4 hydrocarbon mols. migrate to the cathode with each Al atom. With the other solvents the amounts migrating are smaller. R. C.

Position of gold in the potential series in the electrolysis of molten alloys. L. LAMMERMAYR, jun., and R. KREMANN (Monatsh., 1932, **61**, 345—350).—Electrolysis of molten alloys of Au with Bi, Sb, Pb, and Al, respectively, in capillary tubes, followed by analysis of the anode and cathode regions, shows that the position of Au falls in the series Bi, Sb, Hg, Pb, Au, Al. E. S. H.

Electro-potentials of ternary gold–tin–mercury alloys. F. GRIENGL and R. BAUM (Monatsh., 1932, **61**, 330—344).—Isopotential lines for the system

Au–Sn–Hg have been determined. The curves afford no evidence of the existence of AuSn or $AuSn_2$, which are indicated, however, by discontinuities in potential in the binary system. The data suggest that both AuSn and $AuSn_2$ are partly dissociated in the ternary system. E. S. H.

Electro-potentials and constitution of gold amalgams. R. KREMANN and R. BAUM [with L. LAMMERMAYR, jun.] (Monatsh., 1932, **61**, 315—329).—The potential of Au–Hg alloys containing $< 30\%$ Au becomes less noble with time; amalgams containing 30—43·35% change little with time, whilst those containing 60—70% become more noble. When the Au content is $< 75\%$ (the Au_3Hg composition) the equilibrium potential is that of Hg, but when $> 75\%$ of Au is present the potential assumes a val. near that of Au. E. S. H.

Electrode potential of iron. III. Corrosion of iron in water in the absence of oxygen and determination of the solubility product of ferrous hydroxide. K. MURATA (J. Soc. Chem. Ind. Japan, 1932, **35**, 523—530B).—The rate of evolution of H_2 from 10 g. of powdered Fe in pure O-free H_2O reaches a min. of 0·3 c.c. per day after 4 days, then follows a continuous rise to a max. of approx. 1 c.c. reached after nearly a month; there is a subsequent very slow decrease. No blackening of the powder is observed, but small colourless prismatic crystals of $Fe(OH)_2$ appear after a few months. On exposure to air these are immediately oxidised. Opaque violet layers are formed and a metallic lustre similar to that of magnetite appears. Measurements of electrical conductivity, solubility, and p_H at 25° gave 2·90, 1·56, and $2·13 \times 10^{-15}$, respectively, for the solubility product of $Fe(OH)_2$. M. S. B.

Nature of dropping mercury electrode. Non-applicability of thermodynamical equilibrium considerations to solutions of indefinitely small concentration. M. ANDAUER and E. LANGE (Z. physikal. Chem., 1932, **162**, 241—256).—Theoretical. The assumption that thermodynamical and electrochemical equilibrium exists at the interface leads to certain impossible results, particularly in relation to the concn. gradient at the interface. A comprehensive theory, which avoids these difficulties, is arrived at by supposing that the galvanic potential at the interface is a function of the adsorption of $Hg_2^{\cdot\cdot}$, and that the passage of potential-determining ions between the extended and adsorbed phases is subject to a certain hindrance, in consequence of which its speed is limited. Similar considerations are applicable to the electrocapillary curve. The applicability of thermodynamical considerations, in the form of Gibbs' adsorption equation, to the dropping electrode and electrocapillary curve would thus seem to be very limited. R. C.

Electromotive behaviour of nickel and cobalt. E. MULLER and J. JANITZKI (Z. physikal. Chem., 1932, **162**, 385—397).—The behaviour of Ni and Co in neutral solutions of their salts and aq. acids and alkalis is qualitatively similar to that of Fe (A., 1932, 813); the p.d. established at an electrode of the massive metal represents an equilibrium between the dissolution of metal ions at active parts of the surface and the diffusion away of H discharged at other parts of the surface. If the electrode is continually scraped the p.d. becomes more negative, and in Co salt solutions approximates to the reversible potential, which for N-$CoCl_2$ is −0·292 volt. R. C.

Theory of concentrated solutions. V. E. WILKE and W. SCHRANKLER (Z. physikal. Chem., 1932, **162**, 361—371; cf. A., 1932, 700).—The e.m.f.–concn. curves for concn. cells consisting of H halide solutions and H electrodes or alkali halide solutions and alkali-metal amalgam electrodes exhibit discontinuities at the concns. predicted by the theory (cf. A., 1926, 906). R. C.

Polarisation potential of zinc deposited from aqueous solutions. T. ISHIHARA, K. MIHARA, and K. UMETU (Kinz. no Kenk., 1932, **9**, No. 6, 244—278).—The cathodic polarisation potential, the anodic over-voltage, and the total polarisation potential have been measured for $ZnSO_4$ solutions of various concns. and p_H at 35°. The relations between cathodic polarisation potential and c.d. vary with the composition of the solution. The polarisation potential decreases greatly on addition of $H_2SO_4 < N$. Both neutral and acid solutions of $0·5N$-Zn show min. over-voltage. The max. O over-voltage occurs in Zn solutions $> 2N$, the concn. varying with the amount of acid added. CH. ABS.

Electrolytic polarisation. X. Ammines of copper, silver, zinc, and cadmium. S. GLASSTONE (J.C.S., 1932, 2849—2857).—Electrometric titration by aq. NH_3 of solutions of Cu, Ag, Zn, and Cd salts, in presence of excess of $(NH_4)_2SO_4$, indicates the existence of the ions $Cu(NH_3)_4^{\cdot\cdot}$, $Ag(NH_3)_2^{\cdot}$, $Zn(NH_3)_4^{\cdot\cdot}$, and $Cd(NH_3)_3^{\cdot\cdot}$ or $Cd[(NH_3)_3(H_2O)]^{\cdot\cdot}$. Measurements of the cathode potential in $0·1M$ and $0·01M$ solutions for different c.d. show that, for Ag and Cd solutions, none of the stages in the process $M(NH_3)_x^{+} \longrightarrow M$ is slow. In the cupriammine solutions two limiting c.d. were observed, one being a measure of the rate of spontaneous dissolution of the deposited Cu and the other the sum of this and the rate of diffusion of the ammine ions to the cathode, the difference agreeing with the calc. val. of the limiting c.d. No limiting c.d. could be determined for Zn owing to the spontaneous dissolution of this metal with evolution of H. M. S. B.

Electrochemistry of polonium. M. HAISSINSKY (J. Chim. phys., 1932, **29**, 453—473).—The crit. deposition potential of Po on Au from alkaline solution is −0·29 volt; the potential diminishes with increase in the alkalinity, and varies with the nature of the electrode. The crit. anodic potential is approx. const. at $0·53 \pm 0·01$ volt. The mechanism of deposition in alkaline differs from that in acid solution. N. M. B.

Behaviour of hydrogen electrode in chromic–chromous solutions and solubility product of chromous hydroxide. W. H. BENNETT (Trans. Faraday Soc., 1932, **28**, 889—895; cf. A., 1930, 565).—In H_2SO_4 solutions of $Cr^{II} + Cr^{III}$ sulphates to which NaOH is added gradually, the potential of the H electrode is determined by the $Cr^{\cdot\cdot}/Cr^{\cdot\cdot\cdot}$ potential until the $Cr(OH)_3$ is completely pptd., and thereafter

by the [H·] of the solution. Inflexions in the potentiometric titration curve corresponding with the three stages of neutralisation are not sharp enough for quant. purposes. From the p_H of pptn. of $Cr(OH)_2$ from very dil. solutions of $CrSO_4$, viz., 5·6, the solubility product of $Cr(OH)_2$ is calc. to be 2×10^{-20} at 18°. F. L. U.

Utilisation of potentiometric titrations. X. Ampholytes. F. L. HAHN and R. KLOCKMANN (Z. physikal. Chem., 1932, **162**, 318—330).—The "effective" acid and basic dissociation consts. of an ampholyte, in the definition of which no distinction is made between zwitterions and undissociated mols., may be deduced directly from conductivity and p_H measurements, and the vals. used to calculate the isoelectric point and the change in p_H caused by addition to the solution of acid or alkali. The true dissociation consts. of the mols. and zwitterions, respectively, and the ratio of mols. to zwitterions may be derived from an analogy of ampholytes to bivalent acids or bases, and also from certain theoretical considerations. R. C.

Unimolecular reaction velocity. M. G. EVANS (Trans. Faraday Soc., 1932, **28**, 840—845).—A theoretical discussion of the spontaneous decomp. of activated mols. F. L. U.

Chain reactions. M. BODENSTEIN (Z. Elektrochem., 1932, **38**, 911—918).—Historical. D. R. D.

Kinetics of the decomposition of molecules of intermediate complexity. C. N. HINSHELWOOD and C. J. M. FLETCHER (Nature, 1933, **131**, 24).—In a mol. of moderate complexity it is possible that there may be several different modes of activation, corresponding with particular divisions of part of the energy among a limited no. of vibrational or rotational states, and that the most general form of curve obtained by plotting the half-val. of the reacting substance against pressure is of the segmented type. Experiments on the decomp. of N_2O and MeCHO at low pressures indicate the existence of these different types of activated state. L. S. T.

Energy exchange in unimolecular gas reactions. O. K. RICE (J. Amer. Chem. Soc., 1932, **54**, 4558—4581).—Mathematical. The theory is developed with reference to collisions in H_2, He, and org. vapours, and it is concluded that an activated mol. is deactivated by nearly every collision with a mol. of its own kind. In general, the probability of energy transfer decreases with increasing frequency and force const. of the oscillator, but increases with sharpness of collision. Increasing the mass of the particle decreases the probability of energy transfer, but, owing to complications, this factor may not completely account for the contrasting effects of H_2 and He in restoring the velocity coeff. of the decomp. of vapours at low pressures to the vals. at high pressures. J. G. A. G.

"Vibratory movement" in flames. O. C. DE C. ELLIS and E. MORGAN (Trans. Faraday Soc., 1932, **28**, 826—839; cf. A., 1931, 1371).—The method of shadow displacement has been used to determine the gas temp. at different positions in a tube containing a burning mixture of CO and air saturated with H_2O. Flame temp. was measured by the method of reversal of Na lines. From the temp. gradient throughout the tube the acoustic properties of the system can be deduced, and it is shown by mathematical analysis that the vibratory movement in the flame is determined by these and by the dimensions of the tube. F. L. U.

Conditions of ignition of gaseous mixtures. I. Induction period of the thermo-ignition of methane–oxygen mixtures. M. B. NEUMANN and L. N. EGOROV. **II. Region of thermo-ignition of methane–oxygen mixtures.** M. B. NEUMANN and A. I. SERBINOV (J. Phys. Chem., Russia, 1932, **3**, 61—74, 75—82).—I. The induction period for $CH_4:O_2=1:2$ admitted into a SiO_2 tube at 728—853° decreases with rise of temp. or increase in pressure.

II. The above mixture exploded on introduction into SiO_2 tubes at 645—679° only within three different pressure regions. CH. ABS.

Thermal decomposition of ethylamine. H. J. SCHUMACHER and E. O. WIIG (Z. physikal. Chem., 1932, **162**, 419—431).—Contrary to Taylor's observations (A., 1931, 175), the reaction at 510—535° under 10—60 mm. is a heterogeneous chain reaction, its velocity being influenced by H_2O vapour, foreign gases, and the material of the containing vessel. Decomp. involves a pressure increase of 125—180% and results in the formation of a great variety of products, including N_2, H_2, CH_4, NH_3, and resinous and oily substances. The temp. coeff. depends on the containing vessel. Under some conditions the course of reaction can be represented by the unimol. law, but periods of induction and other abnormalities are often observed. R. C.

Role of solvent in unimolecular reactions. M. MAGAT (Z. physikal. Chem., 1932, **162**, 432—448).—A crit. review of available experimental data indicates that the influence of the solvent on a unimol. reaction is determined by its ability to form swarms or complexes with the solute, which in general runs parallel with its self-association; steric peculiarities, electronic interaction, and the sharpness of the resonance of the characteristic frequencies of the solvent and solute may exert a decisive influence in special cases. If Z in the equation $k=Ze^{-E/RT}$ is of the order of 10^{11} or greater the reaction is retarded by an "active" solvent, whilst if $Z=10^3$ to 10^9 the reaction is accelerated. It is tentatively suggested that for reactions of the first class, for which both Z and E are large, the solvent causes a dissipation of energy, whilst reactions for which both Z and E are small are probably "tunnel reactions," the accelerating effect of the solvent being due to its influence on the potential curves. Moelwyn-Hughes' theory (A., 1932, 233) is rejected. R. C.

Decomposition of dilute sodium carbonate solutions at temperatures between 147° and 243°. F. G. STRAUB and R. F. LARSON (Ind. Eng. Chem., 1932, **24**, 1416—1419).—The velocities of decomp. of Na_2CO_3 solutions at 147—243° indicate that there are two reactions $Na_2CO_3+H_2O\rightleftharpoons NaOH+NaHCO_3$ and $NaHCO_3\rightleftharpoons NaOH+CO_2$. On this supposition approx. equilibrium consts. have been calc. J. W. S.

Rate of reaction between chlorate and sulphur dioxide in acid solution. A. C. NIXON and K. B. KRAUSKOPF (J. Amer. Chem. Soc., 1932, **54**, 4606—4608).—The velocity of the reaction $ClO_3' + 3H_2SO_3 = Cl' + 3SO_4'' + 6H^{\cdot}$ in acid solution at 0° is given by $-d[ClO_3']/dt = 2{\cdot}4[H_2SO_3][ClO_3']$. J. G. A. G.

Neutral salt effect in the thiosulphate and monobromoacetate ion reaction. I. A. VON KISS [with P. VASS] (Z. anorg. Chem., 1932, **209**, 236—240).—Solutions of sulphates and nitrates of Na, K, NH_4, and Mg do not alter the mechanism of the reaction. An accelerating effect is observed, but there is no clear relation between its magnitude and the nature or concn. of the salt. E. S. H.

Kinetics of the action of ammonium halides on epichlorohydrin. S. BANERJEE and H. K. SEN (J. Indian Chem. Soc. 1932, **9**, 509—518).—The reactions of epichlorohydrin with NH_4 halides follow the bimol. law if the p_H is const. A. G.

Velocity and mechanism of racemisation. II. Mandelic acid. A. N. CAMPBELL and A. J. R. CAMPBELL (J. Amer. Chem. Soc., 1932, **54**, 4581—4585).—The racemisation of 0·1*M*-mandelic acid has been investigated at 96° in 0·9—7·0*N*-NaOH. The change is very slow in HCl solutions, and some decomp. occurs in 11·24*N*-HCl. There is no evidence of complex formation. J. G. A. G.

Trypanocidal action and chemical constitution. XIV. Relative velocity of oxidation of arylarsenoxides. A. COHEN, H. KING, and (MISS) W. I. STRANGEWAYS (J.C.S., 1932, 2866—2872).—The velocity of oxidation of various arylarsenoxides to arsinic acids by cystine has been determined polarimetrically and bimol. reaction coeffs. have been deduced. The latter bear no apparent relation to the toxicities of the arsinic acids to mice. D. R. D.

Stability of diazo-chlorides. Influence of various substituents, temperature, and concentration. C. C. SNOW (Ind. Eng. Chem., 1932, **24**, 1420—1423).—The rates of decomp. of 32 diazo-compounds have been measured under varying conditions of temp. and concn. Diazo-chlorides containing electropositive groups are more sensitive to rise of temp. than those containing electronegative groups. Diazotisation may in some cases be carried out at temp. > those generally used, facilitating diazotisation of those amines which are very resistant to low-temp. diazotisation. In some cases increased concn. increases the stability of the diazo-chloride. Variation of the negative radical also changes the stability of a diazo-compound, acetates being usually less stable and sulphates more stable than chlorides. J. W. S.

Reactions in solids. Comparison of the methods of deriving the energy of activation. R. S. BRADLEY, J. COLVIN, and J. HUME (Phil. Mag., 1932, [vii], **14**, 1102—1114; cf. A., 1932, 1094).—Theoretical. For flat plates or spherical particles the ratio of the instantaneous tangent to the reaction curve before and after a change from a high to a low temp. in a "split run" gives the true activation energy. The errors in using finite times of measurement are reviewed. H. J. E.

Reaction velocity in reversible systems $solid_1$ $solid_2$ + gas. B. TOPLEY (Phil. Mag., 1932, [vii], **14**, 1080—1090; cf. A., 1932, 26).—A correction is applied to previous results due to the concn. of gas mols. in the reaction zone, even with no impedance due to ($solid_2$). New measurements of the effect of small concns. of H_2O vapour on the velocity of $CuSO_4,5H_2O \longrightarrow CuSO_4,H_2O + 4H_2O$ are recorded. The correction is about 1% at 22·25°. H. J. E.

Influence of the anion on the velocity of dissolution of zinc in acids. E. MÜLLER and J. FÖRSTER (Z. Elektrochem., 1932, **38**, 901—906).—The rate of evolution of H_2 from a Pt wire in contact with amalgamated Zn in various acids at 20° has been measured. With HCl and HBr the velocity is approx. proportional to the concn., but with H_2SO_4, $HClO_4$, $HClO_3$, and H_3PO_4 the velocity–concn. curve passes through a max., which occurs at a higher concn. than that of max. conductivity. The max. velocity does not correspond with a max. concn. of $H^{\cdot}$. Hence, the anions have a sp. action. There is, however, a qual. agreement between velocity of reaction and $[H^{\cdot}]$, the Zn dissolving more rapidly in the stronger acids. There is no induction period. D. R. D.

Rate of dissolution of industrial aluminas in fused cryolite. N. PARRAVANO and O. D'AGOSTINO (Atti R. Accad. Lincei, 1932, [vi], **16**, 186—190).—Measurements of the rate of change of conductivity of cryolite at 1050° produced by the addition of Haglund's, of Bayer's, and of Blanc's Al_2O_3 show that the rate of dissolution increases in the order given. O. J. W.

Calculation of velocity of contact oxidation of ammonia. G. K. BORESKOV.—See B., 1933, 16.

Polymerisation of acetaldehyde. II. W. H. HATCHER and M. G. KAY (Canad. J. Res., 1932, **7**, 337—344).—Pure MeCHO, paraldehyde, and metaldehyde have d^{15} 0·7865, 0·9884, and 1·120—1·127, respectively, and the d curve for mixtures of the former two closely resembles the ideal straight-line curve. The polymerisation of MeCHO in presence of H_3PO_4 (A., 1931, 1273) has been reinvestigated in the absence of O_2, and again found to be a third-order reaction. Metaldehyde appears in the later stages. Preliminary treatment of MeCHO with O_2 retards polymerisation. A. C.

Active oxides. LVIII. Change in the catalytic activity of an aluminium oxide hydrate gel during ageing. G. F. HÜTTIG and J. BRÜLL (Ber., 1932, **65**, [*B*], 1795—1799).—The catalytic dehydration of MeOH by three samples of gel at 300° has been investigated. Activity is at a max. with specimens which have been preserved from 42 to 56 days. The slight change in catalytic activity during the action indicates a stabilising effect of MeOH vapour. H. W.

General method for fluorination of inorganic halides. H. S. BOOTH and C. F. SWINEHART (J. Amer. Chem. Soc., 1932, **54**, 4751—4753; cf. this vol., 134).—SbF_3 and a catalyst effect partial replacement by F of halogens from non-polar inorg. halides. Non-polar oxychlorides and thiohalides react with SbF_3. J. G. A. G.

Influence of the structure of the contact substance of the combustion of carbon monoxide. J. ECKELL (Z. Elektrochem., 1932, 38, 918—920).—The catalytic action of Fe_2O_3 and Fe_2O_3–Al_2O_3 mixed crystals on the reaction $2CO+O_2=2CO_2$ has been investigated over the range 160—204°. The heat of activation falls linearly with increase in concn. of Al_2O_3 until the composition reaches approx. 25% Al_2O_3, after which it remains const. This variation is exactly parallel to the change in lattice const. Increase in fineness of division of the catalyst corresponds with the increase in the velocity coeff. of the reaction. The variation of the latter with temp. agrees well with the log k–$1/T$ law. For pressures of 1—10 mm. the reaction is unimol. with respect to CO. D. R. D.

Decomposition of dimethyl ether on the surface of platinum. E. W. R. STEACIE and H. A. REEVE (J. Physical Chem., 1932, 36, 3074—3084).—The thermal decomp. of Me_2O in contact with Pt filaments at 1150° is unimol. and occurs in a layer of hot gas surrounding the filament. The heat of activation is 67,000 g.-cal., as compared with 58,500 for the homogeneous reaction. The high temp. coeff. is explained by assuming that the accommodation coeff. is low, and hence thermal equilibrium with the filament is not attained by colliding gas mols. E. S. H.

Hydrogenating and dehydrogenating efficiency of platinum catalysts in relation to the supporting substance and the fineness of division of the platinum on the latter. R. KOPPEN (Z. Elektrochem., 1932, 38, 938—942).—A discussion of published work on the use of finely-divided Pt as a catalyst, especially in combination with an adsorbent such as active C, SiO_2 gel, cellulose, starch, gum, etc., for effecting hydrogenation and dehydrogenation of org. compounds. D. R. D.

Benzine synthesis from carbon monoxide and hydrogen at atmospheric pressure. XII. K. FUJIMURA and S. TSUNEOKA.—See B., 1933, 7.

Oxidation of sulphur dioxide in electrodeless discharge. S. D. MAHANT (J. Indian Chem. Soc., 1932, 9, 417—422).—SO_2 is oxidised when mixed with O_2 and exposed to an electrodeless discharge, the max. being about 35% for a mixture containing 60 vol.-% SO_2. The frequency of the discharge has little effect. A. G.

Polarographic studies with the dropping mercury cathode. XXVIII. Evolution of hydrogen from neutral and alkaline solutions. D. ILKOVIČ. **XXIX. Electrodeposition of calcium and magnesium and the determination of calcium.** G. KIMURA (Coll. Czech. Chem. Comm., 1932, 4, 480—491, 492—503).—XXVIII. Current-voltage curves, obtained polarographically during the electrolysis of dil. neutral or alkaline solutions with the dropping Hg cathode, show, above a voltage of approx. 3 volts, a steady rise of current apparently due to the decomp. of H_2O. The true deposition potential is obtained by subtracting the product of the current i and the resistance r of the electrolytic circuit from the applied e.m.f. The cathodic potential of the decomp. of H_2O agrees with that derived on the assumption that the evolution of H at a Hg cathode is due to the reaction $H'+H' \longrightarrow H_2$. The inhibiting effect of alkali metal ions and the catalysing action of $Mg^{\cdot\cdot}$ and $Ca^{\cdot\cdot}$ on the evolution of H are also explained on the basis of this hypothetical reaction and the formation of hydrides.

XXIX. Ca deposits reversibly from alkaline solutions containing quaternary amino bases. The polarographic current–voltage curves show reproducible saturation currents the magnitude of which is proportional to the concns. of $Ca^{\cdot\cdot}$. The amine should be 0·01—0·1N and the concn. of Ca 0·1 of this. Ca may thus be determined electrolytically with an accuracy of ±5% in concns. $> 10^{-5}N$, provided Li is absent and the concn. of other metals does not exceed 15 times that of Ca. It is impossible to deposit Mg without the simultaneous evolution of H_2, since alkali cannot be added in this case to prevent the catalytic action of Mg on H_2 evolution. The use of $(NMe_4)_2C_2O_4$ does not solve the problem satisfactorily, owing to the simultaneous reduction of C_2O_4'' at the dropping Hg cathode. M. S. B.

Electrodeposition of iron–cobalt alloys. I. S. GLASSTONE and J. C. SPEAKMAN.—See B., 1933, 24.

Chromium plating on zinc. M. DE K. THOMPSON and F. C. JELEN.—See B., 1933, 24.

Electrodeposition of chromium from aqueous chromic acid containing hydrofluoric acid. E. MÜLLER and O. ROSSOW.—See B., 1933, 67.

Electrochemistry of chromium. III. Tervalent chromium. A. V. PAMFILOV and O. S. FEDEROVA.—See B., 1933, 24.

Electrodeposition of metals. L. E. STOUT. See B., 1933, 67.

Protective properties of colloids and their behaviour in the electrolytic deposition of metals. P. A. JACQUET.—See B., 1933, 67.

Polarographic studies with the dropping mercury cathode. II. Reduction of acetone. G. SEMERANO. **III. Reduction of benzaldehyde.** G. SEMERANO and G. DE PONTE (Gazzetta, 1932, 62, 959—991, 991—999; cf. A., 1932, 1093).—II. Current-voltage curves have been measured with a dropping Hg cathode during the electrolytic reduction of $COMe_2$ in aq. Li salt solutions in air and in H_2. The effects of varying the concn. of $COMe_2$, of $H^{\cdot}$, and of Li salt are described. The reduction is explained as a direct electronic process, in which hydrated $COMe_2$ decomposes at the electrode surface into OH' and a residue, which reacts with the $CMe_2(OH)_2$ in solution to give pinacone and with $H^{\cdot}$ or H_2O to give $Pr^{\beta}OH$.

III. PhCHO is reduced to hydrobenzoin at a dropping Hg cathode, and the process consists of depolarisation of a metallic cathode in neutral or alkaline solution and of a H cathode in acid solution. PhCHO is strongly adsorbed at the Hg-solution interface. By means of the polarographic measurements, 10^{-7} g. of PhCHO can be detected and determined. O. J. W.

Active nitrogen and formation of ammonia in the silent discharge with reference to the material of the electrodes and to catalytic problems. E. TIEDE and E. HEY (Ber., 1933, 66, [*B*], 85—94; cf. A., 1930, 1139).—The concn. of at. N formed in the neigh-

bourhood of the cathode and leaving the discharge under otherwise similar conditions depends mainly on the re-combining affinity of the surfaces near the region of cathode discharge; owing to the intense evaporation of the cathode, the effect depends more on the deposits on the walls of the vessel than on the electrodes. The ability of the electrodes and their deposits to adsorb N atoms at their surfaces, and hence to accelerate their union to mols., increases in the sequence Al, W, Ni, Fe, Cu, (Pt). The slight adsorptive power of the deposits of Al and W is attributed to the formation of nitrides. NH_3 is formed from N and H atoms adsorbed at the cathodic surfaces; if the sequence of chemical reactions is sufficiently rapid, the rate of formation is proportional to the concn. of adsorbed atoms. The bearing of the results on the thermal contact synthesis of NH_3 is discussed. H. W.

Blue coloration of rock-salt accompanying spark perforation of the crystals. H. STEINMETZ (Neues Jahrb. Min., 1932, **65**, *A*, 119—127; Chem. Zentr., 1932, ii, 1754).—The rock-salt becomes coloured blue along the spark canal. The coloration is in a thin layer, and is sensitive to temp. In air, but not in vac. over H_2SO_4, it disappears in a few days. It gives an alkaline reaction to an aq. solution of the salt. The following mechanism is postulated: (1) formation of Cl′, Na˙, and electrons, (2) Na˙$\longrightarrow$Na, (3) diffusion of Na into the NaCl, (4) formation of amicrons with the constituents of the rock-salt lattice and stabilisation of the diffusing Na atoms towards atm. O_2. A. A. E.

Activation of molecular oxygen by electron impact. G. GLOCKLER and J. L. WILSON (J. Amer. Chem. Soc., 1932, **54**, 4544—4558; cf. A., 1930, 1000; 1931, 1139).—The active species produced by interaction of 0·023—0·05 mm. of O_2 with 3—20-volt electrons react with a Hg surface. Activation by 3—8-volt electrons affords metastable $^1\Sigma_g$ O_2 mols., 8—12-volt electrons afford electronically excited O_2 mols., but the rate of pressure decrease does not increase markedly at the ionisation potential (12·5 volts). The product from higher voltage electrons reacts with KI when adsorbed on glass and may be either at O or O_3. The results are discussed in terms of probabilities of energy transfer from electrons to normal mols. and of reaction between activated states and the Hg surface. J. G. A. G.

Photochemical reaction of hydrogen and chlorine. H. B. BAKER (Nature, 1933, **131**, 27).—A criticism (this vol., 34). The inhibition of the action of light on a mixture of H_2 and Cl_2 after drying is affirmed. L. S. T.

Inhibition of photochemical decomposition of ammonia by atomic hydrogen. H. W. MELVILLE (Trans. Faraday Soc., 1932, **28**, 885—889).—In a mixture of NH_3 with H_2 and Hg vapour illuminated by a Zn spark the rate of decomp. is lowered when at. H is produced by operating a Hg arc. This observation explains the low quantum yield due to the reaction $NH_2+H=NH_3$, and affords a proof of the dissociation of NH_3 into H atoms. F. L. U.

Time lag in the formation of the latent image. L. I. ZIMMERMAN (Physical Rev., 1931, [ii], **37**, 106). Image density gradually decreases with a decrease in time of flash illumination to a crit. point, after which it decreases rapidly. The formation of the latent image is indicated to be a resonance process. L. S. T.

Photochlorination of tetrachloroethylene in carbon tetrachloride solution. J. A. LEERMAKERS and R. G. DICKINSON (J. Amer. Chem. Soc., 1932, **54**, 4648—4657; cf. A., 1932, 1215).—In the absence of O_2, photochlorination is fairly rapid, but about 9% less Cl_2 is absorbed than is required by $Cl_2+C_2Cl_4=C_2Cl_6$. The results for light of wave-length 4358 Å. are reproduced by the relation $-d[Cl_2]/dt=5\cdot1\times I_{abs}^{1/2}[Cl_2](1+0\cdot4[Cl_2]/[C_2Cl_4])^{-1/2}$. Quantum efficiencies between 300 and 2500 were observed. The temp. coeff. is $1\cdot16\pm0\cdot08$ per 10°. The mechanism of the reaction is discussed. J. G. A. G.

Measurement of ultra-violet radiation intensity. I. Photochemical formation of molybdenum-blue. (MLLE.) D. SACHS (J. Chim. phys., 1932, **29**, 474—478).—The formation, in acid solution, of Mo-blue by the partial reduction of Na_2MoO_4 by ultra-violet light, in presence of a weak reducing agent (HCO_2H or CH_2O), is purely photochemical, and affords a convenient quant. method of measuring ultra-violet light intensity. N. M. B.

Halogenated pyridone derivatives in radiography. A. BINZ, C. RATH, H. MAIER-BODE, and K. HERRMANN (Angew. Chem., 1932, **45**, 713—715).—The % transmission of *X*-rays through 0·25*M* and 5% solutions of nine halogenated pyridone derivatives, Na_2SO_4, NaI, NaBr, $CH_2I\cdot SO_3Na$, and $CHBr_2\cdot SO_3Na$, has been determined. For the wave-lengths employed in radiography the Br derivatives are more opaque than the corresponding I derivatives. H. F. G.

Radiochemical decomposition of hydrogen sulphide at room temperature. COLMANT (Bull. Soc. chim. Belg., 1932, **41**, 431—463).—The decomp. of H_2S containing Rn at pressures between 37 mm. and 10 atm. has been studied. The ratio M/I, where M is the no. of mols. decomposed and I the no. of ion pairs formed, calc. on the assumption that all the Ra-*A* and Ra-*C* is deposited on the walls of the vessel, passes through a min. (about 2·2) at 100—200 mm., and tends to reach a const. val. (about 3·6) at high pressures. The variations at low pressure may be attributed to the action of recoil atoms, but it appears that for high pressures the principle of the constancy of M/I must be abandoned, and that the chemical effect of slow α-particles is greater in proportion to their power of ionisation than is the case with rapid α-particles. H. F. G.

High-temperature chemistry. O. RUFF (Angew. Chem., 1933, **46**, 1—7).—A lecture, surveying published work on reactions and stability at high temp. It is inferred that in this region chemical behaviour is not essentially different from that at room temp. E. S. H.

Double iodide ammines. E. VOJIATZAKIS (Bull. Soc. chim., 1932, [iv], **51**, 1310—1312).—The following *compounds* may be crystallised from solutions of

their components in $COMe_2$: $2NaI,CdI_2,6NH_3$; $2NaI,CdI_2,6C_5H_5N$; $2NaI,CdI_2,2m\text{-}C_6H_4Me\cdot NH_2,4H_2O$; $2NaI,CdI_2,2o\text{-}C_6H_4Me\cdot NH_2,4H_2O$; $NaI,CdI_2,2C_9H_7N$; $2KI,2CdI_2,C_9H_7N$. D. R. D.

Formation and decomposition of potassium perchlorate and revision of the heat toning. K. A. HOFMANN (Sitzungsber. preuss. Akad. Wiss. Berlin, 1932, **27**, 3—13).—In the absence of catalysts for the reaction $2KClO_3 \longrightarrow 2KCl+3O_2$ a yield of 73% $KClO_4$ can be obtained by heating $KClO_3$ at 490°. The reaction $4KClO_3 \longrightarrow 3KClO_4+KCl$ is accelerated by KCl and more powerfully by KI or KIO_3, but retarded by molten KNO_3, which, by reason of its solvent action on $KClO_4$, promotes decomp. of the latter according to $2KClO_4 \longrightarrow 2KClO_3+O_2$. $NaNO_2$ reduces $KClO_4$ successively to $KClO_3$ and KCl and is itself oxidised to $NaNO_3$. The reaction $KClO_4 \longrightarrow KCl+2O_2$ is accelerated by salts of various heavy metals, especially of Cu, and occurs with the evolution of 1·73 kg.-cal. The stability of $KClO_4$ compared with $KClO_3$ is due to its higher m.p. and to the large heat of transformation of the rhombic into the cubic modification, viz., 3·29 kg.-cal. at 299·5°. F. L. U.

Hydrothermal synthesis of calcium hydroaluminates. I. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, **35**, 495—500B).—Mol. proportions of CaO and $Al_2(OH)_6$, heated together at pressures ranging from 5 to 20 kg. per sq. cm. and temp. 152—213°, give a mixture of $2CaO,Al_2O_3,xH_2O$ and $3CaO,Al_2O_3,xH_2O$. By varying the proportion of CaO to 1 mol. $Al_2(OH)_6$ at 10 kg. pressure and 180—182°, $2CaO,Al_2O_3,3H_2O$ is obtained from 1 mol. CaO, a mixture of $2CaO,Al_2O_3,3H_2O$ and $3CaO,Al_2O_3,6H_2O$ from 2 and 3 mols. CaO, and $3CaO,Al_2O_3,6H_2O$ from 4 mols. CaO. Mol. proportions of CaO and calcined Al_2O_3, at 5 kg. pressure and 152—154°, give $2CaO,Al_2O_3,(6—7)H_2O$. M. S. B.

Course of the solid reaction between lime and silicic acid. I. WEYER (Z. anorg. Chem., 1932, **209**, 409—428; cf. A., 1931, 921).—The reaction in an equimol. mixture of $CaCO_3$ and SiO_2 has been studied by microscopical and *X*-ray analysis at temp. between 650° and 1250°. At 650° the product is $\beta\text{-}Ca_2SiO_4$. This is also the primary product at 735°, but on tempering is slowly converted into $CaSiO_3$ (wollastonite). At 815—835° both products are formed, whilst at and above 1050° $CaSiO_3$ is alone produced. F. L. U.

Extraction and purification of radium-*E*. P. FOUCAUD (J. Chim. phys., 1932, **29**, 479—487).—The continuous extraction of Ra-*E* (life period 5 days) as it is formed by Ra-*D* obtained from Ra-Pb was effected by pptg. as carbonate the Pb of the impure chloride of Ra-Pb, and converting the carbonate into nitrate. A ppt. containing the Ra-*E* was obtained by the addition of colloidal $Fe(OH)_3$, and this ppt. was purified and the Ra-*E* isolated. N. M. B.

Action of aluminium on solutions of metallic salts. M. J. SALAUZE (Bull. Soc. chim., 1932, [iv], **51**, 1346—1352).—When powdered Al displaces Cu from aq. $CuSO_4$ there is a period of induction of 1—2 hr., after which a violent reaction sets in. This effect is attributed to the presence of a protective film of Al_2O_3. The Al may be activated by treatment with aq. HCl or Au, Hg, or Pt salts, or by boiling with a metallic salt which is hydrolysed giving an acid solution, activation being most efficient in presence of Cl′. Al so treated reacts immediately with aq. $CuSO_4$, $Pb(OAc)_2$, $NiSO_4$, and $CdSO_4$, giving almost quant. yields of finely-divided Cu, Pb, Ni, and Cd. With $FeSO_4$ the yield of Fe is only 50%, since the reaction $2Al+3H_2O=Al_2O_3+3H_2$ occurs to a considerable extent. D. R. B.

Significance of alkali in blue ultramarine. K. LESCHEWSKI and H. MÖLLER (Z. anorg. Chem., 1932, **209**, 369—376; cf. A., 1932, 351).—Blue ultramarine when boiled with $OH\cdot CH_2\cdot CH_2Cl$ for 30—150 hr. loses all but 1·5% of its Na and yields a white or pink substance no longer possessing the cryst. structure of ultramarine. The S content remains unchanged. Subsequent treatment with suitable Na compounds gives a yellow or green substance. In molten HCO_2Na ultramarine takes up Na, its S is reduced, and it is decolorised, the substance thus formed regaining its colour by hydrolysis with H_2O or by the action of HCl at 100°. Finally, ultramarine takes up Na from molten $NaNO_3$ at 500° without oxidation or loss of colour or cryst. structure. F. L. U.

Oxidation and reduction of ultramarine. K. LESCHEWSKI and H. MÖLLER (Z. anorg. Chem., 1932, **209**, 377—382; cf. preceding abstract).—Ultramarine loses only traces of S in O_2 at 500°, and its depth of colour is increased. H_2 at 400° reacts more readily, reducing the S and yielding a substance of brighter colour. Similar differences are observed with the white product formed by the action of $OH\cdot CH_2\cdot CH_2Cl$. The natural colour of ultramarine is related to the firmness of binding of the S due to its alkali content. F. L. U.

Crystal-chemical processess with carbon. U. HOFMANN (Ber., 1932, **65**, [*B*], 1821—1830).—A lecture. H. W.

Production of gaseous hydrogen cyanide. A. SOLDI and A. REGE (Annali Chim. Appl., 1932, **22**, 695—705).—The best yield obtainable from NaCN and H_2SO_4 was 78—79%. T. H. P.

Properties of active charcoal reactivated in oxygen at 400°. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1932, **54**, 4473—4480).—Charcoal activated at 900—1000° ($C_{act.}$) and then heated in O_2 at 300—500° (C_{acid}) forms at the surface a definite acidic compound which could not be identified. The surface acid is also formed slowly on $C_{act.}$ in moist air at room temp., and is stable in vac. at 500—550°. In contrast to C_{acid}, $C_{act.}$ does not adsorb strong bases, but renders salt solutions alkaline by hydrolytic adsorption of acid. Differences in catalytic activity and other adsorptive properties have been investigated. J. G. A. G.

Volatile transport of silica. J. W. GREIG, H. E. MERWIN, and E. S. SHEPHERD (Amer. J. Sci., 1933, [v], **25**, 61—73).—SiO_2 is volatilised from many silicate minerals on heating at about 1100°. C. W. G.

Fluorochlorides of silicon. H. S. Booth and C. F. Swinehart (J. Amer. Chem. Soc., 1932, **54**, 4750—4751; cf. A., 1932, 1218).—By interaction of SbF_3 and $SiCl_4$ in the presence of $SbCl_5$ or Cl_2, $SiFCl_3$, b.p. 12·2°, t_c 165·17°, p_c 34·34 atm., SiF_2Cl_2, t_c 95·75, p_c 34·57, and SiF_3Cl t_c 34·5, p_c 34·42 have been prepared. J. G. A. G.

Germanium and gallium from germanite. II. R. Berg and W. Keil (Z. anorg. Chem., 1932, **209**, 383—384; cf. A., 1926, 589).—Ga can be obtained from germanite by shaking the aq. HCl solution with Et_2O, when $GaCl_3$ passes into the latter, accompanied by $AsCl_3$ and $FeCl_3$, from which it is easily separated. F. L. U.

Preparation of per-acids and their salts. R. R. Coons (Iowa State Coll. J. Sci., 1932, **6**, 419—422).—Treatment of Na_2HAsO_4 with 30% H_2O_2 affords a substance, probably a mixture, having a composition corresponding with $25Na_2HAsO_4,32H_2O_2,16H_2O$. Na_2O_2 and Na_2HAsO_4 in EtOH produced $2Na_3AsO_4,7Na_2O_2,2NaOH\ 75H_2O$, also probably a mixture. Ch. Abs

Decomposition of metallic sulphides, especially those of antimony, tin, and lead, at high temperatures. E. J. Kohlmeyer (Metall u. Erz, 1932, **29**, 105—113; Chem. Zentr., 1932, ii, 653).—Data for Sb_2S_3, PbS, PbS–Sb_2S_3, SnS, SnS–PbS, Cu_2S, PbS–Cu_2S, and Bi_2S_3 have been obtained. The b. p. of Pb and Sb are 1740° and 1645°, respectively. L. S. T.

Chromium pentoxide. E. H. Riesenfeld (Ber., 1932, **65**, [*B*], 1868—1869).—Contrary to Schwarz (A., 1932, 708), CrO_5,C_5H_5N is obtained by the author's process (A., 1907, ii, 357) if cooling is sufficiently careful. The products are identical in composition, but differ somewhat from one another in appearance, in their rate of decomp. by acids, and, particularly, in their behaviour towards alkali. Since each oxide has the simple mol. wt., stereoisomerism is assumed. H. W.

Reactions of complex chlorides of tervalent and quinquevalent tungsten. R. C. Young (J. Amer. Chem. Soc., 1932, **54**, 4515—4519).—In an atm. of N_2, $K_3W_2Cl_9$ is oxidised by H_2O in accordance with the equation $5W_2Cl_9'' + 18H_2O \longrightarrow 45Cl' + 30H^+ + 3H_2 + 2(W_2O_3,3WO_2)$. With 6*N*-KOH, 80% of the W is oxidised, whilst with 50% KOH all of the W is oxidised to W^{IV} and only in presence of air is the W oxidised to a higher state. $K_4W(CN)_8$ is produced by interaction of KCN with $K_3W_2Cl_9$, but H_2 is not evolved. $(NH_4)_2WOCl_5$ reacts with KCN as follows: $2WOCl_5'' + 6OH' \longrightarrow W_2O_5 + 10Cl' + 3H_2O$; $W_2O_5 + H_2O + 8CN' \longrightarrow W(CN)_8'''' + WO_4'' + 2OH'$. The *compound* $K_3W_2Br_9$ was prepared. J. G. A. G.

Influence of filter-paper on hydrochloric acid. E. Grunsteidl (Mikrochem., 1932, **12**, 174—186).—Separation of I in filter-paper moistened with a solution of IO_3'-free KI acidified with HCl is due, not to oxidation of HCl by the filter-paper, but to the combined action of air and light. F. L. U.

Influence of sodium, barium, and aluminium chlorides on the hydrolysis of ferric chloride above 100°. T. Katsurai (Bull. Chem. Soc. Japan, 1932, **7**, 374—375).—The influence of NaCl, $BaCl_2$, and $AlCl_3$ on the hydrolysis of $FeCl_3$ has been investigated by heating the mixed aq. solutions in an autoclave and observing the temp. of pptn. of Fe_2O_3. NaCl and $BaCl_2$ cause this temp. to rise, but $AlCl_3$ has little effect. D. R. D.

Reduction of palladium oxide by carbon monoxide. P. V. McKinney (J. Amer. Chem. Soc., 1932, **54**, 4498—4504; cf. A., 1931, 1366).—A small initial reduction of PdO by CO was observed at 23°, but if adsorbed O_2 is removed, there is no reaction below 76°. At temp. $< 156°$ reduction is never complete and the velocity decreases with time. CO_2 retards the reaction, whilst O_2 is a catalyst, and reduction probably proceeds at an interface. J. G. A. G.

Amino-compounds of platinic chloroammines. B. E. Dixon (J.C.S., 1932, 2948—2955).—The action of alkali on Pt chloroammines, whereby HX is removed and an NH_2 group formed, has been further investigated. Addition of NH_3 to aq. $[Pt(NH_3)_4Cl_2](NO_3)_2$ gives a yellow ppt. of the *compound* $[Pt(NH_3)_3(NH_2)Cl_2]NO_3$. When prepared in the cold, the compound described by Werner ("Neuere Anschauungen," pp. 53, 192) as $[Pt(NH_3)_4ClPO_4]$ has the formula $[Pt(NH_3)_4Cl_2](OH)(H_2PO_4),2H_2O$, but the ppt. obtained in hot solutions is $[Pt(NH_3)_4Cl(HPO_4)]OH$, which loses 1 mol. of H_2O at 130°, forming $[Pt(NH_3)_3(NH_2)Cl(HPO_4)]$. The action of an excess of Ag_2O on aq. $[Pt(NH_3)_5Cl]Cl_3$ yields an aq. solution of $2[Pt(NH_3)_2(NH_2)_3(OH)],3AgOH$, but the solid compound has not been isolated. Using only 2 equivs. of Ag_2O, the *compound* $2[Pt(NH_3)_3(NH_2)_2Cl]Cl,3AgCl$ is obtained, and, using 4 equivs., the *compound* $[Pt(NH_3)_2(NH_2)_3(OH)],2AgCl$. Addition of $(NH_4)_2HPO_4$ to $[Pt(NH_3)_6]Cl_4$ in aq. NH_3 produces a ppt. of the *compound* $[Pt(NH_3)_6]_2(OH)_2(HPO_4)_3,2H_2O$ or $[Pt(NH_3)_5(NH_2)]_2(HPO_4)_3,4H_2O$, which loses $2H_2O$ at 130°. D. R. D.

Supposed anomaly among the plato-tetrammines. H. D. K. Drew and G. H. Wyatt (J.C.S., 1932, 2975—2976; cf. A., 1906, i, 339).—The same compound, β-$[Pt(NH_3)_2(NHMe_2)_2]Cl_2$ (I), is obtained both from β-$Pt(NHMe_2)_2Cl_2$ and NH_3, and from β-$Pt(NH_3)_2Cl_2$ and $NHMe_2$. Whether the red monohydrate, β-$[Pt(NH_3)_2(NHMe_2)_2]PtCl_4,H_2O$, or the buff anhyd. salt (II) separates on adding K_2PtCl_4 depends on the temp. and acidity, and not on the mode of prep. of (I). High temp. and acidity favour the separation of (II). D. R. D.

Spectrum analysis. XI. Method of quantitative and qualitative spectrum analysis. W. Gerlach and K. Ruthardt. **XII. Detection of antimony, arsenic, and tellurium.** E. Riedl (Z. anorg. Chem., 1932, **209**, 337—355, 356—363; cf. A., 1931, 328).—XI. Tables previously given for the quant. analysis of metals and solutions are also applicable to spectra formed by an arc broken 5—10 times per sec., procedure for which is described. General methods for carrying out qual. analysis and details regarding a no. of elements are described.

The high-frequency discharge is specially useful in the examination of material having a high resistance.

XII. Either an intermittent or flame arc can be used to detect As, Sb, or Te in solids or solutions. In the former the limits are 2×10^{-8} g. As and 10^{-7} g. Te, in the latter 0·01% As and 0·002% Te from 2 c.c. of liquid. A preliminary treatment of the solution permits the detection of 5×10^{-7} g. As, 5×10^{-8} g. Sb, and 5×10^{-8} g. Te. F. L. U.

New methods of qualitative micro-analysis. J. WINCKELMANN (Mikrochem., 1932, **12**, 119—128; cf. A., 1932, 358).—Spot reactions are carried out in a substratum of gelatin jelly made with aq. glycerol and mounted for microscopic observation. The method is very sensitive, and is especially useful in that permanent preps. can be made for reference. F. L. U.

Determination of end-point in micro-titrations. F. L. HAHN (Mikrochem., 1932, **12**, 264—268).—A criticism of papers by Partridge and others (A., 1932, 1012, 1013, 1051). F. L. U.

Time required for suitably arranged potentiometric titrations. F. L. HAHN (Z. anal. Chem., 1932, **90**, 417—420).—A criticism of statements by Kordatzki and Wulff (A., 1932, 1013). F. L. U.

Compensating apparatus for avoiding troublesome calculations in p_H determinations. G. HATOS (Magyar Chem. Fol., 1932, **38**, 41—44; Chem. Zentr., 1932, ii, 1477—1478).

Suitability of anhydrous sodium carbonate for volumetric standardisations. J. LINDNER and N. FIGALA (Z. anal. Chem., 1932, **91**, 105—112).—Anhyd. Na_2CO_3, prepared by heating $NaHCO_3$ to const. wt. at 300°, is a suitable substance for the standardisation of volumetric solutions, the quantity of HCl required to neutralise a weighed quantity of Na_2CO_3 being on the average 0·006% < theory. D. R. D.

Use of bimetallic electrodes in potentiometric acidimetry. I. Behaviour in buffer solutions. II. Behaviour during the titrations. A. BANCHETTI (Gazzetta, 1932, **62**, 999—1010, 1011—1018).—I. Measurements have been made of the p.d. in solutions of varying p_H between Pt and N-Hg_2Cl_2, respectively, and electrodes of the following metals and alloys: steel, Ag, Co–Cr, Cr–Ti, Duralumin, Fe, oxidised Fe, Fe–Cr, Fe–Mo, Fe–Ni–Mo, Fe–Ni–W, Fe–Ta, Fe–Ti, Fe–V, Fe–W, Ni, brass, Pb, pyrites, Cu, Cu–Hg, Sn, and Ti.

II. The potentiometric titration of H_2SO_4 with NaOH and of AcOH with $Ba(OH)_2$ by means of bimetallic electrodes consisting of Pt and one of several of the metals and alloys mentioned above is described. O. J. W.

Catalytic determination of hydrogen by means of a contact candle. E. BIESALSKI and H. GIEHMANN (Angew. Chem., 1932, **45**, 767—769).—The candle consists of a porous porcelain tube each end of which has been impregnated with Na_2PtCl_6 and heated in H_2 at 150° to reduce the salt to Pt. The tubes are filled with 25% aq. $NaClO_3$ and are heated in a water-bath to 80—90°, while the gas mixture is passed backwards and forwards through the tube; the H_2 is thus burnt to H_2O, whilst CH_4 and C_2H_6 remain unattacked. The method is useful for the analysis of the gases derived from cracking heavy petroleum oils.

Titration method for the determination of water. R. P. BELL (J.C.S., 1932, 2903—2905).—H_2O in non-hydroxylic org. liquids, moist air, etc. may be determined by reaction with α-naphthoxydichlorophosphine (A., 1894, i, 586), the HCl evolved being absorbed in H_2O and titrated with NaOH. D. R. D.

Volumetric determination of chlorides by means of Ionescu-Matiu and Popesco's reaction. J. FOUCRY (Bull. Sci. Pharmacol., 1932, **39**, 172; Chem. Zentr., 1932, ii, 1663).—The procedure is reversed, standard $HgSO_4$ solution being employed with Na nitroprusside as indicator. The method is applicable to urine. A. A. E.

Determination of chlorine by Volhard's method. M. B. STSCHIGOL (Z. anal. Chem., 1932, **91**, 182—185).—The solution is treated with 5—10 c.c. of C_6H_6, PhMe, or $C_6H_4Me_2$ and then with excess of $AgNO_3$ and HNO_3. The excess of $AgNO_3$ is titrated with NH_4CNS as usual. Use of Et_2O instead of C_6H_6 etc. leads to low results for Cl′. It is concluded that the mutual solubility of Et_2O and H_2O diminishes the interfacial tension between these liquids and hence the power of adsorption of AgCl. J. W. S.

Potentiometric determination of hypochlorite and chlorate with cuprous chloride. B. TROBERG (Z. anal. Chem., 1932, **91**, 161—165).—ClO′ can be potentiometrically titrated directly with Cu_2Cl_2 at room temp. after addition of Na_2CO_3. The titration of ClO_3' must be carried out in acid solution and at a higher temp. Most of the Cu_2Cl_2 is added in the cold and the titration is completed after acidification with H_2SO_4. Addition of a little TlCl accelerates the reaction. J. W. S.

[Reactions of iodine]. E. ABEL (Z. physikal. Chem. 1932, **162**, 372).—Polemical (cf. A., 1932, 920). R. C.

Test for iodides by catalytic reaction. I. F. FEIGL and E. FRANKEL (Z. anal. Chem., 1932, **91**, 12—14).—The decomp. of PhBr by *o*-nitroaniline with the production of HBr is catalysed by KI. This may be used as a test for KI. The presence of HBr is detected by aq. Cl and $CHCl_3$, a comparison test being carried out in the absence of KI. The sensitivity is 1 in 1,000,000. Cl′ and Br′ have no influence. M. S. B.

Determination of iodides in presence of other halides. S. V. GORBATSCHEV and I. A. KASATKINA (Bull. Nauch.-Issledov. Khim.-Farm. Inst., 1930, 7—8).—Excess of HCl and a little $CHCl_3$ are added; the mixture is titrated with 0·1N-$KMnO_4$ until the I at first liberated is converted into ICl and the $CHCl_3$, after shaking, is colourless. CH. ABS.

Detection of fluorine by spot reactions. F. FEIGL and E. RAJMANN (Mikrochem., 1932, **12**, 133—136).—When a drop of an acidified solution containing F′ is brought on to filter-paper impregnated with brown Zr *p*-dimethylaminoazophenylarsinate, a colourless spot surrounded by a red circle is produced. The

sensitiveness is 1 in 2×10^5, 80 times as great as with Zr–alizarin paper. F. L. U.

Determination of fluorine by precipitation as tin triphenyl fluoride. N. ALLEN and N. H. FURMAN (J. Amer. Chem. Soc., 1932, **54**, 4625—4631; cf. A., 1920, i, 340; 1931, 925).—About twice the calc. quantity of $SnPh_3Cl$ solution (0·02 g. per c.c.) is diluted with an equal vol. of 95% EtOH and the boiling liquid is added to the boiling fluoride solution in 60—70 vol.-% of aq. EtOH at p_H 7—9. The ppt. is filtered after about 15 hr. and dried at 110°. 0·05—40 mg. of F can be determined, but large quantities of other salts cause co-pptn. of reagent and give high results. J. G. A. G

Determination of [dissolved] oxygen [in water] in presence of sulphite. L. W. HAASE.—See B., 1932, 94.

Influence of boric acid and of buffer mixtures on the iodometric determination of ozone. R. RUYSSEN (Natuurwetensch. Tijds., 1932, **14**, 245—253).—In presence of HBO_2 the error is erratic and may be as great as 10%; with buffer solutions (p_H 5—7) the result is high and appears to be a function of the p_H. For O_3 concns. up to 5% there is little difference between the results obtained with a KI solution and with a solution buffered at p_H 7. H. F. G.

Volumetric determination of free sulphur. A. CASTIGLIONI (Z. anal. Chem., 1932, **91**, 32—33).—The $COMe_2$ extract of free S (from rubber etc.) is boiled for ½ hr. with KCN under a reflux condenser to form KCNS. $COMe_2$ is removed on the water-bath, the dry residue is dissolved in H_2O, and excess of KCN is destroyed with CH_2O. After acidifying with HNO_3 the solution is titrated with $AgNO_3$, using $Fe(NO_3)_3$ as indicator. Very accurate results are obtained if the pptn. of AgCNS is not too rapid. M. S. B.

Determination of sulphate ion. P. PHOTIADIS (Z. anal. Chem., 1932, **91**, 173—180).—In the volumetric determination of SO_4'' by addition of excess of $BaCl_2$ followed by excess of CrO_4'' and subsequent determination of the residual CrO_4'' in the solution the results are too high for acid solutions and too low for alkaline solutions. The solution containing 0·1—0·12 g. SO_4'' is diluted to 100—120 c.c., neutralised, and treated with 1 c.c. of conc. HCl; 25 c.c. of 0·1*N*-aq. $BaCl_2$ are added dropwise while the solution is stirred, and the solution is then boiled. After cooling, 5 g. NaOAc are added, followed by 25 c.c. of 0·1*N*-aq. $(NH_4)_2CrO_4$ dropwise to the stirred solution. The whole is diluted to 200 c.c., filtered through a dry paper, and 100 c.c. are treated with 15 c.c. of conc. HCl and 2 g. KI, the liberated I being titrated in the usual way. A special procedure for determination of traces of SO_4'', *e.g.*, in H_2O, is detailed. J. W. S.

Preservation of standard thiosulphate. II. F. J. WATSON (J. Soc. Chem. Ind. Victoria, 1932, **32**, 679—680).—Buffering to p_H 9·0—9·5 preserves almost indefinitely the titre of aq. $Na_2S_2O_3$; with 0·01*M*-$Na_2B_4O_7$, 0·1*N*-$Na_2S_2O_3$ remains unchanged after 3 years. A. R. P.

Iodometric determination of thiocyanates. N. P. ALEKSANDROV (Uchen. Zapiski Kazan. Gosud. Univ., 1930, **90**, 1036—1044).—Schwicker's method is satisfactory. Good results are obtained also with insol. thiocyanates (especially Cu). CH. ABS.

Detection and separation of selenocyanates in presence of halides. G. SPACU and V. ARMEANU (Z. anal. Chem., 1932, **90**, 429—432; cf. A., 1925, ii, 1003, 1004).—When $Ni(NO_3)_2$ dissolved in aq. C_5H_5N is added to a solution containing CNSe′, a sky-blue cryst. ppt. of $[Ni(C_5H_5N)_4](CNSe)_2$ separates almost quantitatively. Any halides present may be detected or determined in the filtrate. F. L. U.

Precipitation of telluric acid as the chromium hexammino-salt. T. BERSIN (Z. anal. Chem., 1932, **91**, 170—171).—Addition of a warm freshly-prepared 40% aq. solution of $Cr(NH_3)_6(NO_3)_3$ to an ammoniacal solution of Na_2TeO_4 yields a bright yellow ppt. which after drying has the composition $[Cr(NH_3)_6]_2(H_4TeO_6)_3$. The solution no longer shows any trace of Te with N_2H_4 and H_2SO_4. The determination is not affected by the presence of TeO_3'', Cl', NO_3', or SO_4'', but $[Cr(NH_3)_6](NO_3)_3$ gives sparingly sol. ppts. with P_2O_7'''', SiF_6'', $Fe(CN)_6''''$, $Co(CN)_6'''$, $Cr(CN)_6'''$, and S_2O_6''. J. W. S.

Suppression of sulphuric acid mist in Kjeldahl determinations. A. HENWOOD and R. M. GAREY (Science, 1932, **76**, 524).—A close-fitting alundum tube closed at the bottom and flanged at the top for support on the flange of the digestion flask prevents escape of H_2SO_4 mist when fitted into the neck of the flask. Digestion can then be carried out in the open laboratory. L. S. T.

Determination of ammonia by Ostwald's nitrometer method. F. MUHLERT.—See B., 1933, 16.

Continuous analysis of ammonium salt solution. M. MATSUI, T. NODA, and S. MIYAGI.—See B., 1933, 17.

Colour reaction for nitrites. A. CASTIGLIONI (Z. anal. Chem., 1932, **90**, 427—429).—A large no. of substances containing phenolic OH give a yellow, red, or brown colour with aq. nitrites, especially on heating. The reaction is not given by other oxidising agents, nor by derivatives in which the phenolic H is completely substituted. The most sensitive reaction observed was that with *o*-$C_6H_4(OH)_2$, which can be used to detect 1 part of $NaNO_2$ in 10^6 parts. F. L. U.

Determination of phosphorus in aluminium. W. D. TREADWELL and J. HARTNAGEL.—See B., 1933, 23.

Micro-determination of carbon monoxide by the iodine pentoxide method. G. LJUNGGREN and G. FRANG (Svensk Kem. Tidskr., 1932, **44**, 279—285).—The apparatus of Schlapfer and Hofmann has been simplified and reduced in size, so as to permit the employment of only 25 c.c. of gas if 0·2% of CO is present in the sample. The I set free is collected in CCl_4 and titrated with 0·005*N*-$Na_2S_2O_3$, 6 c.c. of 1% KI and 0·5 c.c. of starch solution being added just prior to the end-point: an accuracy equiv. to 0·0005 c.c. of CO is attainable. The spontaneous liberation of I from I_2O_5 at different temp. has also been investigated; the quantity of I set free in a given time is increased if air is not drawn over the I_2O_5. In

practice, a preliminary heating in a current of air for 1 hr. at 160° is sufficient to reduce the blank to a negligible quantity, when the time occupied in the actual determination does not exceed 25 min. H. F. H.

Determination of cyanide by distillation from sulphuric acid solution. H. A. PAGEL and W. CARLSON (J. Amer. Chem. Soc., 1932, **54**, 4487—4489).—Conditions for the accurate determination of alkali cyanide in the presence of Cl′, Br′, NO_3′, and SO_4″ by distillation from moderately conc. H_2SO_4 without loss due to hydrolysis of HCN etc. have been investigated (cf. A., 1923, ii, 702). J. G. A. G.

Potentiometric determination of a mixture of [silver salts], thiosulphate, and chloride. A. PETIT (Bull. Soc. chim., 1932, [iv], **51**, 1312—1320).—$Ag^{\cdot}$, Cl′, and S_2O_3″ may be determined simultaneously by potentiometric titration with $AgNO_3$ at 90°. Br′ and I′ cannot be determined in this way in presence of S_2O_3″. D. R. D.

Characterisation of chemical species by their catalytic properties. Silver. G. DENIGES (Bull. Soc. Pharm. Bordeaux, 1932, **70**, 13—16; Chem. Zentr., 1932, ii, 747).—The Ag ion acts as a sp. catalyst. 10 c.c. of Ag solution are warmed with 0·7 c.c. H_2SO_4, 11 drops of $MnSO_4$ (4 g. per litre), and 1 drop of $K_2S_2O_8$. 0·02 mg. Ag per litre gives a positive reaction (pink colour). Cu, Fe, Ni, and V do not catalyse this reaction, whilst 50 and 200 times as much Hg and Co, respectively, are required to give an equal effect to Ag. The reaction will detect Ag on a metallic surface. L. S. T.

Determination of calcium by the magneto-optic method. E. R. BISHOP and C. B. DOLLINS (J. Amer. Chem. Soc., 1932, **54**, 4585—4588).—$3·7 \times 10^{-12}$ g. $Ca^{\cdot\cdot}$ per c.c. can be detected by the method described. Larger concns. of $Ca^{\cdot\cdot}$ can be determined to within 10%. The results are not affected by excess of Cl′, NO_3′, SO_4″, PO_4‴, or by the presence of $Mg^{\cdot\cdot}$, $Na^{\cdot}$, or $NH_4^{\cdot}$. J. G. A. G.

Preparation of soap solution for use in determining the hardness of water. K. SCHERINGA.—See B., 1933, 46.

Determination of hardness of water by Wartha's method in the case of water high in chlorides. BRAUER and REISS.—See B., 1933, 46.

Separation and determination of strontium and barium as bromide. L. SZEBELLEDY [with A. DÓRZA] (Magyar chem. Fol., 1932, **38**, 81—83; Chem. Zentr., 1932, ii, 1480).—Winkler's procedure is modified. A. A. E.

Precipitation of barium sulphate in presence of ferric salts. V. M. SHLAPIN (Uchen. Zapiski Kazan. Gosud. Univ., 1928, **88**, 461—464).—The complex $Ba_3[Fe(SO_4)_3]_2$ (I) is formed in quantity increasing with the concn. of $Fe^{\cdot\cdot\cdot}$. With a large excess of $FeCl_3$, Cl′ inhibits the ionisation of $BaCl_2$ and favours formation of complexes of the composition $(BaCl)_3Fe(SO_4)_3$ and $(BaCl)_2SO_4$, this partly compensating for the error resulting from the formation of (I). CH. ABS.

Effect of nitric acid on precipitation of barium sulphate. N. A. RUDNEV (Uchen. Zapiski Kazan. Gosud. Univ., 1930, **90**, 1054—1061).—The use of $Ba(NO_3)_2$ or the presence of HNO_3 gives high results owing to formation of $(BaNO_3)_2SO_4$. With increasing concn. of HNO_3 the error becomes max. and then decreases. Washing with hot water liberates $Ba^{\cdot\cdot}$. CH. ABS.

Malachite-green as indicator in the volumetric determination of zinc. V. N. SKVORTZOV (Uchen. Zapiski Kazan Gosud. Univ., 1930, **90**, 1010—1021).—$ZnSO_4,7H_2O$ is titrated with KOH in presence of malachite-green, the colour of which is discharged by free KOH. Rapid titration is necessary. Results for $>0·07$ g. Zn are too low. CH. ABS.

Determination of zinc in aluminium and its alloys. H. WAGNER and H. KOLB.—See B., 1933, 23.

Solubility of lead chromate in ammonium acetate and acetic acid solutions and the determination of small amounts of lead. E. A. GOODE and W. H. SUMMERS (J. Soc. Chem. Ind. Victoria, 1932, **32**, 686—693).—The solubility of $PbCrO_4$ in H_2O is increased slightly by addition of AcOH and appreciably by NH_4OAc. As little as 1 mg. of Pb may be rapidly pptd. with an error $\ngtr 0·08$ mg. provided that the concns. of NH_4OAc and AcOH are $\ngtr 5\%$, the vol. of solution is $\ngtr 20$ c.c., and the $K_2Cr_2O_7$ concn. is $\nless 0·25\%$. A. R. P.

Potassium iodide as spot reagent for heavy metals. E. GRUNSTEIDL (Mikrochem., 1932, **12**, 169—173).—KI can be used as a sensitive spot reagent for salts of Cu, Au, Pt, or Pd. F. L. U.

Quantitative applicability of spot reactions. J. KISSER and K. LETTMAYR (Mikrochem., 1932, **12**, 235—256).—By comparison with suitable standards spot reactions can be adapted to the rapid approx. quant. examination of a large no. of specimens. The mean error in the case of paper tests varies between ± 15 and $\pm 30\%$. Special reactions suitable for determination of Cu, Ag, Pb, Mn, Sn, Zn, and Mg are described. F. L. U.

Sensitive test for cerium with phosphomolybdic acid and instances of formation of molybdenum-blue in alkaline solution. A. S. KOMAROVSKY and S. M. KORENMANN (Mikrochem., 1932, **12**, 211—214).—If to a solution containing Ce^{III} equal quantities of saturated aq. phosphomolybdic acid and 40% NaOH are successively added, a blue coloration is produced. When used as a spot test, 5×10^{-7} g. Ce can be recognised. The reaction is given by no other rare earth. Several instances of the production of Mo-blue in alkaline solution are given. F. L. U.

Volumetric determination of cerium with arsenious acid. R. LANG and J. ZWEŘINA (Z. anal. Chem., 1932, **91**, 5—12).—Ce^{IV} salts are readily determined by H_3AsO_3 in aq. H_2SO_4 using as catalyst a Mn salt, the action of which must itself be catalysed by KIO_3. In the presence of HNO_3, in place of H_2SO_4, an alkali chloride and a trace of I are used to catalyse the action of Mn. Excess of H_3AsO_3 is used and back-titrated with $KMnO_4$. A Ce^{III} salt must first be oxidised by heating with $(NH_4)_2S_2O_8$. With $NiSO_4$, NaOH, and $K_2S_2O_8$, NiO_2 is formed, which oxidises the Ce^{III} salt in the cold after acidifying with H_2SO_4, added in one quantity. If $Ni(NO_3)_2$ and

HNO_3 are employed, oxidation is not always quite complete. Direct potentiometric titration with H_3AsO_3, either by the compensation method or by the sudden change in potential at the end-point, can also be employed. M. S. B.

Cobalt thiocyanate as a microchemical reagent for mercury. A. DE SWEEMER (Mikrochem., 1932, **12**, 223—226).—The formation of blue cryst. $HgCo(CNS)_4$ is recommended for the micro-detection of Hg^{II}. The solubility of the compound in H_2O is 0·084% and in 0·014*N*-$Co(CNS)_2$ 0·008% at 25°. F. L. U.

Ceric salts in volumetric analysis. R. VANOSSI and R. FERRAMOLA (Anal. Asoc. Quím. Argentina, 1932, **20**, 96—139).—The reagent is 0·1*N*-$Ce(SO_4)_2$ in 1—2*N*-H_2SO_4, and is standardised with H_2O_2 and $KMnO_4$, $Na_2C_2O_4$, or, preferably, $K_4Fe(CN)_6$. More dil. solutions (0·05—0·0005*N*) may be used for micro-analysis, but tend to be unstable. Suitable indicators are malachite-green, methylene-blue, Me-violet, and, as an external indicator, indigo-carmine. The error in titration of 1 c.c. of a 0·0005*N* solution of a reducing substance (*e.g.*, $FeSO_4$) is about 2%. Under certain conditions indigo-carmine may be employed as both reducing agent and indicator in the titration of Ce^{IV}. H. F. G.

Determination of aluminium with 8-hydroxyquinoline in presence of phosphoric acid. G. BALANESCU and (MLLE.) M. D. MOTZOC (Z. anal. Chem., 1932, **91**, 188—191).—Usual methods for the determination of Al with 8-hydroxyquinoline in presence of H_3PO_4 lead to divergent results. The solution is treated with aq. NaOH until the $AlPO_4$ ppt. redissolves and then with excess of 5% 8-hydroxyquinoline in EtOH. After heating the solution to the b.p. the ppt. is collected on a glass filter, washed, redissolved in 4*N*-HCl, and titrated with $KBrO_3$. The method is also suitable for the determination of Al in the absence of H_3PO_4. J. W. S.

Quantitative separation of manganate and permanganate. J. E. ORLOV (Z. anal. Chem., 1932, **91**, 186—187; cf. A., 1932, 1223).—When excess of aq. $BaCl_2$ is added to an alkaline solution containing CO_3'', $BaCO_3$ is first pptd., but finally all the MnO_4'' is pptd. as $BaMnO_4$; after centrifuging, the MnO_4' can be determined. J. W. S.

Microchemical detection of rhenium. E. KRONMANN and V. BIBIKOVA (Mikrochem., 1932, **12**, 187—188).—A drop of solution in which crystals of "nitron" perrhenate have formed and which also contains Na_2S is mixed with a drop of warm 10% gelatin and the mixture is allowed to set. On addition of $TiCl_3$ solution, reduction of the perrhenate crystals takes place and the latter are coloured brownish-yellow through formation of ReS_2. The reaction is localised by the jelly and the perrhenate crystals are thus distinguished from those of other insol. "nitron" compounds. F. L. U.

Microchemical methods in the determination of 1 mg. of rhenium after preliminary separation of molybdenum. O. MICHAILOVA, S. PEVSNER, and N. ARCHIPOVA (Z. anal. Chim., 1932, **91**, 25—28).—Mo and Re are first separated as sulphides and oxidised with alkaline H_2O_2. Excess of the latter is removed, the solution neutralised with H_2SO_4, and Mo separated by 8-hydroxyquinoline in presence of NH_4OAc and AcOH. Re is then pptd. as nitron perrhenate, $C_{20}H_{16}N_4HReO_4$, with aq. nitron acetate at 80°, cooled in ice H_2O, filtered, dried at 110°, and weighed. In the determinations made the error varied from 0·4 to 3%. The micro-method requires 8 hr. as compared with 2 days for the macro-method. M. S. B.

Iron thiocyanate reaction. A. VON HEDENSTROM and E. KUNAU (Z. anal. Chem., 1932, **91**, 17—25).—The disturbing effect of foreign substances on the CNS′ test for Fe^{***} has been investigated by adding Et_2O to solutions prepared from different salts of the two ions, to solutions containing excess of either reagent, or to the reagents in HCl solution, and shaking with sufficient solution of the acid or salt to be examined to decolorise the Et_2O which had taken up the red undissociated $Fe(CNS)_3$. The results are tabulated. Slightly dissociated, complex, or insol. Fe salts are probably formed in presence of excess Fe^{***} by alkali salts and org. and inorg. acids. In presence of excess CNS′ complexes will also be formed and ppts. with Hg^{II} and Ag salts. The disturbing effects are diminished for the most part in aq. HCl. In neutral solutions with no excess of either reagent H_2O has the least effect. Of the org. acids tried AcOH has the least action and $H_2C_2O_4$ the most, and of inorg. acids H_3BO_3 least and HF most. Of metal salts, borates, arsenates, phosphates, and fluorides have the greatest effect and also Hg^{II} and Ag salts. The influence of alkali and alkaline-earth salts is comparatively small. M. S. B.

Electrolytic reduction in analytical chemistry. G. T. GALFAJAN (Z. anal. Chem., 1932, **90**, 421—427).—A collodion diaphragm is used to prevent loss of cathode liquid. Using a Pt cathode satisfactory results were obtained in the determination of Fe^{III}, Ti^{IV}, V^{V}, and Mo^{VI}. Details are given. F. L. U.

Gravimetric determination of cobalt, using dinitrosoresorcinol. O. TOMÍČEK and K. KOMAREK (Z. anal. Chem., 1932, **91**, 90—105).—Cf. A., 1932, 1224. D. R. D.

Solubility of nickel dimethylglyoxime. P. NUKA (Z. anal. Chem., 1932, **91**, 29—32).—The determination of Ni by pptn. of Ni dimethylglyoxime, filtering hot, and washing with hot H_2O gives a result 0·5—1% lower than by the electrolytic method. This is avoided by allowing the solution to cool before filtering, washing with cold H_2O, and avoiding the presence of EtOH or AcOH. Pptn. is then practically complete. M. S. B.

Gasometric determination of chromium. M. COUTURE (Annali Chim. Appl., 1932, **22**, 680—682).—The Cr in minerals, alloys, Cr alum, etc. is converted by treatment with H_2O_2 into CrO_3, which is then treated with a solution of $NaBO_3$ containing Na_2HPO_4 (as stabiliser), the vol. of O_2 evolved being measured. The method is standardised by means of $K_2Cr_2O_7$. Results agree well with those obtained iodometrically. T. H. P.

Volumetric determination of tungsten. B. G. MOKEEV (Uchen. Zapiski Kazan Gosud. Univ., 1930,

90, 1022—1024).—Kanchev's method (pptn. with benzidine chloride and titration with NaOH) is unsatisfactory. CH. ABS.

Complete quantitative micro-analysis of Ceylon thorianites. F. HECHT (Mikrochem., 1932, **12**, 193—204).—A detailed description of procedure, using 20—40 mg. of material. F. L. U.

Determination of bismuth. P. P. SOLODOVNIKOV (Uchen. Zapiski Kazan Gosud. Univ., 1928, **88**, 457—460).—The most satisfactory methods are those of Lowe (basic nitrate $\longrightarrow$ Bi_2O_3) and of Jannasch ($HBiO_3 \longrightarrow Bi_2O_3$). CH. ABS.

Detection of small quantities of bismuth with 8-hydroxyquinoline. R. SAZERAC and J. POUZERGUES (Compt. rend. Soc. Biol., 1932, **109**, 79—82; Chem. Zentr., 1932, ii, 1809).—The compound is cryst. and is readily distinguishable from the Fe compound; the reaction detects 1 p.p.m. A 2% solution of 8-hydroxyquinoline is treated with an equal vol. of 4% KI, and the mixture is added to the Bi solution. A. A. E.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXIV. Separation of tantalum from niobium. W. R. SCHOELLER (Analyst, 1932, **57**, 750—756; cf. A., 1925, ii, 1096).—The technique is based on the fractional pptn. of the aq. NH_3–oxalate solution by tannin. T. McL.

Smoke density meter. R. D. BEAN (J. Sci. Instr., 1932, **9**, 391—392).—The smoke passes between a source of light and a photo-sensitive cell, the current through which is measured. C. W. G.

Fluorescence microscope for strong illumination. E. TIEDE (Mikrochem., 1932, **12**, 269).—A claim for priority over Haitinger (A., 1931, 702, 928). F. L. U.

[Fluorescence microscope for strong illumination.] M. HAITINGER (Mikrochem., 1932, **12**, 270—271).—A reply to Tiede (cf. preceding abstract). F. L. U.

***X*-Ray spectrograph for micro-analysis.** E. S. VON BERGKAMPF (Mikrochem., 1932, **12**, 231—234).—Apparatus is described. F. L. U.

Colorimetric determinations with the use of a special tube stand. G. LOCKEMANN, W. ULRICH, and T. KUNZMANN (Chem.-Ztg., 1933, **57**, 18—20).—A colorimeter tube stand in which the tubes are arranged obliquely is described. Data concerning the accuracy attainable in detecting and determining various ions colorimetrically are tabulated. Only a few c.c. of the sample are used. J. W. S.

Use of colorimeter for absolute colour measurement (spectro-photometry). A. THIEL and R. DIEHL (Sitzungsber. Ges. Beforder. ges. Naturwiss. Marburg, 1932, **67**, 11—30; Chem. Zentr., 1932, ii, 743). L. S. T.

Apparatus for rapid measurement of photomicrographs. J. WOUDA (Z. Physik, 1932, **79**, 511—515). A. B. D. C.

Examination of microscopic crystals with *X*-rays. III. Micro-*X*-ray goniometer. O. KRATKY and K. ECKLING (Z. physikal. Chem., 1932, **B**, **19**, 278—290; cf. A., 1931, 413).—A goniometer suitable for the determination of the lattice structure of microscopic crystals is described. A satisfactory precision is attained, and determinations are made as readily as those with macro-crystals, using the ordinary apparatus. R. C.

Conductivity cell. B. MOORE (J. Sci. Instr., 1932, **9**, 389—390).—Cylindrical electrodes are sealed to a glass tube attached to the ground stopper of the cell, and through it Hg connexion is made with one of them. The other is joined by a Pt wire to Hg in another tube, also sealed to the stopper. C. W. G.

Electro-ultrafilter. D. VON KLOBUSITZKY (J. Physical Chem., 1932, **36**, 3189—3190).—The apparatus is described. E. S. H.

Cathode sputtering. F. H. NEWMAN (Phil. Mag., 1932, [vii], **14**, 1047—1049).—An apparatus for producing sputtered surfaces is described. H. J. E.

Capillary electrometer. G. O. HARNAPP (Z. Elektrochem., 1932, **38**, 900).—A simple type of apparatus is described. D. R. D.

Distillation tube for nitrogen determination. W. LEPPER (Z. anal. Chem., 1932, **91**, 15—16).—The (cheap) distillation tube reduces the possibility of error by loss of NH_3 and ensures quiet distillation. M. S. B.

Precision distillation apparatus. A. HANAK (Chem.-Ztg., 1932, **56**, 984).—Loss of vapour from the distillate during the distillation is prevented by a specially designed condenser. The apparatus (diagrams given) is used for the determination of EtOH. S. M.

Soxhlet type of extraction apparatus for operation at low temperatures under reduced pressure. A. HAMBLETON (J. Biol. Chem., 1932, **99**, 289—294).—An apparatus, the joints of which are of flat glass, and an automatic manometer are described. F. O. H.

Micro-extraction apparatus. G. GORBACH (Mikrochem., 1932, **12**, 161—168).—Extraction apparatus designed for the determination of lipins in bacteria or yeasts, and for working with about 50 mg. of material, is described. F. L. U.

Influence of electrical charge in micro-gravimetric analysis. W. M. SPERRY (Mikrochem., 1932, **12**, 151—152).—Pyrex glass readily acquires a persistent electrical charge, and its use in micro-gravimetric analysis should be avoided unless special precautions are taken. F. L. U.

Determination of mol. wt. by the micro-ebullioscopic method. A. RIECHE (Mikrochem., 1932, **12**, 129—132; cf. A., 1929, 167).—Improved apparatus is described. F. L. U.

Macro-micro-burette. W. EISSNER (Z. anal. Chem., 1932, **91**, 172—173).—A double burette is constructed in the form of a U-tube with a 3-way tap at the bottom. One limb consists of a series of bulbs of 3 c.c. capacity joined by narrow necks carrying the graduation marks, whilst the other is a straight narrow tube of 3 c.c. capacity graduated to 0·01 c.c. Means are provided by which the liquid level in the first limb can be adjusted accurately to a graduation. J. W. S.

Measuring flasks for large volumes of liquid. F. FRIEDRICHS (Chem.-Ztg., 1933, **57**, 20).—A wide-necked flask or bottle fitted with a normal ground joint is recommended as a large-capacity measuring flask. The ground joint is connected to a narrow calibrated tube fitted at the top with a ground stopper. Alternatively the same bottle can be connected by another normal joint with a burette with a device for automatic filling to the zero-mark. J. W. S.

Measurement of differences in level of liquid meniscus, and manometer for low pressures. H. KLUMB and T. HAASE (Z. tech. Physik, 1932, **13**, 372—373; Chem. Zentr., 1932, ii, 2208).

Apparatus for separation of neon–helium mixtures and determination of the helium content of neon. W. MEISSNER and K. STEINER (Z. ges. Kalte-Ind., 1932, **39**, 49—53, 75—78; Chem. Zentr., 1932, ii, 748).—Ne lines are faint in the spectrum of the He separated by the method described. The Ne contains < 0·5 vol.-% of He. The He in Ne is determined by condensation in liquid H_2 and measurement of its partial pressure. L. S. T.

Apparatus for the evolution and detection of gases and vapours. E. EINECKE (Z. anal. Chem., 1932, **91**, 14—15).—The apparatus requires only a few mg. of material and is useful for the rapid detection of carbonates, sulphites, sulphides, cyanides, carbides, etc., and for carrying out the CrO_2Cl_2 reaction. M. S. B.

Simple method of elutriation analysis H. LOBER (Zentr. Min. Geol., 1932, **B**, 364—368; Chem. Zentr., 1932, ii, 1476).—An apparatus is described. A. A. E.

Rapid determination of density. W. KRÄTSCHMAR (Zentr. Min. Geol., 1932, **A**, 221—224; Chem. Zentr., 1932, ii, 1328).—Vals. of d are read directly on the scale of a balance. A. A. E.

Stirring of the bath by bubbling of gas in micro-electroanalysis. A. OKÁC (Mikrochem., 1932, **12**, 205—210).—Two arrangements in which the electrolyte is stirred by a stream of gas are described. F. L. U.

Water-bath for micro-analysis. W. REICH-ROHRWIG (Mikrochem., 1932, **12**, 189—192).—A water-bath constructed entirely of glass is described. The most important features are the use of distilled H_2O electrically heated, a reflux condenser, and a funnel inverted over the vessel being heated whereby vapour is carried off by a filter pump. F. L. U.

Determination of size of small particles by means of electron diffraction. M. VON LAUE (Z. Krist., 1932, **84**, 1—7).—A method for determining the order of magnitude of minute particles, *e.g.*, crystallites 10^{-6} to 10^{-7} cm. diameter, based on Thomson's results (cf. A., 1929, 1209; 1932, 955) is described. C. A. S.

Automatic water-level regulator for autoclaves. N. F. CONANT (Science, 1932, **76**, 522—524). L. S. T.

Lecture experiment on the liquefaction of gases. H. KEEFER (Physikal. Z., 1932, **33**, 967—968).—An apparatus for producing liquid CO_2 is described. A. J. M.

Geochemistry.

Helium in Canada from 1926 to 1931. P. V. ROSEWARNE and R. J. OFFORD (Canada Dept. of Mines, 1932, No. 727, 42—54).—A discussion of the geographical distribution of He in Canada and the U.S.A. and of the economic aspect of production. C. W. G.

Nitrogen content of rain water. H. H. FINNELL and H. W. HOUGHTON (Okla. Panhandle Bull., 1932, **34**, 3—8).—At Goodwell, Okla., in 1931 1·42 lb. N per acre (NO_3' 23·32, NO_2' 6·85, NH_3 69·82%) was added by a rainfall of 15·45 in. Nitrite was greatest during the cooler season; NH_3 was related to the dust content of the air. CH. ABS.

Explanation of the structure of meteoric iron by means of the diagram of state of the ternary system iron–nickel–phosphorus. R. VOGEL (Abh. Ges. Wiss. Gottingen, Math.-phys. Kl., 1932, **3**, No. 6, 1—31; Chem. Zentr., 1932, ii, 1409).—A discussion. A. A. E.

Springwater meteorite. H. H. NININGER (Amer. Min., 1932, **17**, 396—400).—An analysis of the metallic portion is given. CH. ABS.

Age of the Meteor Crater. E. BLACKWELDER (Science, 1932, **76**, 557—560).—The age and evolution of the Meteor Crater, N. Arizona, are discussed. L. S. T.

Titaniferous mica in phlogopite. J. JAKOB and I. PARGA-PONDAL (Anal. Fís. Quím., 1932, **30**, 827—839).—Ti^{III} and Ti^{IV} occur in phlogopites, particularly those poor in Fe, to the extent of up to 4% $(TiO)_2$. It replaces Mg, but never Al or Si. The mineral occasionally contains an excess of SiO_2, and there aro probably groups such as $(SiO_2)_3$ present. H. F. G.

Twinning of magmatic quartz with reference to its temperature of origin. O. MUGGE (Z. Krist., 1932, **84**, 97—108; cf. this vol., 46). C. A. S.

Pitchblende and silver discoveries at Great Bear Lake, Northwest Territories. H. S. SPENCE (Canadian Dept. Mines, No. 727, 1932, 55—92).—Analyses are given. C. W. G.

Danbury granodiorite gneiss of Connecticut. W. M. AGAR (Amer. J. Sci., 1933, [v], **25**, 1—19).—This rock is not a single unit, but consists of biotite schists and quartz-oligoclase-biotite gneisses, intersected by granite and pegmatite. Their history is discussed. C. W. G.

Calculation of the reflectivities of sulphide ore minerals. F. C. PHILLIPS (Nature, 1932, **130**, 998). L. S. T.

Distribution of molybdenum. H. TER MEULEN (Nature, 1932, **130**, 966).—Mo is widely distributed

in plants and animals. Coal, peas and beans, and cereals contained 0·21, 3—9, 0·2—0·6 mg. per kg., respectively, whilst wood, beans, various fruits and vegetables contained traces. A fertile soil contained 0·1—0·3 mg., a moor 0·01, and a barren sandy waste 0·005 mg. per kg. Mineral waters and oils, but not sea-water, contained appreciable amounts of Mo. Liver, blood, bile, milk, eggs, cod's liver, and haddock contained amounts varying from 1·5 to 0·03 mg. per kg. An aquatic plant, *Azolla*, yielded 1·13 mg. per kg. L. S. T.

Contact-metamorphism by syenite-gneiss in the Lao tieh shan district near Ryojun, S. Manchuria. T. Ogura (Mem. Ryojun Coll. Eng., 1932, **5**, 133—186).—A detailed description of the geology of the region is given. The metamorphic rock series has been produced by syenite intrusion. C. W. G.

Hydrogen-ion concentrations caused by dissolution of silicate minerals. R. E. Stevens (J. Washington Acad. Sci., 1932, **22**, 540—547).—Silicate minerals, when ground under H_2O, give alkaline solutions of characteristic and reproducible p_H, the vals. of which form a rough index of the weathering qualities of the minerals. C. W. G.

Thermo-magnetic properties of volcanic rocks. R. Chevallier and J. Pierre (Ann. Physique, 1932, [x], **18**, 383—477).—The fact that the Curie points of specimens of lava from different sources cover the whole temp. range 580—0° and probably extend lower suggests that the magnetic material is a solid solution. The magnetism is determined by the Fe_2O_3 content. The Curie point (° abs.) is proportional to the ratio $Fe_2O_3/(Fe_2O_3+FeO)$ up to magnetite (853° abs.) and then remains const. The effects of TiO_2 and other oxides are also discussed. J. W. S.

Kuznetchikha (Russia) deposits of zinc–copper ores. D. K. Suslov and M. I. Merkulov (Tzvet. Met., 1931, 1329—1347).—The ores (described) contain (average) Cu 1—3, Zn 4—13%, with Au (1—10) and Ag (30—140 grains per ton). Ch. Abs.

Nikitova (S. Russia) mercury deposits. S. N. Danilov and F. A. Abramov (Tzvet. Met., 1931, 763—776). Ch. Abs.

Barite. F. Braun (Neues Jahrb. Min., 1932, **A**, **65**, 173—222; Chem. Zentr., 1932, ii, 1606).—Morphological, genetic, and paragenetic habit studies are described. $a:b:c=1·63:1:1·31$. A. A. E.

Bavenite, a beryllium mineral pseudomorphous after beryl, from California. W. T. Schaller and J. G. Fairchild (Amer. Min., 1932, **17**, 409—422).—The mineral (described), $9SiO_2,Al_2O_3,BeO,4CaO,H_2O$, monoclinic, contains about 3% BeO. Ch. Abs.

Rhodochrosite in the Emilian Apennines. L. Girolami (Annali Chim. Appl., 1932, **22**, 686—691).—This Mn mineral, mistaken first for a limestone encrusted with manganite and then for a manganesiferous siderite, must be regarded as a rhodochrosite containing variable proportions of $FeCO_3$. T. H. P.

Albitite from Ve Skerries, Shetlands. F. Walker (Min. Mag., 1932, **23**, 239—242).—Analysis is given of a rock composed mainly of albite (90%) with little quartz (2%), chlorite (2%), magnetite, and apatite. L. J. S.

Spherulitic rhyolites of Jersey. A. E. Mourant (Min. Mag., 1932, **23**, 227—237).—The origin of the various structures is discussed with particular reference to the rhythmic banding of felspar and quartz. L. J. S.

Metamorphism produced by the combustion of hydrocarbons in the Tertiary sediments of S.W. Persia. W. F. P. McLintock (Min. Mag., 1932, **23**, 207—226).—At various localities in S.W. Persia the escape and combustion of gas or oil has resulted in the brecciation, partial fusion, and crystallisation of calcareous marls with the formation of cryst. rocks consisting of diopside, aegirine, wollastonite, pseudowollastonite (α-$CaSiO_3$, not previously recognised as a mineral), bytownite, melilite, and leucite, with glass, recryst. calcite, and anhydrite. In the field the rocks resemble vesicular igneous rocks, but microscopical examination and chemical analyses prove them to be metamorphosed sediments. L. J. S.

Structure of spherocobaltite. M. Baccaredda (Atti R. Accad. Lincei, 1932, [vi], **16**, 248—252).—Analysis of the mineral from Valle del Neva gave: H_2O 1·30, CO_2 35·87, CuO 1·95, Fe_2O_3 0·27, CoO 55·72, NiO 1·21, CaO 3·12=99·44%, with traces of MnO and MgO. *X*-Ray examination showed a rhombohedral structure, with a 5·72 Å., α 48° 14′, $d_{calc.}$ 4·10, 2 mols. $CoCO_3$ per unit cell. O. J. W.

Zeolites. III. Natrolite and metanatrolite. M. H. Hey [with F. A. B. Bannister] (Min. Mag., 1932, **23**, 243—289).—Analyses of nine natrolites from various localities are accompanied by physical, optical, and *X*-ray data determined on the same samples of material. The unit cell, a 18·31, b 18·66, c 6·60 Å., contains $Na_{16}Al_{16}Si_{24}O_{80},16H_2O$. The Si : Al ratio is const., but there may be a replacement of Na_2 by Ca up to 4 atoms per unit cell and of Na by K up to 2 atoms. Crystallographic measurements agree with orthorhombic symmetry with $a:b:c=0·9807:1:0·3537$, and etch-figures show the c-axis to be polar, but *X*-ray study and v.-p. observations on natrolite and metanatrolite (dehydrated natrolite) suggest that the symmetry is really monoclinic with space-group C_2^3. Base-exchange experiments are described, and the heat of hydration of metanatrolite is measured. L. J. S.

Terpenes as the source of petroleum, and their optically active constituents. M. Freund (Petroleum, 1932, **28**, No. 37, 1—8).—Current theories of the formation of petroleum oils are discussed with reference to the production of petroleum-like mixtures from turpentine. Treatment of lævorotatory French turpentines with $AlCl_3$ yielded dextrorotatory products with physical properties similar to those of crude mineral oils. Prolonged boiling of these products and subsequent fractionation gave dextro-, then lævo-, and again dextro-rotatory fractions with increasing b.p. of the fraction, a phenomenon exhibited by Java petroleum. By further treatment of the products with $AlCl_3$, or by refluxing the original turpentine with $AlCl_3$, oils having a striking resem-

blance in optical and general physical properties to Java and Argentine petroleums were obtained. It is concluded that the dextro-constituents of petroleum are the most stable. H. E. B.

Fish oil theory of the origin of petroleum from a study of brine waters from widely different oilfields in Japan. T. ISHIKAWA and T. BABA (Bull. Chem. Soc. Japan, 1932, **7**, 362—373).—The composition of brine from Japanese oilfields is closely similar to that of the serum of fishes, especially Elasmobranchs. This supports the theory that both the brine and the petroleum have been formed by the decomp. of the bodies of fish. D. R. D.

Organic Chemistry.

Constitution and reaction of organic and especially tautomeric compounds. A. HANTZSCH (Z. anorg. Chem., 1932, **209**, 213—224).—A correction and amplification of the article on tautomerism in Hückel's "Theoretischen Grundlagen der organischen Chemie," based on recent work of Hantzsch and others. A. R. P.

Action of hydrogen on wood charcoal and activated carbon, and methane synthesis. E. BERL and R. BEMMANN (Z. physikal. Chem., 1932, **162**, 71—93).—Charcoal and activated C have a graphitic structure, but the edges of the planes of C hexagons are occupied by groups containing O and H as well as C; on ignition practically pure paracryst. C results. Hydrogenation at 350—675°/50—450 atm. gives good yields of practically pure CH_4, which from ignited C can be regarded as formed by direct synthesis. The observed equilibrium between paracryst. C, CH_4, and H_2 agrees closely with data previously recorded for macrocryst. graphite as solid phase. The H_2 attacks first the edge groups and unsaturated points, causing local overheating, which results in diminution of the activity of the remaining C and increase in size of the crystallites. Hydrogenation occurs the more readily the smaller is the degree of graphitisation and the higher is the content of O and H. There is no simple relation between adsorptive power, measured by the methylene-blue test, and ease of hydrogenation. R. C.

Addition of bromine vapour according to P. Becker. Micro-detection of active and inactive double linkings. E. ROSSMANN (Ber., 1932, **65**, [*B*], 1847—1851).—The substance (1 or 10 mg.), evenly distributed over a weighed glass plate, is placed in a desiccator saturated with Br vapour in complete absence of light. Absorption of Br is usually complete in 30 min. Excess of halogen is mainly lost after exposure to air for 5 min., after which completion is assured with sensitive compounds by preservation over solid KOH, with volatile substances by evacuation at room temp., but usually by heating at 105°/atm. pressure. Determination of the Br val. by this method permits differentiation between smaller C rings and conjugated double linkings. Carotene appears to contain eleven double linkings, but readily loses 3 HBr in vac. or at 110°; it reabsorbs Br when again exposed to the vapour. Sterols and other OH-compounds show the expected number of double linkings after a normal period of exposure, but an additional double linking when action is prolonged, probably owing to loss of H_2O and subsequent addition. Substitution is never observed. Numerous examples are cited. H. W.

Thermal conversion of ethylene and ethane into other hydrocarbons, with special reference to the formation of acetylene. F. FISCHER and H. PICHLER.—See B., 1933, 53.

Reaction between ethylene and bromine in carbon tetrachloride. D. M. WILLIAMS (J.C.S., 1932, 2911—2915; cf. A., 1928, 1351).—Interaction of Br and C_2H_4 in CCl_4 in the dark is autocatalytic, having an inhibition period of many min. in dil. and dry solution. H_2O (0·0065*N*) (concn. kept const. by Na_2SO_4–Na_2SO_4,10H_2O) catalyses the reaction (which, however, remains autocatalytic) to some extent, but is not as active as HBr, which, added in small amounts during the inhibition period, causes > 70% of the C_2H_4 to react in 2 min. The temp. coeff. of the reaction in the moist solvent between 0° and 18° is negative, which supports the view that addition of Br is preceded by addition of HBr (A., 1925, ii, 214). J. L. D.

Polymerisation processes. F. HOFMANN (Chem.-Ztg., 1933, **57**, 5—6).—BF_3 and C_2H_4 give *n*- or *iso*-C_3H_6 or higher polymerides. BF_3, best with a little HF, gives with *cyclo*-pentene and -hexene di-, tri-, tetra-, and poly-merides. R. S. C.

Catalytic vapour-phase hydration of Δ^β-butene under high pressures. L. F. MAREK and R. K. FLEGE (Ind. Eng. Chem., 1932, **24**, 1428—1431).—Vapour-phase hydration of Δ^β-butene at 427—538° under continuous flow at 211—352 kg. per sq. cm. gives small yields of butan-β-ol. Reaction is promoted by Cu_2Cl_2, $Cu_3(PO_4)_2$, ThO_2, and H_3PO_4. Increasing the proportion of H_2O to Δ^β-butene increases the conversion into hydrated products and decreases polymerisation, but the concn. of hydrated products decreases. Increase in pressure from 211 to 352 kg. per sq. cm. favours polymerisation rather than hydration. J. W. S.

Constitution of lycopene. R. KUHN and C. GRUNDMANN (Ber., 1932, **65**, [*B*], 1880—1889).—Doubts regarding the normal structure of lycopenaloxime (A., 1932, 749) are removed by the observation that it resembles other *syn*- and *anti*-aldoximes and ketoximes in its behaviour towards MgMeI and differs from 3 : 5-diphenyl*iso*oxazoline. Lycopenal (I) in C_6H_6–AcOH is oxidised by 0·1*N*-CrO_3 (O = 2) to *bixindialdehyde* (II), m.p. 220° (corr., Berl., vac.), and methylheptenone (*p*-nitrophenylhydrazone, m.p. 101°). Direct oxidation of (I) to the corresponding acid could not be effected, but its *dioxime*, decomp. 250—300°, is dehydrated by Ac_2O to the *dinitrile*, readily hydrolysed to β-norbixin. Lycopene has therefore the constitution

(:CH·CH:[CMe·CH:CH·CH]$_2$:CMe·[CH$_2$]$_2$·CH:CMe$_2$)$_2$, whilst (I) and (II) are respectively CMe$_2$:CH·[CH$_2$]$_2$·[CMe:CH·CH:CH]$_2$·[CH:CMe·CH:CH]$_2$·CHO and (:[CH·CH:CMe·CH]$_2$:CH·CHO)$_2$. The available phytol in plants does not appear adequate to account completely for the production of carotenoids. The amended prep. of lycopene from preserved tomatoes is recorded. Ripe tomatoes contain carotene (III), lycopene (IV), xanthophyll (V) and its ester (VI). The amount of (III) is about 1/10th that of (IV) and appears adequate to explain the vitamin-*A* action. (IV) is present in the unripe fruit in smaller amount than (III), whereas (VI) is absent. In the half-ripe condition the amount of (IV) exceeds that of (III), whilst formation of (VI) has commenced, the amount increasing rapidly, and subsequently exceeding that of (V). (V) contains predominatingly zeazanthin and lutein. (III) is nearly homogeneous β-carotene. The chlorophyll content is > 3 mg. per 100 g. of fresh green tomato. H. W.

Photo-chlorination of tetrachloroethylene in carbon tetrachloride solution. J. A. Leermakers and R. G. Dickinson.—See this vol., 132.

Action of peracetic and perbenzoic acids on unsaturated aliphatic and aromatic iodine compounds. J. Boeseken and C. Schneider (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1140—1143; cf. A., 1931, 207).—Only those aliphatic compounds containing an I atom adjacent to a double linking yield iodoso- or iodoxy-derivatives on treatment with AcO_2H in AcOH or BzO_2H in $CHCl_3$. Thus, CHI_3 is destroyed, liberating I, oxidised to I_2O_5, and C_2I_2 gives C_2I_4, whereas $C_2H_2I_2$ yields a white explosive compound believed to be *di-iodoxyethylene*. Iodofumaric acid gives *iodosofumaric acid* (I), which in boiling H_2O loses CO_2, forming *β-iodosoacrylic acid*, reduced by SO_2 to β-iodoacrylic acid, m.p. 65° (cf. Stolz, A., 1886, 531), and reoxidised by AcO_2H to (I). Di-iodofumaric acid adds 2O on oxidation with AcO_2H in AcOH, giving (?) *di-iodosofumaric acid*. Di-iodostilbene is not oxidised by AcO_2H in AcOH, but in $CHCl_3$ *αβ-dichloro-αβ-diphenylethylene oxide* is obtained. D. R. D.

Oxidimetric determination of small amounts of alcohol. II. L. Smith (Svensk Kem. Tidskr., 1932, **44**, 272—279).—Improvements in the original method (A., 1931, 990) are described. The acid $K_2Cr_2O_7$ solution is diluted directly with the arsenite, and excess of the latter titrated with $KBrO_3$ after addition of Me-orange in HCl. The excess of $K_2Cr_2O_7$ can be determined colorimetrically, provided that the percentage of reduced chromate is not unduly small. H. F. H.

[Preparation of] *iso*propyl alcohol. G. A. Kirchhof and A. D. Stepanov (Chem.-Pharm. Ind., Russia, 1932, No. 1, 21; Chem. Zentr., 1932, ii, 1609).—Electrolysis of $COMe_2$ (37·5 g.) and 15% H_2SO_4 (150 c.c.) is carried out at 6—7 volts for 9 hr. (8 amp. per hr.) using Hg as cathode and Pb in 15% H_2SO_4 as anode, the axis of the stirrer being passed through a porous vessel. The cathode liquid is neutralised with conc. NaOH and distilled; yield 33%.

[Configurative relationships of methyl-, phenyl-, methyl*cyclo*hexyl-, and methylhexyl-carbinols and of their homologues.] P. A. Levene and R. E. Marker (J. Biol. Chem., 1932, **99**, 321; cf. A., 1932, 1027).—The corr. vals. of [*M*] for methyl-, ethyl-, propyl-, butyl-, and amyl-*iso*propyl-carbinols are +4·7°, −16·7°, −27·1°, −35·9°, and −38·2°; and for their phthalates, +98°, +10°, −22°, −36°, and −44°, respectively. J. W. B.

Δ$^\delta$-Pentenol and pentane-αβε-triol. R. Paul (Ann. Chim., 1932, [x], **18**, 304—394).—Me γ-chloro- and -bromo-propyl ether are conveniently obtained from propane-αγ-diol. Grignard reagents obtained from these with $AlCl_3$ as catalyst on condensation with the appropriate nitriles give *αε-dimethoxy-* (I), b.p. 89°/14 mm. (yield 23%) [*semicarbazone*, m.p. 88·5°; *oxime*, b.p. 141—143° (corr.)/15 mm.], ε-methoxy-α-ethoxy-, b.p. 95—96°/13 mm. (yield 23%) (*semicarbazone*, m.p. 59—60°; *oxime*, b.p. 140—141°/9 mm.), *ε-methoxy-α-iso*amyloxy-* (II), b.p. 131—132°/17 mm. (yield 30%) (gives amyloxymethyltetrahydrofuran on distillation with P_2O_5), and *ε-ethoxy-α-iso*amyloxy-pentan-β-one*, b.p. 134°/14 mm. (from chloroethoxypropane; cf. A., 1931, 819). Some ROH corresponding with the RO·CH$_2$·CN employed is always obtained, together with products of the type *di-(γ-methoxypropyl)ethyleneimine*, b.p. 119—132°/9 mm. The mechanism of the interaction of nitriles and Grignard reagents is discussed. No difference could be detected in the rates of oximation of (I) and (II). (II) with gaseous HBr gives MeOH and *iso*amyl alcohol, whilst with $NaNH_2$ and EtI it gives the *γ-Et* derivative, b.p. 135—139°/12 mm. Reduction of the above ketones in AcOH with Pt-black gives *dimethoxy-*, b.p. 94—95°/13 mm. (p-*nitrobenzoate*, m.p. 194—195°), *methoxyethoxy-*, b.p. 99°/13 mm., and *methoxyisoamyloxy-pentanol*, b.p. 126—127°/10 mm., all converted by HBr into *αε-dibromopentan-β-ol*, b.p. 126—128°/11 mm., and 1-bromomethyltetrahydrofuran (A., 1931, 933), also obtained by distillation of the former. Δ$^\delta$-Pentenol (III) (improved prep.) [*Me ether* (IV), b.p. 96—98°/764 mm.] from allylacetic acid contains *β-allyl-Δ$^\delta$-pentenol*, b.p. 182°/760 mm. (*pyruvate*, b.p. 115—117°/13 mm., and its *semicarbazone*, m.p. 99—100°), and gives *αδ-dibromopentane*, b.p. 82°/12 mm., with HBr. δ-Bromo-Δ$^\delta$-pentenol (A., 1931, 1392) gives an *allophanate*, m.p. 136—139°. The corresponding bromide with Br in Et_2O gives *αββε-tetrabromopentane*, b.p. 179—180°/17 mm. (IV) with HOCl gives a little *αβ-dichloro-*, b.p. 81°/13 mm., and *α-chloro-β-hydroxy-ε-methoxypentane* (V), b.p. 102—103°/13 mm., converted by KOH into the *αβ-oxide* of (IV), b.p. 156°/760 mm., which with HCl gives (V), containing 9% of the β-chloro-α-hydroxy-isomeride, detected by kinetic measurements. (III) similarly gives some Cl_2-derivative, and a mixture of monochlorohydrins, giving a small yield of chloromethyltetrahydrofuran with 15% H_2SO_4, and converted by dry KOH into hydroxymethyltetrahydrofuran. The physical properties of some of the above compounds are compared with those of their lower homologues. A. A. L.

Hydrogenolysis of oxygenated organic compounds. R. Connor and H. Adkins (J. Amer.

Chem. Soc., 1932, **54**, 4678—4690).—The effect of structure on the fission (hydrogenolysis) of C·C and C·O linkings in numerous glycols, OH-esters, malonates, and furans by H_2 and a Cu–Cr oxide catalyst is studied. αγ-Glycols undergo hydrogenolysis at a lower temp. or more rapidly than αβ- and αδ-glycols. Both types of fission occur, but the C·C cleavage is facilitated (both for αγ- and αβ-glycols) by branching or lengthening the C chain. Et *cyclo*hexanol-2-carboxylate and β-hydroxybutyrate ($CH_2Ac·CO_2Et$ is used) undergo 100% C·O fission. With Et α-substituted-β-hydroxybutyrates, some C·C cleavage occurs (the amount increases with the size of the substituent), whilst Et αα-dialkyl-β-hydroxybutyrates undergo 100% C·C fission. Et αγ-diacetyl-β-methyl- and -β-phenyl-glutarates undergo little or no C·C fission; di-primary glycols are produced. Hydrogenolysis of $CHR(CO_2Et)_2$ occurs thus: $CHR(CO_2Et)_2+4H_2\longrightarrow CHR(CH_2·OH)_2$ (I); (I) $+H_2\longrightarrow CHMeR·CH_2·OH+H_2O$; (I) $+H_2\longrightarrow CH_2R·CH_2·OH+MeOH$; the amounts of the last two reactions vary with R. $CR_2(CO_2Et)_2$ is completely converted into $CHR_2·CH_2·OH+MeOH$. Hydrogenolysis of furfuryl alcohol occurs at each of the three C·O linkings present; some reduction to tetrahydrofurfuryl alcohol (which is relatively stable to hydrogenolysis) also occurs. The previously reported observation (A., 1932, 599) that PhEt is produced from $CHPhEt·CO_2Et$ is ascribed to the probable presence of $CH_2Ph·CO_2Et$ in the ester used. The following are new: γ-, b.p. 83—86°/10 mm., and ε-, b.p. 84—86°/10 mm., *-methyl-β-ethylhexyl alcohols*; *Et hexahydrosalicylhexahydrosalicylate*, b.p. 192—196°/6 mm. (from *o*-$OH·C_6H_4·CO_2Et$ in absence of EtOH); *hexahydrobenzyl β-hydroxybutyrate*, b.p. 149—150°/17 mm. (from $CH_2Ac·CO_2Et$+*cyclo*hexylcarbinol); *Et β-hydroxy-α-hexahydrobenzylbutyrate*, b.p. 147—148°/10 mm.; *Et β-hydroxy-αα-diethylbutyrate*, b.p. 87—89°/9 mm. H. B.

Preparation of ethers of vinyl alcohol. W. Chalmers (Canad. J. Res., 1932, **7**, 464—471).—Alkyl vinyl ethers are obtained in about 33% yield when alkyl β-bromoethyl ethers (prepared in 10—60% yield from $OAlk·CH_2·CH_2·OH$ and PBr_3 in Et_2O in absence or presence of $NPhMe_2$) are heated with solid NaOH; $(OAlk·CH_2·CH_2)_2O$ is a by-product. Me, b.p. 12—14° (all b.p. are corr.), Et, b.p. 35·5°, *Bu*$^{\alpha}$, b.p. 93·3°, Ph, b.p. 155·5°, and β-chloroethyl, b.p. 108° [from $(CH_2Cl·CH_2)_2O$], vinyl ethers are thus prepared. $OAlk·CH_2·CH_2Cl$ is unaffected by NaOH even at high temp. *Bu*$^{\alpha}$ *β-chloroethyl ether*, b.p. 153—154° (from $OBu·CH_2·CH_2·OH$ and $SOCl_2$); *Bu*$^{\alpha}$ *β-bromoethyl ether*, b.p. 173—174°, and *Bu*$^{\alpha}$ β- -n-*butoxyethoxyethyl ether*, b.p. 245—247°, are new. Physical data are recorded. H. B.

Polymerisation of vinyl ethers. W. Chalmers (Canad. J. Res., 1932, **7**, 472—480).—Et and Bu$^{\alpha}$ vinyl ethers are almost completely polymerised by 0·2% of I in 24 hr.; β-chloroethyl vinyl ether is similarly only slightly affected during 6 days, whilst Ph vinyl ether (I) is unchanged. All the above ethers [except (I)] are polymerised slowly by heat or ultra-violet light and rapidly (explosively) by a trace of the volatile metallic halides; Na has no effect. The polymerides are usually sticky, pitch-like materials which are mobile above 100° and contain 18—82 units (mol. wt. by f.p. in C_6H_6); vals. of *d* and *n* are given. The structure of the polymerides is discussed. H. B.

"Radial" tetrathio-orthosilicic esters. H. J. Backer and F. Stienstra (Rec. trav. chim., 1932, **51**, 1197—1199).—$SiCl_4$ gives the following tetrathio-orthosilicic esters with the corresponding Na alkylmercaptides in C_6H_6 (yield 35—40%): *Me*, b.p. 144—146°/12 mm., m.p. 31°; *Et*, b.p. 169—171°/12 mm., m.p. —5·8°; *Pr*$^{\alpha}$, b.p. 204—206°/17 mm.; *Pr*$^{\beta}$, b.p. 176—178°/13 mm., m.p. 33·5°. A. A. L.

Preparation of sodium argentothioglycerolsulphonate (Lumiere's compound). J. B. Cohen (J. Pharm. Exp. Ther., 1932, **46**, 283).—Epichlorohydrin, treated with $NaHSO_3$ in aq. solution, yields $CH_2Cl·CH(OH)·CH_2·SO_3Na,2H_2O$, from which, when treated with NaHS, $SH·CH_2·CH(OH)·CH_2·SO_3Na$ is obtained. When the solution of this compound is treated with moist Ag_2O, and EtOH is then added, Na argentothioglycerolsulphonate is pptd. as a yellow powder. W. O. K.

Esterification with chloroformic esters. M. J. Kraft and B. A. Alexeev (J. Gen. Chem. Russ., 1932, **2**, 726—729).—Me and CH_2Cl chlorosulphonates are obtained in good yield from the acid and the appropriate chloroformate. BzOH with $ClCO_2CH_2Cl$ gives $BzO·CH_2Cl$ (I), BzCl, and $CH_2(OBz)_2$; the last-named is probably formed from BzCl and CH_2O, produced by the decomp. of (I). $ClCO_2CCl_3$ gives acid chlorides in every case: with $MeHSO_4$ it forms $ClSO_3Me$, also obtained with $ClCO_2CH_2Cl$. G. A. R. K.

Mechanism of oxidation processes. XXXII. Enzymic oxidation of acetic acid by yeast. H. Wieland and R. Sonderhoff.—See this vol., 32.

Raman effect and problems of constitution. III. Carboxylic anhydrides. K. W. F. Kohlrausch, A. Pongratz, and R. Seka (Ber., 1933, **66**, [*B*], 1—12).—Examination of the Raman spectra of eleven acid anhydrides shows (*a*) the presence of two different frequencies in the region of double linkings (1400—1900 cm.$^{-1}$), (*b*) that both frequencies are unusually strongly increased in comparison with the vals. obtained for acids, and (*c*) that the exaltation is about 40 cm.$^{-1}$ greater for cyclic than for simple anhydrides, but that the difference between the two frequencies remains approx. const. Methylsuccinic anhydride is exceptional in showing a third C:O frequency at 1726 cm.$^{-1}$ and Bz_2O in a depression of both vals. consequent on the presence of the aryl group. The exaltation under (*b*) compared with the CO frequency of ketones is consequent on the sp. action of the vicinal O [cf. MeCHO and HCO_2Me; $COMe_2$ and $CO(OMe)_2$; COPhMe and BzOMe]; it is particularly marked when the vicinal O is either very sensitive to hydrolysis or is concerned in ring closure. Exaltation is not observed when O is not in immediate union with CO (cf. furfur- and cinnam-aldehyde; Et cinnamate). Certain duplication of the C:O frequencies of the type observed in anhydrides is not observed when the bridge O is replaced by CH_2 or NH [$CH_2(CO_2Me_2)$; $CH_2(CO_2Et)_2$; $NHAc_2$; succinimide; K phthalimide]. It appears most probable

that the duplication is due to a difference in the constitutional influence on the two CO groups caused by asymmetry of the bridge O. In Me_2O it appears that the internal oscillations of the Me groups differ in spite of their similar structure. H. W.

Unsaturated fatty acids and their derivatives. VIII. Constitution of clupanodonic acid. Y. INOUE and K. SAHASHI (Proc. Imp. Acad. Tokyo, 1932, **8**, 371—374).—Ozonolysis of clupanodonic acid (cf. A., 1929, 294) does not lead to $EtCO_2H$, whilst the proportion of succinic acid is high enough to be due to a repetition of the same grouping of 4 C atoms in the chain. The I val. is low for 5 ethylenic linkings, and consideration of the bromination products of partly hydrogenated clupanodonic acids indicates the presence of 1 acetylenic and 3 ethylenic linkings as in the following suggested formula: $CPr{:}C[CH_2]_5{\cdot}CH{:}CH{\cdot}[CH_2]_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$. A. C.

Preparation of sarcolactic acid. W. FREUDENBERG (J. Biol. Chem., 1932, **99**, 153—154).—This acid (yield 4—5%) is readily prepared by continuous extraction of a suspension of 200 g. of meat extract in 1000 c.c. of H_2O acidified with H_2SO_4 (Congo-red) with Et_2O in a vac. at 25—30°, repetition of the process on the residue from the Et_2O solution, and distillation at 98—100°/0·2 mm. J. W. B.

Desmotropy of some α-keto-acids. C. FROMAGEOT, M. PELLETIER, and P. EHRENSTEIN (Bull. Soc. chim., 1932, [iv], **51**, 1283—1302).—The ultra-violet absorption of dimethyl- (I) and methylethyl- (II) but not of trimethyl-pyruvic acid in H_2O, EtOH, Et_2O, and dioxan varies with the p_H and is not comparable with the content of enolic form determined by titration with Br in presence of $FeCl_3$. It is concluded that (I) and (II) exist partly in the form CRR'.C(OH)$_2$, and that only this form undergoes biological decarboxylation to the aldehyde. R. S. C.

Derivatives of β-keto-γγ-dimethylvaleric acid. E. WAHLBERG (Ber., 1932, **65**, [*B*], 1857—1864; cf. A., 1911, i, 707).—Accumulation of Me groups so masks the CO group that Et β-keto-γγ-dimethylvalerate (I) scarcely reacts with CH_2O or PhCHO, with difficulty and at a high temp. with NH_2Ph or PCl_5, and not with NH_3, $CO(NH_2)_2$, AcCl, HCO_2Et, HCN, or $NaHSO_3$. β-Keto-γγ-dimethylvaleronitrile (II) and HCN afford the unstable *β-hydroxy-β-cyano-γγ-dimethylvaleronitrile*, m.p. 85° after softening when rapidly heated. With NH_2OH in AcOH (II) gives *5-imino-3-tert.-butyl-4 : 5-dihydroisooxazole*, m.p. 93—93·5°. *Et α-imino-γ-keto-δδ-dimethylamyl ether*, m.p. 58—59°, is obtained from the hydrochloride (*loc. cit.*) and Na_2CO_3. The Na derivative of (I) and bromopinacolin in Et_2O afford *Et γ-keto-α-β'-dimethylpropionyl-δδ-dimethylhexoate*, b.p. 155·5—156°/15 mm.; the corresponding *acid*, m.p. 61—62° (decomp.), readily loses CO_2 with formation of *ββηη-tetramethyloctane-γζ-dione*, m.p. 19—19·5° to a cloudy liquid which becomes transparent at 25—25·2° [*dioxime*, m.p. 265° (decomp.)]. $COPh{\cdot}CH_2Br$ and the Na derivative of (I) in Et_2O yield, after hydrolysis, *β-keto-γγ-dimethyl-α-phenacylvaleric acid*, m.p. 108·5° (decomp.), whereas with $CH_2Cl{\cdot}CO_2Et$ *Et β'β'-dimethylpropionylsuccinate*, b.p. 157—160°/16 mm., is produced; the corresponding *acid*, m.p. 108° (decomp.), readily loses CO_2 with production of *γ-keto-δδ-dimethylhexoic acid*, m.p. 66·5—68°. (I) and *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ yield 3-*ββ-dimethylpropionylcoumarin*, m.p. 89·5—90°, from which the *salt* $CMe_3{\cdot}CO{\cdot}C(CO_2Ag){:}CH{\cdot}C_6H_4{\cdot}OH$ is derived. With 3-nitrosalicylaldehyde, *Et β-keto-γγ-dimethyl-α-3-nitro-2-hydroxybenzylidenevalerate*, m.p. 118—119°, is produced, readily transformed into *6-nitro-3-ββ-dimethylpropionylcoumarin*, m.p. 150° (indef., decomp.). *o-Nitro-3-ββ-dimethylpropionylcoumarin*, m.p. 157·5—158°, and *6-nitroacetylcoumarin*, m.p. 194—195°, are described. (I) and NH_2Ph in CO_2 at 160—170° yield *β-keto-γγ-dimethylvaleranilide*, m.p. 82—83°. (I) cannot be nitrosated with N_2O_3 or amyl nitrite but is transformed by $NaNO_2$ in AcOH into *Et β-keto-α-oximino-γγ-dimethylvalerate*, b.p. 162—164°/20 mm., m.p. 92—92·5°. 3-tert.-*Butylisooxazol-5-one*, m.p. 106—107°, is derived from (I), NH_2Ph, and NH_2OH,HCl in MeOH. *Et β-keto-γγ-dimethylvalerate semicarbazone* has m.p. 117—117·5°. β-Keto-γγ-dimethylvaleric acid in EtOH–H_2O is reduced by Na–Hg to *4-β-hydroxy-γγ-dimethylvaleric acid*, m.p. 81·5—82°, resolved by quinine with production of the *l-acid*, m.p. 81—82°, $[\alpha]_D^{19}$ −25° (±2°) (*quinine* salt, m.p. 166—166·5°, $[\alpha]_D^{19}$ −145° in EtOH). H. W.

Walden inversion. IV. Conversion of bromosuccinic acid into malic acid. V. Conversion of aspartic acid into chloro- or bromo-succinic acid. H. N. K. RØRDAM (J.C.S., 1932, 2931—2940, 2940—2945).—IV. Halogenosuccinic acid is converted into malic acid (I) through the lactonic acid (prep. of Et_2O solution described) which can be hydrolysed to (I) both by acid and alkali. $[\alpha]_D$ of the (I) produced under varying concns. of H· and OH′ is determined. In agreement with the author's view (cf. A., 1929, 1041), but contrary to older work (A., 1913, i, 824), acid hydrolysis affords either the (−) or (+) form, depending on the concn., whereas alkaline hydrolysis gives only the (+) isomeride. Other work (A., 1931, 935) supports the view that there is a region of slight basicity in which the stereochemical nature of the product varies with the p_H. The vals. of *n* (cf. A., 1930, 1407) are calc. from α_D.

V. A N_2O_3–N_2 mixture passed into an aq. solution of (+)-aspartic acid (II) containing HCl and HBr at 0° for varying periods affords halogenosuccinic acids of const. [α] in spite of the changing ionic strength, the reaction being of type 2 (*loc. cit.*). The conversion of (II) into (−)-malic acid by diazotisation in HNO_3 (A., 1928, 1216) is a reaction of type 1 (*loc. cit.*) because the stereochemical result of the reaction depends on the hydrolysis of an ester of (I) with HNO_3 and hence on the concn. of HNO_3. The conversion of *l*-phenylmethylcarbinyl *p*-toluenesulphinate into *p*-tolyl-α-phenylethylsulphone (A., 1930, 1177) and cases of auto-racemisation find an explanation in the theory (A., 1928, 1215). J. L. D.

Conjugated double linkings. XXV. Thermal degradation of carotene dyes. R. KUHN and A. WINTERSTEIN (Ber., 1932, **65**, [*B*], 1873—1880).—The carotenoid is heated under 1 mm. pressure first at 110° and then slowly to incipient melting. Bixin,

β-bixin, dihydrobixin, azafrin, m.p. 212—214° (corr., Berl) [*Me* ester, m.p. 193° (corr., Berl)], crocetin, lycopene, carotene, and zeaxanthin yield PhMe and m-$C_6H_4Me_2$, determined approx. by oxidation to the corresponding acids, separated from one another by sublimation in vac. Terephthalic acid is never encountered, thus establishing the absence of Me groups in the αδ position to one another. Azafrin and bixin give, in addition to hydrocarbons, small amounts of *m*-toluic acid, thereby establishing the arrangement ·CH:CH·CH:CMe·CH:CH·CO_2H or ·CH:CMe·CH:CH·CH:CH·CO_2H. Bixin yields also Me *m*-toluate, but not *p*-toluic acid, whereas methylbixin affords solely Me *m*-toluate. The relative position of the next Me to the free and esterified CO_2H group is therefore the same if the possibility of re-esterification is excluded and also the assumption that only one end of the polyene chain tends to ring closure. At least 19 of the 25 C atoms of bixin are accounted for in the thermal degradation—9 between C_1 and C_6 to Me *m*-toluate, 8 from C_{13} to C_{18} to *m*-toluic acid, and 2 further (at C_7 or C_{12}) to m-$C_6H_4Me_2$. The possible production of o-$C_6H_4Me_2$ (from C_7 to C_{12}) could not be certainly established. The symmetrical distribution of the Me groups of bixin is regarded as established. Crocetin Me_2 ester is degraded to the hydrocarbons and the Me_2 ester, m.p. 135°, of a tetramethylocta-tetraenedicarboxylic acid, $C_{14}H_{18}O_4$; no *m*-toluic acid is formed. H. W.

Derivatives of αα′-diketoadipic acid. G. A. R. Kon and B. L. Nandi (J.C.S., 1932, 2958—2959; cf. A., 1932, 1234).—Me and Et diacetyladipates (J.C.S., 1890, **57**, 204) with NO_2·SO_3H in H_2SO_4 at 0° (cf. A., 1904, i, 847) afford Me (diphenylhydrazone identical with the product of ozonisation of Me Δ^1-*cyclo*butene-1 : 2-dicarboxylate) and Et αα′-diketoadipate (*diphenylhydrazone*, m.p. 150°). J. L. D.

Polymerisation of acetaldehyde. II. W. H. Hatcher and M. G. Kay.—See this vol., 130.

New general reagent for enols; mercurous nitrate. II. Absorption spectra of normal and enolic forms of aldehydes and ketones. III. Influence of p_H on the stability of solutions of aldehydes. E. V. Zappi and A. T. Williams (Bull. Soc. chim., 1932, [iv], **51**, 1258—1269).—II. The spectra of aldehydes and ketones in neutral and alkaline aq. solutions are of two types, corresponding with the enolic and ketonic forms. Neutral solutions of freshly-distilled MeCHO and EtCHO are completely ketonic, but the enolic bands appear on keeping and the pure enol is obtained on adding alkali. Acraldehyde is an equilibrium mixture, the influence of alkali being slight, except when polymerisation occurs. $COMe_2$ gives a purely ketonic spectrum, even in presence of alkali. On addition of NH_3, however, the enolic bands appear.

III. Data are given for the velocity of decomp. of MeCHO, EtCHO, and acraldehyde in presence of H_2O and aq. $NaHCO_3$, Na_2CO_3, NaOH, $Na_2B_4O_7$, and AcOH. Ultra-violet light does not accelerate decomp. appreciably. D. R. D.

Relations between acidity and enolisation. F. Arndt and C. Martius (Annalen, 1932, **499**, 228—287).—The tendency of enolisation of a ketone, *i.e.*, the tendency of the (electronic) change R C(H):C:R → R:C(H)–C:R, is termed the "enotropic effect." The SO_2 group is postulated as a non-enolisable group, *e.g.*, R:C(H)(O):S:R, and has, therefore, no enotropic effect; SO_2 groups do, however, confer acidic properties. The work necessary for the transference of a proton from the C- to the enolic O-electrons is termed "prototropic expenditure of work"; this is the smaller the greater is the enotropic effect of the mol. The enotropic effect is independent of the acidity of the mol. The conferment of acidic properties by substituents is found (in accordance with theory) to be SO_3R> SO_2R>SO_2NR_2>CO_2R>CHO, COR, SO, and is influenced by the prototropic expenditure of work. The enotropic effects of the groups CHO, COR, and CO_2R decrease in the order quoted and so differ from their "acidifying action." The relationships between the above factors and constitution are discussed.

The following compounds undergo enolisation as shown by $FeCl_3$ and Br (the limits of accuracy of these methods are discussed): $CH(CO_2Me)_3$ (the Et_2O solution contains 0·7% of enol by indirect Br titration), converted by moist or dry Et_2O–diazomethane into about 80% of *Me* ββ-*dimethoxyethylene*-αα-*dicarboxylate* (I), b.p. 142—145°/13 mm., m.p. 48° [readily hydrolysed to $CH(CO_2Me)_3$], and 20% of *Me ethane*-ααα-*tricarboxylate*, b.p. 123—124°/15 mm., m.p. 39° [also formed when (I) is heated at 180°]; *Me* p-*toluenesulphonylmalonate*, m.p. 65—66°, from $CHCl(CO_2Me)_2$ and p-C_6H_4Me·SO_2Na in MeOH, which is readily sol. in 2*N*-NaOH and with Et_2O–CH_2N_2 gives *Me* α-p-*toluenesulphonylethane*-αα-*dicarboxylate*, m.p. 131° (insol. in 2*N*-NaOH); Et 3-hydroxythionaphthen-1 : 1-dioxide-2-carboxylate (*Me ether*, m.p. 119°), which with CHN_2·CO_2Et in $CHCl_3$ affords the 3-O-*carbethoxymethyl* derivative, m.p. 121°; formylmethanedisulphon-*N*-ethylanilide, $CHO·CH(SO_2NPhEt)_2$ (enol *Me ether*, m.p. 88°); $CO_2Et·CO·CH(SO_2NPhEt)_2$, m.p. 98—99° (lit. 103—105°) (*alcoholate*, m.p. 145—146°), converted by Et_2O–CH_2N_2 into the C-*Me* derivative, m.p. 131—132°, which is non-acidic and with Et_2O–CH_2N_2 affords the *oxide*, $O<^{CH_2}_{C(CO_2Et)·CMe(SO_2NPhEt)_2}$, m.p. 136° (corresponding *glycol diacetate*, m.p. 165°, formed by the action of Ac_2O and anhyd. $FeCl_3$); 4-*hydroxy*-m-*toluenesulphon*-N-*ethylanilide*, m.p. 65°, prepared from 4-acetoxy-*m*-toluenesulphonyl chloride (II) and NHPhEt with subsequent hydrolysis (EtOH–KOH); *Ph* 4-*hydroxy*-m-*toluenesulphonate*, m.p. 55°, from (II) and PhOH in C_5H_5N with subsequent hydrolysis.

The following are non-enolisable (the Me ethers prepared from compounds of the type $RSO_2·CH_2·COR$ and Et_2O–CH_2N_2 are $RSO_2·CH:CR·OMe$ and are hydro-

lysed by acid to the parent ketone) : Me *o*-carbomethoxybenzenesulphonylacetate; *Me di*-p-*toluenesulphonylacetate*, m.p. 160°, from $CHCl_2{\cdot}CO_2Me$, p-$C_6H_4Me{\cdot}SH$, and MeOH–NaOMe followed by oxidation (H_2O_2–AcOH), converted by moist Et_2O–CH_2N_2 into *Me* αα-*di*-p-*toluenesulphonylpropionate*, m.p. 179°, and by diazoethane in Et_2O–CH_2Cl_2 into *Me* αα-*di*-p-*toluenesulphonylbutyrate*, m.p. 193°; *Et di*-p-*toluenesulphonylacetate*, m.p. 131°, which with CH_2N_2 gives *Et* αα-*di*-p-*toluenesulphonylpropionate*, m.p. 92°; *Ph carbomethoxymethanedisulphonate*, m.p. 56°, from $ClCO_2Me$ and $CHNa(SO_3Ph)_2$, converted by Et_2O–CH_2N_2 into *Ph* α-*carbomethoxyethane*-αα-*disulphonate*, m.p. 88—89°; p-toluenesulphonylacetone (*Me ether*, m.p. 122°, which when heated at 100°/vac. passes into an *isomeride*, m.p. 77°); ω-p-*toluenesulphonylacetophenone*, m.p. 110° (*Me ether*, m.p. 89—90°), from $BzCH_2Cl$ and p-$C_6H_4Me{\cdot}SO_2Na$; αγ-di-p-toluenesulphonylacetone (*Me ether*, m.p. 122—123°); 3-hydroxythionaphthen-1 : 1-dioxide (III) [*Me ether*, m.p. 215°, hydrolysed by 2*N*-NaOH to o-$CO_2H{\cdot}C_6H_4{\cdot}SO_2Me$ and converted by MeOH–NaOMe into the *Me*$_2$ *acetal*, m.p. 144°, of the keto-form of (III), which is also formed from (III) and the mercurichloride of formimino Me ether in MeOH]; ωω-*di*-p-*toluenesulphonylacetophenone*, m.p. 196—197° (*Me ether*, m.p. 169°), prepared by oxidation (H_2O_2–AcOH) of the mercaptal from $BzCHCl_2$ and p-$C_6H_4Me{\cdot}SNa$ or from BzCHO, p-$C_6H_4Me{\cdot}SH$, $ZnCl_2$, and AcOH–HCl; Ph benzoylmethanedisulphonate (*Me ether*, m.p. 118—119°; *O-carbethoxymethyl* derivative, m.p. 107—108°, obtained by the action of $CHN_2{\cdot}CO_2Et$ in $CHCl_3$); acetylmethanedisulphon-*N*-ethylanilide (enol *Me ether*, m.p. 131°); p-*toluenesulphonylacetaldehyde*, an oil (*dihydrate*, m.p. 86—88°; *semicarbazone*, m.p. 213—214°), prepared by hydrolysis (conc. HCl–AcOH) of its acetal which is obtained by oxidation ($KMnO_4$–aq. AcOH) of p-$C_6H_4Me{\cdot}S{\cdot}CH_2{\cdot}CH(OEt)_2$, b.p. 166°/15 mm. [from $CH_2Cl{\cdot}CH(OEt)_2$, p-$C_6H_4Me{\cdot}SH$, and EtOH–NaOEt at 120°]. Non-enolisable SO_2-compounds do not react with Br in OH-free solvents but do so (often very rapidly) in H_2O. Bromination of the CO-free SO_2-compounds is retarded or suppressed by acid (whereas acceleration occurs with the SO_2-free ketones).

$CH_2(SO_3Me)_2$, most conveniently prepared from the acid and Et_2O–CH_2N_2, reacts further with Et_2O–CH_2N_2 to give *Me ethane*-αα-*disulphonate*, b.p. 178—180° (slight decomp.)/12 mm. Trimethylenetrisulphone and Et_2O–CH_2N_2 afford tri*iso*propylidenetrisulphone. Disulphones of the type $CH_2(SO_2R)_2$ do not react with CH_2N_2, whilst p-toluenesulphon-amide and -anilide are converted into the *N*-Me derivatives. $NH_2{\cdot}SO_2{\cdot}CH_2{\cdot}SO_3Ph$ is converted by CH_2N_2 into the NN-*Me*$_2$ derivative, m.p. 65°, also prepared from $CH_2(SO_3Ph)_2$ and $NHMe_2$ in C_6H_6 at 135°. $CH_2(SO_2NPhEt)_2$ is unaffected by CH_2N_2. Comparison of sulphonylketones with the analogous diketones, sulphonylaldehydes with oxymethyleneketones, and disulphonylketones with triacylmethanes shows that the effect of SO_2 groups is " acidification " and not enolisation; this is due to the SO_2 group lacking a double linking and thus being unable to form part of a conjugated system. H. B.

Polarographic studies with the dropping mercury cathode. II. Reduction of acetone. G. Semerano.—See this vol., 131.

Mol. wt. of *l*-erythrose. V. Deulofeu (J.C.S., 1932, 2973—2975).—Erythrose triacetate with EtOH–NH_3 during 24 hr. affords erythrosediacetamide (Ac_3 derivative, m.p. 147°, $[\alpha]_D^{20°}$ +31·7°), hydrolysis of which with boiling dil. H_2SO_4 and treatment with $CH_2Ph{\cdot}NPh{\cdot}NH_2$ affords erythrosebenzylphenylhydrazone (I), also obtained from Ca arabonate (A., 1900, i, 139). (I) with CH_2O affords erythrose, $[\alpha]_D^{20}$ in H_2O +1·3° to +22·1°, which gives a normal mol. wt. in H_2O. J. L. D.

Preparation of *l*-arabinose and *l*-ribose by oxidation of *l*-arabinal with perbenzoic acid. W. C. Austin and F. L. Humoller (J. Amer. Chem. Soc., 1932, 54, 4749—4750).—Oxidation of *l*-arabinal with BzO_2H using Levene and Tipson's method (A., 1931, 1400) gives *l*-arabinose and *l*-ribose. H. B.

Utilisation of xylose. H. C. Fang (Iowa State Coll. J. Sci., 1932, 6, 423—424).—Xylose was oxidised to xylonic acid with Cl_2, NH_3 being used as neutralising agent; the yield of NH_4 xylonate (I), which depended on the p_H, was about 30%. Dry distillation of (I) produced 25% of the theoretical yield of pyrrole. A method for the determination of $COMe_2$, EtOH, and BuOH in the products of fermentation of xylose is described. Ch. Abs.

Two new colour tests for hexoses. J. H. Foulger (J. Biol. Chem., 1932, 99, 207—211).—On the basis of Nakashima and Maruoka's colour reaction for $CO(NH_2)_2$ (A., 1924, ii, 708), sp. colour tests for hexoses are obtained with a reagent (I) prepared by boiling 40 g. of $CO(NH_2)_2$ in 80 c.c. of 40 vol.-% H_2SO_4 and 2 g. of $SnCl_2$ until clear, cooling, and diluting to 100 c.c. with 40% H_2SO_4. When 0·5 c.c. of the sugar solution and 3 c.c. of (I) are boiled for 45 sec. and shaken, ketohexoses give a greenish-blue (changing to blue or bluish-violet on cooling), whereas aldohexoses give a yellow or olive-green, changed by alternate boiling and shaking to amethyst. Pentoses and furfuraldehyde give only an intense yellow, and disaccharoses give the colours of their component sugars. A similar reagent prepared from guanidine gives a distinctive colour for each hexose (yellow only with pentoses), but without distinction between keto- and aldo-hexoses. The absorption spectra of the various colours are plotted. J. W. B.

Mechanism of the hydrolytic degradation of sugars. E. Macovski (Bull. Soc. Chim., 1932, [iv], 51, 1306—1309).—Hydrolytic degradation of sugars is probably preceded by ring-opening and then proceeds by the mechanism : $CHO{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}OH \longrightarrow CHO{\cdot}C(OH){:}CH{\cdot}[CH{\cdot}OH]_2{\cdot}CH_2{\cdot}OH \rightleftharpoons CHO{\cdot}CO{\cdot}CH_2{\cdot}[CH{\cdot}OH]_2{\cdot}CH_2{\cdot}OH \longrightarrow$

$CHO{\cdot}CO{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ —— $AcCHO + CHO{\cdot}CH(OH){\cdot}CH_2{\cdot}OH \longrightarrow CHO{\cdot}C(OH){:}CH_2 \rightleftharpoons AcCHO$. Glycerol αβ-$Me_2$ ether with $K_2Cr_2O_7$–H_2SO_4 gives AcCHO. R. S. C.

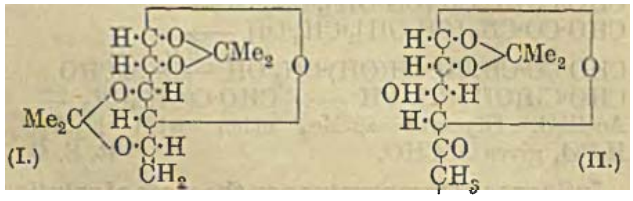
Influence of temperature on the state of solution of methylated carbohydrates. M. Ulmann and K. Hess (Ber., 1933, 66, [*B*], 68—71; cf. A., 1932,

1117).—Determinations of the osmotic pressure of aq. solutions of α-methylglucoside by isothermal distillation at 20° and p_H 4·0—4·5 show evidence of association at a concn. of 0·06%. At 0°, association of the carbohydrate or hendecamethylcellotriose (I) cannot be detected cryoscopically; association appears therefore to increase as the temp. rises. (I) does not appear to be a normal trisaccharide, but a mol. compound from C_6 mols. of unknown constitution. H. W.

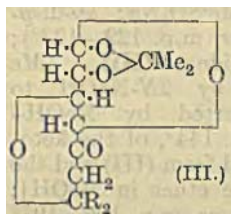
Carbohydrates. XIV. Action of mercaptan on acyl derivatives of cyclic sugars. P. Brigl and R. Schinle (Ber., 1932, **65**, [*B*], 1890—1895; cf. A., 1932, 147).—Glucopyranose pentabenzoate is unaffected by EtSH and HCl, whereas glucofuranose α- or β-pentabenzoate readily affords 2-ethylthiolglucose-1 : 1-diethylmercaptal 3 : 4 : 5 : 6-tetrabenzoate (I), m.p. 82—83°, $[\alpha]_D^{20}$ +57·63° in $COMe_2$. Under similar conditions, glucose 2 : 3 : 4 : 6-tetrabenzoate yields mainly (I) accompanied by small amounts of glucose-1 : 1-diethylmercaptal 3 : 4 : 5 : 6-tetrabenzoate, m.p. 166°, $[\alpha]_D^{20}$ +24·79° (a Bz group wandering from 2 to 5), and a *chloroglucose*-1 : 1-*diethylmercaptal tetrabenzoate*, m.p. 167—168°, $[\alpha]_D^{20}$ +40·06° in $CHCl_3$. *iso*Propylideneglucose 3 : 5 : 6-tribenzoate, EtSH, and HCl, preferably in $CHCl_3$, yield 2 : 4-*diethylthiolglucose*-1 1-*diethylmercaptal* 3 : 5 : 6-*tribenzoate*, m.p. 92°, $[\alpha]_D^{20}$ −1·23° in $COMe_2$. (I) is transformed by alkaline hydrolysis into 2-*ethylthiolglucose*, m.p. 158° after slight softening, $[\alpha]_D^{20}$ +48·8° to +64·4° in H_2O in 24 hr., which at room temp. gives a *phenylhydrazone*, m.p. 187° (decomp.), $[\alpha]_D^{20}$ −157·0° in C_5H_5N, but is converted by $NHPh{\cdot}NH_2$ in AcOH at 100° into EtSH and glucosazone. H. W.

Halogenoses of the β-series and their application to synthesis. VII. Crystalline β-acetobromo-γ-galactose. H. H. Schlubach and E. Wagenitz (Z. physiol. Chem., 1932, **213**, 87—88; cf. A., 1930, 1412).—HBr reacts with γ-galactose β-pentaacetate in 15—20 min. at room temp. giving an 87% yield of β-*acetobromo-γ-galactose*, m.p. 85—86°, $[\alpha]_D^{18}$ −122·7° (±0·5°) in CCl_4. J. H. B.

Synthesis of a C_9 sugar by isomerisation of di*iso*propylideneglucoseen. H. Ohle and R. Deplanque (Ber., 1933, **66**, [*B*], 12—18).—6-*p*-Tolucnesulphonyldi*iso*propylidene*iso*glucose is converted by distillation with NaOH–CaO at 150—195°/high vac. into *glucoseen di*i*sopropylidene ether* (I), m.p. 36—37°, $[\alpha]_D^{18}$ +137° in $CHCl_3$ (highest observed val.), the constitution of which is established by ozonisation to K *iso*propylidene-*d*-xyluronate (95% yield). It adds 13—15% more than the calc. amount of Br. The substance described as (I) (A., 1929, 1279) has a different constitution. (I) is stable towards alkali,



but very sensitive towards acids. It is transformed by 0·01*N*-H_2SO_4 at room temp. into iso*rhamnose* iso*propylidene ether* (II), m.p. 99—100°, $[\alpha]_D^{18}$ −106·7° in $CHCl_3$, which readily undergoes fission between C_4 and C_5 giving about 50% of AcOH in the determination of Ac (Freudenberg) and about 33% of MeCHO in the determination of $COMe_2$ (Elsner). Alkalis transform it into amorphous, complex compounds. With Na it yields an *enolate* from which *iso*amyl acetate results on treatment with *iso*amyl nitrite. The 3-*Ac* derivative, m.p. 65—66°, $[\alpha]_D^{18}$ −76·3° in $CHCl_3$, 3-*Bz* derivative, m.p. 96°, $[\alpha]_D^{18}$ −71·4° in $CHCl_3$, and 3-p-*toluenesulphonyl* compound, m.p. 71°, $[\alpha]_D^{18}$ −99·65° in $CHCl_3$, are described. Treatment of (I) in $COMe_2$ at −5° with conc. H_2SO_4 and immediate neutralisation of the product with KOH affords (II), a K ester sulphate of unestablished constitution, and 7 : 7-*dimethyl*-1 : 2-iso*propylidene*-3 : 7-*anhydro*-d-*gluptonose* (III, R=Me), m.p. 116—117°, $[\alpha]_D^{18}$ +99·4° in $CHCl_3$. [It is proposed to designate compounds this class by reference to the hexose of similar configuration and to express adherence to the heptose series by insertion of pt, the middle consonants being omitted, *e.g.*, glucose ⟶ gluptose; mannose ⟶ maptose; galactose ⟶ galaptose.] (III) is stable towards $KMnO_4$ in boiling $COMe_2$ or H_2O–$COMe_2$, vigorously oxidised after addition of NaOH to CO_2 and AcOH. It could not be acetylated with Ac_2O and C_5H_5N or with boiling Ac_2O. Its 2 : 4-*dinitrophenylhydrazone* has m.p. 176°. It gives non-cryst. products when hydrolysed. When titrated according to Willstatter–Schudel it consumes > 1 mol. of I without formation of CHI_3 in considerable amount. Its *enolate* gives small amounts of Et *iso*valerate when treated with Et nitrite. In the Ac determination (Freudenberg) it yields 30·8% of acid (probably ββ-dimethylacrylic). H. W.



Acetone [*iso*propylidene] sugars and other compounds of carbohydrates. XXIII. Synthesis of cellobiose. K. Freudenberg and W. Nagai (Ber., 1933, **66**, [*B*], 27—29).—A more detailed account of work already reported (A., 1932, 1021), and a reply to Hess and Ulmann (A., 1932, 1117). H. W.

Crystalline ββ-trehalose (*iso*trehalose). H. H. Schlubach and W. Schetelig (Z. physiol. Chem., 1932, **213**, 83—86).—Dry α-acetobromoglucose and β-glucose tetra-acetate, Ag_2CO_3, I, and $CaCl_2$ react in $CHCl_3$ to give a 50% yield of ββ-trehalose octaacetate, m.p. 181° (corr.), $[\alpha]_D^{20}$ −18·6° in $CHCl_3$, quantitatively hydrolysed by 0·003-*N*-NaOMe in MeOH to ββ-trehalose, m.p. 130—135°, $[\alpha]_D^{17}$ −41·5° in H_2O. J. H. B.

Reactions relating to carbohydrates and polysaccharides. XLI. Structure of raffinose lævan. W. Mitchell and H. Hibbert (Canad. J. Res., 1932, **7**, 345—348).—The lævan synthesised by the action of *B. subtilis* on raffinose is identical with that obtained similarly from sucrose and therefore is a polymeric 2 : 6-anhydrofructofuranose (A., 1931, 827, 1276). The view that lævan formation occurs with sugars containing a terminal fructofuranose group is thus confirmed. A. C.

Biochemical synthesis of αγ-butylene glycol β-glucoside. J. VINTILESCO and N. IOANID.—See this vol., 93.

Nucleic acids. Ring structure of the pyrimidine nucleosides. H. BREDERECK (Ber., 1932, **65**, [*B*], 1830—1833).—The applicability of Helferich's CPh_3Cl reaction to the determination of the ring structure of the sugar component of nucleosides and nucleotides is regarded as established, since (1) theophyllineglucoside and CPh_3Cl in C_5H_5N afford *triphenylmethyltheophyllineglucoside*, m.p. 143° (indef.), $[\alpha]_D^9$ +10·1° in $CHCl_3$ {*Ac*$_3$ derivative, m.p. 135—145° (corr. indef.), $[\alpha]^{20}$ + 37·6° in $CHCl_3$} and (2) the mixture of α- and β-methylribopyranoside does not react with CPh_3Cl when kept at room temp. or heated for 2 hr. at 100° as judged by polarimetric observation and the almost quant. recovery of CPh_3Cl as CPh_3·OH. The possibility that the ·CO·NH·CO· group of uridine (I) reacts with CPh_3Cl is excluded by the inactivity of the similarly-constituted diacetamide. (I) affords *triphenylmethyluridine*, m.p. 115—116° (decomp.), $[\alpha]_D^{19}$ +11·0° in $CHCl_3$, and is therefore uracil-*d*-ribofuranoside. Since (I) can be obtained by deamination of cytidine (II), during which ring change is improbable, (II) is cytosine-*d*-ribofuranoside. Cryst. compounds are obtained from (II) and adenosine with CPh_3Cl, but their structure is uncertain because of the presence of the NH_2 group. H. W.

Starch. XXVII. Diamylose and tetra-amylose. H. PRINGSHEIM and A. BEISER (Ber., 1932, **65**, [*B*], 1870—1873).—EtOH may be present to the extent of 4% (calc. on wt. of carbohydrate) in the case of tetra- (I) and of 8% in the case of di-amylose (II) without affecting the f.p. of 1% aq. solutions. $COMe_2$ behaves similarly. The transformation of (II) into (I) is hindered by 2·3%, but not by 1·8%, of EtOH. Contrary to Miekeley (A., 1932, 255), tetra-amylose acetate, $[\alpha]^{20}$ +116° in $CHCl_3$, has been re-prepared. H. W.

[Highly-polymerised compounds. Dependence of the viscosity of cellulose solutions on temperature.] K. HESS and B. RABINOWITSCH (Ber., 1932, **65**, [*B*], 1856).—Contrary to Staudinger (this vol., 55) the viscosity of solutions of limit dextrin acetate 2 is not independent of the temp. 0·5% cellulose solutions cannot be regarded as dil. and it is not valid to apply a relationship established for dil. solutions to such solutions. H. W.

Highly-polymerised compounds. LXXV. Biosan acetate of Hess and Friese. H. STAUDINGER and H. FREUDENBERGER (Ber., 1933, **66**, [*B*], 76—79).—In reply to Hess and Rabinowitsch (see above) it is pointed out that the cryoscopic and viscosimetric methods and the determination of terminal groups show that "limit dextrin acetate 2" is a polytriacetylglucan diacetate of mean degree of polymerisation 12—13. The determination of its viscosity in *m*-cresol by Hess and Rabinowitsch is incorrect. H. W.

Plant colloids. XXXI. Determination of mean particle size of some starch substances and starch derivatives. M. SAMEC [with L. KNOP, B. LAVRENČIČ, and S. PREMRL] (Kolloid-Beih., 1932, **37**, 91—118).—Determination of the apparent mol. wt. of starch ultra-filtrate, erythro-amylose, achrodextrin, amylose acetate, deacetylated amylose and amylopectin acetate, *iso*di- and *iso*tri-hexosans, and other degradation products of starch by various methods showed that cryoscopy and isothermal distillation yield low, whilst diffusion and osmotic measurements yield high results. Consistent results were obtained by all these methods for the products of degradation with HCl. The tendency to association, shown by some of the degradation products, does not lead to reconstruction of the original starch mol. E. S. H.

Cryoscopy of glycogen and inulin in acetamide. J. REILLY and P. P. DONOVAN (Ber., 1932, **65**, [*B*], 1811—1815).—Determinations of the mol. wt. of glycogen (0·176% ash) in freezing NH_2Ac give vals. between 1 and $2C_6H_{10}O_5$ usually approximating more closely to the latter vals. Inulin with 0·07% ash gave vals. corresponding with $4C_6H_{10}O_5$. Further diminution of the ash content led to vals. between 4 and $6C_6H_{10}O_5$, in one instance to $8C_6H_{10}O_5$. An inulin with higher ash content gave the val. $2C_6H_{10}O_5$. H. W.

Cryoscopy of glycogen and inulin in acetamide. H. PRINGSHEIM and H. WEISS (Ber., 1932, **65**, [*B*], 1807—1811).—Re-determination of the mol. wt. of glycogen (0·176% ash) in an all-glass apparatus confirms the aggregation corresponding with a glucose anhydride. Inulin containing about 0·07% ash is much more rapidly dried than that used previously (about 0·23% ash), but exhibits no other essential difference. Mol. wt. determinations fluctuated between $3C_6H_{10}O_5$ and $10C_6H_{10}O_5$ without apparent cause. Berner's criticisms are considered to be invalidated. H. W.

Glycogen triacetate. W. S. REICH (Compt. rend., 1932, **195**, 1029—1031).—Glycogen (I) is converted by Ac_2O in C_5H_5N in presence of NaOAc in complete absence of H_2O and free acid into its *triacetate*, $[\alpha]^{21}$ +160·4° in C_5H_5N, hydrolysed by 0·5*N*-KOH–EtOH at 0° to (I), identical with the original material. The P content of impure liver (I) is considerably reduced by this treatment. A. C.

Acetolysis of cellulose. K. FREUDENBERG and K. SOFF (Ber., 1933, **66**, [*B*], 19—27).—Acetolysis of cellulose (I), β-glucosan (II), cellobiose (III), and glucose (IV) in Ac_2O, AcOH, H_2SO_4, and $CHCl_3$ has been followed polarimetrically. [α] of (IV) falls slowly owing to a slow decomp. (II) is very rapidly acetylated and converted into glucose penta-acetate, but [α] remains higher than that of (IV). The consts. of (I) and (III) do not ultimately reach that of (IV). For (II) $K_2=1{\cdot}7\times10^{-4}$ during 15—80% fission. For (I) $K_n/K_2=2{\cdot}3$, corresponding with a max. yield of rather $<72\%$ of cellobiose octa-acetate. The yield is compatible with the view that the two terminal linkings are split according to K_3, the mean const. of the trisaccharide, and all intermediate linkings according to K_n, and that K_3 is intermediate between K_2 and K_n. On this hypothesis, (I) in

homogeneous system is degraded more at the terminals by 50% H_2SO_4, more in the middle by acetolysis. Starch in aq. acid resembles (I) in that the polysaccharide is hydrolysed more rapidly than the biose; the relationship may be reversed for the starch acetates. The possibility of β linkings in starch to any considerable extent is denied. H. W.

Reactions relating to carbohydrates and polysaccharides. XLII. Synthesis of cellulose *o*-chlorobenzyl ethers and mechanism of their formation. R. H. Ball and H. Hibbert (Canad. J. Res., 1932, **7**, 481—498).—The effects of time of heating, temp., concn. of NaOH in the steeping solution, and time of steeping on the reaction products from "soda cellulose" (I) and *o*-$C_6H_4Cl\cdot CH_2Cl$ (II) are studied. Etherification proceeds to a much greater extent when the excess of NaOH in the steeping solution is removed from (I) before treatment with (II); the reaction is retarded by inert diluents (C_6H_6, PhMe). At 90° and an alkali concn. of 20% NaOH, the amount of etherification increases regularly up to 9 hr. and then decreases. The extent of etherification increases (in a complex manner) with rises in temp. (for fixed concn. of NaOH) and alkali concn. (for fixed temp.); simultaneous increase in both factors gives a good yield of a highly substituted ether. The hemi- and mono-ethers are insol. in $CHCl_3$, whilst higher ethers are sol.; evidence is given for the existence of a sesqui-ether, $C_{12}H_7O_{10}(C_7H_6Cl)_3$. Oxidation and depolymerisation probably occur during long steeping of (I); subsequent etherification gives more sol. ethers. The mechanism of ether formation is discussed with reference to the constitution of (I). H. B.

Higher fatty acid esters of cellulose and starch. II. E. Lorand (Cellulosechem., 1932, **13**, 185—191).—Modified methods (lit.) of prep. of mixed cellulose esters and starch esters are given. H. B.

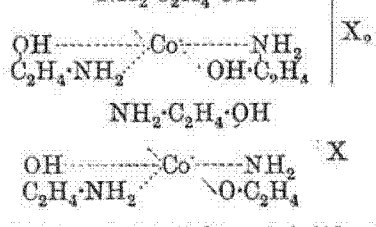
Glycerol degradation of lichenin. E. Berner (Annalen, 1932, **500**, 52—61).—When lichenin is heated with anhyd. glycerol at 240° (bath) in N_2, the resulting solution added to EtOH, the pptd. material extracted with H_2O, and the dissolved solid re-pptd. with EtOH, a substance (lichosan), *M* about 2000, containing about 3·5% of glycerol (even after further purification) is obtained. Acetylation and subsequent hydrolysis do not remove the glycerol, which is probably in combination: $\cdot O\cdot CH\cdot O\cdot C\cdot + C_3H_5(OH)_3 \longrightarrow \cdot O\cdot CH\cdot O\cdot C_3H_5(OH)_2 + OH\cdot C\cdot$; analyses of the lichosan acetate support this view. H. B.

Trimethylenetrinitroamine or "hexogene." L. Desvergnes (Chim. et Ind., 1932, **28**, 1038—1044).—Trimethylenetrinitroamine, $NO_2\cdot N<\begin{matrix}CH_2\\CH_2\end{matrix}>\begin{matrix}N(NO_2)\\N(NO_2)\end{matrix}>CH_2$, m.p. 203·5°, is obtained in 24—32% yield by the action of 96% HNO_3 on $(CH_2)_6N_4$. Nitration in presence of H_2SO_4 or AcOH is impossible. HNO_2 or acid solutions of $NaNO_3$ give di- and tri-nitroso-compounds. The NO_2 content cannot be determined in the nitrometer or by reduction methods. C. I.

Attempted resolution of substituted hydroxylamines into optically active isomerides. J. Meisenheimer and H. Denner (Ber., 1932, **65**, [*B*], 1799—1807).—NHMeEt is oxidised by 6% H_2O_2 to *methylethylhydroxylamine*, b.p. 36—38°/12 mm. {*picrate*, m.p. 104—107°; *α-bromo-*d*-camphor-β-sulphonate* (I), m.p. 97—101°, $[M]_D$ +314° in H_2O}. $NHMe\cdot CH_2Ph$ (*picrate*, m.p. 113—116°) is similarly transformed into *benzylmethylhydroxylamine*, m.p. 41—42° [*H* d-*tartrate* (II), m.p. 86—91°, $[M]_D$ +47° in H_2O; *α-bromo-*d*-camphor-π-sulphonate semihydrate* (III), m.p. 73—79°, $[M]_D$ +273° in H_2O]. Na sulphanilate is converted by Me_2SO_4 (1·1 mol.) and 2*N*-NaOH (1·1 mol.) into dimethylsulphanilic acid, decomp. 270—271° with very rapid, and 263° with normal, heating (*Na* salt, anhyd., $+4H_2O$ and $+6H_2O$; *Ba* salt, anhyd. and $+4H_2O$). NHPhMe and H_2SO_4 give a mixture of methylmetanilic and methylsulphanilic acid (IV), decomp. 250°. The Ba salt of (IV) is transformed by CH_2PhCl and $Ba(OH)_2$ into *benzylmethylsulphanilic acid* (anhyd. and monohydrate), decomp. 248—250° [*Ba* ($+3H_2O$) and *Na* ($+3H_2O$) salts], oxidised by BzO_2H in aq. AcOH to the corresponding *oxide*, decomp. 218°, which is isomerised by hot 4*N*-NaOH to *benzyloxymethylsulphanilic acid* (*Na* salt, anhyd. and $+0{\cdot}5H_2O$; *Ag* salt; *Ba* salt, anhyd. and $+H_2O$; dl-*α-phenylethylammonium* salt, m.p. 153—155°; d-*α-phenylethylammonium* salt (V), m.p. 137—140°, $[M]_D$ +18·4° in EtOH). Benzylmethylmetanilic acid, m.p. 148—152°, is oxidised to the corresponding *oxide*, (anhyd.) decomp. 200°, ($+H_2O$), decomp. 180—183°. Since indications of resolution are not obtained by repeated crystallisation of (I) from EtOAc, (II) from $Pr^{\alpha}OH$, (III) from H_2O, and (V) from EtOAc, it appears that *tert.* hydroxylamines have as little tendency to appear in mirror image isomerides as *tert.* amines. H. W.

Reaction of primary and secondary aminoalcohols and aminophenols with arylsulphonyl chlorides. K. H. Slotta and R. Behnisch.—See this vol., 61.

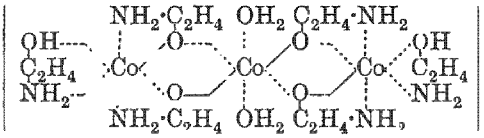
Complex chemical behaviour of the ethanolamines. W. Hieber and E. Levy (Annalen, 1932, **500**, 14—34).—β-Aminoethyl alcohol (I) (0·09 mol.), $CoCl_2$ (anhyd. or $+6H_2O$) (0·03 mol.), and C_5H_5N (0·03 mol.) in EtOH give the red *chloride* (II) ($+2H_2O$) (*A*, X=Cl), which is an electrolyte (conductivity data given), slowly loses $2H_2O$ at 111°/vac. over P_2O_5, and can be crystallised only from cold H_2O. When a hot aq. solution of (II) is cooled, a mixture of (II) and the dark-red *chloride* (III) (*B*, X=Cl) (also $+6H_2O$), results; (III) is also prepared from $CoCl_2,6H_2O$ and a 5*N* solution of (I) in EtOH. The

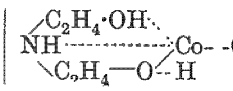
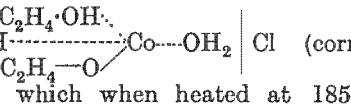
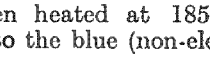


(*A*.)

bromide (anhyd. and $+5H_2O$) and *iodide* of type (*A*) and the *bromide* of type (*B*) are also prepared. The

halides (*A*) are stable to conc. HCl, whilst the halides (*B*) are similarly coloured blue.

(*B*) 

$NH(CH_2{\cdot}CH_2{\cdot}OH)_2$ and $CoCl_2$ in EtOH give a red *chloride* (IV),  Cl or  Cl (corresponding *bromide*), which when heated at 185°/vac. over P_2O_5, passes slowly into the blue (non-electrolytic) *chloride*,  . A *chloride*, *bromide*, and *iodide* (V), all green, of the composition $C_{12}H_{30}O_6N_3Co_2Hal,H_2O$ (alternative structures suggested), are prepared using a 5 : 1 ratio of $NH(CH_2{\cdot}CH_2{\cdot}OH)_2$ and Co; (V) also results during attempted prep. of the iodide analogous to (IV). When (V) is digested with aq. MeOH (1 : 1), one diethanolamine residue is replaced by H_2O giving an *iodide*, $C_8H_{19}O_4N_2ICo_2,4H_2O$, green, which loses $3H_2O$ at 100° and passes into a reddish-violet *iodide*, containing 4- and 6-covalent Co atoms.

$N(CH_2{\cdot}CH_2{\cdot}OH)_3$ furnishes a red *chloride*, $C_{18}H_{45}O_9N_3Cl_3Co_2$ (containing two 6-covalent Co atoms) and a red *bromide*, $C_6H_{14}O_3NBrCo$ (in which Co is 4-covalent). H. B.

Ammines. X. Cobaltous and cupric compounds from tris-(β-hydroxyethyl)amine. New method of formation of ammino-cupric salts. J. C. Duff and E. H. Steer (J.C.S., 1932, 2861—2862).—Tris-(β-hydroxyethyl)amine (I) with $CoCl_2$ and $CoBr_2$ in H_2O at 40° or 5% $CoCl_2$ and 5% KCNS affords respectively *chloro-* (II), *bromo-* and *thiocyanato-cobaltotris-(β-hydroxyethyl)amine*. 20% NaOH containing (II) (saturated solution) during 0·5 hr. at 50° affords a *dihydrate* of the *Na* derivative of *hydroxy-cobaltotris-(β-hydroxyethyl)amine*. (I) in H_2O gives with $NiCl_2$, *ditris-(β-hydroxyethyl)aminonickel chloride* and with $Cu(OH)_2$, *tris-(β-hydroxyethyl)aminocupric hydroxide* (III), which affords only basic Cu" salts with acids. The action of org. NH_4 salts on (III) in aq. EtOH affords the following compounds, hydrolysed by H_2O to basic Cu" salts and NH_3: *diamminocupric formate* and *succinate*; *triammino-cupric maleate* and *fumarate*. J. L. D.

Decomposition points of amino-acids. M. S. Dunn and T. W. Brophy (J. Biol. Chem., 1932, **99**, 221—229).—An apparatus is described whereby a precise determination of the time and temp. required for an NH_2-acid to reach a standard state of decomp. (as judged by the shade of brown colour) may be determined. The time–temp. vals. are plotted, the decomp. point being given by the point where the graph becomes parallel to the time axis. Such decomp. points are claimed to be accurately reproducible and are true characteristics of the NH_2-acid. J. W. B.

Action of glycuronic and galacturonic acid on alanine. C. Neuberg and H. Collatz (Schweiz. med. Woch., 1932, **62**, 4 pp.; Chem. Zentr., 1932, ii, 1431).—Both acids and their salts react with alanine forming CO_2, NH_3, and MeCHO; for 0·005*M*, and boiling for 6 hr., fission occurs to the extent of 6·5% of the theoretical. A. A. E.

Synthesis of glycylglycine. M. S. Dunn, A. W. Butler, and T. Deakers (J. Biol. Chem., 1932, **99**, 217—220).—The improved prep. of glycylglycine (45% yield) by the action of $CH_2Cl{\cdot}COCl$ and *N*-NaOH on crude glycine at 0° is described. J. W. B.

o-Benzoquinone test for cysteine. W. C. Hess and M. X. Sullivan (J. Biol. Chem., 1932, **99**, 95—97).—Although the Dyer–Baudisch colour reaction (A., 1932, 530) differentiates cystine from other NH_2-acids and glutathione, it is not sp., good positive reactions being given by 14 other compounds (tabulated). In all these cases the authors' test (A., 1925, ii, 1211) for cysteine, using Na 1 : 2-naphthaquinone-4-sulphonate in a reducing atm., is negative. J. W. B.

Formation of a homologue of cystine by the decomposition of methionine with sulphuric acid. L. W. Butz and V. du Vigneaud (J. Biol. Chem., 1932, **99**, 135—142).—*dl*-Methionine is decomposed by 18*N*-H_2SO_4 at 125—135° in N_2 to yield *bis-γ-amino-γ-carboxy-*n*-propyl disulphide* (*homocystine*) (I), decomp. 260—265° [Bz_2 derivative, m.p. 184—185° (corr.)], reduced by Na in dry, liquid NH_3 and subsequent treatment with CH_2PhCl to dl-S-*benzyl-homocysteine*, m.p. 190—191° (corr.), and oxidised by Br in H_2O to dl-*homocysteic acid*, decomp. 230—235°. J. W. B.

Mechanism of action of organo-magnesium compounds on *N*-disubstituted amides of αβ-unsaturated acids. II. C. D. Nenitzescu and I. P. Cantuniari (Bul. Soc. Chim. Romania, 1932, **14**, 62—64).—cis-β-*Methyl*-α-iso*propylglutaric anhydride*, m.p. 41—42°, unaccompanied by the *trans*-isomeride, is made by heating the acid, m.p. 112°, with AcCl. Interaction of MgEtBr with crotondiphenylamide (2 mols.) gives β-*methyl*-α-sec.-*butylglutarotetraphenyl-diamide*, decomp. >250° (cf. A., 1930, 1433). H. A. P.

Constitution of carbamide. P. Merklen and H. Gounelle (Bull. Acad. Med., 1931, [iii], **106**, 384—385; Chem. Zentr., 1932, ii, 2171).—The structure $CO(NH_2)_2$ is supported by the fact that only urea derivatives having the carbamide structure have a narcotic action. A. A. E.

Violit, an open-chain analogue of murexide. D. D. Karve (J. Univ. Bombay, 1932, **1**, 48—51).—The Et esters or diamides of mesoxalic (1 mol.) and tartronic (1 mol.) acid with aq. NH_3 give " violit," $(CO{\cdot}NH_2)_2C{:}N{\cdot}C(CO{\cdot}NH_2){:}C(NH_2){\cdot}ONH_4$ (*Na* salt) readily decomposed. R. S. C.

Cyanamide. G. Barsky (Chim. et Ind., 1932, **28**, 1032—1037).—The formation of dicyanodiamide (I) in an aq. solution of $CN{\cdot}NH_2$ is at a max. at p_H 9·6.

At $p_H > 10$ N_2 is lost by decomp. of the polymeride. Pure (I) is prepared by extracting $CaCN_2$ with H_2O, adding H_2SO_4, warming, maintaining the p_H at 9·0, evaporating, and crystallising. In very alkaline solutions $CN{\cdot}NH_2$ is quantitatively hydrolysed at 50° to $CO(NH_2)_2$, the reaction velocity being independent of the alkali concn. $CN{\cdot}NH_2$ is very stable in solution in range p_H 4—7. In solutions acidified with HCl hydrolysis proceeds at a rate proportional to the HCl concn. If $CaCN_2$ is treated in an autoclave with addition of $Ca(CN)_2$ the N_2 is recovered as NH_3 and an appreciable proportion of CaC_2O_4 is produced. The mechanism of this reaction is discussed. If a solution of $CN{\cdot}NH_2$ is treated with H_2S at $p_H < 9{\cdot}6$ $CS(NH_2)_2$ is produced. C. I.

β-Hydroxy-αγ-hexamethyl di-iodoamino*iso*propyl iodobismuthate. G. Aurisicchio (L'Ind. Chimica, 1932, **7**, 1358—1360).—Details are given of the prep. of $OH{\cdot}CH(CH_2{\cdot}NMe_3I)_2,2BiI_3$ from BiI_3 and hexamethyldiamino*iso*propanol. O. F. L.

Action of magnesium ethyl bromide on thallous chloride and thallous ethoxide. R. C. Menzies and (Miss) I. S. Cope (J.C.S., 1932, 2862—2866; cf. A., 1904, i, 656).—TlOEt (1 mol.) and MgEtBr (3 mols.) in dry Et_2O at 0° afford the best yield (22—24%) of $TlEt_2Br$. About 50% of Tl is formed in the reaction. The less sol. TlCl with MgEtBr in Et_2O at 0° affords up to 12% $TlEt_2Br$ and 28·1% Tl. These facts point to the formation of $TlEt_3$ (cf. A., 1904, i, 544). $TlCl_3$ and MgEtBr afford directly $TlEt_2Br$. J. L. D.

Dicyclic hydrocarbons. *cyclo*Hexylidene-*cyclo*hexane and di*cyclo*hexyl. N. D. Zelinski, N. I. Schuikin, and L. M. Fatejev (J. Gen. Chem. Russ., 1932, **2**, 671—680).—*cyclo*Hexenyl*cyclo*hexanone (cf. A., 1927, 153) was converted through the hydrazone into *cyclo*hexenyl*cyclo*hexane, b.p. 236—237°, reduced by H_2 (Pd–C) to di*cyclo*hexyl (II). (II) was also obtained by reduction of *cyclo*hexenyl*cyclo*hexane, resulting from the dehydration of 1-*cyclo*hexyl*cyclo*hexanol by $KHSO_4$, and was very similar to the above and to (II) obtained by the Wurtz reaction: the existence of (II) in stereoisomeric forms is uncertain. Reduction of 2-*cyclo*hexyl*cyclo*hexanol with HI at 100—110° gives (II) and at 260—280° mixtures of (II) with hydrocarbons of lower b.p., *d*, and *n*, perhaps containing 2-*methyl*cyclo*pentyl*cyclo*hexane* (III) (cf. A., 1930, 206). Mg *cyclo*hexyl bromide and 2-methyl-*cyclo*pentanone gave 2-*methyl*-1-cyclo*hexyl*cyclo*pentanol*, b.p. 119°/8 mm., dehydrated by $KHSO_4$ to the unsaturated *hydrocarbon*, reduced by H_2 at 200° (Pd–C) to (III), b.p. 225·5—227°. G. A. R. K.

Action of concentrated sulphuric acid on *cyclo*hexene. S. S. Nametkin and L. N. Abakumovskaja (J. Gen. Chem. Russ., 1932, **2**, 608—613).—The hydrocarbon layer recovered (37%) after treating *cyclo*hexene with conc. H_2SO_4 at 2—5° consists of: (I) $C_{12}H_{22}$, b.p. 216—219°/739 mm., saturated, giving a little $C_{10}H_8$ on dehydrogenation with Ni–Al_2O_3; (II) $C_{18}H_{32}$, b.p. 145—147°/1·5—2 mm., saturated; and (III) $C_{24}H_{40}$, very viscous liquid b.p. 200—203°/1·5—2 mm., containing one double linking. G. A. R. K.

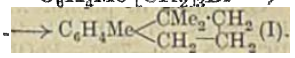
Transformation of benzene, toluene, and *m*-xylene into methane. A. Mailhe (Chim. et Ind., 1932, **28**, 1263—1271).—Hydrogenation of C_6H_6, PhMe, and m-$C_6H_4Me_2$ under standard conditions in presence of Ni gives CH_4, and shows a max. at 280° (% CH_4 obtained, 69·8, 74·0, 75·1, respectively), a decrease, and then a second max. at 330° (% CH_4, 68·0, 68·0, 74·8). A resin, sol. in $COMe_2$, is deposited on the surface of the Ni at 270—280°, paralysing its activity, and this may be removed by H_2 at 325°; at 320—330°, a deposit of C is then progressively formed. At lower temp. homologues of CH_4 are also obtained. F. R. S.

Sodium phenylstyrylmethyl. E. Bergmann and T. Ukai (Ber., 1933, **66**, [*B*], 54—58).—Styrylphenylcarbinol is converted by MeOH–H_2SO_4 into *γ-methoxy-αγ-diphenyl-Δ^α-propene*, b.p. 180—181°/11 mm., readily transformed by Na into *Na phenylstyrylmethyl* (I). $COPh_2$ and (I) yield *δ-hydroxy-αγδδ-tetraphenyl-Δ^α-butene*, dimorphous, m.p. 130—131°, converted by boiling AcCl into *ααβδ-tetraphenyl-Δ^{αγ}-butadiene*, m.p. 148—149°, oxidised to triphenylacraldehyde, m.p. 177—178°. Similarly, (I) and fluorenone yield successively *δ-hydroxy-αγ-diphenyl-δ-diphenylene-Δ^α-butene*, m.p. 145—146°, *αγ-diphenyl-δ-diphenylene-Δ^{αγ}-butadiene*, m.p. 183—184°, and *α-phenyl-β-diphenyleneacraldehyde*, m.p. 164—165°. *δ-Hydroxy-αγδ-triphenyl-Δ^α-butene*, m.p. 109—111°, from PhCHO, affords *αβδ-triphenyl-Δ^{αγ}-butadiene*, b.p. 230—239°/11 mm., m.p. 103—104°. (I) and CH_2PhCl give *αβδ-triphenyl-Δ^γ-butene*, b.p. 240—242°/40 mm., whereas only $C_2H_2Ph_4$ could be isolated from the product of the reaction with $CHPh_2Br$. With $COPh_2$ chloride (I) gives *αγδδεη-hexaphenyl-Δ^{αζ}-heptadiene*, m.p. 145°. *Di-αγ-diphenyl-Δ^α-propenyl ketone*, m.p. 183°, and *αγ*-diphenyl-Δ^α-propene are derived from (I) and $CO(OEt)_2$. The successive action of Hg and CO_2 on (I) leads to *αγ-diphenyl-Δ^γ-butenoic acid*, m.p. 121°, and *αγδζ-tetraphenyl-Δ^{αε}-hexadiene*, m.p. 137—138°. H. W.

Fluorenes. E. Bergmann, H. Hoffmann, and D. Winter (Ber., 1933, **66**, [*B*], 46—54).—2-Nitrofluorenone and PCl_5 at 150—160° yield *2-nitrofluorenone chloride*, m.p. 175—176°, not dehalogenated by Cu powder in $C_6H_4Me_2$ or NaI in boiling $COMe_2$, but transformed by $SH{\cdot}CH_2{\cdot}CO_2H$ (I) in boiling $C_6H_4Me_2$ into *2 : 2′-dinitrobisdiphenylene-ethylene*, m.p. >310°. 2 : 9 : 9-Trichlorofluorene is converted by (I) into *2 : 2′-dichlorobisdiphenylene-ethane*, m.p. 274—275°, and by Cu powder in boiling C_6H_6 into *2 : 2′ : 9 : 9′-tetrachlorobisdiphenylene-ethane*, m.p. 223—225°. 2-Aminofluorenone is transformed through the *diazonium fluoborate*, decomp. 160—170°, into *2-fluorofluorenone*, b.p. 185°/10 mm., m.p. 117° (*oxime*, m.p. 204°). 9 : 9-*Dichloro-2-fluorofluorene*, m.p. 107°, is reduced by (I) in boiling $C_6H_4Me_2$ into *2 : 2′-difluorobisdiphenylene-ethane*, m.p. 241°, and by Cu powder in boiling C_6H_6 to *chloro-2 : 2′-difluorobisdiphenylene-ethylene*, 9 : 9′-*dichloro-2 : 2′-difluorobisdiphenylene-ethane*, m.p. 248°, and unidentified red *needles*, m.p. 227°. 2-Aminofluorene is transformed through the *diazonium fluoborate*, decomp. 145—150°, into *2-fluorofluorene*, m.p. 100°. The intense colour of the substituted ethylenes is attributed to the presence of crossed double linkings. *Benzophenonefluorenoneketazine*,

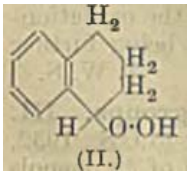
$(C_6H_4)_2C{:}N{\cdot}N{:}CPh_2$, m.p. 115—116°, from $CPh_2{:}N{\cdot}NH_2$ and fluorenone at 150°, resembles $K_2Cr_2O_7$ in colour; fluorenonehydrazone and $COPh_2$ yield fluorenoneketazine and benzophenoneazine. Fluorenone is converted by Mg acetylenyl bromide into *αδ-bisdiphenylene-Δ$^{\beta}$-butin-αδ-diol*, m.p. 238°, transformed by I and HI at 100° into the dark red *αδ-bisdiphenylene-Δ$^{\alpha\beta}$-butatriene*, reduced by Na and boiling amyl alcohol to αδ-bisdiphenylenebutane, m.p. 218—219°. 2 : 2′ : 7 : 7′-*Tetrabromobisdiphenylenebutadiene*, m.p. about 420°, is prepared by autoxidation of 2 : 7-dibromofluorene in presence of alkali. The hypothesis that the colour of the compounds under investigation depends on the partial or complete existence of the ethylenic linkings in the di-radical form (A., 1930, 939) generally requires that pairs of geometric isomerides shall not exist or not be stable. Unsuccessful attempts are described to obtain a second variety of 2 : 5-dinitro-, m.p. 268° (decomp.), or 2-nitro-, m.p. 258°, -fluorenoneoxime. H. W.

Action of sodium in liquid ammonia on derivatives of optically active triarylmethanes. F. H. Adams and E. S. Wallis (J. Amer. Chem. Soc., 1932, **54**, 4753—4754).—The *l*-form, m.p. 184—185°, $[\alpha]_D^{20}$ —48·5° in $COMe_2$, of 12-phenyl-β-benzoxanthene-12-thiolacetic acid, m.p. 187—188°, and Na in liquid NH_3 in absence of O_2 give an optically active Na triarylmethyl, since decomp. with dry NH_4Br affords a trisubstituted methane, $[\alpha]_D^{20}$ —11·7° in $COMe_2$; the three groups and the methane C atom of the ion are, therefore, non-planar. H. B.

Structure of vitamin-*A* and the synthesis of ionenes. M. T. Bogert (Science, 1932, **76**, 475—476).—A study of the NO_2-, nitroamino-, and sulpho-derivatives and the oxidation products of ionene and of its $(NO_2)_2$-derivatives has shown that the Barbier–Bouveault formula for ionene (I) is correct. This has been confirmed by the synthesis of ionene through the steps $C_6H_4Me{\cdot}CHO \longrightarrow C_6H_4Me{\cdot}CH{:}CH{\cdot}CO_2R \longrightarrow C_6H_4Me{\cdot}[CH_2]_2{\cdot}CH_2{\cdot}OH \longrightarrow C_6H_4Me{\cdot}[CH_2]_3Br \longrightarrow C_6H_4Me{\cdot}[CH_2]_3{\cdot}CMe_2{\cdot}OH \longrightarrow$  (I).

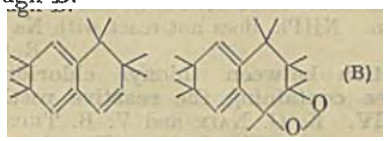
L. S. T.

Autoxidation of hydrocarbons. I. Tetrahydronaphthalene peroxide obtained by autoxidation. H. Hock and W. Susemihl (Ber., 1933, **66**, [*B*], 61—68).—Prolonged passage of air through technical tetrahydronaphthalene (I) at about 75° followed by removal of excess of (I) under greatly diminished pressure leads to the isolation of *tetrahydronaphthalene peroxide* (II), m.p. 56°.



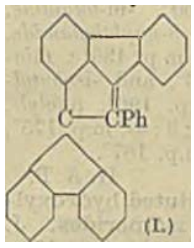
(II.)

Reaction is not accelerated by light or contact substances. The use of active C and O_2 at 20—30 atm. involves danger of decomp. (II) is stable for a short time at 120—125°, loses H_2O at about 130°, and explodes at a higher temp. With $KMnO_4$ in AcOH–H_2O it gives β-*o*-carboxyphenylpropionic acid, m.p. 166—167°. It is reduced by KI in AcOH–H_2O, better by $NaHSO_3$ in MeOH–H_2O, to *ac*-tetrahydro-α-naphthol, which yields 1 : 2-dihydronaphthalene when heated with freshly-melted KOH. Warm 2*N*-NaOH transforms (II) into 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. Cold 22% NaOH yields the *Na* salt, from which (II) is obtained by acidification. It is considered that (II) is derived from a tetrahydronaphthalene of form A through B.

(A)  (B)

H. W.

The indene from β-phenyl-αγ-bisdiphenyleneallyl alcohol. C. F. Koelsch (J. Amer. Chem. Soc., 1932, **54**, 4744—4749).—β-*Phenyl-αγ-bisdiphenyleneallyl alcohol*, m.p. 192—193·5°, from Mg α-phenyl-β-diphenylenevinyl bromide and fluorenone in Et_2O–PhMe, dissolves in AcOH–H_2SO_4 to a violet solution which slowly loses its colour and deposits 2-*phenyl*-3 : 4-*phenylene*-1-*diphenyleneindene* (I), m.p. 196—197° (*Br_7*-derivative, m.p. 328—331°). Oxidation (CrO_3–AcOH) of (I) gives BzOH and 9-*hydroxy*-9-1′-*fluorenonylfluorene* (II), m.p. 222—224° [*chloride*, m.p. 200—203° (becoming red)], which with MgPhBr affords 9-*hydroxy*-9-*phenyl*-1-9′-*hydroxy*-9′-*fluorenylfluorene* (+EtOH), m.p. 260—262°.



(I.)

Oxidation (CrO_3–AcOH) of (II) gives 1-*o*-*carboxybenzoylfluorenone*, yellow, m.p. 208—209°, and orange, m.p. 210—212°, forms; the latter heated with $CuCO_3$ at 250° affords 1-*benzoylfluorenone*, m.p. 114—116°, also prepared from fluorenone-1-carboxyl chloride, C_6H_6, and $AlCl_3$. *o*-$C_6H_4Me{\cdot}MgBr$ and 3-methyl-Δ^2-*cyclo*hexenone yield 3-*o*-*tolyl*-1-*methyl*-Δ$^{1:3}$-*cyclohexadiene*, b.p. 145—148°/21 mm., dehydrogenated (S at 250°) to 2 : 3′-ditolyl. This is oxidised ($KMnO_4$) to diphenyl-2 : 3′-dicarboxylic acid, which with H_2SO_4 gives fluorenone-1-carboxylic acid. (I) contains a ring system hitherto considered impossible. H. B.

Spectrochemical study of the chemical constitution of a reaction product between centralite [diphenyldiethylcarbamide] and gaseous nitrogen peroxide. Dinitrodiphenyldiethylcarbamide. K. Masaki (Bull. Chem. Soc. Japan, 1932, **7**, 353—362).—A substance isolated from the products of the action of NO_2 on *s*-diphenyldiethylcarbamide (I) is shown to be the 4 : 4′-$(NO_2)_2$-derivative. Absorption spectrum data are given for (I), its 4 : 4′-dinitro- and 2 : 4 : 2′ : 4′-tetranitro-derivatives, *p*-nitro- and 2 : 4-nitro-phenylurethane, *o*-, *m*-, and *p*-nitro-, *p*-nitroethyl-, and 2 : 4 : 6-trinitro-acetanilide. D. R. D.

Metallic salts of β-naphthylamine and its hydrochloride. E. B. Detwiler and M. L. Willard (Mikrochem., 1932, **12**, 261—263).—$FeCl_3$, $PdCl_2$, and LiCl give amorphous ppts. with β-$C_{10}H_7{\cdot}NH_2$,HCl, whilst various other salts yield characteristic crvst. residues on evaporation. F. L. U.

Acyl derivatives of arylamines. S. V. Shah and D. G. Pishavikar (J. Univ. Bombay, 1932, **1**, 31—36).—*K* and *Na* derivatives of NHPhAc (I), *o*-(II), and *p*-(III)-$C_6H_4Me{\cdot}NHAc$, α- and β-$C_{10}H_7{\cdot}NHAc$ are obtained by heating the Ac compound with Na or K in PhMe. Reaction is very slow in boiling C_6H_6,

and decomp. occurs in boiling xylene. The K derivatives of (I), (II), and (III) melt at 85°, 95°, and 130°, respectively, the others decomposing at or above 280°. The substances are considered to be derivatives of the enolic form. $NHPh_2$ does not react with Na or K. R. S. C.

Interaction between thionyl chloride and substances containing the reactive methylene group. IV. K. G. Naik and V. B. Thosar (J. Indian Chem. Soc., 1932, **9**, 471—477).—Interaction of $SOCl_2$ in cold, dry Et_2O with compounds $COMe{\cdot}CH_2{\cdot}CO{\cdot}NHAr$ and $CH_2(CO{\cdot}NHAr)_2$ leads to sulphides of the type $S(CHRR')_2$, and with compounds $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}NHAr$ to sulphides of the type S:CRR′ (cf. A., 1890, 582). The following are described: thiobisacetoacetanilide, m.p. 147° (*loc. cit.*); *thiobisacetoacet-o-toluidide*, m.p. 160°, -m-*toluidide*, m.p. 104°, -p-*toluidide*, m.p. 174°, -β-*naphthylamide*, m.p. 185°, and -1 : 3 : 4-*xylylamide*, m.p. 139°: *thiobismalondi*-n-*propylamide*, m.p. 123°, and -iso*butylamide*, m.p. 155°: *Et* o-*tolyl*-, m.p. 196°, p-*tolyl*-, m.p. 203°, β-*naphthyl*-, m.p. 208°, 1 : 3 : 4-, m.p. 175°, and 1 : 4 : 5-*xylyl-thiomalonamate*, m.p. 187°. H. A. P.

Attempted resolution of substituted hydroxylamines into optically active isomerides. J. Meisenheimer and H. Denner.—See this vol., 150.

Solubility relationships amongst optically isomeric salts. II. Camphorates of α-*p*-tolylethylamine. A. W. Ingersoll and F. B. Burns (J. Amer. Chem. Soc., 1932, **54**, 4712—4715).—*dl*-α-*p*-Tolylethylamine [*dl*-camphorate, m.p. 180° (all m.p. are corr.)] is resolved by *d*-camphoric acid into *d*-, b.p. 205°, $[\alpha]_D^{23}$ +34·6° (*d*-camphorate, m.p. 187°), and *l*-forms, b.p. 205°, $[\alpha]_D^{23}$ −34·3° [d-*camphorate* (+H_2O), m.p. (anhyd.) 173°; dl-*camphorate* (+H_2O), m.p. (anhyd.) 169°]. The four camphorates described illustrate case 7 (or 10) of the scheme previously given (A., 1932, 263); the order of solubility is *lBdA* < *lBdlA* < *dlBdlA* < *dBdA*. H. B.

Nitration of *p*-dimethylaminoacetanilide by nitrous acid. H. H. Hodgson and J. H. Crook (J.C.S., 1932, 2976—2977).—*p*-Dimethylaminoacetanilide (I) (*picrate*, m.p. 224°) with HNO_2 (cf. A., 1930, 466) affords nearly 100% of 3-*nitro*-4-*dimethylaminoacetanilide*, m.p. 132° [*hydrochloride*, m.p. 180° (decomp.); *picrate*, m.p. 172°; *chloropicrate*, m.p. 149°] (also formed by heating 4-chloro-3-nitroacetanilide with $NHMe_2$ at 100° during 6 hr.), and only a trace of an *N*-NO-compound due to the NHAc group strongly inhibiting the displacement of an *N*-Me group (cf. A., 1932, 842). (I) with conc. HNO_3 in H_2SO_4 at 0° affords 2-*nitro*-p-*dimethylaminoacetanilide*, m.p. 116° (*picrate*, m.p. 185°; *chloropicrate*, m.p. 184°), hydrolysed to 3-*nitro*-4-*aminodimethylaniline*, m.p. 112° (*picrate*, m.p. 205°; *chloropicrate*, m.p. 204°). J. L. D.

Peroxidative action. II. Constitution of purpurobenzidine. H. Willstaedt, F. Reuter, and K. L. Zirm (Annalen, 1932, **500**, 61—69).—*o*-Tolidine (I) and H_2O_2, with phæophorbide (*a*+*b*) Fe salt as catalyst, in AcOH–NaOAc give a blue *compound* (II), m.p. 70—72°, probably the quinhydrone-like compound of equimol. amounts of (I) and the corresponding *NN*′-diacetyldimethyldiphenoquinone-di-imine (III), a freshly-prepared specimen of which is reduced ($SnCl_2$, HCl) to *NN*′-diacetyl-*o*-tolidine (IV). Treatment of solutions of (II) with alkali affords a brownish-red ppt., which is considered to be (III), and is re-convertible into (II) by dil. AcOH (rapid working). (III) does not show the calc. reduction equiv. (Schlenk, A., 1909, i, 36) probably because of its partial decomp. during the prolonged action of alkali. Attempted prep. of (III) by dehydrogenation of (IV) with PbO_2 was inconclusive. Purpurobenzidine (A., 1932, 426), prepared by the action of alkali on the solution of the dye from benzidine, H_2O_2, and hæmin in AcOH (after some time the colour of this solution changes from blue to Bordeaux red), is considered to be *NN*′-*diacetyldiphenoquinonedi-imine*; the mechanism of its formation is discussed. H. B.

Isomeric dinitrophenylhydrazones. H. Brederreck (Ber., 1932, **65**, [*B*], 1833—1838).—Instances are recorded of the occurrence of 2 : 4-dinitrophenylhydrazones of furfuraldehyde compounds in red and yellow forms. Since they differ in m.p. and one variety depresses the m.p. of the other, chromoisomerism is excluded. The stability of the forms in boiling org. solvents and in EtOH–KOH renders desmotropy improbable and *cis–trans* isomerism is provisionally assumed. The following 2 : 4-*dinitrophenylhydrazones* are described: *furfuraldehyde*, red, m.p. 230° (corr.) [*Ac* derivative, m.p. 171—172° (corr.)], yellow, m.p. 212—214° (corr.); 5-*ethoxymethyl*-, red, m.p. 208—210° (corr.) [*Ac* derivative, m.p. 166—167° (corr.)], yellow, m.p. 160—161° (corr.); 5-*triphenylmethoxymethyl*-, red, m.p. 246—248° (corr.), yellow, m.p. 212—215° (corr.) [*triphenylmethoxymethylfurfuraldehyde* has m.p. 139—141° (corr.)]; and 5-*methoxymethylfurfuraldehyde*-, red, m.p. 183—184° (corr.), yellow, m.p. 137—138° (corr.)]. The Ac derivative, obtained from both the red and yellow variety, belongs to the red series, into which it is re-converted by hydrolysis. H. W.

Oxidation of phenol with peracetic acid. J. Böeseken (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 750—755).—PhOH is oxidised by AcO_2H to a mixture of *cis-cis*-muconic acid (I) (new m.p. 187°), benzoquinone, and a little fumaric acid (II). Similar oxidation of pyrocatechol and quinol gives a mixture of (II) and (I) and quinhydrone, respectively, the latter being further oxidised with difficulty to (II) and a little maleic acid. As the yield of (I) from pyrocatechol is less than from PhOH it is suggested that the first tangible products of the oxidation are *p*- and *o*-quinones, the former yielding the oxidation-resisting benzoquinone and the latter being further oxidised to (I). J. W. S.

Reactivity of aromatic hydroxyl groups. III. H. L. Bassett and (Miss) A. O'Leary (J.C.S., 1932, 2945—2946).—The half-reaction period of 22 phenols with AcBr in EtOAc at 0° (cf. A., 1930, 1033; 1931, 1410) is determined. In monosubstituted phenols a *m*-directing group accelerates the reaction when *m*- to the OH group, and retards it when in the *p*-position, whilst *op*-directing groups have the converse effect. *o*-Substituents cause greater retardation than any others, the retarding effect being in the order Alk <

OR<hal<NO_2, CO_2Alk. An electronic explanation is advanced. H. A. P.

Chlorination of iodophenols. V. *m*-Iodophenol. S. BUCHAN and H. MCCOMBIE (J.C.S., 1932, 2857—2860).—Chlorination of *m*-iodophenol in CCl_4 gives an unstable *iododichloride*, m.p. 59° (decomp.), which with KI in AcOH gives 6-*chloro*-3-*iodophenol*, m.p. 56°, and on keeping over-night 4 : 6-*dichloro*-3-*iodophenol* (I), m.p. 104°, the *iododichloride*, m.p. 68—69° (decomp.), of which is converted by keeping into 2 : 4 : 6-*trichloro*-3-*iodophenol*, m.p. 104°; further chlorination of this gives finally tetrachloroiodo- and pentachloro-phenols without intermediate formation of an iododichloride. The constitution of (I) was proved by its synthesis from 4 : 6-dichloro-3-nitrophenyl 2-nitro-*p*-toluenesulphonate, by reduction, diazotisation, introduction of I (Sandmeyer), and fission by piperidine. 4-*Chloro*-3-*iodophenol*, m.p. 78°, is prepared from 2-iodo-4-nitroaniline by the Sandmeyer reaction. The following are also described: m-*iodophenyl acetate*, m.p. 38° [*iododichloride*, m.p. 91—92° (decomp.)], *benzoate*, m.p. 72—73° [*iododichloride*, m.p. 106° (decomp.)], p-*toluenesulphonate*, m.p. 60—61° [*iododichloride*, m.p. 97—99° (decomp.)], *Et carbonate*, b.p. 163—164°/11 mm. [*iododichloride*, m.p. 79—80° (decomp.)], *carbonate*, m.p. 141° [*bis-iododichloride*, m.p. 115° (decomp.)], *benzyl ether*, m.p. 52° [*iododichloride*, m.p. 70° (decomp.)], *Me ether*, b.p. 123°/14 mm. [*iododichloride*, m.p. 74° (decomp.)], *Et ether*, b.p. 133—134°/15 mm. [*iododichloride*, m.p. 64° (decomp.)], *allyl ether*, b.p. 154—156°/11 mm. [*iododichloride*, m.p. 86—87° (traces only formed)], *dibromopropyl ether* [*iododichloride*, m.p. 78° (decomp.)], and *phenylcarbamate*, m.p. 138° [*iododichloride*, m.p. 120° (decomp.)]; 3-*iododiphenyl ether*, b.p. 184°/14 mm. [from *m*-$C_6H_4Br{\cdot}NO_2$, NaOPh, and Cu (3-*nitrodiphenyl ether*, b.p. 189—200°/14 mm.), followed by reduction and Sandmeyer] (*iododichloride*, m.p. 58°); ω-3′-*iodophenoxyacetophenone*, m.p. 104° (*iododichloride*, m.p. 94°); 6-*chloro*-3-*iodophenyl acetate*, b.p. 149°/11 mm. [*iododichloride*, m.p. 89° (decomp.)], *benzyl ether*, b.p. 250—260°/11 mm. [*iododichloride*, m.p. 72° (decomp.)]; 4 : 6-*dichloro*-3-*iodophenyl acetate*, m.p. 95° [*iododichloride*, m.p. 104° (decomp.)], and *benzyl ether*, m.p. 82° [*iododichloride*, m.p. 86° (decomp.)]; 2 : 4 : 6-*trichloro*-3-*iodophenyl acetate*, m.p. 87°, and *benzyl ether*, m.p. 80—81°. H. A. P.

Reduction and hydrolysis of *o*-, *m*-, and *p*-nitrophenetoles. D. H. RICHARDSON and F. W. SMITH (J.C.S., 1932, 2955—2958).—The yields of reduction products (azoxyphenetoles + phenetidines) obtained by heating the nitrophenetoles at 60° for 96 hr. with MeCHO-free 1·6*N*-KOH in EtOH are: *m*-, 92%, *o*-, 50%, and *p*-, 10%; very similar yields of azoxyphenetidines are obtained by electrolytic reduction. Hydrolysis to the nitrophenol accompanies reduction in the former case to the extent of *p*-, 24%, *o*-, 11·4%, and *m*-, 7·4%. Hydrolysis of the nitrophenetoles with 20% HCl at the b.p. for 72 hr. gives 10% *p*-, 8% *o*-, and 6% *m*-nitrophenol. H. A. P.

Bromination of 2-nitro-*p*-cresol. W. O. KERMACK and W. T. SPRAGG (J.C.S., 1932, 2946—2948).—Bromination of 2-nitro-*p*-cresol in $CHCl_3$ gives a mixture of 5-*Br*- (I), m.p. 104° (*Me ether*, m.p. 94°; *Ac* derivative, m.p. 121°), and (probably) 3-*Br*-derivative, m.p. 77° (*Me ether*, m.p. 74°; *acetate*, m.p. 81°); the former is identified by synthesis of its Me ether from 2-nitro-5-amino-*p*-tolyl Me ether by the Sandmeyer reaction. Nitration of 3-*bromo*-p-*tolyl* p-*toluenesulphonate*, m.p. 121°, or carbonate, m.p. 77°, in conc. H_2SO_4 also gives (I), but 3-bromo-*p*-cresol itself gives the 5-NO_2-derivative. H. A. P.

Action of nitrous acid on aminophenyl-2-hydroxy-α-naphthylmethane. Correction. F. E. RAY (J. Amer. Chem. Soc., 1932, **54**, 4753).—The compound previously obtained (A., 1932, 263) from aminophenyl-2-hydroxy-α-naphthylmethane and HNO_2 is not a diazo-compound, but is a *N*-NO-derivative of a heterocyclic compound. H. B.

Alkylation of dihydroresorcinols. A. SONN (Ber., 1932, **65**, [*B*], 1865—1866).—5-Methyldihydroresorcinol is converted by 20% KOH and allyl bromide into 5-*methyl*-2-*allyldihydroresorcinol*, m.p. 133—134°, and by 20% KOH and CH_2PhCl into 2-*benzyl*-, m.p. 132—134° after softening, and 2 : 2-*dibenzyl*-, m.p. 129°, -5-*methyldihydroresorcinol*. H. W.

Mechanism of the catalysis of autoxidation processes by iron. A. BACH (Ber., 1932, **65**, [*B*], 1788—1789).—Solutions of pyrogallol, quinol, and pyrocatechol in presence of $Fe^{\cdot\cdot}$ absorb O_2 with production of black, humus-like products. Pyrogallol Me_3 ether, quinol Et_2 ether, pyrocatechol Me and Me_2 ethers are not affected under like conditions, but give the same products as the free phenols when O_2 is replaced by H_2O_2. Autoxidation of the phenols is accelerated by $Fe^{\cdot\cdot}$ only when the OH groups are not replaced by alkyl, and this fact is not in harmony with the assumption of the primary formation of FeO_2. If the necessary conditions for the initial formation of H_2O_2 are not fulfilled, the autoxidation process is not accelerated by $Fe^{\cdot\cdot}$ and the hypothesis is justified that the catalytic action is due to acceleration of the effect of initially formed H_2O_2. H. W.

Derivatives of 1 : 2 : 3 : 4-tetrahydroxybenzene. II. W. BAKER, A. W. W. KIRBY, and (MISS) L. V. MONTGOMERY (J.C.S., 1932, 2876—2879).—1 : 2 : 3 : 4-Tetramethoxybenzene, m.p. 88—89°, is prepared by hydrolysis of 4-iodo- (I) or 4-bromopyrogallol Me_3 ether with aq. alkali at 210—215° [the addition of Cu-bronze is not deleterious with (I)], or oxidation of resorcinol-2 : 4-dialdehyde (II) with alkaline H_2O_2, and methylation of the respective products; the orientation assigned to (II) (cf. A., 1878, 423) arises from its mode of oxidation. The action of aq. Ag_2O on (I) at 245° gives *vic*-$C_6H_3(OH)_3$. (I) is conveniently prepared by iodination of *vic*-$C_6H_3(OMe)_3$ in presence of HgO. 2 : 4-*Diaminoresorcinol Me*$_2$ *ether hydrochloride*, m.p. about 210° (decomp.) (free base not isolated), could not be hydrolysed to a *vic*-$C_6H_2(OH)_4$ derivative. 4-*Nitropyrocatechol dibenzyl ether*, m.p. 98° (cf. A., 1884, 432), yields only 4-nitropyrocatechol by hydrolysis with HCl in AcOH; the corresponding NH_2-compound, m.p. 112° [*Ac* derivative, m.p. 228° (decomp.)], could not be oxidised to benzyloxy-*p*-benzoquinone, nor could *o*-aminophenyl benzyl ether (prep. improved). 4-

Nitro-2-benzyloxyanisole is slowly demethylated by 10% KOH at 150—200° to 4-*nitropyrocatechol* 2-*benzyl ether*, m.p. 83—85°. H. A. P.

2-Amino*cyclo*pentanol and its resolution. Resolution of 2-amino*cyclo*hexanol. M. Godchot and M. Mousseron (Bull. Soc. chim., 1932, [iv], **51**, 1270—1277, 1277—1282).—The first paper is a recapitulation (cf. A., 1932, 844). 2-Amino*cyclo*hexanol (I), m.p. 66° (*H tartrate*, m.p. 152—153°, $[\alpha]_D$ ±17·30°) (prepared, with some *cyclo*hexadiene, from *cyclo*hexene oxide), is resolved by *d*- and *l*-tartaric acids. The d- and l-*bases* have m.p. 83—84°, $[\alpha]_D$ +40·12° and −40·06° (*hydrochlorides*, m.p. 147—148°, $[\alpha]_D$ +31·47° and −31·57°; *H tartrates*, *l*-acid-*d*-base and *d*-acid-*l*-base, m.p. 177—178°, $[\alpha]_D$ +2·75° and −2·70°, *d*-acid-*d*-base and *l*-acid-*l*-base, m.p. 170—171°, $[\alpha]_D$ ±31·20°). *d*-(I) with PCl_5 in $CHCl_3$ affords l-2-*chloro*cyclo*hexylamine*, $[\alpha]_D$ −31·60°, changed by Ag_2O into *l*-(I). R. S. C.

Synthesis of substances related to ephedrine. C. Mannich and H. Budde (Arch. Pharm., 1933, **271**, 51—55).—Ph α-bromo*iso*propyl ketone and NH_2Me in C_6H_6 (not in EtOH) give Ph α-hydroxy-*iso*propyl ketone, b.p. 122—123°/12 mm. (giving, when kept, a substance, m.p. 186°), and *Ph* α-*methylamino*iso*propyl ketone*, m.p. 215°, each in 40—45% yield; the hydrochloride of the base is hydrogenated (PtO_2) in H_2O to β-*hydroxy*-β-*phenyl*-αα-*dimethylethylmethylamine*, m.p. 231°. *p*-Anisyl α-bromo*iso*propyl ketone, b.p. 169°/18 mm. (from *p*-anisyl Pr$^\beta$ ketone and Br), leads similarly to p-*anisyl* α-*methylamino*iso*propyl ketone* (I), m.p. 49—50° (*hydrochloride*, m.p. 237°), p-*anisyl*-α-*hydroxy*iso*propyl ketone*, b.p. 184°/20 mm., and β-*hydroxy*-β-p-*anisyl*-αα-*dimethylethylmethylamine*, m.p. 143—144° (*hydrochloride*, m.p. 204—205°). (I) with HI gives p-*hydroxyphenyl* α-*methylamino*iso*propyl ketone*, m.p. 210° (*hydriodide*, m.p. 218—219°; *hydrochloride*, m.p. about 235°), reduced to β-*hydroxy*-β-p-*hydroxyphenyl*-αα-*dimethylethylmethylamine*, m.p. 188° (*hydrochloride*, m.p. about 212—213°). All the OH-bases are less active pharmacologically than is ephedrine. R. S. C.

Isomerism of the ketones in ring *B* of the cholesterol ring system. R. Tschesche (Ber., 1932, **65**, [*B*], 1842—1845).—The substance described previously as cholestan-6-one is oxidised to a dicarboxylic acid (I), which passes at 190—200°/1 mm. into an anhydride (cf. Schulze, Diss., Gottingen, 1928), but at 290—300° into a ketone. (I) is identical with the dihydro-acid of Diels and Abderhalden, now formulated $\begin{matrix}-CH-CH-CMe\cdot[CH_2]_2\cdot CO_2H,\\ CH_2\cdot CH_2\cdot CH\cdot CO_2H\end{matrix}$ "Cholestan-6-one" from nitro-ψ-cholestene, must therefore be regarded as cholestan-4-one. Consequently ψ-cholestene is a 4 : 5-unsaturated cholestene. Only two ketones, 6- and 7-, are therefore known in which the CO group is present in ring *B*, and the difficulty of the new cholesterol formula vanishes. The true cholestan-6-one is reduced by Na and EtOH to *cholestan*-6-*ol* (II), m.p. 128—129°, $[\alpha]_D^{19}$ +34·8° in $CHCl_3$ (*Ac* derivative, m.p. 95°, $[\alpha]_D^{19}$ +69·5° in $CHCl_3$). (II) does not appear to be epimerised by NaOEt at 200°; it does not combine with digitonin. H. W.

Cerevisterol, a sterol accompanying ergosterol in yeast. E. M. Honeywell and C. E. Bills (J. Biol. Chem., 1932, **99**, 71—78).—The improved isolation and purification of the hexane-insol. cerevisterol, $C_{28}H_{47}O_3$, m.p. 265·3° (corr.), $[\alpha]_{5461}^{21}$ −57·4° in $CHCl_3$, from yeast (10 g. from 4500 kg.) is described (cf. A., 1929, 104). Solubility and crystallographic data are given, and the ultra-violet absorption spectrum shows a single band, max. 248 mμ. With Ac_2O it gives a *Ac*$_2$ derivative, m.p. 171°, $[\alpha]_{5461}^{21}$ −163° in $CHCl_3$, the nature of the third O being undetermined. The sterol contains two double linkings, one of which is probably $\Delta^{1:2}$ (or $\Delta^{1:13}$) as in ergosterol and *iso*ergosterol, since with Rosenheim's $CCl_3\cdot CO_2H$ reagent the initial red colour develops immediately. Irradiation confers no antirachitic properties. J. W. B.

***aci*-Nitro-compounds. IV. Mechanism of conversion of nitro-derivatives into hydroxamic acids.** C. D. Nenitzescu and D. A. Isacescu (Bul. Soc. chim. Romania, 1932, **14**, 53—62).—Interaction of phenyl*aci*nitromethane (I) or of its Na salt with HCl in dry Et_2O gives benzhydroxamic chloride, with intermediate formation of a blue coloration. The transformation is explained as follows: $CHPh{:}NO\cdot OH + HCl \longrightarrow$ $[Cl\cdot CHPh\cdot NH(:O)\cdot OH] \xrightarrow{O} Cl\cdot CHPh\cdot NO$ (blue) $\longrightarrow Cl\cdot CPh{:}N\cdot OH$. With acid chlorides (AcCl, BzCl, $POCl_3$) (I) gives the same product, but its Na salt gives the acyl derivative of the hydroxamic acid, *e.g.*, $CPh(OH){:}N\cdot OAc$. The Na salt of 9-*aci*nitrofluorene (II), however, gives with AcCl in Et_2O at 0° a stable, yellow *Ac* derivative, $C_{12}H_8{:}C{:}NO\cdot OAc$, m.p. 99—100°, and similarly, a *Bz* derivative, m.p. 134—135°; the former is also obtained from (II) and keten at about −70°. With (I) keten gives an unstable *Ac* derivative, m.p. 98° (diffuse), decomposed by warm H_2O to acetylbenzhydroxamic acid. The *Me ether* of (II), $C_{12}H_8{:}C{:}NO\cdot OMe$, m.p. 84° (decomp. into CH_2O and fluorenoneoxime), is prepared from its K salt and Me_2SO_4. H. A. P.

Temporary formation of the azlactone ring in the racemisation of acyl derivatives of amino-acids with acetic anhydride. V. du Vigneaud and C. E. Meyer (J. Biol. Chem., 1932, **99**, 143—151).—That the failure to racemise proline by the Ac_2O method (A., 1932, 1238) is due to the presence of ·NH· is confirmed by the similar failure to racemise the N-*Ac* derivative, m.p. 144—145° (corr.), $[\alpha]_D^{25}$ −76·5° in EtOH, of *N*-methyl-*l*-phenylalanine (prepared by Fischer and Lipschitz's method, A., 1915, i, 242). This confirms the suggested mechanism of racemisation, which involves the intermediate formation of an azlactone: $CHR\langle^{CO_2H}_{NHAc} \rightleftharpoons CHR\langle^{CO\cdot O}_{N=CMe} \rightleftharpoons CR\langle^{C(OH)\cdot O}_{N=CMe}$ or $CR\langle^{CO\cdot O}_{N-CHMe}$, thus destroying the asymmetry. Such a mechanism is possible only with derivatives containing primary NH_2 groups. The similar mechanism proposed by Ashley and

Harington (A., 1930, 253) for the simultaneous acetylation–esterification of NH_2-acids is confirmed, since *d*-phenylalanine with NaOEt in EtOH–Ac_2O gives the Et ester of acetyl-*dl*-phenylalanine (racemisation occurring as expected), whereas *l*-proline similarly treated gives only acetyl-*l*-proline, no esterification taking place. Under similar conditions β-phenylpropionic acid undergoes only 30% esterification. J. W. B.

Attempted detection of free radicals with univalent sulphur. A. SCHONBERG (Ber., 1932, 65, [*B*], 1864).—Di-α-thionaphthoyl disulphide (I) (cf. Houben, A., 1906, i, 847) possibly undergoes radical dissociation, since its solutions in $C_{10}H_8$ at 95° do not obey Beer's law. Solutions in hot solvents show reversible change in shade and intensity of colour with alteration of temp. With metals the change, (I)$\longrightarrow$$C_{10}H_7$·CS·SX, can be effected. H. W.

Lactone formation in sunlight. D. B. LIMAYE (J. Univ. Bombay, 1932, 1, 52—53).—*o*-Bz·C_6H_4·CO_2H and *o*-*p*-toluoylbenzoic acid in EtOH in sunlight give the dilactones of αβ-dihydroxy-αβ-diphenyl- and -αβ-di-*p*-tolyl-αβ-di-(*o*-carboxphenyl)ethane. The latter (m.p. 247—248°) is new. R. S. C.

Synthesis of alkamino-acids by cyanohydrin method. A. I. KIPRIANOV and G. I. KIPRIANOV (J. Gen. Chem. Russ., 1932, 2, 585—589).—β-Aminoethyl alcohol hydrochloride (I) can be employed in place of NH_3 in the Strecker NH_2-acid synthesis, giving β-hydroxyethylamino- (" alkamino- ") acids. (I) and PhCHO in presence of aq. KCN give a viscous nitrile hydrolysed by HCl to the *hydrochloride*, m.p. 178—191°, of α-(β-*hydroxyethylamino*)*phenylacetic acid*, m.p. 217—218°. (I) and *cyclo*hexanone with aq. KCN give 1-(β-*hydroxyethylamino*)cyclo*hexane*-1-*carboxynitrile*, m.p. 78—80° (*hydrochloride*, m.p. 95—98°), hydrolysed by HCl to the *acid*, m.p. 252—254°. (I) and $COMe_2$ give α-(β-*hydroxyethylamino*)iso*butyric acid*, m.p. 243—245°, and α-(β-*hydroxyethylamino*)*acetic acid*, m.p. 174—175°, is similarly obtained from CH_2O and (I); in both cases the cyanohydrins are hydrolysed *in situ*. G. A. R. K.

Syntheses by means of the magnesium derivatives of phenyl- and *o*-chlorophenyl-acetic acid and saturated and unsaturated ketones. II. M. D. IVANOV, (MISS) M. MIHOVA, and (MISS) T. CHRISTOVA (Bull. Soc. chim., 1932, [iv], 51, 1321—1325; cf. A., 1931, 726).—*o*-C_6H_4Cl·CH(MgX)·CO_2MgCl and $COPr^{\alpha}_2$ give β-*hydroxy*-α-*o*-*chlorophenyl*-β-*propylhexoic acid*, m.p. 130—131°, yielding with hot NaOH *o*-chlorophenylacetic acid. COPhMe yields similarly β-*hydroxy*-ββ-*diphenyl*-α-*o*-*chlorophenylpropionic acid*, m.p. 141—141·5°. CHPh(MgX)·CO_2Na (I) and mesityl oxide give β-*hydroxy*-α-*phenyl*-ββδ-*dimethyl*-Δ$^{\nu}$-*hexenoic acid*, m.p. 128—129°, hydrolysed by NaOH to CH_2Ph·CO_2H; however, with phorone and dypnone 1:4-addition occurs, the products being δ-*keto*-α-*phenyl*-ββζ-*trimethyl*-Δ$^{\delta}$-*octenoic acid*, m.p. 110·5—111·5° (*oxime*, m.p. 160—161°), and δ-*keto*-αβδ-*triphenylvaleric acid*, m.p. 201—202° (decomp.) [*oxime*, m.p. 219° (decomp.)]. Benzoin and 2 mols. of (I) give the γ-*lactone*, m.p. 202—203°, of βγ-*dihydroxy*-αβγ-*tripnenylbutyric acid*. R. S. C.

Syntheses by means of the magnesium derivative of sodium phenylacetate. I. Preparation of aryl-β-hydroxyaliphatic acids (substituted β-lactic acids). II. Preparation of mixed benzyl ketones and symmetrical trisubstituted β-hydroxyglutaric acids. D. IVANOV and N. I. NICOLOV (Bull. Soc. chim., 1932, [iv], 51, 1325—1331, 1331—1337).—I. CHPh(MgX)·CO_2Na (I) (modified prep.) and aldehydes, R·CHO, give good yields of α-phenyl-β-lactic acids, CHR(OH)·CHPh·CO_2H; phenolic aldehydes with 2 mols. of (I) give 15—25% of the acid and about 30% of the stilbene derivative, CHR:CHPh; the latter is probably formed by loss of $MgCO_3$ and NaX from the primary product, *e.g.*, (MgX)O·C_6H_4·CH(OMgX)·CHPh·CO_2Na, since this reaction occurs to a greater extent at a higher temp. The following were prepared: β-*hydroxy*-α-*phenylhexoic* (m.p. 155—156°) and *-nonoic* (m.p. 107—108°) *acids*; β-*hydroxy*-α-*phenyl*-γ-*methylvaleric acid*, forms A and B (in yields 5:1), m.p. 139—140° and 171—172°, respectively; β-*hydroxy*-αγ-*diphenylpropionic acid*, m.p. 175° (*Me ether* of *Me* ester, m.p. 78·5—79·5°); β-*hydroxy*-α-*phenyl*-γ-p-*chlorophenyl*- (m.p. 138—139·5°), -γ-p-*anisyl*- (m.p. 136·5°), -γ-*piperonyl*- (m.p. 166—167°), -γ-*p-hydroxyphenyl*- (m.p. 172°), -γ-*vanillyl*- (4OH) (m.p. 185°), and -γ-*furyl*- [m.p. about 175° (decomp.)] -*propionic acid*; β-*hydroxy*-αδ-*diphenyl*-Δ$^{\nu}$-*pentenoic acid*, m.p. 136—137° (from cinnamaldehyde); 4-*hydroxy*- (m.p. 189°) and 4-*hydroxy*-3-*methoxy*-*stilbene*, m.p. 132—133°. β-*Hydroxy*-α-*o*-*chlorophenylbutyric acid*, m.p. 129°, was similarly prepared.

II. (I) and acid chlorides give 50—75% yields of the ketones, CH_2Ph·CO·R, and 10—25% yields of β-hydroxyglutaric acids, OH·CR(CHPh·CO_2H)$_2$; the amount of the latter formed is not increased by use of an excess of (I). The following were thus prepared: benzyl Me, Pr^{β}, and Bu^{β} ketones; deoxybenzoin; *p*-bromophenyl benzyl ketone; CO(CH_2Ph)$_2$ (oxime, m.p. 122·4—123·6°); *benzyl* β-*phenylethyl ketone*, m.p. 43·5—44° (*oxime*, m.p. 120°); and the following β-substituted derivatives of β-*hydroxy*-αα′-*diphenylglutaric acid*: *Me*, m.p. about 204° (decomp.), Pr^{β}, m.p. about 174° (decomp.), Bu^{β}, m.p. about 170° (decomp.), p-C_6H_4Br, m.p. about 175—177° (decomp.), CH_2Ph, m.p. about 187° (decomp.), and β-*phenylethyl*, m.p. about 187° (decomp.); β-*hydroxy*-αα′β-*triphenylglutaric acid*, m.p. about 175° (decomp.). Cinnamoyl chloride, however, reacts partly by 1:4-addition, yielding benzyl styryl ketone, m.p. 72·5—73° (lit. 71°), and δ-*keto*-αβε-*triphenylhexoic acid*, m.p. 184—185°. R. S. C.

Oxidation products of 2:4:6-trinitro-*m*-xylene. M. I. MURAVIEVA (J. Gen. Chem. Russ., 1932, 2, 691—696).—2:4:6-Trinitro-*m*-xylene in H_2SO_4 is oxidised by CrO_3 at 50—80° to 2:4:6-*trinitro*-m-*toluic acid* (I), m.p. 196—200° (decomp.), decomposed by boiling H_2O into 2:4:6-trinitrotoluene, together with 2:4:6-trinitro*iso*phthalic acid (II) (cf. A., 1922, i, 534); the yield of (II) increases with rise of temp. and increase in amount of CrO_3. (I) alone is obtained with HNO_3–H_2SO_4 at 140° or CrO_3 in HNO_3 solution. G. A. R. K.

Thermal and alkaline decomposition of symmetrical trisubstituted β-hydroxyglutaric acids.

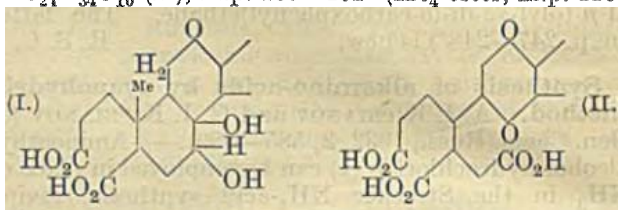
M. D. IVANOV and N. I. NICOLOV (Bull. Soc. chim., 1932, [iv], **51**, 1337—1340).—Acids of the type $OH{\cdot}CR(CHPh{\cdot}CO_2H)_2$ decompose to give $CH_2Ph{\cdot}CO_2H$, CO_2, and $R{\cdot}CO{\cdot}CH_2Ph$, when heated above the m.p. or in alkaline solution. Both methods can be used quantitatively by determining the CO_2 evolved. This decomp. occurs more readily if R is aryl than if R is alkyl. R. S. C.

Condensation of chloral with 2-hydroxy-*p*-toluic acid and its methyl ether. A. N. MELDRUM and B. M. KAPADIA (J. Indian Chem. Soc., 1932, **9**, 483—491).—Interaction of 2-hydroxy-*p*-toluic acid with $CCl_3{\cdot}CH(OH)_2$ in 95% H_2SO_4 at room temp. gives *3-hydroxy-4-methyl-α-trichloromethylphthalide*, m.p. 232° (*Ac*, m.p. 142°, and *Bz*, m.p. 154°, derivatives), hydrolysed by 20% aq. NaOH to *2-hydroxy-6-carboxy-3-methylmandelic acid*, m.p. 115° (*Ba* salt), and reduced by Zn and AcOH to *2-hydroxy-3-ββ-dichloroethyl-p-toluic acid* (I), m.p. 184° [*Ac*, m.p. 185°, and *Bz*, m.p. 140°, derivatives; *Ba* salt (+3H$_2$O)], which with H_2SO_4 evolves HCl and gives *2-hydroxy-4-carboxy-m-tolylacetic acid*, m.p. 213° (II) [*Ba* salt (+1H$_2$O); *Bz*, m.p. 126°, and *Ac* derivatives, m.p. 110°; *Me ether*, m.p. 206°]. This can react further with $CCl_3{\cdot}CHO$ in H_2SO_4 to give *5-hydroxy-4-methyl-α-trichloromethylphthalide-6-acetic acid*, m.p. 249° [similarly obtained in poor yield from (I)], which is hydrolysed by alkali to *4-hydroxy-2-carboxy-3-carbomethoxy-5-methylmandelic acid*, m.p. 246°, and converted as before into *2-hydroxy-4-carboxy-5-ββ-dichloroethyl-m-tolylacetic acid*, m.p. 203—205°, and *2-hydroxy-4-carboxytolylene-3 : 5-bisacetic acid*, m.p. 220°.

2-Methoxy-*p*-toluic acid condenses with $CCl_3{\cdot}CHO$ under similar conditions in the 5-position. The following are thus prepared: *5-methoxy-4-methyl-α-trichloromethylphthalide*, m.p. 132° {hydrolysed by aq. NaOH to *5-methoxy-4-methyl-α-carboxyphthalide*, m.p. 222° [*Ba* salt (+2H$_2$O)]}; *2-methoxy-5-ββ-dichloroethyl-p-toluic acid*, m.p. 195° (*Ba* salt); and *6-hydroxy-4-carboxy-m-tolylacetic acid* (III), m.p. 209° (demethylation having occurred during hydrolysis of the $\cdot CH_2{\cdot}CHCl_2$ group) (*Ba* salt; *Bz* derivative, m.p. 170°). The orientation of these derivatives is arrived at by the non-identity of (II) and (III), the oxidation of (III) by alkaline $KMnO_4$ to *4-hydroxy-5-methylphthalic acid*, m.p. 244—245° (*Ba* salt) (different from the known 5-hydroxy-6-methyl*iso*phthalic acid), and the conversion of (III) by $CCl_3{\cdot}CHO$ in abs. H_2SO_4 into the known 3-hydroxy-4 : 6-dimethylbenzoic acid, m.p. 170—171° (*Ba* salt; *Ac* derivative, m.p. 134°), which is accompanied by a *polymeride* of $CCl_3{\cdot}CHO$, m.p. 120°. H. A. P.

Synthesis of 1 : 2 : 7-trihydroxy-5-methylanthrone-8-carboxylic acid. P. K. PAUL (J. Indian Chem. Soc., 1932, **9**, 493—497).—Condensation of meconine with Et 3-methoxy-*p*-toluate in $CHCl_3$ by means of $AlCl_3$ results in the demethylation of 2 OMe groups, and formation of a *dihydroxymethoxy-2'-carboxy-2-benzyl-p-toluic acid* (I), m.p. 207°, converted by MeI and NaOMe into *Me*$_2$ *5 : 3' : 4'-trimethoxy-2'-carboxy-2-benzyl-p-toluate* (II), m.p. 98—99°. Cyclisation of (I) with H_2SO_4 at room temp. gives the *Me ether*, m.p. 225°, of *1 : 2 : 7-trihydroxy-5-methylanthrone-8-carboxylic acid*, m.p. 255° (decomp.); the free $(OH)_3$-compound did not give any recognisable product on oxidation with alkaline H_2O_2. Condensation of opianic acid with Et *m*-cresotate gives *Et 5-hydroxy-3' : 4'-dimethoxy-2'-carboxy-2-benzoyl-p-toluate*, m.p. 93°; the free *acid*, m.p. 255°, also obtained from *m*-cresotic acid, is reduced by Zn–NaOH to the corresponding *-benzyl-p-toluic acid*, m.p. 183°, complete methylation of which gives (II). Condensation *products*, $C_{18}H_{18}O_8$, m.p. 137°, and $C_{18}H_{18}O_7$, m.p. 203—204°, from Et 3-methoxy-*p*-toluate and 3 : 4 : 5-trimethoxy- and 3 : 5-dimethoxy-6-methyl-1 : 2-phthalide, respectively, are described. H. A. P.

Constitution of bile acids. XLV. 3 : 12-Dihydroxycholenic acid and *apo*cholic acid. H. WIELAND and E. DANE. **XLVI. Acetylation of cholic acid and some reactions of its acetylated derivatives.** H. WIELAND and W. KAPITEL (Z. physiol. Chem., 1932, **212**, 263—268, 269—277; cf. this vol., 64).—XLV. Oxidation of the dihydroxyketotricarboxylic acid $C_{24}H_{36}O_9$ (I) (A., 1932, 614) with CrO_3 in AcOH gives a *tetracarboxylic acid* $C_{21}H_{34}O_{10}$ (II), m.p. 189—192° (*Me*$_4$ ester, m.p. 119°)

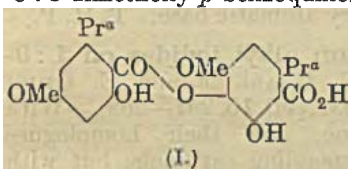


Oxidation of *apo*cholenic acid with BzO_2H in $CHCl_3$ gives apo*cholenic acid oxide*, m.p. 167°. Oxidation with $KMnO_4$ gives a non-cryst. *resin*, $C_{24}H_{40}O_4$ (?). The double linking of *apo*cholic acid appears to lie between C_8 and C_9.

XLVI. Acetylation of Me cholate with Ac_2O in C_5H_5N affords *Me triacetylcholate* (I), m.p. 94°, $[\alpha]_D$ +78°. The free acid with AcCl gives the Ac_2 derivative (II). Thermal decomp. of (I) at 340—360° gives Me cholatrienate (III), converted into Me cholanate by hydrogenation (with PtO_2). (III) forms a *hexabromide*, m.p. 158—160° (decomp.). Me deoxycholate yields with Ac_2O and C_5H_5N or with AcCl a *diacetyl* derivative (IV), m.p. 117°. Thermal decomp. of (IV) at 300—335° affords Me choladienate, which forms a *tetrabromo*-derivative, m.p. 172°, decomp. 179—181°. Oxidation of (II) with CrO_3 gives *12-keto-3 : 7-diacetoxycholanic acid* (V), m.p. 221—222° [*Me* ester (VI), m.p. 179°]. Hydrolysis of (VI) with KOH in MeOH gives 3 : 7-dihydroxy-12-ketocholanic acid, m.p. 218° [probably identical with Borsche and Feske's product (cf. A., 1928, 1008)]. After 1 hr. with 0·5*N*-NaOH (V) gives *3-hydroxy-12-keto-7-acetoxycholanic acid* (VII), m.p. 239° (*Me* ester, m.p. 184°). At 310—335°, (VII) gives *12-ketocholadienic acid* (VIII), m.p. 182° (*Me* ester, m.p. 138—140°). On hydrogenation (Pd-black) (VIII) gives 12-ketocholanic acid and a by-product, probably *ketocholenic acid*, m.p. 203°. Oxidation of (VII) with CrO_3 in AcOH gives *3 : 12-diketo-7-acetoxycholanic acid* (IX), m.p. 190°, which on alkaline hydrolysis yields *7-hydroxy-3 : 12-diketocholanic acid*, m.p. 196°. With Na in EtOH the disemicarbazone of (IX) affords 7-hydroxycholanic acid. (II) is hydrolysed by 0·5*N*-

NaOH to 7-*acetylcholic acid*, non-cryst. (*Me* ester, m.p. 181°), which on oxidation with CrO_3 gives (IX).

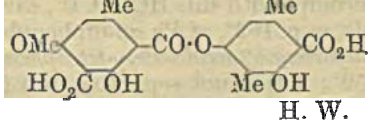
Lichen substances. XVI. Components of *Ramalina* species with particular reference to sekikaic acid. Y. ASAHINA and S. NONOMURA **XVII. Squamatic acid,** Y. ASAHINA and M. YANAGITA (Ber., 1933, **66**, [*B*], 30—35, 36—39).—XVI. Extraction of *Ramalina geniculata* with Et_2O at room temp. and concn. of the extract yields *d*-usnic acid, m.p. 202°, $[\alpha]_D$ +480·4° in $CHCl_3$, and sekikaic acid (I), m.p. 143—144° (Ac_2 derivative, m.p. 162—163°; *Me* ester, m.p. 124°). Treatment of (I) with EtOH at 125—130° yields hydroxydivaricatic [2 : 3-dihydroxy-4-methoxy-6-propylbenzoic] acid, m.p. 158°, unchanged material, and divaricatic acid, m.p. 148°. (I) and CH_2N_2 in Et_2O yield *Me sekikaate* Me_2 *ether*, m.p. 80—81°, hydrolysed to divaricatic acid Me ether, m.p. 63·5°, and *Me hydroxydivaricatate Me ether* (II), m.p. 88°, which is indifferent towards $FeCl_3$ but contains a free OH group; the corresponding *acid*, m.p. 119—120°, is decarboxylated to 4-hydroxy-3 : 5-dimethoxypropylbenzene (Ac derivative, m.p. 87—88°), oxidised to 3 : 5-dimethoxy-*p*-benzoquinone, m.p. 249°. Hence



(I.)

(I) has the annexed formula. (I) and possibly usnic acid are obtained by extraction of a species of *R. farinacea* with Et_2O. *R. pollinaria* when similarly treated affords obtusatic acid, m.p. 203°, *d*-usnic acid, m.p. 195°, $[\alpha]_D$ +488·4° in $CHCl_3$, and evernic acid, m.p. 170°.

XVII.—Extraction of the thalli of *Cladonia uncialis* (L.) with warm Et_2O affords *l*-usnic acid, m.p. 200°, $[\alpha]_D$ −500·2° in $CHCl_3$, and squamatic acid, $C_{19}H_{18}O_9$ (I) (instead of $C_{19}H_{20}O_9$ recorded by Hesse), m.p. 215° (decomp.), which contains 2 CO_2H groups. (I) is smoothly hydrolysed to 2-*hydroxy*-4-*methoxy*-6-*methyliso*phthalic *acid*, decomp. 207—208° (whence Me_2 2 : 4-dimethoxy-6-methyl*iso*phthalate, m.p. 59°), β-orcinol, and CO_2. (I) and CH_2N_2 afford *Me squamatate* Me_2 *ether*, m.p. 132°, hydrolysed to 2 : 4-dimethoxy-6-methyl*iso*phthalic acid, m.p. 212° (decomp.), and Me 4-hydroxy-2-methoxy-3 : 6-dimethylbenzoate, m.p. 146°. (I) is therefore



H. W.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. IV. Oxonium phosphates of the carbonyl group, and derivatives of the type $CH_2Ph{\cdot}COR$. J. W. BAKER and L. HEY (J.C.S., 1932, 2917—2923).—Cryst. *phosphates* of PhCHO and *p*-OMe·C_6H_4·CHO (m.p. 82°) are described (cf. A., 1898, i, 477); they are presumably of the type $Ar{\cdot}CR(OH){\cdot}O{\cdot}PO_3H_2$. Similar phosphates could not be obtained cryst. from BzOEt or *p*-OMe·$C_6H_4{\cdot}CO_2Et$, but their existence is indicated by partition of the esters between H_3PO_4 and light petroleum. The salts with H_3PO_4 are less stable than those with H_2SO_4 (cf. A., 1931, 485, 486; 1932, 612), but the effect of a common ion [$(NH_4)_2HPO_4$] is the same, and their greater stability in the case of the OMe-compounds is in accordance with the polar behaviour of the OMe group. The partition of $CH_2Ph{\cdot}COMe$ and $CH_2Ph{\cdot}CO_2Et$ between H_2SO_4 or H_3PO_4 and light petroleum, and their nitration in H_2SO_4 of varying concns. in absence and presence of $(NH_4)_2SO_4$, confirm the expected higher stability of the oxonium ion brought about by the +*I* effect of the $\cdot CH_2Ph$ group. *Benzyl Me ketone* p-*nitrophenylhydrazone* has m.p. 143°.

H. A. P.

[Aluminium chloride, 3-methyl*cyclo*pentanone, *cyclo*pentanol, and 3-methyl*cyclo*pentanol.] C. D. NENITZESCU and C. N. IONESCU (Bul. Soc. chim. Romania, 1932, **14**, 65—68).—An apparatus for the sublimation of $AlCl_3$ is described. 3-Methyl*cyclo*pentanone is prepared in 83% yield by distillation of β-methyladipic acid with 6·6% of its wt. of CuO at 280—300°. Pinacone formation during reduction of *cyclo*pentanone and 3-methyl*cyclo*pentanone to the alcohol with Na and aq. Et_2O is suppressed by added MeOH.

H. A. P.

Asymmetric syntheses. I. Action of optically active nitrites on cyclic ketones. M. PEZOLD and R. L. SHRINER (J. Amer. Chem. Soc., 1932, **54**, 4707—4711).—4-Methyl*cyclo*hexanone, *d*-β-octyl nitrite, and NaOEt in EtOH–Et_2O at −15° to −10° give a lævorotatory *Na* derivative of 2-oximino-4-methyl*cyclo*hexanone; a dextrorotatory *Na* derivative is similarly prepared using *l*-β-octyl nitrite. Possible mechanisms for this type of asymmetric synthesis are discussed. The same inactive *Na* derivative is obtained from *cyclo*hexanone and *dl*- or *d*-β-octyl nitrite.

H. B.

Peculiar bromination reaction. E. BERGMANN and W. SCHREIBER (Ber., 1933, **66**, [*B*], 44—46).—3-Phenylindene, amyl nitrite, and NaOEt yield 3-*phenylindoneoxime*, m.p. 143—144°, transformed by AcOH–HBr in presence of CuO into 2-bromo-3-phenylindone, m.p. 112°. 2-*Phenylindoneoxime*, m.p. 178—180° (slight decomp.), similarly affords (?) 3-*bromo*-2-*phenylindone*, m.p. 73—74° (decomp.). When heated with AcOH and aq. HBr, CuO yields CuBr; the liberated Br attacks the phenylindones. Me α-phenylcinnamate (I) and Br in $CHCl_3$ give *Me* α*β-dibromo*-α*β-diphenylpropionate*, m.p. 246° (decomp.), with the known isomeride, m.p. 110°, reconverted by NaOH–EtOH into (I).

H. W.

Reducing action of the Grignard reagent. III. Hydrocarbons formed during reduction. C. R. NOLLER, W. E. GREBE, and L. H. KNOX (J. Amer. Chem. Soc., 1932, **54**, 4690—4696).—Reduction of $COPh_2$ by $MgBu^sBr$ in Bu^a_2O gives 1 mol. of *iso*butene (I) per 1 mol. of $CHPh_2{\cdot}OH$. The non-production of benzpinacol and the occurrence of only 0·1% of C_4H_{10} in (I) indicate that it is unlikely that free radical formation precedes reaction.

H. B.

Colour and structure of oximes and semicarbazones. (MME.) RAMART-LUCAS and (MME.) M. GRUMEZ (Compt. rend., 1932, **195**, 959—962).—The oximes of $CH_2Alk{\cdot}COPh$ all show the same ultraviolet absorption curve as do the oximes of

$CAlk_3$·COPh; the two series show large differences in colour and in the position and form of the absorption bands. The curve for α-methylstyrene is very similar to that for the former series (thus indicating CH_2R·CPh:N·OH or CHR:CPh·NH·OH), whilst that of βγ-oxido-βγ-diphenylbutane resembles that of the latter series (indicating CR_3·CPh$<^{NH}_{O}$). Oximes (and semicarbazones) appear to exist not only in stereochemical forms, but also in two isomeric forms containing different functional groups. H. B.

Deoxybenzoin as a substance containing a reactive methylene group. M. V. Ionescu and O. G. Popescu (Bull. Soc. chim., 1932, [iv], **51**, 1215—1227, 1231—1245).—Deoxybenzoin (I) contains a weakly reactive CH_2 group, since it reacts with aryl aldehydes in presence of gaseous HCl, but not of piperidine, and, additively, with substances containing the grouping C:CH·CO, sometimes in presence of piperidine and always in presence of NaOEt. Mesityl oxide and (I) thus give αε-*diketo*-αβ-*diphenyl*-γγ-*dimethylhexane*, m.p. 193—195°, which partly condenses further to yield 2 : 3-*diphenyl*-4 : 4-*dimethyl*-Δ^{2}-cyclo*hexenone*, m.p. 128—131°. The following substances were similarly obtained: *Et*$_2$ γ-*keto*-αβγ-*triphenylpropylmalonate* (II), m.p. 129—130°; *Et*$_2$ γ-*keto*-βγ-*diphenyl*-α-p-*anisyl*- (m.p. 127—129°), -α-*piperonyl*- (m.p. 112—114°), -α-p-*dimethylaminophenyl*- (III) (m.p. 149—151°), and -α-m-*nitrophenyl*- (m.p. 167—169°), -*propylmalonate*; αε-*diketo*-αβγ-*triphenylhexane*, m.p. 209—211°; αε-*diketo*-αβ-*diphenyl* γ-p-*anisylhexane*, m.p. 195—196°; 2-γ-*keto*-αβγ-*triphenylpropylindan*-1 : 3-*dione* (IV), m.p. 188—190°; 2-γ-*keto*-βγ-*diphenyl*-α-p-*tolylpropylindan*-1 : 3-*dione*, m.p. 151—153°; 2-γ-*keto*-βγ-*diphenyl*-α-p-*anisylpropylindan*-1 : 3-*dione*, m.p. 144—146°; the following substituted phenylmethylpyrazolone derivatives: γ-*keto*-βγ-*diphenyl*-α-p-*anisyl*- (m.p. 200—202°), -α-*piperonyl*- (m.p. 206—207°), and -α-p-*dimethylaminophenyl*- (m.p. 201—202°) -*propyl*; 3 : 4 : 5-*triphenyl*-Δ^{2}-cyclo*hexenone*, m.p. 139—140°; 3 : 4-*diphenyl*-5-p-*anisyl*-Δ^{2}-cyclo*hexenone*, m.p. 137—139°; and the lactone (V), m.p. 164—166°, derived from (III). Reduction of (IV) with Zn dust and AcOH

(V.) O—CO—CH·CO_2Et
CPh:CPh·CH·C_6H_4·NMe_2

(VI.) $C_6H_4<^{C(OH)\cdot CPh(OH)}_{CO\cdot CH}>^{CHPh}_{CHPh}$

gives the *substance* $C_{30}H_{24}O_3$ (VI), m.p. 83° (*phenylhydrazone*, m.p. 246—247°), dehydrated by Ac_2O or AcOH–H_2SO_4 to the *substance* $C_{30}H_{20}O$ (VII), m.p. 222°. The additive products dissociate in EtOH in presence of piperidine, since addition of another reactive component leads to separation of the least sol. of the various possible condensation products. Thus, (IV) with indandione gives benzylidenebisdiindone and *benzylidenebisdi-indandione*, m.p. 167—169°, and with dimethyldihydroresorcinol yields benzylideneindandionedi-indone, m.p. 305°, and a benzylidenebisdimethyldihydroresorcinol *derivative*, $C_{23}H_{26}O_3$ (VIII). (II) and indandione give diindone, $CH_2(CO_2Et)_2$, and 2-(γ-*keto*-αβγ-*triphenyl*-

(VIII.) CH_2—CO—C·CHPh·C·CO—CH_2
CMe_2·CH_2·C—O—C·CH_2·CMe_2

(IX.) $CO<^{C_6H_4}_{CH-}>C{:}C<^{CO}_{CO}>C_6H_4$
CHPh·CHPhBz

propyl)*di-indone* (IX), m.p. 186°. Similar dissociation occurs in cold, conc. H_2SO_4, (IV) giving benzylideneindandione and (I), and (II) giving benzylidenedeoxybenzoin and $CH_2(CO_2Et)_2$. *Et*$_2$ p-*dimethylaminobenzylidenemalonate*, m.p. 111—112°, and *Et* m-*hydroxybenzylideneacetoacetate*, m.p. 138—140°, were prepared by condensation in EtOH in presence of piperidine. R. S. C.

Economies effected in the synthesis of benzanthrone and its homologues by means of Friedel and Crafts' reaction. M. Gallotti and A. Beretta (Annali Chim. Appl., 1932, **22**, 691—694).—The direct synthesis of benzanthrone (90% yield) is effected, without isolating *o*-C_6H_4Bz·CO_2H, by treating the product of interaction of *o*-$C_6H_4(CO)_2O$, C_6H_6, and $AlCl_3$ with H_2SO_4 and glycerol in presence of Al powder or a primary aromatic base. T. H. P.

Action of magnesium alkyl iodides on 1 : 9-benzanthrone(-10). G. Charrier and E. Ghigi (Atti R. Accad. Lincei, 1932, [vi], **16**, 257—262).—With anthraquinone, anthrone, and their homologues MgMeI gives the corresponding carbinols, but with benzanthrone it yields 4-methylbenzanthrone and 10-*methylene*-3 : 4-*dihydrobenzanthrene*, m.p. 155—156°; the latter readily loses 2H to form 10-methylenebenzanthrene. The action of MgEtI on benzanthrone gives 4-*ethylbenzanthrone*, m.p. 100°, which yields an *ethylanthraquinonecarboxylic acid*, m.p. 195°, when oxidised with CrO_3. T. H. P.

Reaction between αβ-unsaturated ketones and organic magnesium compounds. Structure of the additive products. E. P. Kohler and W. E. Mydans (J. Amer. Chem. Soc., 1932, **54**, 4667—4678).—Treatment of the Mg derivative from MgPhBr and Ph α-phenylstyryl ketone with O_2 or 0·5 mol. of the peroxide OH·CPh·CPh·$CHPh_2$, and subsequent decomp. with dil. HCl at 0°, gives a 1 : 1-*compound* (*A*), m.p. 162°, of Ph αβ-diphenylstyryl ketone (I) and α-*hydroxy*-αβ-*oxido*-αβγγ-*tetraphenylpropane* (II), m.p. 159°; (*A*) is not separable into (I) and (II) by fractional crystallisation. Oxidation of (*A*) with CrO_3–AcOH affords the oxide of (I) together with benzil and $COPh_2$ [which are derived from (II)], whilst treatment with AcCl at 100° (sealed tube) yields 3-*chloro*-1 : 2 : 3-*triphenylindene*, m.p. 115—116°, convertible (MeOH–KOH) into 3-methoxy-1 : 2 : 3-triphenylindene, m.p. 144° (lit. 153°). Treatment of (*A*) with 20% MeOH–KOH gives Ph α-hydroxy-αββ-triphenylethyl ketone (III) [derived from (II)] and unchanged (I), whilst reduction with 45% HI affords 1 : 2 : 3-triphenylindene [from (I)] and unchanged (II) (which is separable). Reduction of (*A*) with red P and HI yields 1 : 2 : 3-triphenylhydrindene and ααβγ-*tetraphenylpropane*, m.p. 121°, also prepared by reduction.

(Na–Hg and EtOH–C_6H_6) of Ph αββ-triphenylethyl ketone (IV) to the corresponding *carbinol*, m.p. 160—161°, and further reduction of this with red P and HI. Reduction of (*A*) with Zn dust and hot AcOH gives (IV) and unchanged (II) (which is separable by fractional crystallisation). MgPhBr and (*A*) afford (III) and (mainly) αβ-dihydroxy-ααβγγ-pentaphenylpropane; with MgEtBr, unchanged (II) and an unidentified compound [derived from (I)] are produced. Treatment of the product from MgEtBr and Ph α-phenylstyryl ketone with O_2 and subsequent decomp. (dil. HCl at 0°) gives hydrocarbons, m.p. 123° and 143°, Ph αβ-diphenylbutyl ketone, and (mainly) *Ph α-hydroxy-αβ-diphenylbutyl ketone*, m.p. 154° (*acetate*, m.p. 160—161°; *chloride*, m.p. 93—95°; *Me ether*, m.p. 81—82°), also prepared from benzil and Mg α-phenylpropyl chloride.

The structures of the Mg derivatives formed by addition of Grignard reagents to unsaturated ketones cannot, therefore, be determined by conversion into peroxides. H. B.

Hydration of primary acetylenic alcohols. E. D. Venus-Danilova and S. N. Danilov (J. Gen. Chem. Russ., 1932, **2**, 645—658).—The hydration of acetylenic alcohols of the type CR:C·CH_2·OH (I) in presence of $Hg(OAc)_2$ yields in every case an alcohol of the type R·CO·CH_2·CH_2·OH (II), together with the unsaturated ketone R·CO·CH:CH_2 (III), none of the alternative α-keto-alcohol, R·CH_2·CO·CH_2·OH, being formed; the acetates behave in the same way. When R=Ph, (I) gives impure *Ph β-hydroxyethyl ketone*, b.p. 143—144°/20 mm. (*semicarbazone*, m.p. 170°), accompanied in some cases by a *substance* $C_{18}H_{18}O_3$, m.p. 89—90°, and Ph vinyl ketone (IV), b.p. 111—112°/20 mm., in a ratio of 1 : 3·5. (IV) gives a *semicarbazidosemicarbazone*, m.p. 206° (decomp. with sintering at 195°); with NHPh·NH_2 it forms 1 : 3-*diphenylpyrazoline*, m.p. 153·5—154°, and with the theoretical amount of NH_2OH a *base* $C_{18}H_{19}O_3N$, m.p. 122·5° (*hydrochloride*, m.p. 138°, becoming yellow at 128°; *sulphate*, m.p. 156°, becoming yellow at 133°). On further treatment with NH_2OH this forms a *substance* $C_{18}H_{21}O_3N_3$, m.p. 153°, also obtainable from (IV) with an excess of NH_2OH, and hydrolysed by HCl or H_2SO_4 to a salt of the base $C_{18}H_{19}O_3N$. For the latter the formulæ (COPh·CHMe)$_2$N·OH or (COPh·CH_2·CH_2)$_2$N·OH are suggested; the higher-melting substance is probably the corresponding dioxime. The acetate of (I) gives equal amounts of (IV) and the *acetate* of Ph β-hydroxyethyl ketone, b.p. 119—121°/19 mm., which cannot be purified and gives the same derivatives as (IV).

tert.-Butylacetylene, MgEtBr, and trioxymethylene in Et_2O yield tert.-*butylpropinol* (δδ-*dimethyl*-Δ^{β}-*pentinyl alcohol*) (I, R=CMe_3), b.p. 78—79°/27 mm. (*acetate*, b.p. 106°/72 mm.). On hydration it gives equal quantities of β-*hydroxyethyl* tert.-*butyl ketone* (II, R=CMe_3), b.p. 94—97°/22 mm. [*semicarbazone*, m.p. 223° (decomp.)], giving a substance, m.p. 128·5—129·5°, after several distillations, and tert.-*butyl vinyl ketone* (V), b.p. 78—81°/100 mm., oxidised to CMe_3·CO_2H by CrO_3 and giving with NHPh·NH_2 a *substance* $C_{19}H_{26}N_4$, m.p. 134°, which is probably a phenylhydrazidophenylhydrazone. The acetate of (I) (R=CMe_3) gives on hydration (V) and the *acetate* of (II), (R=CMe_3), b.p. 120—122°/50 mm. (*semicarbazone*, m.p. 127°), forming the substance m.p. 134° with NHPh·NH_2. G. A. R. K.

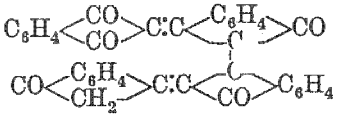
Oxidative processes. VI. Mechanism of autoxidation and racemisation of α-ketols and steric hindrance. A. Weissberger (Ber., 1932, **65**, [*B*], 1815—1820; cf. A., 1929, 1301).—Autoxidation of benzoin in presence of excess of alkali is a reaction of the first order, the velocity of which is proportional to the concn. of alkali. The change is therefore expressed: R·CH(OH)·COR + OH′ = R·CHO′·COR + H_2O and R·CHO′·COR + O_2 ⟶ R·CO·COR + HO_2′. The second change can be further resolved into R·CHO′·COR ⟷ R·CO′:C(OH)R and R·CO′:C(OH)R + O_2 ⟶ R·CO·COR + HO_2′. The rate of reaction is governed by that of enolisation. The coloration observed in the solutions when O is only slowly available is attributed to the union of part of the enediol ions with diketone; if O is freely available this change does not occur and the solution remains colourless. If the rates of autoxidation of substituted benzoins are divided by the dissociation consts. of the carboxylic acids with the corresponding residues attached to the CO_2H group, a small systematic variation is observed which disappears when the 1·8th power of the const. is employed. With *o*-mono- and di-substituted benzoins reaction proceeds more slowly than expected, steric hindrance being very marked. Racemisation of *d*-benzoin proceeds through the same intermediate stages and, under like conditions, with the same velocity as autoxidation. With optically active 2 : 2′-*diethoxybenzoins* (details subsequently) autoxidation and racemisation occur very sluggishly and at equal rates. Steric hindrance of the autoxidation is not caused by difficulty of approach of O to the reacting group, but occurs at ionisation or enolisation. Evidence is adduced in favour of the view that the doubly-charged enediol ion, R·CO′:CO′R, reacts with O. H. W.

Thermal interconversion of mixed benzoins. P. L. Julian and W. Passler (J. Amer. Chem. Soc., 1932, **54**, 4756).—Anisbenzoin (I), prepared by the methods of Asahina and Terasaka (A., 1923, i, 1023) and McKenzie *et al.* (A., 1929, 1067), has m.p. 89°. When (I) is heated slowly and then cooled the m.p. rises to about 101°. The anisbenzoin, m.p. 101°, of McKenzie *et al.* (*loc. cit.*) is considered to be a mixture of (I) and benzanisoin, m.p. 106°. H. B.

Chemical characterisation of stryphnone (4-ω-methylaminoacetopyrocatechol). H. K. Barrenscheen and W. Filz (Biochem. Z., 1932, **255**, 344—350).—Stryphnone, m.p. 215° (decomp.) (hydrochloride, m.p. 237—245°), gives with Folin's phenol reagent an intense blue colour which may be used for its colorimetric determination. Attempts to obtain the semicarbazone and thiosemicarbazone were unsuccessful, but the *phenylhydrazone*, m.p. 135—136° (decomp.), was obtained, the reaction thus differentiating it readily from adrenaline. P. W. C.

Anhydrobisbindone and the chemistry of the production of tribenzoylenebenzene (truxenequinone). W. M. Fischer and A. Cirulis (Ber.,

1932, **65**, [*B*], 1852—1855).—Bindone (anhydrobisindandione) is converted by 96% H_2SO_4 at room temp. into tribenzoylenebenzene and cis-*anhydrobisbindone* (I), m.p. 408°, which passes into the *enol* (*Na*



(I.)

salt) when heated with NaOMe or when its solution in $CHCl_3$ evaporates on exposure to air. (I) yields a Br_6-compound, m.p. (indef.) 382—385°, which regenerates (I) when heated in solvents of high b.p. Prolonged boiling of (I) with EtOH in a SiO_2 flask results in quant. production of tribenzoylenebenzene and 1 mol. of indan-1 : 3-dione (II). This is taken to be the course followed in the transformation of indan-1 : 3-dione into tribenzoylenebenzene (contrast Stobbe and Zschoch, A., 1927, 347). In C_5H_5N or in AcOH, (II) is partly converted into bindone.

H. W.

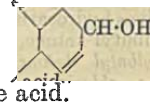
Derivatives of di-indone. II. Action of alcoholic alkalis and alkali alkoxides on bisdi-indones. M. V. Ionescu and H. Slusanschi (Bull. Soc. chim., 1932, [iv], **51**, 1245—1258; cf. A., 1932, 1252).—Alkyl- and aryl-idenebisdi-indones (*A*) with NaOEt give di-indone and successively chocolate-coloured, amorphous products (*B*), yellow products (*C*), m.p. about 240°, and yellow products (*D*), m.p. about 300°. (*A*) and KOH–EtOH give only (*D*). The reaction consists in the elimination of 1 mol. of indandione, which is converted into di-indone; the successive products all have the same empirical formula, R·$C_{28}H_{15}O_5$, as the corresponding arylidene-indandione-di-indone, R·CHO being the aldehyde. The following m.p. are recorded: R=Ph, (*C*) m.p. 243°, (*D*) m.p. 325° (*K*, *Na*, and *piperidine* salts); R=MeO·C_6H_4, (*C*) m.p. 245°, (*D*) m.p. 307° (*K* and *piperidine* salts; additive *compound* with EtOH); R=CH_2O_2:C_6H_3, (*C*) m.p. 246°, (*D*) m.p. 315° (*Na*, *K*, and *piperidine* salts); and R=Me, (*C*) m.p. 227°, (*D*) m.p. 298° (*piperidine* salt). The salts are formed by addition of 1 mol. of base and regenerate (*D*) when acidified. (*B*), (*C*), and (*D*) are also differentiated by their behaviour (colour) with alkalis.

R. S. C.

Production of [di]aminoanthraquinone derivatives. Imperial Chem. Industries, Ltd., R. J. Loveluck, and J. Thomas.—See B., 1932, 1115.

Action of ammonia on acenaphthenequinone. G. Charrier and E. Ghigi (Atti R. Accad. Lincei, 1932, [vi], **16**, 262—265).—The action of NH_3, as gas or in H_2O, on acenaphthenequinone gives acenaphthazine and naphthalimide; other *o*-quinones behave similarly.

T. H. P.

Lupeol. II. H. Dieterle and A. Salomon [with C. Coester, A. Wilcke, and W. Daum] (Arch. Pharm., 1932, **9**, 540—549).—Lupeol (I), $C_{30}H_{49}$·OH, m.p. 212—213°, with CrO_3–AcOH gives $COMe_2$ and an unsaturated ketone, *lupone*, $C_{27}H_{42}O$, m.p. 170° (2 : 4-*dinitrophenylhydrazone*, m.p. 214°; *dibromide*, m.p. 246°), with O_3 in CCl_4 a dibasic acid, $C_{23}H_{28}(CO_2H)_2$, m.p. 135—137°, and with O_3 in AcOH an unsaturated *ketone* (II), $C_{21}H_{34}O_2$, m.p. 218° (2 : 4-*dinitrophenylhydrazone*, m.p. 137°; *dibromide*, m.p. 255°), and an *aldehydo-acid* (III), $C_{19}H_{30}O_3$ (2 : 4-*dinitrophenylhydrazone*, m.p. 168—169°; *Me* ester, m.p. 80—81°). (II) contains an indifferent O atom; with MgMeI it yields the *carbinol*, $C_{22}H_{38}O_2$, m.p. 192° (*acetate*, m.p. 234°), oxidised by CrO_3–AcOH to the dibasic *acid*, $C_{19}H_{30}O_4$, m.p. 262—264°, corresponding with (III). (II) and alkaline $K_3Fe(CN)_6$ give a dibasic *acid* (IV), $C_{17}H_{26}O_4$, m.p. 137—139° (*Na* salt), which with Zn dust gives 2-methylanthracene and possibly phenanthrene. (I), therefore, contains the grouping  and (IV) is probably a phenanthrene acid.

R. S. C.

Constitution of podophyllotoxin and picropodophyllin. W. Borsche and J. Niemann (Ber., 1932, **65**, [*B*], 1846; cf. A., 1932, 1258).—A reply to Spath and others (this vol., 72).

H. W.

[**Dye from acacia wood.**] K. Brass and H. Kranz (Ber., 1932, **65**, [*B*], 1867; cf. B., 1932, 760).—A claim for priority against Schmid and Tadros (this vol., 72).

H. W.

Reduction of phosphorus tetrachlorobromide and phosphorus pentachloride during their action on menthol and sodium menthoxide. J. H. Kolitowska (Rocz. Chem., 1932, **12**, 896—901).—PCl_4Br converts menthol (I) or Na menthoxide (II) into menthyl chloride and bromide; at the same time about 14 or 30% of the PCl_4Br taken is reduced to PCl_3. A similar reaction takes place with PCl_5 and (II), but not (I).

R. T.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. V. Rotation of camphor in strong mineral acids. J. W. Baker (J.C.S., 1932, 2923—2927).—Partition of *d*-camphor between ligroin (b.p. 100—120°) and H_2SO_4 of different concns. indicates the formation of the oxonium cation: $HO{\cdot}SO_3H+C_9H_{16}C{:}O$ (sol.) $C_9H_{16}C(OH)O{\cdot}SO_3H$ (insol.) $\rightleftharpoons$ $C_9H_{16}C{:}OH+O{\cdot}SO_3H$, the equilibria being displaced from right to left either by adding H_2O or $(NH_4)_2SO_4$. This refutes the argument put forward by Lucas (A., 1928, 816). Similar salt formation occurs with H_3PO_4. *l*-Camphor exhibits *d*-rotation in H_2SO_4 and the rotation of Me *d*-camphorate is reduced from $[\alpha]_{5461}$ +60·3° in ligroin to +7·5° in H_2SO_4, both attributed to conversion of C:O into ·C:OH.

F. R. S.

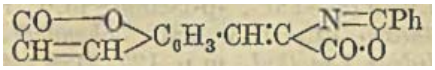
Condensation of pernitrosocamphor with primary amines. P. Latini (Annali Chim. Appl., 1932, **22**, 728—730).—With *o*-$C_6H_4Br{\cdot}NH_2$ (cf. A., 1932, 517), *camphor-o-bromoanil*, b.p. 236°/700 mm., is obtained. The more acid substituents in the amine, the more difficult such condensation becomes.

T. H. P.

A triterpenediol monostearate from coca fruit (*Erythroxylon novogranatense*). J. Zimmermann (Rec. trav. chim., 1932, **51**, 1200—1203).—The EtOH extract of coca fruit contains a *triterpenediol monostearate*, m.p. 124°, $[\alpha]_D^{25}$ +49·90°, hydrolysed to stearic acid and the triterpenediol, *erythrodiol*, m.p. 231°, $[\alpha]_D^{25}$ +75·38° (*diacetate*, m.p. 188°, $[\alpha]_D^{25}$ +59·41°).

A. A. L.

Azlactone from 6-aldehydocoumarin and its condensation with aromatic amines. S. K. BANERJEE (J. Indian Chem. Soc., 1932, 9, 479—481).—The *azlactone* (I), m.p. 245°, is formed in



(I.)

small yield from coumarin-6-aldehyde, hippuric acid, Ac_2O, and NaOAc at 100°, and is hydrolysed by boiling aq. NaOH to *coumarin-6-pyruvic acid* (isolated as the *quinoxaline*, m.p. 288—290°). Condensation *products* from (I) and *o*-$C_6H_4Me{\cdot}NH_2$, m.p. 258°, α-$C_{10}H_7{\cdot}NH_2$, and NH_2Ph, m.p. 178—180°, are prepared by heating it with the amine and Cu-bronze at 130—160°. H. A. P.

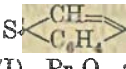
Comparison of the directive powers of elements having consecutive atomic numbers. IV. Nitration of 2 : 4 : 6-triphenylpyrylium perchlorate. (MRS.) C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1932, 2894—2899).—2 : 4 : 6-*Triphenylpyrylium perchlorate*, m.p. 288—290°, prepared from the ferrichloride, could not be mononitrated, but gave a $(NO_2)_3$-derivative, about 70% of which was 2 : 6-*di*-m-*nitrophenyl*-4-*p*-*nitrophenylpyrylium perchlorate* (I), m.p. 276—278°, from which by oxidation *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ has been obtained. *p*-Nitrochalkone and COMePh treated with HCl and $FeCl_3$ yield 4-*p*-*nitrophenyl*-2 : 6-*diphenylpyrylium ferrichloride*, m.p. 209—212°, which gives the *perchlorate* (II), m.p. > 300°. 4-m-, m.p. 237°, 2-m-, m.p. 216—218°, and 2 : 6-*di*-m-*nitrophenyl*-4-*phenylpyrylium ferrichloride*, m.p. 229—232°, and 4-m-, m.p. 241—242°, 2-m- (III), m.p. 277—278°, and 2 : 6-*di*-m-*nitrophenyl*-4-*phenylpyrylium perchlorate* (IV), m.p. 291°, are similarly obtained. Nitration of (II), (III), and (IV) yields (I), and the course of the nitrations is discussed. F. R. S.

Nitration of di-*p*-tolyl- and di-*p*-chlorophenylphenylpyrylium perchlorates. (MISS) H. E. JOHNSTON and R. J. W. LE FEVRE (J.C.S., 1932, 2900—2902).—4-*Phenyl*-2 : 6-*di*-*p*-*tolylpyrylium ferrichloride*, m.p. 257—258°, prepared from *p*-methylacetophenone, PhCHO, Ac_2O, and $FeCl_3$, is converted by NaOAc into 4-phenyl-2 : 6-di-*p*-tolylpyranol [*picrate*, m.p. 259—260° (decomp.)], which forms the *perchlorate* (I), m.p. 278—280°, corresponding with the ferrichloride. Trinitration of (I) affords a $(NO_2)_3$-derivative, m.p. 271—273°, oxidised to *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, and identical with the product of nitrating 2 : 6-*di*-(2′-*nitro*-p-*tolyl*)-4-*phenylpyrylium perchlorate*, m.p. 275—277°, obtained from PhCHO and 3-nitro-4-methylacetophenone. 2 : 6-*Di*-p-*chlorophenyl*-4-*phenylpyrylium perchlorate*, m.p. > 300°, obtained through the ferrichloride, m.p. 295°, from $C_6H_4Cl{\cdot}COMe$, gives a $(NO_2)_3$-derivative, m.p. 240—245° (decomp.), oxidised to *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, and converted by $C_5H_{11}N$ with loss of Cl into 4-p-*nitrophenyl*-2 : 6-*di*-(m-*nitro*-p-*piperidinophenyl*)*pyranol*, m.p. 76—78°. These results confirm the constitution assigned to the nitration product of 2 : 4 : 6-triphenylpyrylium perchlorate (cf. preceding abstract). F. R. S.

1 : 3-Dioxins. III. Condensation of *p*-nitroanisole with formaldehyde and the mechanism of the formation of 6-nitro-1 : 3-benzdioxin. F. CALVET and M. N. MEJUTO (Anal. Fís. Quím., 1932, 30, 767—777).—*p*-Nitroanisole and CH_2O in 75% H_2SO_4 at 100° yield 5 : 5′-*dinitro*-2 : 2′-*dimethoxydiphenylmethane* (I), m.p. 180—182°. At 0° there is also obtained the intermediate product, 5-*nitro*-2-*methoxybenzyl alcohol* (II), m.p. 122° (*acetate*, m.p. 72°), which condenses with *p*-nitroanisole to give (I). Oxidation of (II) with $KMnO_4$ gives 5-nitro-2-methoxybenzoic acid. Demethylation of (II) could not be carried out; HCl has no action, HBr yields the *bromide*, m.p. 84°, HI reduces the NO_2-group. 5-Nitro-2-hydroxybenzyl alcohol (III) and MeI yield (II). (III) and CH_2O yield 6-nitro-1 : 3-benzdioxin. Oxidation of (I) with CrO_3 yields 5 : 5′-*dinitro*-2 : 2′-*dimethoxybenzophenone*, m.p. 184° [*phenylhydrazone*, m.p. 286° (decomp.)]. Reduction of (I) with Zn and HCl yields the $(NH_2)_2$-compound, m.p. 124—126° [*dihydrochloride*, m.p. 315° (decomp.); Ac_2 derivative, m.p. 200°]. Demethylation of (I) with HBr yields the amorphous (?) 2 : 2′-$(OH)_2$-compound, m.p. 230° (decomp.).

The course of these new condensations with CH_2O indicates that the formation of 1 : 3-benzdioxins in this and other cases takes place by direct entrance of CH_2O into the position *ortho* to the OH-group, followed by condensation of CH_2O with the OH-group and ring-closure. The analogous condensations of chloral and dichloroacetal (A., 1926, 1242; 1927, 458, 967; 1928, 632, 750; 1929, 65, 573) may be similarly explained. R. K. C.

Rotenone. XXIV. Synthesis of tetrahydrotubanol. H. L. HALLER (J. Amer. Chem. Soc., 1932, 54, 4755).—2 : 6-$(OMe)_2C_6H_3{\cdot}CN$ and $MgBu^{\beta}Br$ give (after hydrolysis) 2 : 6-dimethoxyphenyl Bu^{β} ketone, reduced to 2 : 6-dimethoxy*iso*amylbenzene, which is demethylated to 2-*iso*amylresorcinol. This is identical with tetrahydrotubanol (cf. A., 1932, 165, 739). H. B.

Dismutation of some disulphides. II. J. L. D'SILVA and E. W. MCCLELLAND (J.C.S., 1932, 2883—2887).—2 : 2′-Thiobenzoic acid (I), Ac_2O, and KOAc give 3-hydroxy-2-acetyl- and 3-acetoxy-1-thionaphthen, which is accounted for by an intramol. arrangement of S  C·OH, obtained by dismutation of (I); (I), Pr_2O, and KOPr yield 3-propionoxy-2-methyl-1-thionaphthen (also similarly obtained from 2 : 2′-dithiobenzamide). Condensation of 2 : 2′-dithiobenzamide with Ac_2O and KOAc gives the same products as (I) and 3-acetamido-1-thionaphthen (II), showing that it undergoes dismutation to 2-keto-1 : 2-dihydrobenz*iso*thiazole and 2-thiobenzamide. (II) is oxidised by H_2O_2 in AcOH to 3-hydroxy-1-thionaphthen 1-dioxide and nitrated to 2-*nitro*-3-*acetamido*-1-*thionaphthen*, m.p. 205—206°, hydrolysed to the 3-*OH*-compound, m.p. 104—105° (decomp.) (*Na* salt), which is reduced and subsequently oxidised to thionaphthaquinone. The Br-compound, $C_{10}H_8ONBrS$, obtained by bromination of (II) (McClelland, A., 1929, 1084) is oxidised by H_2O_2 to 2 : 2-dibromo-3-keto-2 : 3-dihydrothionaphthen 1-dioxide, confirming the entry of Br in position 2. Hydrolysis of $C_{12}H_{13}ONS$ (III), obtained

by condensing 2-keto-1 : 2-dihydrobenz*iso*thiazole, Pr_2O, and NaOPr (A., 1932, 64), affords 3-hydroxy-2-methyl-1-thionaphthen, identified as the bis-compound. Oxidation of (III) with H_2O_2 gives 3-*propionamido*-2-*methyl*-1-*thionaphthen* 1-*dioxide*, m.p. 173°, and bromination yields a *Br*-derivative, m.p. 195—196°. (III) must be $S<\begin{matrix}CMe\\C_6H_4\end{matrix}>C\cdot NH\cdot COEt$. F R S

New cyclic dipeptide of aspartic acid. C. Ravenna and R. Nuccorini (Gazzetta, 1932, **62**, 1019—1024).—Diketopiperazinediacetic acid (I) (A., 1922, i, 180) with *N*/3-$Ba(OH)_2$ yields the β-dipeptide (A., 1920, i, 601), and a monocyclic *dipeptide*, decomp. 140—160° (*Ba*, *Cu* salts; *Et* ester), which at 210° slowly gives (I), and is therefore $\begin{matrix}CH(NH_2)\cdot CO\\CH\cdot CO\end{matrix}>N\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, or possibly $\begin{matrix}CH(CO_2H)\cdot NH\cdot CO\\CH_2\cdot CO\cdot NH\end{matrix}>CH\cdot CH_2\cdot CO_2H$. E W. W.

Synthetical experiments in the indole group. IX. Synthesis of indolenines. T. Hoshino. **X. Synthesis of the eserine ring-system.** T. Hoshino and K. Tamura (Annalen, 1932, **500**, 35—42, 42—52).—IX. A more detailed account of work previously reviewed (A., 1932, 952).

X. Partly an account of work previously reviewed (*loc. cit.*). The following is new. Mg 2 : 3-dimethylindolyl iodide and $CH_2Cl\cdot CN$ give 2 : 3-*dimethyl*-3-*indoleninylacetonitrile*, m.p. 81—83° (*picrate*, m.p. 177—178°), which when reduced (Na, EtOH) affords 2 : 3-dimethylindole and not the expected amine. 2-*Methyl*-3-*indolylacetonitrile*, m.p. 85—86° (from Mg 2-methylindolyl iodide and $CH_2Cl\cdot CN$), is hydrolysed (20% KOH) to the *-acetic acid*, decomp. 198—199°, and reduced (Na, EtOH) to β-2-*methyl*-3-*indolylethylamine*, m.p. 107—108° (*hydrochloride*, m.p. 194—195°; *acetate*, m.p. 158—159°; *picrate*, decomp. 218—219°; *benzylidene* derivative, m.p. 94—95°), and a little 2 : 3-dimethylindole. 9-Methyldinordeoxyeseroline (*salicylate*, m.p. 178°; *benzoate*, m.p. 133—133·5°; *formate*, m.p. 119°; *oxalate*, decomp. 250°; resinous NO-derivative, reduced by Zn dust–AcOH to the original base) is resolved by successive treatment with *d*-tartaric and *d*-camphorsulphonic acids into *d*-, $[\alpha]_D^{20}$ +55·7° in EtOH (d-*tartrate*, m.p. 205°), and *l*-, $[\alpha]_D^{20}$ −54·1° in EtOH (d-*camphorsulphonate*, m.p. 219°), forms, both of which are non-cryst. H. B.

Condensation of acetophenone with isatin by the Knoevenagel method. H. G. Lindwall and J. S. Maclennan (J. Amer. Chem. Soc., 1932, **54**, 4739—4744).—Isatin (I) and COPhMe (II) in EtOH–$NHEt_2$ (piperidine, NH_3, or KOH) give 3-*hydroxy*-3-*phenacyloxindole* (III), m.p. 169—172° (decomp.) (all m.p. are corr. unless stated otherwise), which when heated alone or with 10% EtOH–KOH regenerates (I) and (II). More prolonged heating of (III) with EtOH–KOH affords 2-phenylquinoline-4-carboxylic acid (IV). (III) is dehydrated by conc. HCl in EtOH or AcOH to 3-*phenacylideneoxindole* (V), m.p. 193—194°, which is not converted into (IV) by EtOH–KOH and is, therefore, not an intermediate in the Pfitzinger synthesis (A., 1898, i, 207) of substituted cinchoninic acids. (V) is reduced ($Na_2S_2O_4$–aq. EtOH) to 3-*phenacyloxindole*, m.p. 177° [*oxime*, m.p. 198—199° (uncorr.)], which is unaffected by conc. EtOH–KOH. The following are prepared by the above methods: 3-*hydroxy*-3-*phenacyl*-1-*methyl*-, m.p. 168—170° (decomp.), 3-*hydroxy*-3-p-*chloro*-, m.p. 175—176°, -p-*bromo*-, m.p. 178—181°, -p-*methyl*, m.p. 185—186°, and -p-*methoxy*-, m.p. 186—187°, *-phenacyl-oxindoles*; 3-*phenacylidene*-1-*methyl*-, m.p. 127—128°, 3-p-*chloro*-, m.p. 209—210°, -p-*bromo*-, m.p. 218—219°, -p-*methyl*-, m.p. 182—183°, and -p-*methoxy-phenacylidene-oxindoles*; 3-*phenacyl*-1-*methyl*-, m.p. 134—135°, 3-p-*chloro*-, m.p. 182—183°, -p-*bromo*-, m.p. 191—192°, -p-*methyl*-, m.p. 145—146°, and -p-*methoxy*-, m.p. 164—165°, *-phenacyl-oxindoles*. H. B.

Action of nitric acid on the 1-acyl-2 : 3-diphenylindoles. R. C. G. Fennell and S. G. P. Plant (J.C.S., 1932, 2872—2876).—The p-*nitrophenylhydrazone*, m.p. 158—160°, of $CH_2Ph\cdot COPh$ is converted by Fischer's reaction into 5-nitro-2 : 3-diphenylindole, m.p. 211° (*Ac* derivative, m.p. 158°), whilst the o-*nitrophenylhydrazone*, m.p. 143°, does not similarly lose NH_3; the *m*-NO_2-derivative, m.p. 157—158°, gives a mixture of 4(or 6)- (I), m.p. 227—228°, and 6(or 4)-*nitro*-2 : 3-*diphenylindole*, m.p. 205° (1-*Ac* derivative, m.p. 187°). 1-*Acetyl*-2 : 3-*diphenylindole* (II), m.p. 138°, in AcOH is nitrated by HNO_3, at 80° to 4(or 6)-*nitro*-1-*acetyl*-2 : 3-*diphenylindole* (III), m.p. 210°, but when the solution is boiled for 5 min. there is obtained 15-*nitro*-16-*hydroxy*-15 : 16-*dihydrophenanthracarbazole* (IV), m.p. 262° (decomp.), converted by boiling AcOH into the isomeric ?-*nitro*-16-*hydroxy*-15 : 16-*dihydrophenanthracarbazole*, m.p. 227° (*Ac* derivative, m.p. 175—176°). Nitration of (II) in AcOH at 50° gives a mixture of (III), 15-*nitro*-9-*nitroso*-16-*hydroxy*- (V), m.p. 170° (decomp.), ?-*nitro*-15 : 16-*dihydroxy*-, m.p. 192°, and ? ?-*dinitro*-15 : 16-*dihydroxy*-15 : 16-*dihydrophenanthracarbazole*, m.p. 215°. 1-*Benzoyl*-2 : 3-*diphenylindole*, m.p. 153°, is nitrated to the 4(or 6)-NO_2-compound, m.p. 215°, hydrolysed to (I), and similarly *Et* 2 : 3-*diphenylindole*-1-*carboxylate*, m.p. 110°, yields the 4(or 6)-NO_2-derivative, m.p. 184°. 1-*Cinnamoyl*-2 : 3-*diphenylindole*, m.p. 192°, on nitration at 80° affords (IV), and at 50° gives a mixture of 4(or 6)-*nitro*-1-*cinnamoyl*-2 : 3-*diphenylindole*, m.p. 254°, and (V). The complexity of the reaction makes it unsuitable for determining how far the simple indole nucleus undergoes additive reactions during nitration. F. R. S.

Octahydropyrrocoline. G. R. Clemo and G. R. Ramage (J.C.S., 1932, 2969—2973).—*Et* β-2-*carbethoxypiperidinopropionate*, b.p. 116—118°/0·2 mm., prepared from Et piperidine-2-carboxylate, $CH_2Cl\cdot CH_2\cdot CO_2Et$, and anhyd. NaOAc, and hydrolysed to β-2-*carboxypiperidinopropionic acid*, m.p. 210°, gives with Na in xylene 1-*keto-octahydropyrrocoline*, b.p. 93°/18 mm. Octahydropyrrocoline (I), b.p. 65—67°/18 mm., obtained by Clemmensen reduction of the keto-compound, gives a mixture of two *picrates*, m.p. 135° and 226° (decomp.), the latter being more readily obtained by keeping (I). The formation of two picrates suggests that (I) occurs as *cis*- and *trans*-forms. *Et* 2-*pyridylacrylate*, b.p. 153°/16 mm., prepared from pyridyl-ω-trichloro-β-hydroxypropane hydrochloride by hydrolysis and esterification, is reduced catalytically to 3-keto-octahydropyrrocoline.

This is reduced by the Bouveault method to (I) (cf. Löffler and Flugel, A., 1909, i, 831), which gives only the picrate, m.p. 226°. Et piperidine-2-carboxylate and anhyd. K_2CO_3 give with $CH_2Cl{\cdot}CO_2Et$, *Et* 2-*carbethoxypiperidinoacetate*, b.p. 149°/17 mm., and with $CHMeBr{\cdot}CO_2Et$, *Et* α-2-*carbethoxypiperidinopropionate*, b.p. 151°/17 mm., 110°/0·2 mm. F. R. S.

[Supposed acetoneanil.] K. VON AUWERS (Ber., 1933, **66**, [*B*], 59—60; cf. Auwers and Wunderling, A., 1932, 253).—The conception of Reddelien and Thurm (A., 1932, 1142) that the "acetoneanil" of Knoevenagel (A., 1921, i, 785) is 2 : 2 : 4-trimethyl-1 : 2-dihydroquinoline and its reduction product is a 2 : 2 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoline is in harmony with the spectrochemical behaviour of the compounds. H. W.

Synthesis of quinoline derivatives. II. K. DZIEWONSKI, J. MOSZEW, G. DORTHEIMERÓWNA, and W. RÓŻYCKI (Rocz. Chem., 1932, **12**, 925—935).—The *o*-tolil of COPhMe heated with PhNCS yields 4-*anilino*-2-*phenyl*-8-*methylquinoline*, m.p. 171° (*hydrochloride*, m.p. 191°; *picrate*, m.p. 260—261°; *NO*-derivative, m.p. 194°), which on fusion with KOH gives 4-*hydroxy*-2-*phenyl*-8-*methylquinoline*, m.p. 245—246°. 4-*Anilino*-2-α-*naphthylquinoline*, m.p. 219° (*hydrochloride*, m.p. 200—201°; *nitrate*, m.p. 163—164°; *compound* with $C_2H_4Br_2$, m.p. 258°; *NO*-derivative, m.p. 199—200°; *Ac* derivative, m.p. 132—133°; 6-(?)NO_2-derivative, m.p. 314°), is obtained from α-naphthyl Me ketone or its *anil*, m.p. 134°, and $CS(NHPh)_2$. 4-p-*Tolylamino*-2-α-*naphthyl*-6-*methylquinoline*, m.p. 229—230° (*hydrochloride*, m.p. 297—298°; *picrate*, m.p. 247—248°; *NO*-derivative, m.p. 220°; *Ac* derivative, m.p. 218°), is prepared from α-naphthyl Me ketone and di-*p*-tolylthiocarbamide. β-Naphthyl Me ketone and $CS(NHPh)_2$ yield 4-*anilino*-2-β-*naphthylquinoline*, m.p. 176° (*picrate*, m.p. 264—265°), and 3-acenaphthenyl Me ketone and $CS(NHPh)_2$ yield 4-*anilino*-2-(3′-*acenaphthenyl*)*quinoline*, m.p. 230° (*hydrochloride*, m.p. 236—237°; *picrate*, m.p. 263—265°; *NO*-derivative, m.p. 193—194°; *Ac* derivative, m.p. 178—179°). R. T.

Quinoline derivatives. XL. Synthesis of 2-phenyl-4-quinolylaminoacetic acid. H. JOHN and G. BEHMEL (J. pr. Chem., 1932, [ii], **135**, 215—221).—4-Amino-2-phenylquinoline, 40% CH_2O, and NaCN in EtOH at 100° give 2-*phenyl*-4-*quinolylaminoacetic acid*, m.p. 256—261° [26 *salts* described briefly; *Me*, m.p. 108—109°, *Et*, m.p. 128° (*hydrochloride*, m.p. 217—218°), *Pr*$^{\beta}$, m.p. 109·5°, and *benzyl*, m.p. 106°, esters; *amide*, m.p. 227° (sinters at 224°), from the Et ester and conc. aq. NH_3], decarboxylated to 4-*methylamino*-2-*phenylquinoline*, m.p. 135·5°. H. B.

Alkylation of azomethine compounds. E. BERGMANN and W. ROSENTHAL (J. pr. Chem., 1932, [ii], **135**, 267—281).—*iso*Quinoline methosulphate and MgPhBr in C_6H_6 give 1-phenyl-2-methyl-1 : 2-dihydro*iso*quinoline, whilst *iso*quinoline and MgPhBr afford some 1-phenyl*iso*quinoline (by dehydrogenation of its 1 : 2-dihydro-derivative). $CH_2Ph{\cdot}MgCl$ and C_5H_5N in dioxan give some 2-benzylpyridine; quinoline similarly affords 2- (*picrate*, m.p. 151°) and 4-benzyl- and 2 : 4-dibenzyl-quinoline (*picrate*, m.p. 193°); *iso*quinoline yields 1-*benzyl*-1 : 2-*dihydroisoquinoline*, b.p. 213—215°/18 mm. (*picrate*, m.p. 153°) (in absence of dioxan, the yield is smaller and some 1-benzyl*iso*quinoline is formed); acridine furnishes 9-benzyl-9 : 10-dihydroacridine (I). Addition of $CHNaPh_2$ to C_5H_5N, quinoline, or *iso*quinoline does not occur; acridine affords (after decomp. with EtOH and H_2O) 9-*benzhydryl*-9 : 10-*dihydroacridine*, m.p. 266°, which, like (I), is not dehydrogenated by HgO in EtOH. The product from 2-methylpyridine and LiPh treated with EtBr gives 2-n-*propylpyridine*, b.p. 165—168°, reduced (Na–EtOH) to *dl*-coniine; treatment with BzCl affords 2-phenacylpyridine, whilst PhCHO yields 2-β-*hydroxy*-β-*phenylethylpyridine*, m.p. 110°. The product from 2 : 6-dimethylpyridine and LiPh treated with CH_2PhCl gives 2 : 6-*di*-β-*phenylethylpyridine*, b.p. 230—240° (*picrate*, m.p. 137—138°), showing that two CH_2Li groups are present in the original product. CPh_2:NPh and LiPh afford *o*-phenylbenzhydrylaniline (Gilman *et al.*, A., 1929, 1056), whilst CHPh.NPh and $CHNaPh_2$ give β-*anilino*-αα*β*-*triphenylethane*, m.p. 164—166°. 9-α-*Naphthyl*-, m.p. 242°, 9-*anisyl*-, m.p. 213°, 9-*o*-*tolyl*-, m.p. 207°, and 9-m-*tolyl*-, m.p. 159—160°, -*acridines* are prepared by dehydrogenation of their 9 : 10-dihydro-derivatives with HgO in EtOH. H. B.

Double linkings. V. Thermochromic ethylenes. E. BERGMANN and H. CORTE (Ber., 1933, **66**, [*B*], 39—43).—The behaviour of thermochromic ethylenes is completely analogous with that of fulvenes, attributed to the occurrence of diradical forms. The presence of a crossed, conjugated system, particularly if associated with a ring, appears essential for the existence of a coloured variety. Repetition of the ring system usually favours the diradical state. The formation with Br of halogen-rich, labile compounds of the perbromide type is parallel with the thermochromic phenomenon. The thermochromism of benzhydrylideneanthrone (I) cannot be due to thermal disaggregation of an associated product, since it has an approx. normal mol. wt. in freezing dioxan and C_6H_6.

Na diphenylmethyl is caused to react with the requisite ketone and the carbinol is dehydrated with AcCl. Xanthone thus gives 9-*hydroxy*-9-*benzhydrylxanthen*, m.p. 226°, whence *benzhydrylidenexanthen*, $X<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C{:}CPh_2$ (II) (II, X=O), m.p. 197°, yielding an unstable additive *product*, $C_{26}H_{18}OBr_4$, m.p. 143° (decomp.). Thioxanthone gives successively 9-*hydroxy*-9-*benzhydrylthioxanthen*, m.p. 208°, 9-*benzhydrylidenethioxanthen* (II, X=S), m.p. 243°, giving a *dibromide*, m.p. 210° (decomp.), and a red *compound*, decomp. 170°. *N*-Methylacridone yields impure 9-*hydroxy*-9-*benzhydryl*-N-*methylacridan*, m.p. about 218° (slight decomp.), whence 9-*benzhydrylidene*-N-*methylacridan* (I, X=NMe), m.p. 249°, giving a *hexabromide*, decomp. 147°, passing when cryst. from AcOH into a *pentabromide*, m.p. >250°. 9 : 9-Diphenylanthrone yields 10-*hydroxy*-9 : 9-*diphenyl*-10-*benzhydryl*-9 : 10-*dihydroanthracene*, m.p. 229—230°, whence the corresponding hydrocarbon (II, X=CPh_2), which is not thermochromic and does not absorb Br. 9-*Hydroxy*-2-*methoxy*-9-*benzhydrylthioxanthen*, m.p.

207—209°, from 2-methoxythioxanthone, and 2-*methoxy*-9-*benzhydrylidenethioxanthen*, m.p. 204—205°, are described. Bromination of (I) in $CHCl_3$ affords anthraquinone; ill-defined compounds are formed in CS_2. H. W.

Tyrosine-*N*-acetic acid. General method for preparing symmetrical and asymmetrical imino-dibasic acids. D. A. HAHN and A. LITZINGER (J. Amer. Chem. Soc., 1932, **54**, 4663—4667).—Hydrolysis of 5-*p*-hydroxybenzyl-3-methylhydantoin-1-acetic acid with aq. $Ba(OH)_2$ at 100° (bath) gives *tyrosine-N-acetic acid* ($+H_2O$), m.p. 228—230° (decomp.) [*hydrochloride*, m.p. 212·5—213°; *Me*$_2$ ester *hydrochloride*, m.p. 163—165°, decomp. 200°; *K* ($+2H_2O$), m.p. 250—255° (decomp.), *K*$_2$ ($+1{\cdot}5H_2O$), m.p. 174—200° (decomp.), *Na* ($+H_2O$), m.p. 180—186° (decomp.), *NH*$_4$, m.p. 218·5—220° (decomp.), *Ag* ($+H_2O$), m.p. 148·5—149·5° (decomp.), and *Ba* ($+3H_2O$), m.p. 223—227° (decomp.), salts; *complexes* $C_{11}H_{11}O_5NPb,H_2O$, m.p. 260—262° (decomp.), $(C_{11}H_{11}O_5NBa)_2,Ba(OH)_2,H_2O$, m.p. > 315°, $(C_{11}H_{11}O_5NCu)_2,H_2O$, m.p. 241—242·5° (decomp.), $[(C_{11}H_{12}O_5N)_2Cd,5H_2O],4H_2O$, m.p. > 315°, and $C_{11}H_{11}O_5NCd,2H_2O$, m.p. 205—208° (decomp.)]. *Phenylalanine-N-phenylacetic* ($+H_2O$), m.p. 224—226° (decomp.), and -*N-acetic acid*, m.p. 220—228° (decomp.), are prepared by similar hydrolysis of 5-benzyl-3-methylhydantoin-1-phenylacetic and -1-acetic acid, respectively. H. B.

Optically active 5 : 5-disubstituted hydantoins. H. SOBOTKA, M. F. HOLZMAN, and J. KAHN (J. Amer. Chem. Soc., 1932, **54**, 4697—4702).—5-Phenyl-5-ethylhydantoin is resolved by brucine into d- (I), m.p. 237°, $[\alpha]_D$ +123° in EtOH, and l- (II), m.p. 235—237°, $[\alpha]_D$ −121° in EtOH, forms. *dl*-α-Amino-α-phenylbutyric acid (III) [*Cu* salt ($+2H_2O$)] is resolved through its *formyl* derivative, m.p. 193°, by quinine into d- (*formyl* derivative, m.p. 212°; *Et* ester, decomp. about 270°, $[\alpha]_D$ +36° in H_2O) and l-*forms*; these are very resistant to racemisation and are convertible into, and also produced by hydrolysis of, (I) and (II), respectively. *iso*Propylcyanoacetamide (from $CN{\cdot}CHPr^{\beta}{\cdot}CO_2Et$ and conc. aq. NH_3), allyl iodide, and NaOEt give iso*propylallylcyanoacetamide*, m.p. 87°, converted by NaOBr into 5-iso*propyl*-5-*allylhydantoin*, m.p. 187°, which is resolved by quinine into the d-*form*, $[\alpha]_D$ +7° in EtOH. 5-*iso*Propyl-5-β-bromallylhydantoin, m.p. 214—215°, and 3 : 5-*diphenyl*-5-*ethyl*-2-*thiohydantoin*, m.p. 143° [from (III) and PhNCS], are described. Pharmacological data are given for (I), (II), and the *dl*-form. H. B.

Preparation of optically active thiohydantoins and the racemisation of amino-acids as their azlactones. F. A. CSONKA and B. H. NICOLET (J. Biol. Chem., 1932, **99**, 213—216).—When *d*-alanine is heated with NH_4SCN and 10% AcOH in Ac_2O at 100° d-2-*thio*-1-*acetyl*-5-*methylhydantoin*, m.p. 161—162°, $[\alpha]^{20}$ +118·5° in EtOH, is obtained, but if the NH_4SCN is added only after heating with AcOH–Ac_2O for 0·5 hr., only the *dl*-compound is obtained. Thiohydantoin formation also occurs when < 2 mols. of Ac_2O are used, partial racemisation occurring. It is suggested that the active azlactone initially formed is then racemised by Ac_2O, such racemisation being prevented by its rapid quant. reaction with NH_4SCN (cf. this vol., 156). J. W. B.

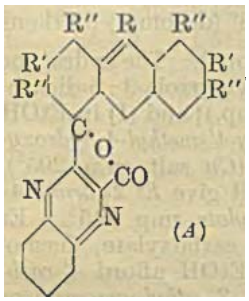
Hydroxyarylazo-derivatives of the pyrazole group. G. B. CRIPPA and M. LONG [with G. PERRONCITO] (Gazzetta, 1932, **62**, 944—953).—4-Benzeneazo-1-phenyl-3-methyl-5-pyrazolone with Me_2SO_4 or Et_2SO_4 gives 5-*Me* and 5-*Et ethers*, m.p. 42° and 80°, respectively, both of which are reduced by Zn in AcOH to rubazonic acid, m.p. 181° (A., 1882, 602), Me being eliminated. The following 4-arylazo-1-phenyl-3-methyl-5-pyrazolones are obtained by coupling 1-phenyl-3-methyl-5-pyrazolone with diazonium salts: o-, m-, and p-*tolyl*, m.p. 187°, 116°, and 137°; 1 : 3- and 1 : 4-*dimethyldiphenyl*, m.p. 159° and 131°; p-*chlorophenyl*, m.p. 140°; p-*bromophenyl*, m.p. 151° (*Me ether*, m.p. 119°); o- and p-*anisyl*, m.p. 109° and 135°; o- and p-*phenetyl*, m.p. 89° and 136°; p-*acetamido*- and p-*benzamido-phenyl*, m.p. 139° and 149°; p-*acetophenyl*, m.p. 136° (*oxime*, m.p. 187°; *phenylhydrazone*, m.p. 148°; *semicarbazone*, m.p. 260°); o-, m-, and p-*nitrophenyl*, m.p. 209°, 183°, and 196°; α-*naphthyl*, m.p. 200° (*Et ether*, m.p. 98°); β-*naphthyl*, m.p. 184°; β-*nitro*-α-*naphthyl*, m.p. 139°; 4′-*nitro*-α-*naphthyl*, m.p. 125°; 3-*acenaphthyl*, m.p. 146°, and pp′-*azodiphenylbis*-4-(1-*phenyl*-3-*methyl*-5-*pyrazolone*), m.p. 275° (*Me ether*, m.p. 204°). E. E. J. M.

Oxidation colours derived from 5 : 6-diaminouracil. M. T. BOGERT and D. DAVIDSON (J. Amer. Chem. Soc., 1932, **54**, 4754).—5 : 6-Diaminouracil reacts with *m*-$C_6H_4(NH_2)_2$, *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$, and *m*-$C_6H_4(OH)_2$ in presence of H_2O_2 to give substances which dye animal fibres purple, old rose, and salmon, respectively. H. B.

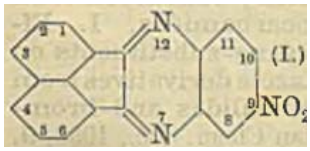
Application of calorimetry to pyrroles and pyrrole dyes. II. Calorimetric determinations with simple and polynuclear pyrrole derivatives. A. STERN and G. KLEBS (Annalen, 1932, **500**, 91—108).—The following nos. give the mol. heats of combustion (kg.-cal. at 15°) at const. pressure and vol., respectively: Me 2 : 4-dimethylpyrrole-5-carboxylate, 1029·4, 1028·7; Me 5-carbomethoxy-2 : 4-dimethyl-3-pyrrylpropionate, 1509·4, 1508·3; Et 2 : 4-dimethyl-3-propylpyrrole-5-carboxylate, 1645·3, 1643·4; 3 : 3′- dicarbethoxy-2 : 4 : 2′ : 4′-tetramethylpyrromethene, 2414·4, 2412·6, -dipyrrylmethane, 2472·0, 2470, and -dipyrrylethane, 2628·5, 2626·2; Et 3-propionyl-2 : 4-dimethylpyrrole-5-carboxylate, 1549·7, 1548·4; Et 5-propionyl-2 : 4-dimethylpyrrole-3-carboxylate, 1549·3, 1548·0; Et 4-methyl-2-α-hydroxyethylpyrrole-3 : 5-dicarboxylate, 1603·6, 1602·1; 1-, 1286·6, 1285·6, and 2-, 1283·0, 1282·0, -phenylpyrroles; Me 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate, 1184·9, 1184·5; 5-carbomethoxy-2 : 4-dimethyl-3-pyrrylacrylic acid, 1288·2, 1287·8; Et (?)-hydroxy-2 : 4-dimethylpyrrole-3-carboxylate, 1129·1, 1128·5; 2 : 4 : 2′ : 4′-tetramethyl-3 : 3′-diethyldipyrryl ketone, 2361·8, 2359·2; dicryptopyrrylphorone, 3614·9, 3610; Me 2 : 4-dimethylpyrrole-3-carboxylate, 1029·4, 1028·7; Et 3-formyl-2 : 4-dimethylpyrrole-5-carboxylate, 1233·8, 1233·1; Et 5-formyl-2 : 4-dimethylpyrrole-3-carboxylate, 1233·7, 1233·0; Et 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate, 1436·4, 1435·1; 3 : 5-dipropionyl-2 : 4-diethyl-

pyrrole, 1922·2, 1920; Me 5-carboxy-2 : 4-dimethylpyrrole-3-carboxylate, 1023·4, 1023·2; Et 4-methyl-2-hydroxymethylpyrrole-3 : 5-dicarboxylate, 1459·9, 1459·2; Et 2 : 4 : 5-trimethylpyrrole-3-carboxylate, 1338·1, 1336·8; Et 5-carbethoxy-2 : 4-dimethylpyrrole-3-glyoxylate, 1564·0, 1563·3; dipyrrylmethane, 1220·3, 1219·4; dipyrryl ketone, 1115·8, 1115·5; indole, 1021·1, 1020·4. The heats of formation of the above compounds are also given. The contributions of various groups to the mol. val. are calc. H. B.

Dyes derived from quinoxaline-2 : 3-dicarboxylic acid. P. C. Dutta (Ber., 1932, 65, [*B*], 1791—1793; cf. A., 1926, 1153; 1927, 977; 1932, 66).—Resorcinol, quinoxaline-2 : 3-dicarboxylic acid, and anhyd. $ZnCl_2$ at 180—190° afford *resorcinolquinoxalinedicarboxylein* (I) (*A*, R=O, R′=OH, R″=H), m.p. 248° after softening at 196°. *Orcinol*-, m.p. 206°, *phloroglucinol*-, m.p. above 290°, m-*aminophenol*- (*A*, R=NH, R′=OH, R″=H), m.p. above 290°, and m-*diethylaminophenol*- (*A*, R=O, R′=NEt_2, R″=H), m.p. 178° after softening at 164°, -*quinoxalinedicarboxylein* are similarly prepared. (I) and Br in EtOH yield *tetrabromoresorcinolquinoxalinedicarboxylein* (*A*, R=O, R′=OH, R″=Br), m.p. above 290°. The dyes are paler than the pyrazinedicarboxyleins and their fluorescence is less intense. H. W.



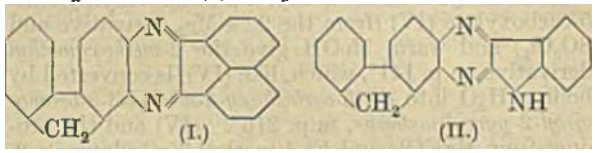
Dyes derived from acenaphthenequinone. III. Azines and indigoid vat dyes. S. K. Guha (J. Indian Chem. Soc., 1932, **9**, 423—427).—9-*Nitro*- (I), m.p. > 310°, 3-*chloro*-9-*nitro*-, m.p. 287°, 3-*bromo*-9-*nitro*-, m.p. 295°, and 3 : 4 : 9-*trinitroacenaphthaphenazine*, m.p. 300—301°, are prepared by condensation of appropriately substituted derivatives of acenaphthenequinone and *o*-$C_6H_4(NH_2)_2$. 9-*Aminoacenaphthaphenazine*, m.p. > 310°, is prepared either from (I) or by condensation of reduced chrysoidine with acenaphthenequinone. All are yellow dyes for wool. 3-*Chloro*-, m.p. 280°, 3-*bromo*-, m.p. 287°, and 3 : 4-*dinitro*-8-*keto*-7-*acenaphthylidene*-3′-*oxythio*(1′)-*naphthen*, m.p. > 300° (named thionaphthenacenaphthyleneindigos), are obtained from the acenaphthenequinones and oxythionaphthen in AcOH–HCl, and are red vat dyes of Ciba-scarlet G. type (cf. A., 1908, i, 674, 1011; G.P. 282,170). H. A. P.



Isatide and isatol. G. Heller (J. pr. Chem., 1932, [ii], **135**, 222—224).—The conclusions of Sumpter (A., 1932, 951) are criticised. Structures are suggested for α- and β-isatols (cf. A., 1925, i, 1166; 1929, 1315). H. B.

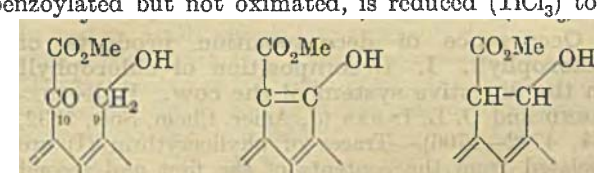
Active hydrogen atoms of polymeric indoles. O. Schmitz-Dumont and K. Hamann (Ber., 1933, 66, [*B*], 71—76).—The behaviour of di-indole (I), diskatole (II), di-7-methylindole, and tri-indole (III) towards MgMeI in amyl ether, $C_6H_4Me_2$, and mixtures of Ph_2O and $C_6H_4Me_2$ indicates the presence of 2, 2, 2, and 3 active H atoms, respectively, whilst monomeric indoles are found to have 1 active H. Depolymerisation of the polymerides under the action of MgMeI does not occur, since they can be almost quantitatively recovered. Simple addition of the monomerides to *cyclo*butane and *cyclo*hexane derivatives in the respective cases of (I) and (III) appears excluded, since with PhNCO, (I), (II), and (III) afford the *carbamides*, $C_{23}H_{19}ON_3$, m.p. 179—180°, $C_{27}H_{23}ON_3$, m.p. 219°, and $C_{31}H_{26}ON_4$, m.p. 217°, respectively. H. W.

Dyes derived from acenaphthenequinone and isatin : fluorenoacenaphthazines and fluorenoindazines. P. C. Dutta (Ber., 1932, **65**, [*B*], 1793—1795; cf. A., 1932, 1043).—Acenaphthenequinone and 1 : 2-diaminofluorene in boiling AcOH afford *fluorenoacenaphthazine* (I), m.p. 288°. The 5-*nitro*-, m.p.



> 295°, and 5 : 6-*dinitro*-, m.p. > 295°, compounds, are derived similarly from the corresponding acenaphthenequinones. *Fluorenoindazine* (II), m.p. > 295°, is prepared from isatin and 1 : 2-diaminofluorene in boiling AcOH. From substituted isatins the following fluorenoindazines are derived; 5-*nitro*-, m.p. > 295°; 5-*bromo*-, m.p. > 295°; 5 : 7-*dibromo*-, m.p. > 290°; 5-*bromo*-7-*nitro*-, m.p. > 295°; 5-*chloro*-, m.p. 290°. Comparison of the compounds of this series with the fluorenophenanthrazines shows that the depth of colour increases with the complexity of the mol. even without the presence of chromophoric or auxochromic groups. H. W.

Conversion of chlorophyll *b* into chlorophyll *a*. A. Stoll and E. Wiedemann (Naturwiss., 1932, **20**, 889).—Phæophorbide *b* [as (I)] (or phæophytin *b*) and conc. HCl containing Et_2O give an anhydrophæophorbide *b*, $C_{35}H_{37}O_5N_4$ (±4H) [as (II)], which can be benzoylated but not oximated, is reduced ($TiCl_3$) to



phæophorbide *a* [as (III)], and is reduced (H_2, Pd) to hydrophæophorbide *a*. The formulæ previously proposed (A., 1932, 1266) are thus confirmed. The conversion of chlorophyll *b* (IV) into chlorophyll *a* (V) can be accomplished as follows: (IV) ⟶ (I) ⟶ (II) ⟶ (III) —— chlorophyllide *a* $\xrightarrow{\text{l. tol}}$ (V). H. B.

Chlorophyll. XXVIII. Synthesis of deoxophylloerythrin; bromovinylpyrroles. H. Fischer and J. Riedmair (Annalen, 1932, **499**, 288–301).—Synthetic deoxophylloerythrin (I) (A., 1931, 1431) (*hæmin*; *Cu* salt) is $C_{33}H_{36}O_2N_4$; the *Me* ester, m.p. 264° (corr.) (*hæmin*), is identical with

" analytical " deoxophylloerythrin Me ester. Catalytic reduction of (I) (or the " analytical " product) results in the uptake of 5—6 mols. of H_2; some fission to dipyrrylmethane derivatives occurs. 1 : 3 : 5 : 8-Tetramethyl-2 : 4 : 6-triethyl-7-β-carboxyethylporphin (II) and 6-bromopyrroporphyrin (III) are by-products in the synthesis of (I). The amount of (II) is a min. when succinic acid is used at 140° (cf. *loc. cit.*), but is the main product with methylsuccinic acid at 140° or AcOH–HBr at 180°. The formation of (II) and (III) shows that the bromovinyl group (of the pyrromethene used) is partly eliminated and partly reduced to Et. The above results support the constitution assigned to (I). The mixture of basic porphyrins obtained from 5-carboxy-4 : 3′ : 5′-trimethyl-4′-ethyl-3-bromovinyl- and 5-bromo-4 : 3′-dimethyl-3 : 4′-diethyl-5′-bromomethyl-pyrromethene hydrobromides could not separated (without decomp. or change in structure).

Et 4-methyl-2-chloromethyl-3-β-bromovinylpyrrole-5-carboxylate (IV) (from the 2 : 4-Me_2 derivative and SO_2Cl_2) and warm MeOH give the 2-*methoxymethyl* derivative, m.p. 141°, which, like (IV), is converted by boiling H_2O into *di-(5-carbethoxy-4-methyl-3-β-bromovinyl-2-pyrryl)methane*, m.p. 216°. (IV) and the product from MgEtBr and Et 4-methyl-3-ethylpyrrole-2-carboxylate give 5 : 5′-*dicarbethoxy*-4 : 3′-*dimethyl*-4′-*ethyl*-3-β-*bromovinyldi*-2-*pyrrylmethane*, m.p. 178°. 2-Formyl-4-methyl-3-β-bromovinylpyrrole-5-carboxylic acid (V) and cryptopyrrolecarboxylic acid with AcOH–48%HBr afford *o-carboxy*-4 : 3′ : 5′-*trimethyl*-4′-β-*carboxyethyl*-3-β-*bromovinylpyrromethene hydrobromide*, converted by Br in AcOH–HCO_2H into a *compound*, $C_{17}H_{20}N_2Br_4$ (*Me* ester). 5-*Carboxy*-4 : 4′ : 5′-*trimethyl*-3′-β-*carboxyethyl*-3-β-*bromovinylpyrromethene hydrobromide*, from (V) and hæmopyrrolecarboxylic acid, is similarly brominated to a *substance*, $C_{17}H_{20}O_2N_2Br_4$. 5-Carboxy-4 : 3′ : 5′-trimethyl-4′-ethyl-3-β-bromovinylpyrromethene hydrobromide and Br in AcOH–HCO_2H give *o-bromo*-4 : 3′ : 5′-*trimethyl*-4′-*ethyl*-3-β-*bromovinylpyrromethene hydrobromide*, which when treated with KI in AcOH and then basified (10% aq. NH_3 in MeOH) affords the free *base*, m.p. 144° [reduced (H_2, PtO_2, AcOH) to a *compound*, $C_{16}H_{19}N_2Br_3$, m. p. > 280°]. H. B.

Occurrence of decomposition products of chlorophyll. I. Decomposition of chlorophyll in the digestive system of the cow. P. Rothemund and O. L. Inman (J. Amer. Chem. Soc., 1932, **54**, 4702—4706).—Traces of phylloerythrin (I) are isolated from the contents of the first and second stomachs of freshly-killed cows; (I), rhodo-, phyllo-, and pyrro-porphyrins, and traces of two other pigments (probably porphyrins) are extracted from the contents of the third and fourth stomachs. Prophorbides and (I) are isolated from the third and fourth stomachs of sheep. The stomach contents of a calf on a milk diet contain no porphyrins, indicating that these arise from chlorophyll. The view that the five-membered ring attached to the porphin structure occurs in both (I) and chlorophyll *a* is favoured by the above results. H. B.

Porphyrin syntheses. XLVI. Synthesis of the parent substance [ætioprotoporphyrin] of protoporphyrin and hæmin. H. Fischer, A. Kirstahler, and B. von Zychlinski (Annalen, 1932, **500**, 1—14).—The hæmin of 1 : 3 : 5 : 8-tetramethyl-6 : 7-diethylporphin (improved prep. given; cf. A., 1931, 967), Ac_2O, and $SnCl_4$ give (after removal of Fe with HBr–AcOH) *diacetylætiodeuteroporphyrin*, m.p. >335° (*Cu* salt; *hæmin*), converted by conc. EtOH–KOH in H_2 at 140° into *ætiohæmatoporphyrin* [*di-α-hydroxyethylætiodeuteroporphyrin*], which, when heated at 165°/high vac., is dehydrated to *ætioprotoporphyrin* [1 : 3 : 5 : 8-*tetramethyl*-6 : 7-*diethyl*-2 : 4-*divinylporphin*] (*hæmin*).

During the (nuclear) carbethoxylation of cryptopyrrole and 2 : 4-dimethyl-3-propylpyrrole, 20—30% of the respective N-*carbethoxy*-derivatives, b.p. 125—135°/11 mm. and 144—149°/14 mm., are produced. Et 2-formyl-4-methylpyrrole-3 : 5-dicarboxylate (I) and N_2H_4,H_2O in AcOH give the *pyridazine*, NH·CO·C——CMe / N=CH·C·NH·C·CO_2Et, m.p. 3'8° (decomp.) (darkens at 295°) (all m.p. except this are corr.). The hydrazone of Et 2-formyl-4-hydroxymethylpyrrole-3 : 5-dicarboxylate [*oxime*, m.p. 194° (decomp.)] and (I) in EtOH afford 3 : 5 : 3′ : 5′-*tetracarbethoxy*-4′-*methyl*-4-*hydroxymethylpyrroaldazine*, m.p. 197° (*Cu* salt, m.p. 205°). (I), Br, and aq. $KBrO_3$ in AcOH give *Et* 2-*formyl*-4-*bromomethylpyrrole*-3 : 5-*dicarboxylate*, m.p. 145°. Et 5-formyl-2 : 4-dimethylpyrrole-3-carboxylate, hæmopyrrole, and HBr (*d* 1·49) in EtOH afford 4′-*carbethoxy*-4 : 5 : 3′ : 5′-*tetramethyl*-3-*ethylpyrromethene hydrobromide*, decomp. 214°. 3-*Carbethoxy*-4 : 5 : 3′ : 5′-*tetramethyl*-4′-*ethylpyrromethene hydrobromide*, m.p. 176° (decomp.), is similarly prepared from cryptopyrrole and Et 5-formyl-2 : 3-dimethylpyrrole-4-carboxylate or (in small amount with m.p. 245°) from cryptopyrrolealdehyde (II) and Et 2 : 3-dimethylpyrrole-4-carboxylate. 2-Methyl-4-ethylpyrrole and (II) similarly give 5 : 3′ : 5′-*trimethyl*-3 : 4′-*diethylpyrromethene hydrobromide*, m.p. 183° (decomp.). H. B.

Directive effect of [nuclear] substituents on cyclisation of *s*-diarylthiocarbamides. I. Effect of fluoro-, iodo-, and cyano-substituents on formation of anilinobenzthiazole derivatives from *p*-monosubstituted thiocarbanilides and bromine. R. F. Hunter (J. Indian Chem. Soc., 1932, **9**, 435—440).—*p*-Fluoro- and *p*-iodo-*s*-diphenylthiocarbamides, analogously with the *p*-Cl- and *p*-Br-compounds, undergo cyclisation with Br in the unsubstituted ring; the *p*-CN-group has a like effect. In every case the constitution of the resulting thiazole was confirmed by synthesis from 1-chlorobenzthiazole and the appropriately substituted aniline. The following are described: p-*fluoro*-, m.p. 175—176°, p-*iodo*-, m.p. 168°, and p-*cyano*-s-*diphenylthiocarbamide*, m.p. 161—162°; 4′-*fluoro*-, m.p. 200—201°, 4′-*iodo*-, m.p. 213°, and 4′-*cyano*-1-*anilinobenzthiazole*, m.p. 208° (the intermediate *perbromides* are described). H. A. P.

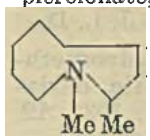
Constitution and classification of sulphur dyes. H. E. Fierz-David (Naturwiss., 1932, **20**, 945—947).—A discussion. R. K. C.

Actinodaphnine: an alkaloid from *Actinodaphne Hookeri*, Meissn. S. Krishna and T. P. Ghose (J. Indian Chem. Soc., 1932, **9**, 429—433).—

Actinodaphnine, $C_{18}H_{19}O_4N$, m.p. 210—211°, $[\alpha]_D^{20}$ +37·77° in abs. EtOH [*hydrochloride*, m.p. 280—281° (decomp.); *hydriodide*, m.p. 264—265° (decomp.); *picrate* (+$1H_2O$), decomp. 220—222°; *sulphate* (+$3H_2O$), m.p. 249—250° (decomp.); *methiodide*, m.p. 243—244°; *Bz*, m.p. 232—233°, and *Ac* derivatives, m.p. 229—230° (Ac_2O, not AcCl)], is extracted from the bark of *A. Hookeri* with 90% EtOH and Na_2CO_3, and purified by crystallisation from aq. $COMe_2$. It is considered (Zeisel) to contain an OMe and NMe group. H. A. P.

Syntheses in the homoneurine series. II. Homoneurines of the *Cinchona* alkaloids. E. Macovski and A. Silberg (J. pr. Chem., 1932, [ii], **135**, 237—244).—*Dihomoneurine halides* [*diallyl halides*] of the following are described: quinine: *iodide*, m.p. 160° (decomp.); *bromide*, m.p. 159—160° (becoming yellow) (*dihydrate*, m.p. 152—155°); quinidine: *iodide* (+1·5H_2O), m.p. 155—156° (decomp.); *bromide*, m.p. 152° (decomp.); cinchonine: *iodide*, m.p. 248—250° (decomp.); *bromide*, m.p. about 222° (decomp.); cinchonidine: *iodide*, m.p. 238—239° (decomp.); *bromide*, m.p. 225° (decomp.). Successive treatment of the above iodides with AgCl and H_2PtCl_6 gives the corresponding *chloroplatinates* (all +$2H_2O$), blackens at 220°, —, blackens 235—240° (decolorised about 220°), and blackens and decomp. about 225°, respectively. The quaternary *bromide* from cinchonine (1 mol.) and allyl bromide (1 mol.) has m.p. 240—241° (decomp.). H. B.

Lupin alkaloids. VI. G. R. Clemo, G. R. Ramage, and R. Raper (J.C.S., 1932, 2959—2969).—Et pyridine-2-carboxylate (improved prep.), Et succinate, and NaOEt afford *Et* β-2-*pyridoylpropionate*, b.p. 135—140°/0·2 mm. (*picrolonate*, m.p. 104°), reduced (Clemmensen) to *Et* γ-2-*pyridylbutyrate* (I), b.p. 145—150°/18 mm., 100°/0·2 mm. (I), on hydrolysis and subsequent reduction with Na–EtOH, yields 4-*keto-octahydropyridocoline*, b.p. 146°/20 mm., and reduction with Na–EtOH alone gives δ-2-*piperidyl*-n-*butyl alcohol*, b.p. 149°/17 mm., which with PBr_5 in C_6H_6 followed by aq. NaOH forms *octahydropyridocoline* "A," b.p. 72°/16 mm. [picrate, m.p. 194°, methiodide, m.p. 335°, chloroaurate, m.p. 167°, identical with those derived from norlupinane (A., 1931, 499; 1932, 178); *picrolonate*, m.p. 245°]. Octahydropyridocoline "*B*" (*loc. cit.*) gives a *picrolonate*, m.p. 191°. The Hofmann reaction on the methiodide of "*A*," followed by catalytic reduction, gives a mixture of three bases, $C_{10}H_{21}N$, "*C*" (*picrolonate*, rhombs, m.p. 153°, converted by two crystallisations into monoclinic prisms, m.p. 147°; *picrate*, m.p. 88°; *methiodide*, m.p. 164°), "*D*" (*picrolonate*, m.p. 167°; *picrate*, m.p. 94°; methiodide, m.p. 168°), and "*E*" (*picrate*, m.p. 197°; *picrolonate*, m.p. 129°; *methiodide*, m.p. 263°), "*C*" and "*D*" being separated as the picrolonates and "*E*" as the picrate. Similar reduction of the methiodide of "*B*" affords a mixture of "*D*" and "*E*." CNBr gives with "*A*" a cryst. substance, m.p. 283°, but this is not formed with "*B*." 2-Crotylpyridine (improved prep.) is reduced catalytically to 2-*n*-butylpiperidine, b.p. 75°/14 mm. (*hydrochloride*, m.p. 182°; *picrolonate*, m.p. 182°), which gives, with CH_2O and HCO_2H, 1-*methyl*-2-n-*butylpiperidine* (II), b.p. 78—80°/15 mm. (*chloroaurate*, m.p. 90°; picrolonate, picrate, and methiodide are identical with those obtained from "*C*"). "*C*" is therefore identical with (II) and "*D*" and "*E*" are isomeric forms of 1-methyl-*cyclo*azadecane or "*E*" may have the structure (III). This indicates that "*A*" and "*B*" are structurally identical stereoisomerides and norlupinane occurs as *cis*- and *trans*-isomerides of the decalin type.



(III.)

Me lupinate affords a mixture of α-, m.p. 240° (decomp.), and β-*methiodides*, m.p. 170°. Hofmann degradation of the α-methiodide results in a mixture of two bases, $C_{10}H_{19}N$ (IV), b.p. 48°/1 mm. [*picrate*, m.p. 179°; *methiodide*, m.p. 258—259° (decomp.)], and a second fraction, b.p. 95°/1 mm. (IV), reduced (Pt–H) to "*E*." Similar treatment of the β-methiodide yields a β-base, b.p. 45°/1 mm. (picrate, m.p. 148—149°), also reduced to "*E*." The methochloride of "*E*" when heated isomerises to an open-chain *tert.* base $NMe_2{\cdot}C_9H_{18}Cl$, the methiodide, m.p. 91°, of which gives with Ag_2O, NMe_3, and an oil, possibly 9-hydroxy-Δ^{α}-nonene, since it is oxidised to suberic acid. Aminolupinane and HNO_2 afford *iso*norlupinene, $C_9H_{15}N$, b.p. 43—45°/1 mm. [forming a *picrolonate*, m.p. 189° (changing to the *picrolonate* of norlupinene, m.p. 229—230°, on repeated crystallisation), and a *picrate*, m.p. 147°], and a small quantity of hydroxynorlupinane, m.p. 109°. Norlupinene and Br give a Br_4-derivative, m.p. 174°, from which a Br_5-compound, m.p. 84—85°, is obtained, whilst *iso*norlupinane forms a Br_3-derivative, m.p. 156—157°. The bearing of these facts on the structure of lupinine is discussed. F. R. S.

Attempted synthesis of oxyprotoberberine and a synthesis of 3-methoxyoxyprotoberberine. S. Chakravarti and A. P. M. Nair (J. Annamalai Univ., 1932, **1**, 186—189; cf. A., 1927, 1096).—The acid chloride of phthalidecarboxylic acid in cold dry C_6H_6 during several hr. affords with β-phenyl- and β-*m*-anisyl-ethylamine, *phthalidecarboxy*-β-*phenylethylamide* (I), m.p. 155°, and *phthalidecarboxy*-β-m-*anisylethylamide* (II), m.p. 105°, respectively. (I) when treated with $POCl_3$ or P_2O_5 and then with Zn dust in AcOH affords no oxyprotoberberine; but when cyclised with PCl_5 gives a *substance*, m.p. 153°. (II) when heated at 100° with $POCl_3$, and the product reduced by Zn in boiling AcOH affords 3-*methoxyoxyprotoberberine*, m.p. 143°. J. L. D.

Synthesis of 3 : 10-dimethoxytetrahydroprotoberberine. S. Chakravarti, N. Ananthaivaidyanathan, and A. Venkatasubban (J. Annamalai Univ., 1932, **1**, 190—193; cf. A., 1929, 335).—β-*m*-Anisylethylamine with *p*-anisylacetic acid at 180° during 2 hr. affords p-*anisylaceto*-β-m-*anisylethylamide*, m.p. 81°, converted by $POCl_3$ during 2 hr. at 100° into 6-methoxy-1-(4′-methoxybenzyl)-3 : 4-dihydro*iso*quinoline (*picrate*, m.p. 146°), which with Zn dust and dil. H_2SO_4 gives 6-methoxy-1-(4′-methoxybenzyl)-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (I) [*hydrochloride*, m.p. 196°; *picrate*, m.p. 192° (decomp.)]. (I) is converted into its *N*-formyl derivative, which with $POCl_3$ in boiling PhMe during 1·5 hr. affords 3 : 10-dimethoxydihydroprotoberberine (not isolated),

reduced (Zn–dil. HCl, 2 hr.) to 3 : 10-dimethoxytetrahydroprotoberberine, identical with a product previously described. J. L. D.

Strychnine and brucine. II. Dihydromethoxymethylhexahydrostrychnine and its derivatives. O. Achmatowicz (Rocz. Chem., 1932, 12, 936—942).—Methoxymethyldihydroneostrychnine on electro-reduction yields in addition to methoxymethyltetrahydrostrychnidine (I) (A., 1932, 406), *dihydromethoxymethylhexahydrostrychnine* (II), m.p. 116—118° (*methiodide*, m.p. 249—250°; *methochloride*, m.p. 210—212°; *nitrosoamine*, impure; NO-*diacetate*, an oil). (II) yields (I) when treated with $POCl_3$, and methyldihydrostrychnidinium sulphate on prolonged treatment with 50% H_2SO_4. R. T.

***Strychnos* alkaloids. LXIX. Further experiments on the fission of brucine with cyanogen bromide and fission of dihydrobrucine.** H. Leuchs and H. S. Overberg (Ber., 1933, 66, [*B*], 79—84; cf. A., 1932, 866).—Treatment of brucine with CNBr and of the product with $COMe_2$ yields the cyanoamide $C_{24}H_{26}O_4N_3Br$ (I), $[\alpha]_D$ +76·4°/*d*; the undissolved material with boiling MeOH gives brucine hydrobromide and a neutral *compound*, $C_{25}H_{29}O_5N_3$, m.p. about 80°, decomp. 90°, $[\alpha]_D^{21}$ −88°/*d* in AcOH. (I) is transformed by $KMnO_4$ in $COMe_2$ into much resinous matter and an *acid*, $C_{24}H_{26}O_7N_3Br$, $[\alpha]_D^{21}$ +87·5°/*d* in AcOH, by AgOBz in boiling $COMe_2$ mainly into brucine, also obtained by the action of C_5H_5N at 100°. Dihydrobrucine and CNBr in C_6H_6 smoothly yield the cyanoamide $C_{24}H_{28}O_4N_3Br$ (II), m.p. 240—242° (decomp.) after softening at 230°, $[\alpha]_D$ +58·2°/*d* in $CHCl_3$, apparently identical with the compound of Wieland and Gumlich (A., 1932, 629). (II) is converted by C_5H_5N into the *salt*, $C_{24}H_{28}O_4N_3Br,C_5H_5N$, decomp. about 280° after becoming discoloured at 250°, $[\alpha]_D^{21}$ −39·2°/*d* in H_2O, by $NPhMe_2$ into *dihydrobrucine methobromide*, $[\alpha]_D^{20}$ +31·6°/*d* in H_2O, and a neutral *substance*, $C_{32}H_{38}O_4N_4$, m.p. 168—170° after softening, $[\alpha]_D^{20}$ −41·7°/*d* in $CHCl_3$, and by NHPhMe into dihydrobrucine hydrobromide and the *compound* $C_{31}H_{36}O_4N_4$, m.p. 178—180° (slight decomp.) after softening at 170°, $[\alpha]_D$ +40·8°/*d* $CHCl_3$. (II) and NH_2Ph yield diphenylguanidine and resin. H. W.

Reaction with Grignard reagent and other reactions of *Strychnos* alkaloids. XII. H. Wieland and F. Hölscher (Annalen, 1932, **500**, 70—91).—The no. (mean val.) of active H atoms (Zerevitinov method using PhOMe as solvent in N_2) in the following are quoted in parentheses (where two nos. are given, the second is for C_5H_5N as solvent): strychnine (I) (1·3, 0·7); brucine (II) (1, 1); vomicine (2, 1); dihydrostrychnine (III) (1), dihydrobrucine (IV) (1); dihydrovomicine (1·5); strychnidine (V) (0); tetrahydrostrychnine (1·7); vomicidine (1); deoxyvomicine (1·7); the base $C_{16}H_{22}O_3N_2$ (A., 1932, 179) (1); the base $C_{16}H_{26}O_2N_2$ (*loc. cit.*) (1·1); the iodo-base, $C_{22}H_{25}O_3N_2I$ (A., 1929, 708) (1·1). The negative val. with (V) indicates that production of CH_4 is concerned with the lactam group of, *e.g.*, (I). MgMeI and (I) in PhOMe–*iso*amyl ether and N_2 give *deoxymethylstrychnine methiodide*, $C_{22}H_{24}ON_2,MeI$, m.p. 245—246° (decomp.), $[\alpha]_D^{18}$ +137·3° in H_2O [reduced (H_2, PtO_2, aq. EtOH) to its *tetrahydro*-derivative, m.p. 287° (decomp.), $[\alpha]_D^{19}$ −69° in H_2O], which may result from the change $>N\cdot CO\cdot CH_2\cdot \rightarrow >N\cdot CMe(OMgI)\cdot CH_2\cdot \rightarrow >N\cdot CMe{:}CH\cdot + MgI\cdot OH$; this also explains the production of CH_4 in the Zerevitinov determination, *i.e.*, it is not due to active H. The Grignard solution used could not be freed from MeI even in vac. Vomicine (which does not form a methiodide) does not give a deoxymethyl derivative. MgEtBr and (I) similarly give *deoxyethylstrychnine ethobromide*, m.p. 235° (decomp.) (sinters at 220°); MgPhBr does not react. MgMeI and (III) afford *deoxymethyldihydrostrychnine methiodide*, decomp. 241° (darkens at 200° and sinters at 231°), $[\alpha]_D^{18}$ +741° in 20% EtOH [*dihydro*-derivative, m.p. 295° (decomp.) (sinters at 285°), $[\alpha]_D$ +93° in 20% EtOH], whilst (II) gives *deoxymethylbrucine methiodide*, decomp. 263°, $[\alpha]_D^{18}$ +173° in H_2O [*tetrahydro*-derivative (anhyd. and +H_2O), m.p. 262—264° (decomp.), $[\alpha]_D^{21}$ (anhyd.) −36·2° in 20% EtOH]. 1-Ethyloxindole, which contains one active H (Zerevitinov) is recovered unchanged after treatment with MgMeI. These new derivatives are very unstable. The methiodides of (I) and (II) have α=0°, whilst those of (III) and (IV) (prepared by catalytic reduction) have $[\alpha]_D^{21}$ +30·3° and $[\alpha]_D$ +29·4° in 50% MeOH, respectively.

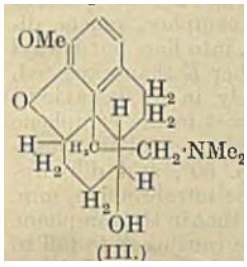
Dihydrovomicine and 20% MeOH–KOH in N_2 give (after neutralisation with dil. HCl) *dihydrovomicinic acid*, $C_{22}H_{28}O_5N_2,H_2O$, m.p. 291° (sinters at 165°), oxidised by CrO_3 (as previously described; A., 1932, 179) to *bisdihydrovomicyl*, $C_{44}H_{50}O_8N_4$, m.p. >310° (darkens gradually from 260°) (*dihydrochloride*). *Deoxyvomicinic acid*, $C_{22}H_{26}O_4N_2,2H_2O$, m.p. 205° (sinters at 165°), prepared from deoxyvomicine [*Br*-derivative, m.p. 266° (decomp.) (darkens at 200° and sinters at 260°)], is similarly converted into *dideoxyvomicyl*, $C_{44}H_{46}O_6N_4,H_2O$, m.p. >300° (darkens gradually above 200°). Bisdihydrodeoxyvomicyl, $C_{44}H_{50}O_6N_4$ [*dihydrochloride* (+H_2O), darkens above 200°], is prepared from dihydrodeoxyvomicine.

[With W. Munster.] The acids $C_{17}H_{22}O_5N_2$ and $C_{17}H_{24}O_5N_2$ from vomicine (A., 1932, 179) and CH_2N_2 in Et_2O–MeOH give the *Me* esters, m.p. 261—262° (decomp.) and 178—179° (slight decomp.) (sinters at 176°), respectively, which with MeI afford *substances*, $C_{37}H_{51}O_{10}N_4I,H_2O$, m.p. 207° (decomp.), and $C_{37}H_{55}O_{10}N_4I,2H_2O$, sinters at 183°, froths at 184°, and melts later to a clear liquid, respectively. The acid $C_{18}H_{24}O_7N_2$ (*loc. cit.*) and CH_2N_2 give a *methylbetaine Me* ester, $C_{20}H_{28}O_7N_2$, m.p. 283—285° (decomp.).

The formation of additive (1 : 1) compounds, decomp. 170—171° and 239—240°, respectively (cf. A., 1932, 629; Leuchs and Overberg, *ibid.*, 866), of brucine and dihydrobrucine with CNBr is confirmed.

Reductions in the morphine series. I. Dihydro-ψ-codeine. R. E. Lutz and L. F. Small (J. Amer. Chem. Soc., 1932, **54**, 4715—4730).—Catalytic reduction of ψ-codeine (I) and related compounds varies with the catalyst, solvent, and especially [H·]. Thus, reduction (H_2, PtO_2, AcOH) of the hydrochloride of (I) at temp. up to 60° gives 76—85% of the non-phenolic *dihydro-ψ-codeine* (II) (+H_2O), m.p. 121—

122° (all m.p. are corr.), m.p. (anhyd.) 155°, $[\alpha]_D^{20}$ −41·4° in EtOH [*hydrochloride* (+0·5H_2O), m.p. 239—241° (decomp.); *hydriodide*, m.p. 287° (rapid), 268—269° (decomp.) (slow heating)], and 5—15% of tetrahydro-ψ-codeine. The *methiodide* (+H_2O), m.p. 190—195° (rapid), 241—243° (decomp.) (slow heating), of (II) is converted by hot 12% NaOH into the non-phenolic dihydro-ε-methylmorphimethine (de-*N*-methyldihydro-ψ-codeine) [*hydriodide*, m.p. 232—235° (decomp.); *hydrochloride*, m.p. 222—224°], reduced (H_2, Pd–$CaCO_3$, EtOH) to the non-phenolic tetrahydro-ε-methylmorphimethine (dihydrode-*N*-methyldihydro-ψ-codeine) (III) [*hydrochloride* (+0·5 and 3H_2O), m.p. 187°; *hydriodide*, m.p. 225—226° (decomp.); *salicylate*, m.p. 198°; *H tartrate*, m.p. 195·5° (decomp.)]. Tetrahydro-ψ-codeine, m.p. 115—120° (sinters at about 100°) [hydrochloride, m.p. 263° (decomp.) *salicylate* (+2H_2O), m.p. 135—136°, (+H_2O), m.p. 165—166°], is best obtained by reduction (H_2, PtO_2, or Pd–$BaSO_4$, dil. AcOH) of (I); its methiodide is degraded by conc. aq. KOH to the phenolic tetrahydro-ε-methylmorphimethine, m.p. 196—197° (decomp.) (lit. 162—163°), $[\alpha]_D^{20}$ +192° in EtOH, which is reduced (H_2, Pd–$CaCO_3$, EtOH) to hexahydro-ε-methylmorphimethine (IV), m.p. 166·5—167·5° (lit. 155°), $[\alpha]_D^{20}$ +28° in EtOH [hydrochloride, m.p. 250—254° (decomp.) (lit. 213°); *H tartrate* (+H_2O), m.p. 114—115° (decomp.)]. Catalytic reduction of the *hydrochloride*, m.p. 211—212°, of ε-methylmorphimethine gives (III) and (IV); the amounts vary with the conditions used. (II) results by addition of 2H to a double linking and is then as stable as dihydrocodeine and -*iso*codeine to further reduction. Tetrahydro-ψ-codeine must result from a primary 1 : 4-addition of H_2 to O and C_7 or by direct reductive fission of the oxidic O; in the latter case, the 6 : 7-double linking of (I) is not directly concerned with the addition of the first mol. of H_2, but is saturated in the second stage of the reduction. (II) can be demethylated (HI) to the hydriodide of a new dihydro-γ-*iso*morphine (no details given). iso*Codeine H tartrate*, m.p. 185—186° (decomp.), and *dihydro*isocodeine *H tartrate* (+3H_2O), m.p. about 180°, are described.


OMe
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H
H
H

const. combining capacity of each protein for $H^{\cdot}$, the non-combination with Cl', and a linear relation of the log. of the mean activity coeff. of the acid with increasing protein concn. (A., 1932, 802). The combining capacities for $H^{\cdot}$ are $9{\cdot}6\times10^{-4}$ for (I), $13{\cdot}4\times10^{-4}$ for (II), and $8{\cdot}0\times10^{-4}$ for (III) in equivs. of combined $H^{\cdot}$ per g. of protein. F. O. H.

Effect of temperature on the titration curve of caseinogen. V. A. PERTZOFF and S. C. CARPENTER (J. Gen. Physiol., 1932, **16**, 257—265).—The data of Hoffman and Gortner (A., 1925, i, 1479) indicate that the effect of temp. is accounted for by the Bjerrum and not by the classical theory of ampholytes. F. O. H.

Reaction of proteins with iodic acid. H. BAUER and E. STRAUSS (Biochem. Z., 1932, **255**, 287—288).—When excess of HIO_3 is added to aq. solutions or suspensions of most proteins, oxidation of cystine, cysteine, and tryptophan occurs, I being therefore liberated. No reaction is obtained with glycine, proline, phenylalanine, tyrosine, histidine, and glucosamine. P. W. C.

Isolation of citrulline, δ-carbamido-ornithine, from tryptic digestion products of caseinogen. M. WADA (Proc. Imp. Acad. Tokyo, 1932, **8**, 367—370).—This isolation (A., 1930, 1224) is described. Digestion in 0·2% Na_2CO_3 solution produces ornithine, presumably by alkaline hydrolysis of citrulline. The latter gives proline with boiling conc. acids, and is not obtained by tryptic digestion of arginine.

Laws regulating the behaviour of organic dyes towards proteins, proteids, albuminoids, and nucleins. F. HUNDESHAGEN (Collegium, 1932, 854—861).—By testing these different substances with a solution of a mixture of an acid and a basic dye, "basophilic" substances which combine with acid dyes, "acidophilic" or "oxyphilic," which combine with basic dyes, and "amphophilic" or "neutrophilic" substances can be differentiated. Triacid or eosin dyes are the most suitable acid dyes for the purpose of this test. The N compounds can be arranged in the following order: proteins (most oxyphilic), nucleoalbumins, nucleoproteins, nucleins, nucleic acids (most basophilic). The oxyphilic character depends on the basic N groups in the proteins. The basophilic property is attributed to an acid complex, which contains H_3PO_4, present in nucleic acids but not in the first-mentioned proteins. The basophilic nature of proteins is intensified by introducing acid groups into the protein mol. An intensely basophilic product is produced in vegetable tannin of collagen. Dormant basophilic groups may be present in purely oxyphilic and amphophilic compounds, respectively, which can be made to function under conditions as described, and these are termed "pseudochromatic." D. W.

Contributions of synthesis to the investigation of proteins and their enzymes. M. BERGMANN (Naturwiss., 1932, **20**, 941—943).—A discussion. Certain synthetic dipeptides, including those of proline (A., 1932, 935), are not attacked by dipeptidases. No increase in Van Slyke N occurs when proline peptides are hydrolysed. In tryptic digestion of gelatin CO_2H and Van Slyke N increase equally, but in subsequent erepsin treatment the increase is in the ratio 1 : 0·3—0·5. Proline and oxyproline therefore occur in the interior of peptide chains.

Synthetic glycyldehydrophenylalanine is not attacked by dipeptidases, but an enzyme from kidney yields glycine, phenylpyruvic acid, and NH_3. The kidney is, therefore, a source of keto-acids and NH_3 derived from dehydrogenated NH_2-acids. R. K. C.

Phosphatides of human brain. II, III. Y. YOKOYAMA and B. SUZUKI.—See this vol., 176.

Micro-determination of mol. wt. Relationships between constitution and mol. depression of the m.p. of organic compounds. J. PIRSCH (Ber., 1932, **65**, [*B*], 1839—1842; cf. A., 1932, 713, 714, 925).—The ratio E/M is approx. const. for dicyclic compounds in which the 1 : 4-ring atoms are united by their *cis*-valencies through a $>CMe_2$ bridge (bornylamine, bornyl chloride, camphor, pinene dibromide). Borneol falls approx. into line, but bornyl bromide, m.p. 89°, shows a higher E than expected. 3-Bromocamphor diverges widely in its behaviour. Similar regularities appear to exist in the camphene series. The val. of E/M is approx. const. for *trans*-dipentene dihydrochloride, m.p. 50°, and dihydrobromide, m.p. 64°, and dipentene tetrabromide, m.p. 125°, but markedly smaller than that in the camphane series, fission of the CMe_2 bridge causing E to fall to $\frac{1}{6}$ of its val. H. W.

Sucharda and Bobranski's semimicro-method of elementary analysis. F. CALVET and L. MOSQUERA (Anal. Fís. Quím., 1932, **30**, 853—864).—The method ("Sammlung Vieweg," 1929, Heft 94) has been used with petrol gas as the source of heat. Ascarite (Na asbestos) is used instead of soda-lime, and decalin is used in the PbO_2 thermostat. Improvement has been obtained by mixing the substance with CuO. R. K. C.

Determination of halogens in organic substances. G. ILLARI (Annali Chim. Appl., 1932, **22**, 673—679).—Further tests confirm the validity of the author's method (A., 1930, 101). Heller's criticisms (A., 1929, 528, 1158) are answered. T. H. P.

Detection and determination of fluorine in organic compounds. W. BOCKEMÜLLER (Z. anal. Chem., 1932, **91**, 81—90).—A review of published methods. D. R. D.

Micro-determination of methoxyl. V. BRUCKNER (Mikrochem., 1932, **12**, 153—160).—Improvements in technique are described. F. L. U.

Gravimetric determination of formic acid in presence of higher fatty acids. R. RIGAMONTI (Annali Chim. Appl., 1932, **22**, 744—746).—Scala's method of determining HCO_2H by the reduction of $HgCl_2$ to HgCl (A., 1891, 248) may be made more rapid and more exact by addition of NaOAc. T. H. P.

Detection of lactic acid. E. TIKKANEN (Farm. Notisbl., 1927, No. 5, 4 pp.; Chem. Zentr., 1932, ii, 2213).—Brauer's reaction (A., 1920, ii, 517) is sp. Preferably, to 0·5 c.c. of dil. lactic acid are gradually added, with cooling, 3 c.c. of H_2SO_4, and on to the mixture are floated at $>50°$ 2 c.c. of freshly prepared

1% pyrocatechol (I) (or, better, guaiacol) solution. Gastric juice is first shaken with 4 vols. of Et_2O, and the extract, after evaporation of the Et_2O, is dissolved in H_2O and treated as above. With (I) CH_2O, paraldehyde (cherry-red), EtCHO, PhCHO, and vanillin give blood-red colorations. A. A. E.

Folin–Denis and naphtharesorcinol reagents. H. VON EULER, D. BURSTROM, and H. HELLSTROM (Svensk Kem. Tidskr., 1932, **44**, 288—290).—Small amounts of the following substances do not react with the Folin–Denis reagent (A., 1913, ii, 163): tyrosine, phenylalanine, histamine, thyroxine, tryptophan, *l*-histidine, yeast-nucleic acid, and glutathione. Equiv. to 1 mg. of uric acid are adrenaline (0·3 mg.), cysteine hydrochloride (2·4 mg.), and hexuronic acid (I) (0·8 mg.). (I) in aq. solution and in absence of O_2 does not respond to the Tollens reaction (A., 1908, ii, 638), but does so after oxidation by atm. O_2. With <4 mg. of (I) the depth of colour produced by the reagent increases with time. Unlike (I), *d*-fructose yields only a brown colour which shows no absorption in the neighbourhood of the *D*-line. F. O. H.

Titrimetric determination of sugars. S. KRAUZE (Wiadom. Farm., 1932, **59**, 267—269, 283—285).—Lactose is best determined by Fellenberg's modified method, which is now applied to the determination of sugar in urine. Adsorption of sugar is partly avoided by decolorising with $Hg(NO_3)_2$ instead of $Pb(OAc)_2$. The transition point is sharpened by addition of anhyd. Na_2SO_4 to the titrated liquid. CH. ABS.

Colour reactions of some nitro-compounds. I. V. KULIKOV and S. V. PANOVA (J. Gen. Chem. Russ., 1932, **2**, 736—740)—An adaptation of Flürscheim's method (J.C.S., 1908, **93**, 1463, 1772) can be used to detect 2 : 3- and 3 : 4-dinitrophenols in 2 : 5-dinitrophenol; the coloured solution is acidified and shaken with $CHCl_3$, which is coloured yellow if these impurities are present. The test is sensitive to 1 in 660,000. Compounds reducible to *o*-diamines can also be detected by treating the acid solution with Zn dust and adding CH_2Ac_2, an intense violet colour being produced. The test is sensitive to 1 in 200,000. G. A. R. K.

Use of ferrous sulphates and bromine water in detection of some substituted phenols. R. FOLCH and O. FERNANDEZ (Anal. Fís. Quím., 1932, **30**, 851—852).—Dil. solutions of adrenaline, adrenalone, and thiocol give permanent colorations with $FeSO_4$ solution followed by Br-H_2O. R. K. C.

Microchemical detection of novocaine. M. WAGENAAR (Mikrochem., 1932, **12**, 143—150).—Substances giving characteristic micro-cryst. ppts. with solutions of novocaine are enumerated. The most sensitive tests are those with H_2PtCl_6 (0·01 mg.) and aq. Br (0·001 mg.). Furfuraldehyde gives an intense red colour and can be used in examining minute quantities of a solid specimen. F. L. U.

Reactions for caffeic and chlorogenic acids. W. HOEPFNER (Chem.-Ztg., 1932, **56**, 991).—In aq. acid (AcOH, H_3PO_4) solution, caffeic acid (I) gives with $NaNO_2$ a deep cinnabar-red or, in very high dilution, orange coloration; sensitiveness 1 : 10^5. Under similar conditions, chlorogenic acid or its salts give a bright yellow coloration, becoming carmine on addition of excess of NaOH; sensitiveness at least 1 : 10^6. Possible destruction of either colour by NO_2 is obviated by addition of much $CO(NH_2)_2$. EtOH disturbs the reactions. The first reaction serves to detect free (I) in treated coffee beans, and the second may be made quant. with the help of a Pulfrich photometer. Detailed procedure is given. T. H. P.

Microchemical identification of caffeine. H. J. SANDRUS and M. L. WILLARD (Mikrochem., 1932, **12**, 137—142).—Of 23 residues obtained by evaporating mixed solutions of caffeine and metallic salts in presence of an acid the most characteristic are obtained with $PtCl_2$ and with nitrates of Al, Sr, Ba, Bi, Hg^{II}, Ag, and Tl^{I}. Photomicrographs are given. F. L. U.

Nephelometric determination of caffeine. E. HERNDLHOFER (Mikrochem., 1932, **12**, 227—230).—The turbidity produced in a solution of caffeine by Na phosphotungstate is measured in a nephelometer. The method can be applied to 0·25 g. of plant material containing about 1% of caffeine. F. L. U.

Modification of the iodometric determination of caffeine by Wallrabe's method. G. MIKÓ (Magyar Gyog. Tars. Ert., 1932, **8**, 291—294; Chem. Zentr., 1932, ii, 1484).—The caffeine salt (0·3 g.), dried at 100°, is dissolved in H_2O (20 c.c.), treated with 0·1*N*-$KH(IO_3)_2$ solution (50 c.c.), KI (2 g.), and 5*N*-H_2SO_4 (5 c.c.), diluted after 1 hr. to 100 c.c., shaken, and filtered. The first 25 c.c. of filtrate are rejected, and of the rest 50 c.c. are titrated with 0·1*N*-$Na_2S_2O_3$ [1 c.c. 0·1*N*-$KH(IO_3)_2$=0·00485 g. anhyd. caffeine]. A. A. E.

Identification of organic compounds. IX. L. ROSENTHALER (Pharm. Ztg., 1933, **78**, 23—24).—KI–$SbCl_3$–HCl solution gives cryst. ppts. with arecoline, brucine, caffeine, ephedrine, ephetonine, mezcaline, scopolamine, theobromine, and theophylline. Other alkaloids yield amorphous ppts. unsuitable for characterisation. R. S. C.

Microchemical identification of alkaloids [dilaudide]. F. AMELINK (Pharm. Weekblad, 1933, **70**, 2—3).—Dilaudide (dihydromorphinone) gives characteristic, microcryst. ppts. (illustrated) in 0·1% solutions with Dragendorff's reagent (needles and quadratic platelets) and Na nitroprusside (hexagonal prisms). $PtCl_4$, $AuCl_3$, $HgCl_2$, KOH, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and picrolonic acid give indefinite or sol. compounds. S. C.

Biochemistry.

Oxidation of hæmoglobin-iron by potassium ferricyanide and the equilibrium of the reaction. H. SCHÜLER (Biochem. Z., 1932, **255**, 474—488).—When $K_3Fe(CN)_6$ reacts with CO-hæmoglobin more $K_3Fe(CN)_6$ is used than corresponds with the CO liberated, the extra utilisation being equiv. to 2 mols. $K_3Fe(CN)_6$ per g.-atom of hæmoglobin-Fe. Globin separated from hæmin utilises 2 mols. $K_3Fe(CN)_6$ per

mol. of globin. The manometric and optical determinations of the dissociation const. and of the equilibrium const. are described. P. W. C.

Absorption of light by globin-hæmochromogen and its use for determination of blood-pigment. A. DENES (Biochem. Z., 1932, **255**, 378—386).—The absorption curves for horse-, dog-, and cat-globin-hæmochromogen are similar in form to, but differ somewhat from, those for pig and man. They show absorption max. at 555·8 and 527·1 mμ and min. at 540·0 mμ. A method for calculating the pigment content of blood using the extinction coeffs. and *A*-vals. is given. P. W. C.

Mol. wt. of the hæmocyanin of *Octopus vulgaris*. T. SVEDBERG and I. B. ERIKSSON.—See this vol., 171.

Change in physico-chemical properties of hæmoglobin and in the acid-base equilibrium after splenectomy in dogs. G. GROSCURTH and J. GLASS (Klin. Woch., 1932, **11**, 1071; Chem. Zentr., 1932, ii, 1318).—HCO_3' increases and CO_2 tension falls. A. A. E.

Change in isoelectric point of hæmoglobin and its relation to acid-base economy. J. GLASS and G. GROSCURTH (Klin. Woch., 1932, **11**, 1070—1071; Chem. Zentr., 1932, ii, 1196).

Osmotic pressure of globin. J. ROCHE, A. ROCHE, G. S. ADAIR, and M. E. ADAIR (Biochem. J., 1932, **26**, 1811—1828).—There is a striking difference at p_H 7·7 and p_H 5·6 between the relationship of osmotic pressure to concn. of ox-globin (I) and hæmoglobin (II) equilibrated with the same buffer solution. In (I) the ratio of partial pressure of protein to concn. tends to diminish as the protein concn. is increased. At p_H 7·7 the mean mol. wt. of (I) may be greater than that of (II). At p_H 5·6 paraglobin is more highly aggregated than native globin. S. S. Z.

Vanadium chromogen of *Ascidia* blood. M. HENZE (Z. physiol. Chem., 1932, **213**, 125—135).—The chromogen contains 39·0% C, 4·6% H, 7·4% N, and 10·1% V. After acid hydrolysis the humin-N was high (18·8% of the total). The V in the chromogen is bivalent and is oxidised to the V^{III} state by methylene-blue or indigo. The CO_2 content of *Phallusia* blood is < that of sea-water. J. H. B.

Modification of Yoshimatsu's potassium method with 0·1 c.c. of blood. S. YOSHIMATSU and Y. UGA (Tohoku J. Exp. Med., 1932, **19**, 156—161).—K in the Kramer-Tisdall protein-free filtrate is pptd. as cobaltinitrite and redissolved in HNO_3; the colour is developed by adding dimethylglyoxime and Na_2S. The average error with 0·1 c.c. is 3%. CH. ABS.

Diffusible calcium in the blood-stream. V. Influence of agents which affect blood-calcium on calcium distribution and inorganic phosphate of serum. D. M. GREENBERG and L. GUNTHER (Arch. Int. Med., 1932, **50**, 855—875).—The authors' method (A., 1930, 361) for determination of diffusible Ca (I) gives reproducible and concordant results. In absence of bile (dog with fistula), there was little change in total Ca and in (I) over 2 months, and there was no daily rhythm of change in blood-Ca and -PO_4. On ingestion, the increase in Ca was equiv. to the Ca given and was due to an increase in (I); the non-diffusible Ca (II) does not change. After injection of parathyroid extract, the increase in Ca was due to equal increases in (I) and (II). H. G. R.

Blood-phosphate compounds in health and disease. S. GEREB and D. LASZLO (Klin. Woch., 1932, **11**, 800—802; Chem. Zentr., 1932, ii, 1032).—Hyperphosphatæmia is regarded as a readily demonstrable symptom of phosphate poverty. A. A. E.

Determination of oxygen required to combine with oxidisable material in blood and to oxidise the intermediate products of metabolism. L. N. LAPIN (Biochem. Z., 1932, **256**, 20—36).—A method for determining the amount (I) of O required to combine with the oxidisable substances in 100 c.c. of blood is described. By subtracting from (I) the amount of O consumed by the blood-sugar present (a table is given) the O required (II) for oxidising the intermediate products of degradation is obtained. (In the blood of birds account must be taken of the O required to oxidise uric acid.) Average figures for (I) and (II) in man, rabbits, guinea-pigs, and wethers are given. (II) is not identical with "difference val." Serum contains 2·5 times as much sugar as do erythrocytes, but the val. of (I) is about the same in both. In human blood (I) usually increases as blood-sugar increases, but no relation has been found between (I) and (II). W. McC.

Manometric determination of residual and total nitrogen. R. IWATSURU, Y. NAKAI, T. ITO, and K. KOBAYASHI (Biochem. Z., 1932, **256**, 18—19; cf. A., 1928, 912).—Prepared material (*e.g.*, from 1·0 c.c. of serum or plasma) is heated with H_2SO_4 as in the micro-Kjeldahl method, and the solution, after being made first alkaline with conc. NaOH and then almost acid with 0·1*N*-H_2SO_4, is diluted to known vol. 20 c.c. of the dil. solution are then treated with NaOBr in a Barcroft apparatus. Residual N is thus determined. Total N is determined in the same way but with addition of a few drops of 10% Na tungstate to the H_2SO_4 used for destruction of the org. matter. W. McC.

Determination of residual nitrogen and its fractions. I. Micro-determination of residual nitrogen in blood. F. RAPPAPORT (Klin. Woch., 1932, **11**, 688—689; Chem. Zentr., 1932, ii, 747).—0·2 c.c. of blood or serum is hæmolysed with Na_2SO_4 containing H_2SO_4 and treated with phosphomolybdic acid. After Kjeldahlisation the filtrate is distilled in a Parnas-Wagner apparatus. NaOBr is added and the excess determined iodometrically. L. S. T.

Determination of residual nitrogen and its fractions. II. Micro-determination of urea in blood and serum. F. RAPPAPORT and A. GLASER (Klin. Woch., 1932, **11**, 814; Chem. Zentr., 1932, ii, 747; cf. preceding abstract).—Urea-N is converted into NH_3 by urease on warming. Urease and proteins are pptd. by Na tungstate and H_2SO_4. The NH_3 formed is distilled and determined iodometrically. L. S. T.

Micro-determination of blood-urea-nitrogen. A. G. KELLER (J. Lab. Clin. Med., 1932, **17**, 1146—1147).—A modification of Karr's method (A., 1925, i, 323) permits the use of 0·2 c.c. CH. ABS.

Colorimetric determination of the true glucose content of body-fluids. E. HERZFELD (Biochem. Z., 1932, **256**, 127—133; cf. A., 1932, 416).—0·1—0·5 c.c. of fluid (serum, plasma) is treated with $NHPh{\cdot}NH_2,2HCl$ and NaOAc and the osazone produced is dissolved during 1 hr. at 100°, after purification, in HCl–96% EtOH. For the colorimetric determination which follows, aq. $K_2Cr_2O_7$ is used as standard. The results, which are as accurate as those obtained in the Hagedorn and Jensen method, represent glucose but not other reducing substances. W. McC.

Normal renal threshold for glucose. R. A. CAMPBELL, E. E. OSGOOD, and H. D. HASKINS (Arch. Int. Med., 1932, **50**, 952—957).—Filtrates by Somogyi's method (A., 1930, 801) of removing blood-proteins give true sugar vals. within a range of ±7 mg. per 100 c.c. Tungstate pptn. averages 21 mg. higher. A probable range for the normal renal threshold is 105—200 mg. H. G. R.

Leech method of blood analysis. I. Cholestérol. T. SATO. **II. Potassium.** Y. UGA (Tôhoku J. Exp. Med., 1932, **19**, 162—164, 165—167).—Vals. for rabbit or human blood recovered from leeches are correct to within 2% or 3%, respectively. CH. ABS.

Process for demonstrating lability in serum. G. A. BROSSA (Biochem. Z., 1932, **256**, 55—63; cf. Sahlbom, A., 1911, ii, 100).—Normal serum can be distinguished from labile by addition of equal amounts of each to a solution of a positive hydrosol (*e.g.*, night-blue) into which filter-paper is then dipped. The dye always rises higher in the case of the normal than in that of the labile serum. W. McC.

Critical temperature of serum. VI. Absorption spectra in the ultra-violet, visible, and near infra-red regions. P. LECOMTE DU NOÜY and M. LECOMTE DU NOÜY (Ann. Inst. Pasteur, 1932, **49**, 762—777).—The wave-lengths of the max. and min. points on the absorption curves in ultra-violet light of normal horse or sheep serum are not affected by warming to 55—65°, although at the latter temp. the actual densities are increased. In strongylosis in sheep the curve is considerably flattened in the terminal stages of the disease. The curves in the visible and infra-red regions are far less const. even for normal serum, and no definite changes were observed in serum heated at 60° for 10 min. P. G. M.

Alleged transformation of serum-albumin into serum-globulins. S. B. HOOKER and W. C. BOYD (Science, 1932, **76**, 517).—The addition of heparin to crude but not to pure horse-serum albumin at p_H 5 ppts. a substance sol. in salt solution and precipitable by half saturation with $(NH_4)_2SO_4$. The albumin–heparin mixture or compound still reacted to the same degree as albumin with an anti-albumin serum, but did not react with anti-globulin sera prepared either by injecting isolated globulin or by absorbing an anti-horse serum with albumin. The latter reacted readily with globulin. L. S. T.

Determination of serum-albumin and -globulin without using precipitating electrolytes. P. MERKLEN, E. LE BRETON, and A. ADNOT (Compt. rend. Soc. Biol., 1931, **107**, 758—760; Chem. Zentr., 1932, ii, 1483).—Serum, diluted with an equal quantity of H_2O, is treated with 8 pts. of $COMe_2$ at 0°; the ppt. is centrifuged, dissolved in H_2O to the original vol., and again pptd. with 10 pts. $COMe_2$. If the serum contains much fat, 3 pptns. are necessary. The dried ppt. gives the total protein; it is pptd. in cold H_2O (10 pts. of H_2O to 1 pt. of serum) and CO_2 is passed through the solution for 6 min. The p_H val. becomes const. at 5·5. The ppt. contains the globulin. The albumin is calc., or is determined by pptn. of the acidified residual solution with $COMe_2$. A. A. E.

Suspensions of proteins precipitated from serum by acetone. C. ACHARD and A. BOUTARIC (Compt. rend., 1932, **195**, 1196—1197).—Comparisons of the physical properties of sera with fresh suspensions of the proteins freshly pptd. from them by $COMe_2$ show that proteins are not denatured by $COMe_2$ pptn. A. C.

Determination of direct and indirect bilirubin in blood-serum. B. VARELA and J. ESCULIES (Compt. rend. Soc. Biol., 1931, **107**, 884—886; Chem. Zentr., 1932, ii, 1483).—Serum (1 c.c.) is mixed and centrifuged with $CHCl_3$ (4 c.c.), which dissolves the "indirect" bilirubin. After several repetitions the $CHCl_3$ is evaporated and the bilirubin determined in the residue by Ehrlich's reagent, whilst the aq. layer is freed from $CHCl_3$ and used for determination of the "direct" bilirubin (originating in the liver). A. A. E.

Formation of leucocyte protease during immunisation. M. GAROFEANU and H. IOAN (Compt. rend. Soc. Biol., 1931, **108**, 297—298; Chem. Zentr., 1932, ii, 1638).—In normal rabbits little or no protease was found; injection of horse serum causes an increase, the amount becoming const. or diminishing after several injections. A. A. E.

Hæmotoxic behaviour of glutamic acid. F. SULMANN (Z. Immunitat., 1932, **74**, 459—468; Chem. Zentr., 1932, ii, 735).—*d*-Glutamic acid (1 : 6000) *in vitro* is hæmotoxic towards the blood-corpuscles of warm-blooded animals. Urea in conc. solution and many protein degradation products, mainly NH_2-acids, are not hæmolytic. L. S. T.

Relationship between structure of antigen and specificity of antibody. H. ERLENMEYER and E. BERGER (Biochem. Z., 1932, **255**, 429—433).—The antigens prepared from diazotised *p*-aminophenylphosphinic and -arsinic acids, but not that from *p*-aminophenylantimonic acid, react with two antisera prepared against the antigen produced from diazotised atoxyl by coupling with horse serum and with cryst. ovalbumin. P. W. C.

Specific union of precipitins and chemospecific antigens *in vivo* by injections of simply constituted substances. E. BERGER and H. ERLENMEYER (Biochem. Z., 1932, **255**, 434—445).—When rabbits are immunised with diazotised atoxyl coupled with cryst. ovalbumin, precipitins are obtained the specificity of which is determined by the arsinic acid and not by the injected protein. In neutralisation experi-

ments the appearance of a sp. union is detected *in vivo*. A reduction or complete disappearance of precipitin from the blood-stream was obtained by injection of pure aminophenylarsinic acid (I), or of diazotised (I) coupled with tyrosine or with horse serum. Pure atoxyl is less active than the azoprotein and the arsinic acid coupled with tyrosine. P. W. C.

Role of lipoidal substances in complement fixation. W. S. STONE (Milit. Surg., 1932, **71**, 61—66).—Lipins normally present in the antiserum are essential to its reactivity. A hypothetical explanation of the Wassermann reaction is advanced. CH. ABS.

Antibodies in the fibrinogen of immune serum. K. CHIHARA (Japan. Z. Mikrobiol. Path., 1932, **26**, 733—739).—Agglutinin for typhoid bacilli, hæmolysin for goat's red blood-cells, and precipitin for horse serum were found in the fibrinogen of sera containing these antibodies. CH. ABS.

Metallic colloids. I. Influence on production of antibodies. Effect on production of agglutinins. II. Precipitins. III. Hæmolysins. R. YOSHIDA (Japan. Z. Mikrobiol. Path., 1932, **26**, 196—218, 449—468, 561—582).—The behaviour of colloidal Ag, Sn, Sb, Hg, Bi, Au, Se, Pt, Fe, Pb, and Cu is recorded. CH. ABS.

Immunological reaction to the enzyme papain. R. P. WALTON and C. M. SEGURA (Biochem. J., 1932, **26**, 1750—1753).—Continued injections (intravenous and intraperitoneal) of papain did not produce an anti-enzymic serum in dogs. S. S. Z.

Chemistry of the aqueous humour. Z. STARY and R. WINTERNITZ (Z. physiol. Chem., 1932, **212**, 215—233).—The aq. humour of the horse contains 7·4 mg. of Ca, 1·7 mg. of Mg, 20·1 mg. of K, and 348 mg. of Na per 100 c.c. (average vals.). These figures (except Na) differ from those for serum and cerebrospinal fluid, but approx. to those obtained for the ultra-filterable portion of serum, and suggest this origin. J. H. B.

Phosphatides of human brain. II. Isolation of lecithins of the α-series. III. Isolation of lecithins of the β-series. Y. YOKOYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, **8**, 358—360, 361—363).—II. The α-lecithins have been brominated in Et_2O, and fractionated by $CHCl_3$ and $COMe_2$, affording *dioleo-α-lecithin tetrabromide*, an oil; *palmito-oleo-α-lecithin dibromide*, an oil; *oleoarachidono-α-lecithin decabromide*, m.p. 189° (decomp.); *palmitoarachidono-α-lecithin octabromide*, m.p. 112° (decomp.).

III. The mixture of bromo-β-lecithins yields, on fractionation with solvents, *dioleo-β-lecithin tetrabromide*, an oil; *palmito-oleo-β-lecithin dibromide*, an oil; *oleoarachidono-β-lecithin decabromide*, m.p. 119°; and *linoleoarachidono-β-lecithin dodecabromide*, m.p. 124° (decomp.). A. C.

Cholesterol of the human brain. C. ANTONIANI and F. ZANELLI (Atti R. Accad. Lincei, 1932, [vi], **16**, 150—153).—Cholesterol from the brain of the fœtal or adult human has the same mol. wt. and % composition as that of the bile, but a slightly higher m.p. (150—151°), probably owing to its greater purity. Small (but insignificant) differences occur in the $[\alpha]_D$ of the two products. T. H. P.

Applications of the diamine dye group in histology. I. Vital stains. II. Electric charge of dyes, their chemical structure, and vital staining. III. Diffusibility and solubility in lipin of dyes and vital staining. K. FUJITA (Japan. Z. Mikrobiol. Path., 1931, **25**, 1477—1504, 1505—1518, 1519—1536). CH. ABS.

Active substance from the lung. J. DADLEZ and W. KOSKOWSKI (Compt. rend. Soc. Biol., 1931, **107**, 75—77; Chem. Zentr., 1932, ii, 1318).—The comminuted lung was repeatedly extracted with EtOH, the extract conc. in vac., the concentrate extracted with Et_2O, conc., centrifuged, and poured into much EtOH. The ppt. was repeatedly washed with EtOH and abs. EtOH. The last traces of histamine were removed by treatment of a 5% aq. solution with active C and centrifuging. The solution has a pressor effect in the chloralosed cat, and causes uterine contraction in the virgin guinea-pig, and expansion of the melanophores of the frog, thus behaving like posterior pituitary extracts. A. A. E.

Lipins of mammalian liver. II. Occurrence of lignocerylsphingosine in pig's liver. E. FRANKEL and F. BIELSCHOVSKY (Z. physiol. Chem., 1932, **213**, 58—62; cf. A., 1932, 294).—Lignocerylsphingosine, $[\alpha]_D^{24}$ −2·5°, was isolated from pig's liver (0·06%). J. H. B.

Iron in the liver and spleen after destruction of blood and transfusions. S. A. GLADSTONE (Amer. J. Dis. Children, 1932, **44**, 81—105).—The large amounts of Fe present in the livers of infants 1—10 weeks after birth appear to be due both to hæmorrhages into the tissues or cavities of the body of the fœtus or infant and to post-natal intravascular destruction of blood. Transfusion of blood in infants aged $\not<$ 3 months is followed by increased deposition of Fe in the liver and spleen. The total non-hæmoglobin Fe content of the liver of infants aged $<$ 3 days is 32 mg. CH. ABS.

Glycogen in cartilage. H. A. HARRIS (Nature, 1932, **130**, 996—997).—Mainly a discussion on the association of glycogen (I) with phosphatase (II) in the senescent cell for the purpose of bone formation. In human and other embryos cartilage cells in the neighbourhood of the epiphysis store (I) in direct proportion to their age. The osteoblasts and highly vascularised bone contain no (I). It is suggested that the senescent or hypertrophic cartilage cells provide both the (II) and the (I); the latter yields on hydrolysis hexosephosphoric esters which by the action of (II) and the Ca of the circulating body-fluids deposit Ca phosphate on the matrix. L. S. T.

Muscle extractives. XXXII. Extractives of crucian flesh. H. TALANOVA (Z. physiol. Chem., 1932, **213**, 8—10).—The flesh of *Carassius carassius* contains methylguanidine and traces of guanine, but carnosine and carnitine could not be detected. J. H. B.

Melanin acids in binary systems. O. ADLER (Biochem. Z., 1932, **256**, 228—235; cf. A., 1930, 493).—Mixed m.-p. or softening-point curves of melanin

acids with pyramidone, benzidine, or urea indicate the possibility of distinguishing between these acids by the extents of the depressions produced. The sepia acid and the acid from sarcoma seem to be very similar. W. McC.

Natural melanins. H. WAELSCH (Z. physiol. Chem., 1932, **213**, 35—57).—Melanins were obtained from various sources (chorioid and retinal pigment of the horse's eye, liver metastases of malignant human eye melanoma) and were purified by digestion with pepsin hydrochloride, flotation of impurities, and extraction of fat. The elementary composition varied considerably. All samples contained a protein group, not hydrolysed by enzymes but removed by digestion with HCl. It has high amide- and non-NH_2-N, but low NH_2-acid content. It is digested after treatment with Br in AcOH. The chorioid melanin contained traces of Fe and all contained S. The pigmenting groups of sarcoma melanin were const. in composition, but differed from those of chorioid melanin and fuscin. J. H. B.

Cholesterol and water content of the adrenal cortex in mammals. C. I. PARHON and M. CAHANE (Compt. rend. Soc. Biol., 1931, **107**, 836—837; Chem. Zentr., 1932, ii, 1462).—In females the H_2O content is > in males; generally a high H_2O content is associated with a low cholesterol content. A. A. E.

Lipolytic properties of the adrenals. I. PARFENTIEV and B. SOKOLOV (Compt. rend. Soc. Biol., 1931, **107**, 114—115; Chem. Zentr., 1932, ii, 1317).—H_2O, glycerol, and EtOH extracts have no lipolytic action or lipase-inhibiting properties. A. A. E.

Iodine content of ox thyroids. I. I. NITZESCU and E. BINDER (Compt. rend. Soc. Biol., 1931, **108**, 281—282; Chem. Zentr., 1932, ii, 1794).—The I content of the fresh gland is 0·076—0·088%; seasonal variations were not observed. A. A. E.

Effects of high-protein diets on the thyroid-gland iodine. R. MCCARRISON and K. B. MADHAVA (Indian J. Med. Res., 1930, **18**, 619—661).—High-protein diets *per se* do not regularly cause thyroid enlargement in growing rats, even if the diet is poor in fat-sol. vitamins or I. The increase occasionally noted is referable to deficiency of fat-sol. vitamin, and not to impaired absorption of I. The diets caused polyuria and albuminuria and stimulated urinary excretion of I. CH. ABS.

Comparison of the body constituents of parasite and host. II. Electrometric titration of extracts of *Balanimus dentipes*. T. SASAKI (Keijo J. Med., 1932, **3**, 354—359).—The similarity between constituents of the chestnut (I) and those of its parasite, *B. dentipes* (II) (cf. A., 1932, 1275), is extended by the parallelism of the titration curves of extracts (10% NaCl, 1% AcOH, and 1% NaOH) of the fat-free (I) and (II). This is due to the protein constituents, for the N contents are 1·84 (I) and 9·61% (II). F. O. H.

Vanadium in some Tunicates. J. CANTACUZÈNE and A. TSCHEKIRIAN (Compt. rend., 1932, **195**, 846—849).—The H_2O-washed ash of nine species of Tunicates contains V in amount varying from 15·4% in *Ciona intestinalis* to 0·05% in *Styllopsis grossularia*. The V is detectable in an EtOH extract of the uncalcined animal. It seems to take the place of Cu, which is absent from these animals. No V was found in three Polyclinids (cf. A., 1911, ii, 740; 1930, 361). C. A. S.

Occurrence of the paralytic shell-fish poison in the common sand-crab. H. SOMMER (Science, 1932, **76**, 574—575).—The poison may occur in a high concn. in *Emerita analoga*. L. S. T.

Detection of toxins in the milk of lactating women during menstruation. E. ELTZ (Jahrb. Kinderheilk., 1932, **86**, 82—115; Chem. Zentr., 1932, ii, 1464).—A substance which arrests the growth of *Lupinus albus* seedlings is present. The substance can pass undecomposed through the intestinal wall. A. A. E.

Influence of different levels of fat intake on milk secretion. L. A. MAYNARD and C. M. MCCAY (New York [Cornell] Agric. Exp. Sta. Bull., 1932, No. 543, 40 pp.).—Cows fed on rations from which all but 1% of fat was extracted and replaced by an equiv. of starch produced heavily decreased milk and fat yields. In similarly treated rations in which 3% fat remained, milk yields were still subnormal. Partial replacement of fat in rations by starch produced milk-fat having a higher I val. There was also a gradual lowering of the total fatty acids, phospholipin fatty acids, and the cholesterol of the blood-plasma, the changes being closely parallel for the three constituents. The glucose contents of the whole blood, cells, and plasma were not affected by the above changes in the ration. A. G. P.

Effect of different planes of protein intake on milk production. E. S. HARRISON and E. S. SAVAGE (New York [Cornell] Agric. Exp. Sta. Bull., 1932, No. 540, 24 pp.).—Supplied in amounts > equiv. to 127% of the protein output in milk (after deduction for live wt. maintenance) there was no evidence that protein stimulated milk production. A. G. P.

Influence of arsenical dipping on yield of milk by dairy cows. P. T. D. ARNOLD, W. M. NEAL, and R. B. BECKER (J. Dairy Sci., 1932, **15**, 407—412).—Dipping for the eradication of cattle fever ticks resulted in a small decrease (1·9%) in milk flow. The greatest reduction occurred in the second milking after dipping and is ascribed to absorption of As. A. G. P.

Effect of feeding irradiated ergosterol to cows on the vitamin-*D* content of milk. W. E. KRAUSS, R. M. BETKE, and C. F. MONROE (J. Nutrition, 1932, **5**, 467—477).—Irradiated ergosterol dissolved in maize oil, when fed to cows, increased the vitamin-*D* content of the milk. The vitamin-*D* of such milk was less effective than that of cod-liver oil for calcification in chicks. A. G. P.

Adsorption of calcium ions on caseinogen in milk. K. BALLOWITZ (Biochem. Z., 1932, **256**, 64—74).—The p_H of milk is not altered by boiling but is lowered by addition of $CaCl_2$, which, at p_H 5·95—6·05, ppts. the caseinogen (I). The boiling causes adsorption of the Ca in such a way that max. adsorption coincides with max. pptn. The inability of boiled milk to coagulate with rennet is removed by addition of an amount of $CaCl_2$ equiv. to the Ca

adsorbed by the (I) during boiling. This explains why boiled milk is more difficult to assimilate than unboiled. The coagulation of milk by rennet is not affected by K and Na salts, but is accelerated by Ca > Ba > Mg. The order corresponds with the order of the sp. pptg. effect on (I) of these metals. W. McC.

Effect of parathyroid hormone on milk-calcium. C. I. PARHON and I. ORNSTEIN (Compt. rend. Soc. Biol., 1932, **110**, 921—822; Chem. Zentr., 1932, ii, 1317).—With bitches no change was observed. A. A. E.

Determination of calcium and phosphorus in saliva. F. KRASNOW, M. KARSHAN, and L. E. KREJCI (J. Lab. Clin. Med., 1932, **17**, 1148—1152).—Salivary Ca is titrated with 0·005*N*-$KMnO_4$ after ashing or treatment with $CCl_3{\cdot}CO_2H$. Tisdall's method is employed for the determination of P in ashed or unashed material; Fiske and Subbarow's method is applicable only to ashed material. CH. ABS.

Bile-stimulating action of iodosalicylic acids. L. KAUFTHEIL and F. RAPPAPORT (Arch. exp. Path. Pharm., 1932, **168**, 654—667).—Administration of Na 5-iodo-, 5-iodo-acetyl-, and iodosalicyl-salicylates to dogs with a bile fistula markedly increases the amount of bile secreted, but other halogeno-salicylic acids are without appreciable action. W. O. K.

Dependence of the fermenting power of intestinal juice on the diet. I. Amylolytic enzyme. S. ANDREEV and S. GEORGIEVSKY (Pflüger's Arch., 1932, **230**, 33—41; Chem. Zentr., 1932, ii, 1313).—The amylolytic val. (Wohlgemuth) rises on a bread–milk diet, falls when the carbohydrate is diminished, and is lowest on a meat diet. A. A. E.

Acid response of the stomach to test meals of protein, fat, and carbohydrate. W. H. BARROW (J. Lab. Clin. Med., 1932, **17**, 1094—1100).—The character of the food does not affect the acid response of the stomach. CH. ABS.

Isolation of citrulline, δ-carbamido-ornithine, from tryptic digestion products of caseinogen. M. WADA.—See this vol., 172.

Bile acid of bear's bile. K. TANAKA (Z. physiol. Chem., 1932, **213**, 199—200).—The chief constituent is taurocholic acid. J. H. B.

Cholagoguic action of guaiacol derivatives. E. CHABROL, R. CHARONNAT, M. MAXIMIN, and R. WAITZ (Compt. rend. Soc. Biol., 1931, **107**, 1240—1243: Chem. Zentr., 1932, ii, 1652).—Guaiacol, eugenol, vanillin, vanillic acid, and vanillyl alcohol, and also *o*-vanillin, have the same cholagoguic action. A. A. E.

Influence of food on the nutrition of insects [silkworms]. S. BITO (Bull. Sericult. Japan, 1932, **5**, 5).—Leaves of *Cudrania triloba* contain less protein than mulberry leaves. Silkworms fed on the former have slower larval growth and poorer production of silk than those fed on the latter. Pupæ fed on *Cudrania* leaves contain more protein but less fat and glycogen than those fed on mulberry leaves. B. P. R.

Relation between food plants and the properties of the cocoons of *Antheræa Yamamai* and *A. Pernyi*. K. KITAZAWA (Bull. Sericult. Japan, 1932, **5**, 6).—Leaves of *Quercus dentata* contain less H_2O, ash, fat, and protein, but more fibre, tannin, and sol. N-free extract, than those of *Q. serrata*. Tussah silkworms fed with the former spin larger cocoons, whilst Yamamai silkworms fed on the latter spin the larger cocoons with a higher percentage of silk. The cocoons of both wild silkworms fed on leaves of *Q. dentata* are poor in silk and difficult to reel. B. P. R.

Wild silks. II. Isoelectric point of liquid silk. III. Viscosity of fibroin sol. S. BITO (Bull. Sericult. Japan, 1932, **5**, 3, 3—4).—II. The isoelectric points of the liquid silk from the wild silkworms *Antheræa pernyi* and *Dictyoploca japonica* occur at p_H 2·6 and 2·8—2·92, respectively.

III. Wild silk is more resistant to Loewe's reagent than is true silk, the order of increasing resistance to dissolution being: true silk, Kuriwata, Yamamai, tussah, and *Attacus cynthia*. The viscosity of the fibroin sols decreases with increasing time and is represented by the equation $\eta = at^b$, where η is the viscosity, t the time in hr., and a and b are consts. B. P. R.

Effect of figs and small amounts of raisins on urinary acidity. L. G. SAYWELL (J. Nutrition, 1932, **5**, 519—525).—Addition of raisins or figs to the ration increased the p_H of urine and decreased the total acids and NH_3 excreted. A correlation between ash alkalinity and physiological reaction is recorded. A. G. P.

[Qualitative analysis of] urinary sediments. G. KLEYER (Pharm. Ztg., 1932, **77**, 1312).—The sediment is extracted with warm dil. HCl and the residue tested for uric acid. The extract is diluted and tested for Ca oxalate and phosphate, Mg phosphate, and "triple phosphate," using a technique which dispenses with filtration. F. O. H.

Determination of contrast media [iodine compounds] in urine. J. H. C. NIEVERGELD (Pharm. Weekblad, 1932, **69**, 1422—1425).—Na 5-iodo-2-pyridoneacetate (Uroselectan), iodomethanesulphonate (Abrodil), "*N*-methyl-2 : 5-di-iodopyridoxyl-2 : 6-dicarboxylate" (Uroselectan B), and diethanolamine 3 : 5-di-iodo-4-pyridone-*N*-acetate (Perabrodil), used as contrast media in *X*-ray diagnosis, are excreted in the urine, but not as iodides. To determine the amount excreted, 5 c.c. of urine are evaporated with 2 g. of K_2CO_3 and ignited. The melt is extracted with H_2O, I oxidised with $KMnO_4$ to HIO_3, and the latter determined by KI and $Na_2S_2O_3$. S. C.

Phosphorus metabolism. III. Determination of phosphorus in urine. G. E. YOUNGBURG (J. Lab. Clin. Med., 1932, **17**, 1145—1146).—Phosphomolybdate is reduced by $SnCl_2$. CH. ABS.

Effect of hydrolysis on the sugars of normal urine. A. HASSAN and M. A. S. EL AYYADI (Biochem. J., 1932, **26**, 1851—1856).—Hydrolysis with 10% HCl of charcoal-treated urine, except when sucrose is present, diminishes the reducing power. This is due at least in part to the destruction of "*iso*-maltose" occurring normally in urine. S. S. Z.

Sugars of urine. I. Determination of reducing sugars of urine. E. S. WEST and V. L. PETERSON. **II. Factors affecting excretion of fermentable and non-fermentable sugars in urine.** E. S. WEST, A. C. LANGE, and V. L. PETERSON. **III. Nature of the fermentable sugar of normal and starvation urine.** E. S. WEST and A. STEINER (Biochem. J., 1932, **26**, 1720—1727, 1728—1741, 1742—1749).—I. The method is based on the prep. of $HgSO_4$–$BaCO_3$ filtrates followed by determination of fermentable and non-fermentable sugar using washed yeast and a sensitive Shaffer–Hartmann reagent. Fermentable sugar was present in almost all 24-hr. samples of normal urine, averaging 142 mg. per 100 c.c. (as glucose). The average non-fermentable sugar in such samples was 395 mg. calc. as glucose.

II. Non-fermentable sugars (I) are derived in some measure from most common foodstuffs, but in particular from dried fruits, apples, honey, and carbohydrate-containing foods which have been subjected to high temp. Their excretion is not increased by high nucleoprotein diets, by the ingestion of yeast-nucleic acid, or by stimulation of the digestive glands. The excretion is continued at a somewhat lower level during starvation of man or dog. Intestinal stasis in dogs causes an increased output of (I). (I) of urine are very little changed by hydrolysis. Patients with kidney impairment show a decreased output of (I) in the urine. Conditions which lower the carbohydrate tolerance increase (I) and *vice versa*. A non-reducing polysaccharide is excreted in urine, which on hydrolysis yields a fermentable sugar.

III. The sugar is glucose. S. S. Z.

Detection of glucose in urine by means of potassium permanganate. I. B. SCHUR (Munch. med. Woch., 1932, **79**, 679—681; Chem. Zentr., 1932, ii, 747).—The glucose alone in urine gives a sp. red colour with alkaline $KMnO_4$. L. S. T.

Clinical determination of urinary sugar. H. STEINMAURER (Med. Klinik, 1932, **28**, 932; Chem. Zentr., 1932, ii, 1048).—The urine is boiled with KOH and the yellow to dark brownish-red colour is compared with that similarly developed in sugar solutions. A. A. E.

Occurrence in the urine of phenolic substances detected by Millon's reaction. O. FURTH, R. SCHOLL, and H. HERRMANN (Klin. Woch., 1932, **11**, 1231; Chem. Zentr., 1932, ii, 1195—1196).—The increase in phenolic substances, insol. in Et_2O, is associated with increased degradation of protoplasm, and with disturbance of liver function. They are related to increased excretion of neutral S. A. A. E.

Rapid determination of phenol in urine. G. DENIGÈS (Bull. Soc. Pharm. Bordeaux, 1931, **69**, 233—236; Chem. Zentr., 1932, ii, 1047—1048).—The urine (2 c.c.) is shaken with 2 drops of 1% $CuSO_4,5H_2O$ solution, 2 drops of H_2O_2 (10 vol.-%), and 2 drops of aq. NH_3 and after 10 min. is treated with 4 drops of glacial AcOH and then shaken with 2 c.c. H_2O. The colour is compared with that produced by standard PhOH solutions (50, 100, and 200 mg. per litre) similarly treated, except that the last 2 c.c. H_2O are replaced by 2 c.c. of the urine. Fæces are first diluted (1 : 40—50) and filtered with talc powder. The reaction indicates only free PhOH; combined PhOH needs preliminary hydrolysis. A. A. E.

Detection of porphyrin in urine. G. HOLLAND and A. SCHURMEYER (Klin. Woch., 1932, **11**, 1221—1222; Chem. Zentr., 1932, ii, 1331).—With Wood's filter urine containing porphyrin gives a red fluorescence, whilst otherwise the fluorescence is blue or bluish-green. A. A. E.

Colorimetric examination of sweat. W. RIEDER and A. NEUMANN (Klin. Woch., 1932, **11**, 1027—1028; Chem. Zentr., 1932, ii, 1209).—The skin is painted with a paste containing $FeSO_4$, tannin, and ZnO; this acquires a bluish-black colour in presence of sweat. A. A. E.

Influence of acidosis on carbohydrate metabolism. M. L. GILCHRIST (Arch. Dis. Childhood, 1932, **7**, 169—180).—The ability of the organism to utilise carbohydrates is unaffected by ingestion of NH_4Cl, but is markedly reduced after ingestion of ketogenic diets. The effect of the latter appears due to diminution of stored carbohydrate rather than to production of acidosis. CH. ABS.

Acid–base balance of new-born infants. II. Low alkaline reserve. E. MARPLES and V. W. LIPPARD (Amer. J. Dis. Children, 1932, **44**, 31—39).—The acidosis which frequently occurs in breast-fed infants during the first 10 days of life appears to be due to accumulation of blood-Cl. The blood-p_H is normal and the serum-CO_2 is decreased. CH. ABS.

Albuminuria in pregnancy and its treatment. J. V. O'SULLIVAN (Lancet, 1932, **223**, 1326—1328).—Fe given in addition to the usual treatment diminishes the amount of albumin and improves blood counts and hæmoglobin. L. S. T.

Allergically active substance in pollen. *Phleum pratense* (timothy) pollen. A. STULL, R. A. COOKE, and R. CHOBOT (J. Allergy, 1932, **3**, 341—351).—The substance is an albumin similar to that of ragweed pollen (cf. A., 1931, 1186). It is the only active substance. H_2O extracts of 10-year-old timothy pollen were low in protein, N, and activity as compared with those of new pollens. Treatment of the pollen with EtOH greatly reduced the activity and the amount of extractable N. Heating lessened the activity of the extract. The precipitin test was negative with the purified albumin and a specifically sensitive serum. No albumin was found in cat-tail pollen, which has no clinical or skin reactivity. CH. ABS.

Pollen and pollen extracts. VIII. Dialysability of pollen allergens. L. UNGER, H. W. CROMWELL, and M. B. MOORE (J. Allergy, 1932, **3**, 252—256).—Active substances in pollen extracts are diffusible through celloidin, cellophane, or parchment membranes at various p_H. Dialysis occurs more freely in slightly acid solutions. There is not a complete correlation in response of sensitive rabbits and man to the dialysable skin-reactive material. CH. ABS.

Biological identity of certain grass pollens causing hay fever. A. STULL, R. A. COOKE, and J. H. BARNARD (J. Allergy, 1932, **3**, 352—356).—A single active substance is common to all extracts. CH. ABS.

Effect of ovarian lipins on cholesterolæmia in amenorrhœa. C. I. PARHON and I. ORNSTEIN (Compt. rend. Soc. Biol., 1931, **107**, 841—842; Chem. Zentr., 1932, ii, 1462).—Blood-cholesterol is increased by injection of the total Et_2O extract. A. A. E.

Calcium, phosphorus, and potassium of the serum and spinal fluid in asthma. D. M. LIERLE and R. A. SAGE (J. Allergy, 1932, **3**, 325—331).—Normal vals. were found. CH. ABS.

Experimental anæmia by artificial diets rendered free from iron. H. NAKAMURA (Keijo J. Med., 1932, **3**, 375—384).—In mice fed on an Fe-free artificial diet with added vitamin-*B* the erythrocyte count decreases, whilst with *A*+*B* the count is unchanged. With such diets the absence of Fe has little influence on the rate of growth, the main changes occurring in the hæmoglobin index. F. O. H.

Treatment of anæmia with copper, quantitative comparison of anti-anæmic drugs, and a new copper-iron-protein preparation. H. HANDOVSKY (Klin. Woch., 1932, **11**, 981—984; Chem. Zentr., 1932, ii, 1036).—Cu, particularly when combined with aromatic NH_2-acids, greatly stimulates erythrocyte formation in anæmic animals, and slightly stimulates hæmoglobin formation. With Fe the reverse holds; its stimulating power is much < that of Cu. Good results are obtained with "cuvitan," which contains protein, Cu (0·1%), and Fe (1%). A. A. E.

Microbial metabolism and its bearing on the cancer problem. A. J. KLUYVER (Science, 1932, **76**, 527—532).—A lecture. L. S. T.

Insulin and carbohydrate metabolism in cancer of the skin. S. F. G. DA COSTA (Compt. rend. Soc. Biol., 1931, **107**, 85—87; Chem. Zentr., 1932, ii, 1317).—Local application of insulin caused marked retrogression, particularly at the surface, but not complete disappearance of the tumour. A. A. E.

Technique of micro-incineration: its advantages in histochemical study of normal and malignant tissues. E. S. HORNING (J. Cancer Res. Comm. Univ. Sydney, 1932, **4**, 118—121).—When sections of tissue are ashed on a glass slide and mounted dry the constituents of the ash can often be recognised under the microscope. Cancer cells yield more ash than normal cells, and its arrangement and nature are different. A. G.

Fat absorption in cœliac disease. C. E. KELLETT (Lancet, 1932, **223**, 1270—1272).—Fat absorption curves in cases of cœliac disease are determined by a direct method which is described. Their shape can be explained by assuming impaired fat absorption which is enhanced by an increase of fat in the diet. L. S. T.

Metabolism of carbohydrate. D. S. WALLER (J. Amer. Dietet. Assoc., 1932, **8**, 119—132).—The proportion of fat in a diabetic diet has no effect on the amount of available glucose which can be metabolised by a definite amount of insulin. The action of insulin on glucose, like enzyme action, is more efficient in a high concn. of glucose, up to 100 g. > the tolerance of the patient. CH. ABS.

Phosphates in the sugar-tolerance test. D. R. MCCULLAGH and L. VAN ALSTINE (Amer. J. Clin. Path., 1932, **2**, 277—286).—Curves indicating blood-inorg.-P after ingestion of 100 g. of glucose are normally regular; in metabolic disorders irregular variations are observed. CH. ABS.

Decreased glucose tolerance in acute infectious diseases. J. L. WILLIAMS and G. F. DICK (Arch. Int. Med., 1932, **50**, 801—818).—Glycosuria, accompanied by a low carbohydrate tolerance, occurred in 41% of cases with acute infectious diseases. Administration of insulin improves the glucose tolerance. It is suggested that there is often an injury to the islets of Langerhans, with a lessened production of insulin. H. G. R.

Clinical evaluation of blood-phosphates and sugar tolerance curves. F. W. HARTMAN and D. P. FOSTER (Amer. J. Clin. Path., 1932, **2**, 289—297). CH. ABS.

Eclampsia. V. Effect of placental antiserum on the glycogen content of the placenta. M. MURAKAMI (Tohoku J. Exp. Med., 1932, **19**, 113—128).—Rabbit antisera were produced against human and rabbit placental tissue, and a duck antiserum against rabbit liver. Injection of the liver antiserum into pregnant rabbits caused convulsions, but the blood-N and -sugar remained normal; the liver- and placental glycogen decreased. These effects were accentuated by simultaneous injection of an anti-placental serum, especially of the anti-rabbit serum. CH. ABS.

Carbohydrate metabolism in exophthalmic goitre. P. KRAMER (Z. klin. Med., 1932, **121**, 472—475; Chem. Zentr., 1932, ii, 1929—1930).—After injection of insulin in hypoglycæmia and after administration of sugar in hyperglycæmia the difference, in exophthalmic goitre, between capillary and venous blood-sugar is < the normal; the absorption of sugar by the tissues is much retarded. Thus the thyroid takes part in the regulation of the carbohydrate metabolism of muscle, and is antagonistic to insulin. A. A. E.

Enzootic hæmaturia (*Hæmaturia vesicalis*) of cattle in S. Australia. L. B. BULL, C. G. DICKINSON, and A. T. DANN (Counc. Sci. Ind. Res. Australia, Pamphlet, 1932, No. 33, 24 pp.).—Occurrence of "red-water" cannot be ascribed to any sp. abnormality of soil or herbage. Urine analyses indicate that low protein and S intakes are characteristic of affected animals. A. G. P.

Arrest of hæmorrhage by hypertonic glucose solution. J. EASON (Lancet, 1932, **223**, 1272).—Various types of hæmorrhage are arrested by the application of a 50% aq. solution of glucose. L. S. T.

Use of disodium hydrogen phosphate as an antidote for hypercalcæmia in dogs. I. H. PAGE and J. P. SCOTT (J. Pharm. Exp. Ther., 1932, **46**, 431—434).—Intravenous administration of solutions of Na_2HPO_4 lowers the serum-Ca in normal dogs and in dogs in which this has been raised by parathyroid extract. Na_2HPO_4 is an antidote against the symptoms of hyperparathyroidism. W. O. K.

Hyperproteinæmia due to Bence-Jones protein in myelomatosis. J. W. SHIRER, W. DUNCAN, and R. L. HADEN (Arch. Int. Med., 1932, **50**, 829—835).—In two cases of myelomatosis the blood-serum was high in protein, due to large amounts of Bence-Jones protein, and in Ca. H. G. R.

Endemic nutritional œdema. I. Clinical findings and dietary studies. J. B. YOUMANS, A BELL, D. DONLEY, and H. FRANK (Arch. Int. Med., 1932, **50**, 843—854).—The œdema was due to a chronic dietary deficiency, particularly to a shortage of protein. H. G. R.

Formation of renal calculi. I. TRAUBE, K. SKUMBURDIS, and V. GOLDBERG (Munch. med. Woch., 1932, **79**, 1083; Chem. Zentr., 1932, ii, 1034).—Chondroitinsulphuric acid contains a substance which hinders the formation of flocks and calculi. A. A. E.

Plasma-phosphatase in rickets and scurvy. J. SMITH and M. MAIZELS (Arch. Dis. Childhood, 1932, **7**, 149—159).—Normally the average plasma-phosphatase is 0·23 unit during the first year of life, 0·24 in the second, and 0·17 up to the twelfth; in active rickets it is 0·3—1·4, the vals. decreasing during treatment. In scurvy, vals. increase with the onset of calcification of the hæmorrhages. Vals. are at first normal after fracture, but become higher as the callus appears. CH. ABS.

Treatment of rachitic infants with milk produced by cows fed with irradiated ergosterol. H. J. GERSTENBERGER and A. J. HORESCH (J. Nutrition, 1932, **5**, 479—483).—The milk examined had a definite but small antirachitic action when fed to infants. A. G. P.

Autogenous urinary proteose in rheumatoid arthritis. G. R. P. ALDRED-BROWN and J. M. H. MUNRO (Lancet, 1932, **223**, 1211—1214).—Autogenous urinary proteose does not produce skin reactions in rheumatoid arthritis similar to those produced by antigens in allergy. L. S. T.

Nitrogen metabolism in skin diseases. G. TEMESVARY (Magyar Orvosi Arch., 1932, **33**, 194—210; Chem. Zentr., 1932, ii, 1651).—Retention of uric and NH_2-acid was chiefly observed, but in many cases of eczema no disturbance of N metabolism was detected. A. A. E.

Relation between creatinine and lactic acid in horse's blood in tetany. S. GRZYCKI (Klin. Woch., 1932, **11**, 865; Chem. Zentr., 1932, ii, 1032).—Increase in creatinine is accompanied by decrease in lactic acid, blood-Cl remaining const. A. A. E.

Magnesium content of blood, especially in tetany. B. SJOLLEMA and L. SEEKLES (Klin. Woch., 1932, **11**, 989—990; Chem. Zentr., 1932, ii, 1037).—Human blood in tetany contained 0·5—0·7 mg. Ca per 100 c.c. A. A. E.

Carbohydrate metabolism in human trypanosomiasis. A. WORMALL (Biochem. J., 1932, **26**, 1777—1787).—There is no general hypoglycæmia during the earlier stages of this disease, although in certain cases a definitely low blood-sugar val. was obtained. Treatment with "Baeyer 205" gave variable results. There is no relationship between blood-sugar level and the presence in or absence from the blood of trypanosomes. There is no very marked impairment of the capacity of the liver to deal with glucose in trypanosomiasis. S. S. Z.

Urticaria. I. Acid–base balance. II. Blood chemistry. L. H. CRIEP (J. Allergy, 1932, **2**, 219—226).—The CO_2-combining power of the plasma does not definitely indicate a disturbance in the acid–base balance in urticaria. The blood-sugar, non-protein-N, and urea are normal. The uric acid is slightly high and the blood-Cl is low during the acute paroxysm. Total blood-Ca is normal. Diffusible Ca may be slightly high. CH. ABS.

Chemistry and metabolism in experimental yellow fever in monkeys. VI. Bromsulphalein liver function test and the Van den Bergh reaction. A. M. WAKEMAN and C. A. MORRELL (Arch. Int. Med., 1932, **50**, 876—883).—Loss of hepatic function is indicated by reduced rate of excretion of bromsulphalein and the onset of jaundice. The clotting time of the blood is increased, associated with lower fibrinogen content. $COMe_2$ is not excreted in the urine, supporting the view that the liver is the chief site of $COMe_2$ formation. H. G. R.

Growth and chemical constituents. I. Silkworms. A. AKAO (Keijo J. Med., 1932, **3**, 360—374).—The silk-worm attains a max. wt. (greater in the male than in the female) just before cocoon-formation, following which it decreases in wt. and remains fairly const. during metamorphosis. The total N and P contents follow a somewhat parallel course, but divergences occur in the purine- and uric acid-N during the period following cocoon-formation. These variations are related to phases of the worm's development. F. O. H.

Effect of a high intake of manganese on the growth of rats. J. T. SKINNER (J. Nutrition, 1932, **5**, 451—457).—Retarded growth of rats ascribed to the toxicity of Mn (Skinner *et al.*, A., 1931, 516) was due to an unsuitable source of milk solids. With suitable diet addition of 2000 p.p.m. of Mn did not affect growth rates. A. G. P.

Artificial diet for experiments of long duration on the relation between nutrition and growth, maintenance, and, particularly, reproduction. L. RANDOIN and H. SIMONNET (Compt. rend., 1932, **195**, 1328—1330).—For experiments extending over a period of years, a diet of 10—15 g. per rat per day of the following mixture maintains uniform growth and reproduction through several generations: pancreatic peptone 15, caseinogen 2, dry yeast 3, pure butter-fat 12, pure rice starch 32, sucrose 32, and Osborne and Mendel salt mixture 4%. A. C.

Regeneration. IV. Oxidation–reduction potential of the tissue of the regenerating extremity of the axolotl. N. OKUNEV (Biochem. Z., 1932, **255**, 387—392).—The oxidation–reduction potential is lower for tissue of the regenerating than for tissue of the normal extremity, due probably to the local accumulation of reducing substances (glutathione). P. W. C.

Variation of p_H of brain tissue. E. G. HOLMES (Biochem. J., 1932, **26**, 2010—2014).—The p_H vals. of mouse brains which have been fixed in liquid air are higher in the case of hypoglycæmic than of normal or hyperglycæmic animals. The changes in p_H are of the same order as those calculated from the titration curve of brain tissue and lactic acid. S. S. Z.

Metabolic activity of the cells of the trigeminal ganglion. E. G. HOLMES (Biochem. J., 1932, **26**, 2005—2009).—The trigeminal ganglia of sheep show very poor powers of oxidation, although the cells contain indophenol-oxidase. Their power of forming lactic acid from glucose is < that of the white matter of the central nervous system. S. S. Z.

Action of uric acid on metabolism of tissues. L. KURTI and C. SELLEI (Biochem. Z., 1932, **256**, 209—213).—In mice, uric acid, especially when intramuscularly injected, inhibits the aerobic and anaerobic metabolism of the liver and also acts on the kidneys as a mild poison. W. McC.

Diets of college women in relation to their basal metabolism. C. M. COONS and A. T. SCHIEFELBUSCH (J. Nutrition, 1932, **5**, 459—465).—Lowered habitual food consumption of the present day as compared with 20 years ago is shown more notably by the deficiency of protein rather than calorie content. A. G. P.

Influence of alcohol on oxidation [in the animal organism]. A. BICKEL and I. KANAI (Biochem. Z., 1932, **255**, 289—294).—When smaller (1·7 c.c.) and larger (2·7 c.c.) amounts of EtOH are added to the rabbit's diet, the oxidation quotient in the former cases usually decreased and in the latter in two cases decreased, in one remained unchanged, and in one increased. P. W. C.

Combustion of alcohol by the small mammal. Mouse. M. NICLOUX (Compt. rend. Soc. Biol., 1931, **108**, 14—17; Chem. Zentr., 1932, ii, 1651).—Combustion is much more rapid than with large mammals. Of 1 mg. EtOH per g. injected, the animal being kept at 30°, 20·4% had undergone combustion in 15 min. and 95·6% in 2·5 hr. A. A. E.

Combustion of alcohol by poikilothermic animals. Effect of temperature. M. NICLOUX (Compt. rend. Soc. Biol., 1931, **108**, 17—21; Chem. Zentr., 1932, ii, 1652).—Combustion of EtOH by the frog is much slower than by the mouse. At 1° combustion amounts to 14·7% in 24 hr., and at 29° to 97%. A. A. E.

Reaction velocity and van 't Hoff's temperature coefficient of the combustion of alcohol in the organism of the poikilothermic animal. M. NICLOUX (Compt. rend. Soc. Biol., 1931, **108**, 21—24; Chem. Zentr., 1932, ii, 1652).—Between 1° and 29° the temp. coeff. is approx. 2. A. A. E.

Morphology of sclerotic cartilage. V. Influence of aqueous nutrients on the development of sclerotic cartilage in *Hynobius leechii*. T. YATABE (Keijo J. Med., 1932, **3**, 393—402).—The growth of the sclerotic cartilage in *H. leechii* is retarded by restriction to aq. (1%) nutrients which form the following increasing order of inhibition: EtOH, peptone, vitamin-*B* prep., glucose. A still greater retardation is effected by starvation. F. O. H.

Urinary composition and acid–base equilibrium. IV. Acid excess of urine. V. Effect of muscular work on the composition of the urine. S. M. NEUSCHLOSZ (Biochem. Z., 1932, **256**, 37—50, 51—54; cf. A., 1931, 1444).—IV. Theoretical considerations as well as examination of the urine of persons suffering from acidosis and of that of dogs receiving intravenous injections of acid show that most of the acid excreted leaves the organism as NH_4 salt, and that the function of the acid excess in the urine is to provide for the rapid and sharply-defined regulation necessary for maintaining the normal reaction of the blood.

V. Vigorous bodily exercise results in increase in the acidity and NH_3 content of human urine, preferential excretion in it of the weaker amongst the moderately strong acids concerned, and decrease in the ratio of excess of acid to NH_3. The views previously expressed are thus confirmed. W. McC.

Nitrogen excretion of the hypophysectomised dog after a meat meal. B. BRAIER (Compt. rend. Soc. Biol., 1931, **108**, 128—130; Chem. Zentr., 1932, ii, 1793—1794).—During fasting, hypophysectomised dogs excrete 30% less N per hr. and kg. than do normal animals. By feeding with meat the N excretion of hypophysectomised dogs is at first retarded, but afterwards accelerated, so that the total N excretion in 24 hr. is unchanged. A. A. E.

Cystine and wool production. H. E. WOODMAN and R. E. EVANS (Nature, 1932, **130**, 1001).—A criticism (cf. A., 1932, 646). In England, the cystine content of the pasturage, although low, is sufficient to account for wool production. L. S. T.

Fatigue of skeletal muscle. M. OSAWA (Arbeitsphysiol., 1932, **5**, 357—369; Chem. Zentr., 1932, ii, 1470).—The toad's gastrocnemius yields to perfusion liquid a substance identical with Haberlandt's heart hormone. Acids reduce the contractability of the muscle; alkalis increase it. Lactic acid increases the sugar-mobilising action of adrenaline on the perfused toad liver. A. A. E.

Nutrient value of certain animal protein concentrates. P. B. CURTIS, S. M. HAUGE, and H. R. KRAYBILL (J. Nutrition, 1932, **5**, 503—517).—Nutrient vals. of various tankages and meat scrap are determined. The hot-H_2O-sol. protein (I) contents are recorded and their significance is discussed. The (I) in a tankage ration having 15% protein is inadequate even for maintenance and is deficient in tryptophan and cystine. Tankage may be used as a supplement to certain grain rations. A deficiency of tryptophan is associated with a type of blindness in rats. A. G. P.

Biological values of proteins. III. Method used to measure the nitrogenous exchange of rats. IV. Biological values of the proteins of wheat, maize, and milk. M. A. B. FIXEN and H. M. JACKSON (Biochem. J., 1932, **26**, 1919—1922, 1923—1933).—III. Modifications of the previous method are described (cf. A., 1931, 256, 271).

IV. The following vals. have been obtained: whole wheat (6% protein in diet) 68, wheat embryo (7%) 69, wheat endosperm (7%) 61, whole yellow maize (8%) 67, (5%) 84, yellow maize endosperm (7%) 70, whole milk (7%) 86, lactalbumin (7%) 65, caseinogen (6%) 76, heated caseinogen (7%) 54·5, "whole rat" prep. (7%) 55. S. S. Z.

Influence of administration of arginine and histidine on excretion of creatinine. B. G. SHAPIRO and H. ZWARENSTEIN (Biochem. J., 1932, **26**, 1880—1885).—Injection of arginine and histidine into adult male rabbits gives rise to 10—40% increase in the elimination of urinary creatinine. Feeding with glycocyamine has no effect on creatinine excretion, but leads to a large output of creatine. Injected glycine and alanine or ingested tyrosine, cystine, and glutamic acid have no effect on creatine or creatinine excretion. S. S. Z.

Possible formation of glucose from lecithin. M. VRIART (Compt. rend. Soc. Biol., 1931, **108**, 136—137; Chem. Zentr., 1932, ii, 1651).—Increased excretion of sugar from depancreatised or phloridzinised dogs was not observed. A. A. E.

Tryptophan content of the thyroid gland and other organs after a meat meal. D. POTICK and P. M. RE (Compt. rend. Soc. Biol., 1931, **108**, 135; Chem. Zentr., 1932, ii, 1646).—In dogs the tryptophan content of the thyroid and the red blood-corpuscles was markedly increased, whilst that of certain other organs was decreased. A. A. E.

Nitrogenous and fat metabolism. Influence of muscular work on the blood-nitrogen and -fat content. T. HIRAMATSU (Biochem. Z., 1932, **255**, 304—306).—The N and fat contents of the blood of rats fed on a rice diet in the fasting condition are considerably < those of animals on a flesh diet. The total and residual N and the fat contents of the blood of the rice-fed rats do not change with muscular work, whereas with flesh-fed rats the N contents increase and the fat content decreases. P. W. C.

Effects of fatty acid on nutrition. U. TANGE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **20**, 13—28).—Rats fed on a fat-free diet develop a condition characterised by extensive dermatitis, loss of hair, and loss of wt., but the administration of small quantities of linoleic or linolenic acid prevents and cures the condition. Oleic and elaidic acids produce a growth response, but do not effect complete cure. Stearic and clupanodonic acids are also non-curative. W. O. K.

Fat metabolism in fishes. I. Fatty acid composition of the fats of a number of fishes. II. Peritoneal, pancreatic, and liver fats of the sturgeon (*Acipenser sturio*). J. A. LOVERN (Biochem. J., 1932, **26**, 1978—1984, 1985—1988).—II. The most noticeable differences in fatty acid composition between the oils from fresh-water fish and from marine species are the increased proportions of oleic, linoleic, and palmitoleic acids and the reduced amounts of acids of the and C_{22} series in the former oils. There is no linoleic acid and the low ratio of C_{20} to C_{22} acids does not occur in halibut-liver oil.

II. The analytical data of the component fatty acids do not support the theory of desaturation in the liver. They show an interrelationship between palmitic and palmitoleic acids. A relationship is maintained between the amount of total saturated acids (24%) and total unsaturated acids (76%). S. S. Z.

Fat metabolism of the herring. I. H. J. CHANNON and M. K. EL SABY (Biochem. J., 1932, **26**, 2021—2034).—The % of fatty acids in the liver and "mesentery" increases for about 3 weeks after the gonads are empty to a max. (15 and 39%, respectively) and then falls to about 1% by the time of spawning. In the case of the muscles the max. of 17·4% is reached after about 5 weeks and then progressively falls to approx. the initial val. The % of fatty acids of the ovaries and testes varies during the period of maturation, whilst that of cholesterol continuously rises to a max. The cholesterol in the liver and mesenteric fat disappears at a much slower rate than do the fatty acids of these tissues. The % in the muscle remains approx. const. The degree of unsaturation of the fatty acids of the ovaries and testes rises steadily to a max. (I val. 137—200) before the fish spawns. The I vals. of other tissues (liver 128, "mesentery" 108, muscle 118) remain const. S. S. Z.

Carbohydrate metabolism. Influence of muscular work on the blood-sugar and glycogen contents and of injection of sugar and phosphate on the blood-sugar and glycogen contents after muscular work. T. HIRAMATSU (Biochem. Z., 1932, **255**, 295—303).—A table gives the blood-sugar (I) and glycogen [of the liver (II) and of the rest of the animal (III)] contents of normal fasting white rats on rice and flesh diets. All the vals. decrease during muscular work. With rice-fed animals 1 hr. after cessation of work (I) is not greatly increased, (II) is unchanged, whilst half the loss of (III) has been replaced. With flesh-fed animals, (I) has regained normal vals., half the loss of (II) has been replaced, but (III) is unchanged. After 3 hr. rest, (I) is normal with both types of diet, but with the rice diet (II) and (III) have not shown further change, whereas with the flesh diet (II) is almost normal and loss in (III) is > half replaced. When glucose is injected into animals on a rice diet during work, the amounts of (I), (II), and (III) utilised are small and the time of recovery after work is shortened. With flesh-fed animals during injection, (I) and (II) increase and hyperglycæmia results, whilst the amount of (III) used is very small. P. W. C.

Antiketogenic action of carbohydrates. A. GOTTSCHALK (Klin. Woch., 1932, **11**, 978—980; Chem. Zentr., 1932, ii, 1034).—The point of attack is the $CH_2Ac{\cdot}CO_2H$ stage, probably by the formation of a condensation product of this with a degradation product of the carbohydrate. A. A. E.

Nutritive value of wheat embryos. V. FAMIANI (Atti R. Accad. Lincei, 1932, [vi], **16**, 275—278).—Rats fed on wheat alone show limited growth and lowered powers of resistance. Addition of 25% of wheat embryo to the diet effects improved growth and increased resistance, and further addition of 4% of Pappenheimer, McCann, and Zucker's saline mix-

ture results in almost normal growth and reproduction, but does not render suckling possible; further addition of 5% of caseinogen is without effect. T. H. P.

Re-formation of muscle-glycogen after exercise is an insulin action. J. Hoet and H. Ernould (Compt. rend. Soc. Biol., 1931, **107**, 921—923; Chem. Zentr., 1932, ii, 1469).

Glucosone. K. C. Dixon and K. Harrison (Biochem. J., 1932, **26**, 1954—1958).—Glucosone was prepared from fructose by oxidation with selenious acid. It can be detected and determined in dil. solution (0·03%) by pptn. with 2 : 4-dinitrophenylhydrazine in HCl after keeping at 37° for 1 hr. Glucosone occurs to an extent of < 0·01% in the blood of rabbits suffering fron convulsions caused by insulin. It is not formed by the liver even in presence of insulin, nor does it occur in the fresh liver (cf. A., 1927, 480). S. S. Z.

Behaviour of the piperidine ring in metabolism. H. Steudel (Z. physiol. Chem., 1932, **213**, 11—15).—Treatment of 1-piperidinomethyl-5 : 5-diethylbarbituric acid (I) with aq. NaOH affords veronal, CH_2O, and methylenedipiperidine. When (I) was administered to dogs δ-methylaminovaleric acid was isolated from the urine. J. H. B.

Oxidative metabolism in hunger and on an insufficient diet. Influence of replacement of food protein by amino-acids on intermediate metabolism. I. Kanai (Biochem. Z., 1932, **255**, 307—318).—In a fasting animal and on an insufficient diet, less material is oxidised, but the oxidation is more complete than normal. By replacement of the food protein with glycine or glycylglycine, incomplete utilisation, especially of the N, was recorded, whereas replacement with a mixture of NH_2-acids led to incomplete utilisation, particularly of the C. P. W. C.

Regulation of sodium by muscle. R. Mond and H. Netter (Pfluger's Archiv, 1932, **230**, 42—69; Chem. Zentr., 1932, ii, 736—737).—Frog's muscle is free from Cl; it contains 30 (max.), 15 (average) mg. Na per 100 g., depending on the season and the condition of the animal. The Na is localised at the surface of the muscle fibre. In muscular activity this Na does not serve directly as a buffer for the excreted lactic acid. During recovery Na becomes associated with the muscle. A. A. E.

Apparent digestibility of, and nitrogen, calcium, and phosphorus balance of dairy heifers fed on, artificially dried pasture herbage. R. E. Hodgson and J. C. Knott (J. Agric. Res., 1932, **45**, 557—563).—Grass dried at 38—93° for 12 hr. had the following digestibility coeffs. (heifers): crude protein, 74·9%; N-free extract, 74·5%; Et_2O extract, 21·9%; crude fibre, 72·7% The N balance of heifers was negative (average 0·63 g. per day) in two cases out of three. Ca and P balances were positive in two cases and negative in the third. A. G. P.

Spectrographic proof of the formation of substances by excitation of the cardiac nerves. Z. M. Bacq and V. Henri (Compt. rend., 1933, **196**, 135—137).—The absorption curve of the Ringer's solution used for perfusing a stimulated (excitation of the vago-sympathetic trunk) frog's heart shows a max. at about 3150 Å., a min. at about 3000, and then rises rapidly towards the ultra-violet; the positions of the bands are similar to those of the polyphenols. The perfused solution from a non-stimulated heart shows general absorption in the far ultra-violet. H. B.

Potential toxicity. I. G. Kahlson. **II. Significance of the polarity of the concentration gradient in the activity of a potential poison.** H. Haag and G. Kahlson (Arch. exp. Path. Pharm., 1932, **169**, 44—55, 56—69).—I. The potential toxicity of choline is dynamic in nature and is exhibited only during the penetration phase.

II. Acetylcholine has all the properties of a potential poison, in the action of which the direction of the concn. gradient is important. P. G. M.

Relation of taste and chemical constitution. S. Michael (Biochem. Z., 1932, **255**, 351—377).—The taste intensity (I) of undissolved inorg. salts is for the most part determined by and follows their heats of dissolution. In org. substances (I) is dependent on the no. and position of O- and N-containing substituents. With the same no. of such substituents, (I) decreases with increasing no. of C atoms and increases the more closely together are the substituents. With saturated dicarboxylic acids, (I) increases the nearer the carboxyl groups are together, and those acids with an odd no. of C atoms have a greater (I) than those with an even no. Of the unsaturated dibasic acids, the *cis* have a greater (I) than the *trans*. With di-substituted C_6H_6 compounds, the *m*-substituted are more intense than the *o*- or *p*-. P. W. C.

Toxicology of *o*-tolyl phosphate. E. Gross and A. Grosse (Arch. exp. Path. Pharm., 1932, **168**, 473—514).—*o*-Tolyl phosphate (I) exerts a marked toxic action with extensive lesions in various organs in animals and in man, whilst the *m*- (II) and *p*-isomerides (III) are relatively harmless. (I) is relatively readily absorbed through the mucous membrane or unbroken skin and from the peritoneal cavity, whereas the (II) and (III) are not. After intravenous administration (I) disappears from the blood-stream within 40 min. and is stored partly in the wall of the stomach and intestine and in the liver and spleen, and partial excretion of unchanged (I) takes place through the kidneys. W. O. K.

Synergism and antagonism of drugs. I. Non-parasympathetic antagonism between atropine and the miotic alkaloids. T. Koppanyi (J. Pharm. Exp. Ther., 1932, **46**, 395—405).—Atropine antagonises the action of pilocarpine and other miotic alkaloids even in cases where parasympathetic action is excluded. W. O. K.

Changes in diastase of blood and urine after various types of surgical anæsthesia. T. Castro (Arch. Ist. Biochim. Ital., 1932, **4**, 361—374).—An increase in the diastatic activity of blood and urine is found in human patients after Et_2O or spinal anæsthesia, but with C_2H_4–N_2O little or no change occurs. Local anæsthesia has no effect. The changes

are probably due to the toxic action of the anæsthetic on the pancreatic cells. R. K. C.

Relative pre-anæsthetic values of the sodium salts of ethyl*iso*amylbarbituric acid (amytal), pentobarbital, phenobarbital, and barbital. E. E. SWANSON (J. Pharm. Exp. Ther., 1932, **46**, 387—394).—The pre-medication vals. of Na amytal and Na pentobarbital, *i.e.*, their powers in terms of their respective toxic doses to facilitate anæsthesia by N_2O–O_2 and C_2H_4–O_2 in animals (rats or cats), are approx. equal, but Na barbital and Na phenobarbital have lower vals. W. O. K.

Colloid chemistry of the nervous systems. VI. W. D. BANCROFT and J. E. RUTZLER, jun. (J. Physical Chem., 1932, **36**, 3162—3174; cf. A., 1932, 1061).—Anæsthesia and recovery phenomena have been studied on goldfish anæsthetised by Na amytal, Et_2O, nembutal, EtOH, or urethane. Although Na citrate, Na tartrate, and $Al_2(SO_4)_3$ revive the fish more rapidly than does NaCNS, NaCl, or NaBr, the effects of the former compounds are due to processes other than the counteraction of anæsthesia. The action of the peptising agents NaCNS, NaCl, and NaBr is consistent with the reversible coagulation theory of anæsthesia. Osmotic pressure changes appear to have no influence. E. S. H.

Response of the isolated intestine to cocaine and novocaine at different p_H levels. W. SALANT and W. M. PARKINS (J. Pharm. Exp. Ther., 1932, **46**, 435—446).—The effect of cocaine on the isolated intestine (cats, rabbits, and rats) varies with the p_H, but the action of novocaine on the rat intestine is not influenced by p_H. W. O. K.

Action of some hypnotics on blood-sugar and blood-lactic acid. L. HONIGHAUS (Arch. exp. Path. Pharm., 1932, **168**, 561—568).—In rabbits, subcutaneous administration of morphine hydrochloride raises the blood-sugar (I) and -lactic acid (II), whilst luminal lowers (I) and dionin (II). Codeine phosphate and urethane are without definite effect on (I) or (II). Similar results are obtained when Na lactate solution is injected intravenously 1 hr. after the administration of the hypnotic. W. O. K.

Parasympathicotonics and blood-lactic acid. I. I. NITZESCU and N. MUNTEANU (Compt. rend. Soc. Biol., 1932, **109**, 314—315; Chem. Zentr., 1932, i, 1799).—Pilocarpine and eserine and, to a smaller degree, choline increase blood-lactic acid similarly to the blood-sugar increase. L. S. T.

Pharmacological action of eseridine. R. ST. A. HEATHCOTE (J. Pharm. Exp. Ther., 1932, **46**, 375—385).—Eseridine (I) in general acts by stimulating the parasympathetic nerves, but its slowing action on the heart of the toad or rabbit is probably exerted directly on the muscle. The action of (I) runs closely parallel to, but is only about one tenth as strong as, that of eserine. W. O. K.

Comparative pharmacological study of some related ephedrine compounds. E. E. SWANSON (J. Amer. Pharm. Assoc., 1932, **21**, 1125—1134).—The pharmacological activity of six analogues of ephedrine, two stereoisomeric forms of 3-α-hydroxybenzylpiperidine, and 2-amino-1-hydroxyindane is recorded. R. S. C.

Ergotamine and the adrenaline-controlled increase of blood-lactic acid. I. I. NITZESCU and N. MUNTEANU (Compt. rend. Soc. Biol., 1932, **109**, 311—313; Chem. Zentr., 1932, i, 1799).—Ergotamine arrests adrenaline hyperglycæmia but not the lactic acid excretion in blood. Glycogen accumulation in the muscles has a mechanism different from that produced by adrenaline in the liver. L. S. T.

Action of tyramine on the excitability of the cardiac vagus, and influence of this amine on the effects of nicotine. M. RAYMOND-HAMET (Compt. rend., 1932, **195**, 1330—1333).—The electric excitability of dog's cardiac vagus is progressively diminished by intravenous injection of tyramine (I) in doses increasing from 20 to 300 mg. per kg., the highest dose completely abolishing excitability. (I) simultaneously destroys the effect of nicotine on arterial pressure and intestinal motility. The effect of a moderate dose of acetylcholine is, however, not influenced by 444 mg. of (I) per kg. body-wt., and adrenaline (0·05 mg.) still induces a distinct, though reduced, hypertension. A. C.

Determination of alkaloids, especially atropine, in the animal body. H. A. OELKERS, W. RAETZ, and K. RINTELEN (Arch. Pharm., 1932, **9**, 520—539).—Various alkaloids give with KI–I and phosphomolybdic acid ppts., which can be used for approx. nephelometric determination of the alkaloid. Centrifuging of the ppt. with the latter reagent and titration with alkali allows accurate determination of very small quantities. Details are given for determination of atropine (I) in the blood, serum, organs, and urine of the guinea-pig and rabbit. The concn. of (I) in the blood of rabbits after subcutaneous injection rises to a max. in 20—30 min., and thereafter falls to 0 in about 2 hr.; 24—33·7% of the (I) injected (independent of the dose) is excreted in the urine in 72 hr. (I) is unstable in aq. or alkaline solution. R. S. C.

Detection of choline and acetylcholine. G. KAHLSON (Arch. exp. Path. Pharm., 1932, **169**, 34—43).—Choline can be quantitatively extracted from tissue by $COMe_2$. After removal of the solvent it is acetylated and the acetylcholine is determined by its action on the frog's heart. P. G. M.

Action of various uric acid eliminants on experimental uric acid storage in the kidney. H. O. SCHROEDER (J. Pharm. Exp. Ther., 1932, **46**, 461—469).—In various animals the accumulation of uric acid in the kidneys after its administration is decreased by cincophen and neocincophen and to a smaller extent by $NaHCO_3$ and Na salicylate (I), but not by $(CH_2)_6N_4$ or piperazine. The increased elimination of uric acid produced by (I) in man is probably due to increased purine metabolism and also possibly to decreased uricolysis. W. O. K.

Rapid detection of diethylbarbituric acid and phenylethylbarbituric acid in neural substance. G. VITTE (Bull. Soc. Pharm. Bordeaux, 1931, **69**, 279—283; Chem. Zentr., 1932, ii, 1048).—Pulped cerebral substance is ground to homogeneity with

5 c.c. of 20% $CCl_3 \cdot CO_2H$, further quantities of acid being gradually added until the total vol. is about 100 c.c. After 30 min. 50 c.c. H_2O are added, and the mass is stirred for 30 min. After filtration, extraction with Et_2O, and filtration of the extract, the Et_2O is evaporated and the residue is dissolved in dil. aq. NH_3 and heated for 15 min. on the water-bath with a little animal C. The residue is again taken up with dil. aq. NH_3, slightly acidified with HCl, and again extracted with Et_2O. The Et_2O residue is treated with 1 drop of aq. NH_3 (1 : 10) and 1 drop is treated under the microscope with H_2SO_4 (1 : 10). Diethyl- and phenylethyl-barbituric acid crystals are readily distinguishable. A. A. E.

Influence of Chinese antidiabetic drugs on rabbit's blood-sugar. I. P. Min (Korean Med. J., 1932, **2**, 50—56).—Rapid hyperglycæmia followed the oral administration of *Lonicera japonica, Paeonia abovata, Trichosanthes kirilowii, Coptis teeta, Licium chinense, Phyllostachys bambusoides, Liriope graminifolia*, and *Bupleurum falcatum*. Ch. Abs.

Clinical evaluation of convallatoxin. B. Weicker (Arch. exp. Path. Pharm., 1932, **168**, 731—742).—The action of convallatoxin from *Convallaria majalis* on frogs and cats has been examined quantitatively and its effect on human cardiac cases investigated. It resembles strophanthin and exhibits the phenomenon of cumulation. W. O. K.

Evaluation on the frog of glucosides acting on the heart. K. Fromherz (Arch. exp. Path. Pharm., 1932, **168**, 743—744).—Evaluation of the activity of glucoside preps. by the frog method may lead to different results depending on whether spring or autumn frogs are employed (see preceding abstract). W. O. K.

Catatonin, a toxic substance of the lipoid extract of urine, tissue-fluids, and organs. J. Freud and E. Dingemanse (Biochem. Z., 1932, **255**, 464—473).—The prep. of catatonin from urine is described. It is extracted quantitatively by fat solvents from alkaline media. Injected into rats in oil or aq. solution it brings about all the symptoms of experimental catatonia in a few min. P. W. C.

Anaphylaxis and calcium. I. S. Yun (Korean Med. J., 1932, **2**, 14—18).—The serum-Ca increases after sensitising by normal horse serum (I) in the guinea-pig and decreases after reinjection of (I). Anaphylactic shock was inhibited by injection of "vigantol," "parathormone," and $CaCl_2$. Ch. Abs.

Effects of certain toxic gases on the blood of the cockroach, *Periplaneta orientalis*, Linn. W. E. Shull, M. K. Riley, and C. H. Richardson (J. Econ. Entom., 1932, **25**, 1070—1072).—Of a no. of org. materials examined few produced any visible changes in the blood of cockroaches. In those killed by AcOH vapour the blood did not coagulate, and cells were fixed in an apparently normal condition. Crystals of $MgNH_4PO_4$ occurred in blood from insects killed by NH_3. A. G. P.

Relation of respiratory metabolism of insects to their susceptibility to fumigants. R. T. Cotton (J. Econ. Entom., 1932, **25**, 1088—1103).—The susceptibility of an insect to a fumigant varies with the rate of respiratory metabolism. Among known factors increasing susceptibility, the most important are rise of temp. and an increased CO_2 or decreased O_2 content of the atm. A. G. P.

Action of carbon dioxide on the human organism and its importance in public health. H. Lehmann (K. Mitt. Ver. Wasser-, Boden-, Luft-hyg., 1932, **8**, 145—158; Chem. Zentr., 1932, ii, 1197).—8—10% or more of CO_2 in inhaled air can be tolerated. Many animals can tolerate 50% for 1—1·5 hr. Town and country air both contain about 0·04% CO_2. A. A. E.

Carbon monoxide poisoning, with special reference to chronic injury to health. Beintker (Gasmaske, 1932, **4**, 75—77; Chem. Zentr., 1932, ii, 1037).—Chronic CO poisoning cannot be diagnosed with certainty, since CO vanishes rapidly from the blood. A. A. E.

Alkaline-earth salts and their biological action. K. Mulli and F. Standenath (Klin. Woch., 1932, **11**, 990—991; Chem. Zentr., 1932, ii, 1035).—Citric acid should not be regarded as a Ca-pptg. acid, since it probably forms in the organism a sol. Na Ca citrate complex. A. A. E.

Chemotherapeutic examination of rare metals. V. Fischl (Z. Hyg., 1932, **114**, 284—288).—Relationships between the periodic classification of metals and their therapeutic action are examined. A. G. P.

Assimilation of dust by the respiratory passages. I. Assimilation of dust containing lead and copper. O. Ehrismann (Z. Hyg., 1932, **114**, 224—268).—After exposure to Cu-containing dusts the Cu content of dogs' stomachs varied considerably, that of the lungs remained practically const. (approx. 0·1 mg.), and other organs examined were Cu-free. Cu is quickly eliminated and disappeared from the lungs within 8 days after exposure. Similar conditions were observed after exposure to dusts containing PbO. A. G. P.

Mortality of *Rhagoletis completa*, Cress., through ingestion of certain solid materials. A. M. Boyce (J. Econ. Entom., 1932, **25**, 1053—1059).—Solid particles of common insecticides and of diluents (bentonite, talc, etc.) are shown to pass, undissolved, into the stomachs of adult flies. Colloidal dilutents (CaO and S) were highly injurious. Pb arsenate had a somewhat slower action. Fish oil incorporated with $BaSiF_6$ dust reduced its speed of action. Natural cryolite had a smaller lethal action than the synthetic product. Nicotine preps. were relatively slow-acting as stomach poisons. A. G. P.

Radiation and enzyme activity. M. Copisarow (Nature, 1932, **130**, 1001—1002).—Metabolic radiation is a general function of normal org. metabolism; it is exhibited by blood, milk, eggs, brain, bone-marrow, lung, the pituitary lobes, the parathyroid gland, urine, yeast, etc. It decreases with a fall in temp., is inhibited at −5° to 10°, and destroyed by heating at 98—100° for 2 hr., by CO in the dark, H_2O_2, $KMnO_4$, and KCN. Pure cholesterol, vitamins-*C* and

-*D*, sucrose, hormones, and alkaloids as such show no radiation. Radiation is an inseparable part of normal enzymic activity. The bearing of this conclusion on malignant growth is discussed. L. S. T.

Triose-dehydrogenase. I. F. P. CLIFT and R. P. COOK (Biochem. J., 1932, **26**, 1804—1810).—An extract from ox-liver possesses three distinct dehydrogenases, one acting on glucose, another on glyceraldehyde and dihydroxyacetone, and a third on hypoxanthine and MeCHO. S. S. Z.

Hydrogenlyases. II. Some factors concerned in the production of the enzymes. J. YUDKIN (Biochem. J., 1932, **26**, 1859—1871).—Whilst aerating washed suspensions of bacteria does not destroy the enzymes, aerobic conditions during growth prevent their formation in some cases and greatly decrease it in others. In most cases no hydrogenlyases are present in organisms grown on a simple inorg. medium; those grown in broth contain them. The presence of substrates on which hydrogenlyases act favours the production of the enzymes. S. S. Z.

Amylase in barley and malt. K. MYRBACK and S. MYRBACK (Woch. Brau., 1932, **49**, 246—247).—The functions of α- (I) and β-amylase (II) in barley (III) and malt (IV) are discussed. Non-germinated (III) contains practically only (II) whilst after 2—5 days' germination considerable amounts of (I) are present. Differences in the limit of sugar formation do not appear to be due to amylokinase. With (III) and green malt of short growth, but not with (IV), there is a marked difference between the rate of hydrolysis of sol. starch and that of potato-starch paste. The amylase of (IV) is totally sol. in H_2O, whilst that of (III) is partly in a bound and inactive form which, together with the sol. form, is extracted by digestion in presence of papain. A method for the determination of (II) in (III) and (IV) is given. F. O. H.

Effect of hydrogen-ion concentration on the activity of amylase. A. OPARIN and A. KURSSANOV (Biochem. Z., 1932, **256**, 190—195).—Within the limits p_H 3·5—6·2 the changes in the activity of amylase produced by altering [H$^+$] are only apparent, and depend on changes in the physical condition of the impurities. Outside these limits changes in [H$^+$] irreversibly decrease the activity of the enzyme. W. McC.

Enzymic amylolysis. III. Amylokinase. E. WALDSCHMIDT-LEITZ and A. PURR (Z. physiol. Chem., 1932, **213**, 63—70; cf. A., 1932, 304).—The action of amylokinase (I) on pancreatic amylase is due to its Ca salt content, and is destroyed by purification (adsorption and elution). The purest (I) obtained activates α- and β-amylase; it is non-dialysable and gives carbohydrate but not protein reactions. J. H. B.

Do p_H changes play a part in the loss of activity of diastase solutions submitted to prolonged electrolysis? F. MAIGNON and D. CROIZE (Compt. rend. Soc. Biol., 1932, **109**, 195—197; Chem. Zentr., 1932, ii, 1925).—They do not. Diastase differs in this respect from trypsin. A. A. E.

Comparative effect of electrolysis on diastase and inactivated protein solutions. F. MAIGNON (Compt. rend. Soc. Biol., 1932, **109**, 93—95; Chem. Zentr., 1932, ii, 1925).—For 100 volts 4—5 hr. suffice for complete demineralisation of ovalbumin or serum-protein solutions, whilst 4—5 days are necessary for that of pancreatic juice or an extract of germinated barley. A. A. E.

Rôle of thiol compounds in carbohydrate degradation. H. K. BARRENSCHEEN and H. BENESCHOVSKY (Biochem. Z., 1932, **255**, 453—463).—$AcCO_2H$ added to mammalian muscle pulp or muscle extract is only to a small extent converted into lactic acid, the conversion being, however, greatly increased by addition of thioglycollic acid and cysteine, but unaffected by addition of adenosinetriphosphoric acid. P. W. C.

Fate of added methylglyoxal in blood and muscle. H. K. BARRENSCHEEN, K. SCHEPPACH, and J. CLAUDATUS (Biochem. Z., 1932, **256**, 196—208; cf. A., 1931, 766, 1455).—The very rapid disappearance of added AcCHO (I) in blood in the presence or absence of $CH_2Br{\cdot}CO_2H$ is confirmed. This disappearance is not due to combination with NH_2-acids or proteins, since the amount of NH_3 produced is not appreciably > when there is no addition. In the earlier stages (up to about 1 hr.) of the process lactic acid (II) equiv. to about 50% of the (I) consumed is produced in the blood; later, production of (II) is slower. $CH_2Br{\cdot}CO_2H$ does not affect the disappearance of (I), but restricts production of (II). Muscle (pulp and extract) decomposes (I) more slowly than does blood, and at first the amount of (II) produced is equiv. to > half of the (I) consumed; later (1 hr.) this amount likewise becomes equiv. to 50% of the (I) added. The production of (II) in the muscle extract is < that in the pulp, although in both cases (I) disappears at the same rate. W. McC.

Mechanism of deamination in heart and skeletal muscle. P. OSTERN (Naturwiss., 1933, **21**, 14—15).—At 40° frogs' heart-muscle pulp deaminates muscle-adenylic acid (I), adeninenucleotide (II) from yeast-nucleic acid, and adenosine (III) equally rapidly, but mammalian heart-muscle does not proportionately deaminate (II). From this and other cases of sp. action it is concluded that a mechanism exists in which the H_3PO_4 compounds are deaminated after dephosphorylation. The addition of phosphate inhibits the deamination of (II) by frog heart-muscle, but at the same p_H increases the deamination of (I). This is also true for skeletal muscle. It appears that (II) directly undergoes dephosphorylation and deamination, whilst the (I) is first combined with H_3PO_4 to form adenosinetriphosphoric acid (IV). Three deaminases probably exist in muscle acting respectively on (III), (I), and (IV). Extracts made from rabbit muscle with $NaHCO_3$ solution deaminate (I), but have practically no action on (IV), whilst the residual muscle contains an enzyme which deaminates (I) only in presence of added phosphate and presumably acts on (IV). W. O. K.

Cellulase from the symbiotic intestinal flagellates of termites and of the roach, *Cryptocercus*

punctulatus. W. TRAGER (Biochem. J., 1932, 25, 1762—1771).—The enzyme is present in four flagellates. It hydrolyses cellulose or cellobiose to glucose. It can be adsorbed on $Al(OH)_3$ and eluted with 3% KH_2PO_4. The effect of enzyme concn. and of temp. has been studied. S. S. Z.

Hydrolysis of caseinogen by pepsin and by trypsin-kinase. J. D. STIRLING and G. M. WISHART (Biochem. J., 1932, 26, 1989—1999).—The action of trypsin-kinase (I) and pepsin on caseinogen produces substances which are not completely sol. in $CCl_3{\cdot}CO_2H$. With pepsin the rate of liberation of acid-sol. N is > that of acid-sol. P, whilst with (I) the opposite is true. S. S. Z.

Action of pectase. II. A. MEHLITZ (Biochem. Z., 1932, 256, 145—157; cf. A., 1930, 957).—Although slight purification of pectase (I) from extracts of lucerne can be effected by filtration through membranes, the process has no practical val. Pptn. of (I) with EtOH and subsequent drying increases the time required for (I) to cause coagulation, but has little effect on the stiffness of the jelly produced. Treatment of the extracts with decolorising C does not affect the activity of (I). Jellies containing < 50% of sugar can be produced with (I). The time required for jelly formation increases with increasing sugar content, but the stiffness of the jelly remains unaffected. In the presence of AcOH also, jellies are produced, the time required for jelly formation being dependent on the $[H^{\cdot}]$ only. Alteration of the p_H from 4·88 to 3·95 by addition of the acid results in a ten-fold increase in this time. W. McC.

Specificity of phosphatase. Enzymic fission of a heterocyclic phosphoric ester by animal phosphatase. K. P. JACOBSOHN and F. B. PEREIRA (Compt. rend. Soc. Biol., 1931, 107, 1168—1170; Chem. Zentr., 1932, ii, 1925).—Kidney- and liver-phosphatase cause fission of di-8-hydroxyquinoline pyrophosphate. A. A. E.

Specificity of phosphatases. Enzymic hydrolysis of a hydroxyquinoline phosphate by vegetable phosphatase. F. B. PEREIRA and A. DA CRUZ (Compt. rend. Soc. Biol., 1931, 107, 1170—1171; Chem. Zentr., 1932, ii, 1925).—Phosphatase of dried yeast caused 37%, that of pea-flour 79%, fission. A. A. E.

Specificity of mammalian phosphatases. J. ROCHE (Compt. rend. Soc. Biol., 1931, 107, 1144—1145; Chem. Zentr., 1932, ii, 1925).—Tests of phosphatases from red and white blood-corpuscles, serum, kidney, intestine, and bone with various PO_4-compounds differentiated several types. A. A. E.

Photochemical methods for investigation of oxygen-transportases (use of acetic acid bacteria and yeast-cells). F. KUBOWITZ and E. HAAS (Biochem. Z., 1932, 255, 247—277).—A further 22 wave-lengths are added to the 15 already described (A., 1929, 1475) of the respiratory enzyme, the spectral range being now from 193 to 671 mμ. The methods whereby the 37 wave-lengths are determined and the absorption coeffs. calc. are described. The absorption spectra of the CO compound of the respiratory enzyme of *B. Pasteurianum* and *Torula utilis* are given and compared with those of hæmoglobin, chlorocruorin, and cytochrome. P. W. C.

Conversion of acetaldehyde by yeast. Action of co-zymase. II. F. ZUCKERKANDL and L. MESSINER-KLEBERMASS (Biochem. Z., 1932, 255, 330—343).—The reduction of MeCHO to EtOH is always dependent on the presence of glucose or glycogen, glucose being first split into a 3C complex (I). Poisoning the yeast with NaF or $CH_2I{\cdot}CO_2H$ prevents the formation of (I), and therefore of EtOH. The formation of (I) is again made possible by addition of PO_4''' or substances containing an imine group and the reduction then again takes place. (I) passes partly into $AcCO_2H$ by oxidation. Enzymic processes which are not inhibited by NaF or $CH_2I{\cdot}CO_2H$ are not affected by addition of imines. P. W. C.

Mechanism of oxidation processes. XXXII. Enzymic oxidation of acetic acid by yeast. H. WIELAND and R. SONDERHOFF.—See this vol., 32.

Enzymes and salt ions. IV. Invertase concentration in *Penicillium glaucum* in nitrogen deficiency. G. VON DOBY (Z. physiol. Chem., 1932, 213, 71—83; cf. A., 1932, 665).—The variation in invertase production by *P. glaucum* was studied when the nutrient solution was varied in respect of sucrose concn. (4—20%) and in source and concn. of N (0·0035—0·28%). The optimum p_H of the invertase was 4·5, the temp. optimum 50° in all cases. The invertase concn. on 5% sucrose was an inverse function of the N concn., and was higher for org. N sources. It was less dependent on the N concn. with 20% sucrose. J. H. B.

Presence of factor *Z* in grape juice and fermented liquors. J. BRISOU and L. GENEVOIS (Compt. rend. Soc. Biol., 1931, 107, 865—867; Chem. Zentr., 1932, ii, 1641).—Euler's observation of the presence of factor *Z* in liquids fermented aerobically with yeast was confirmed for Gironde wine yeast and grape juice (I). Fresh (I) contains as much *Z* as yeast juice; fermented (I) contains much less, and the finished wine contains very little. A. A. E.

Chemical composition of *Aspergillus niger* as modified by zinc sulphate. N. PORGES (Bot. Gaz., 1932, 94, 197—205).—Addition of 0·01% of $ZnSO_4$ to a 10% sugar medium tended to retard spore formation and increase vegetative growth in *A. niger*. Under these conditions there was a greater utilisation of sugar and larger yield of citric acid. Treatment with $ZnSO_4$ increased the Et_2O-sol. and cold-H_2O-sol. constituents and the hemicellulose content of the mycelium. The lignin content was considerably depressed. A. G. P.

Influence of potassium salt anions on the mycelium growth of *Aspergillus niger*. E. LOWIG (Landw. Jahrb., 1932, 76, 181—210).—The presence of 0·1—1·0% of citric acid in the nutrient or soil extract does not affect the growth of mycelium of *A. niger*. The growth increases caused by K citrate, silicate, chloride, and sulphate are attributable to the action of the cation alone. The greatest relative growth increase due to K was shown in solutions containing 0·0035% K_2O. Max. growth intensity is reached in 3—4 days. The abs. and relative K_2O

and P_2O_5 contents of the mycelium decrease and the Cl' and SO_4'' contents increase with age. In the early stages the K_2O and P_2O_5 contents of the mycelium are approx. 10 times those of the nutrient medium. Where K is supplied as sulphate the SO_4'' content of the fresh mycelium in the early stages is approx. the same as that of the nutrient, but rises considerably with increasing age of the culture, and finally exceeds the equiv. of the K content. Where KCl is supplied the Cl' content of the mycelium never exceeds that of the nutrient, and ultimately equals ¼—⅓ of the K content. A. G. P.

Chemical production of a growth-promoting substance of the *B* group. N. Nielsen and V. Hartelius (Biochem. Z., 1932, **256**, 2—10; cf. A., 1932, 661).—A substance which promotes the growth of *Aspergillus niger* is produced by the interaction of carbohydrate (glucose, fructose, or arabinose, but not inositol, mannitol, or EtOH), org. acids (tartaric, citric, succinic, lactic, oxalic) or their NH_4 salts, and filter-paper or filter-paper ash, especially at high temp. (135°). The substance contains no N and, like the similar (or identical) substance produced by *Rhizopus suinus*, is insol. in Et_2O and is destroyed by H_2O_2. W. McC.

Biochemistry of micro-organisms. XXV. 3 : 5-Dihydroxyphthalic acid, a product of the metabolism of glucose by *Penicillium brevi-compactum* and related species. A. E. Oxford and H. Raistrick. **XXVI. The formation from glucose by members of the *Penicillium chrysogenum* series of a pigment, an alkali-soluble protein, and penicillin.** P. W. Clutterbuck, R. Lovell, and H. Raistrick (Biochem. J., 1932, **26**, 1902—1906, 1907—1918).—XXV. The product $C_8H_6O_6$ (A., 1932, 1289) is 3 : 5-dihydroxyphthalic acid.

XXVI. The pigment chrysogenin, $C_{18}H_{22}O_6$, $[\alpha]_{5161}$ —762°, gives a brown coloration with $FeCl_3$ and contains two weakly acidic groups. The protein resembles a typical alkali-sol. leaf-protein. Penicillin is an extremely labile substance very readily inactivated by oxidation. It is moderately stable at p_H 5—6 and less stable in acid or alkaline solutions. The synthetic media contained glucose and mineral salts with $NaNO_3$ as a source of N. S. S. Z.

Chemistry of mould tissue. I. Soluble carbohydrate constituents. A. G. Norman, W. H. Peterson, and R. C. Houtz. **II. Resistant cell-wall material.** A. G. Norman and W. H. Peterson (Biochem. J., 1932, **26**, 1934—1945, 1946—1953).—I. The H_2O- and alkali-sol. fractions of *Aspergillus fischeri* grown on a glucose–NH_4NO_3 medium have been examined. Except for a trace of pentose the only sugar unit found was glucose. Interrupted hydrolysis of one of the fractions indicated the presence of two types of sugar linking, one easily hydrolysed and the other more resistant.

II. The resistant cell-wall material of *A. fischeri* does not contain ordinary cellulose. It is probably a mixture of two components, one containing hexosamine, glucose, and Ac units, and the other more readily hydrolysed glucose units alone. S. S. Z.

Chemistry of the white rots of wood. III. Effect on wood substance of *Ganoderma applanatum* (Pers), Pat., *Fomes fomentarius* (Linn.), Fr., *Polyporus adustus* (Willd.), Fr., *Pleurotus ostreatus* (Jacq.), Fr., *Armillaria mellea* (Vahl.), Fr., *Trametes pini* (Brot.), Fr., and *Polystictus abientinus* (Dicks), Fr. W. G. Campbell (Biochem. J., 1932, **26**, 1829—1838).—The examination of this series shows that fungi of the white rot type decompose carbohydrates as well as lignin, although there is no general uniformity with regard to either the order or proportion in which the several wood components are decomposed. In white rots the total alkali-solubility of the decayed wood as a % of oven-dry sound wood rises to a max. and begins to decline at a much earlier stage than in brown rots. S. S. Z.

Arsenic fungi of Gosio. C. Thom and K. B. Raper (Science, 1932, **76**, 549—550).—As fungi are more numerous in soil than has previously been supposed. Many species or strains of *Scopulariopsis* and *Aspergillus sydowi* produce As-containing gas. Other common fungi such as *Penicillium expansum*, *P. chrysogenum*, etc. grow well on As substrates without producing gas. Accumulation of As in soil may be expected to occur only when large amounts of As are used, or under special conditions favourable to the development of a varied microflora. L. S. T.

Aeration train for the study of products of bacterial metabolism. H. H. Walker (J. Bact., 1932, **24**, 169—184).—Apparatus for determining the NH_3 and CO_2 produced in aerated bacterial cultures is described. A. G. P.

Effect of iodoacetic acid on bacterial lactic acid production. K. Meyer (Biochem. Z., 1932, **256**, 105—114).—$CH_2I{\cdot}CO_2H$, in doses far below the lethal, specifically inhibits the production of lactic acid by otherwise unaffected bacteria. W. McC.

Lactic acid fermentation. Effect of potassium chloride. G. P. Le Gallic (Compt. rend. Soc. Biol., 1932, **108**, 1138—1140; Chem. Zentr., 1932, ii, 1642).—The yield of lactic acid is diminished; it is max., independently of the quantity of KCl, in 65 hr. A. A. E.

Fermentation products of *Actinomyces* sp. Saito. T. Takahashi and T. Asai (J. Agric. Chem. Soc. Japan, 1932, **8**, 652—655).—Glucose afforded $CHAcMe{\cdot}OH$ and *l*-lactic acid (I); the yield of (I) was 36% of the glucose consumed. Ch. Abs.

Formation of fructose and kojic acid by acetic acid bacteria. T. Takahashi and T. Asai (Proc. Imp. Acad. Tokyo, 1932, **8**, 364—366).—Fructose and kojic acid have been isolated from mannitol cultures of several species of AcOH-bacteria which also produce gluconic acid from glucose. A. C.

Gluconic acid fermentation. IV. *Bacterium hoshigaki* var. *glucuronicum* II and III nov. sp. T. Takahashi and T. Asai (J. Agric. Chem. Soc. Japan, 1932, **8**, 703—719).—II produces acid from arabinose, glucose, fructose, galactose, sucrose, raffinose, glycerol, mannitol, sorbitol, EtOH, and PrOH, but not from maltose, lactose, dextrin, starch, inulin, or MeOH. It inverts sucrose and oxidises AcOH. The yield of gluconic acid is 89% of the glucose used, or 100% for the culture solution containing glucose

and peptone or NH_4 phosphate. III does not produce acid from raffinose, glycerol, mannitol, or sorbitol, and it does not oxidise AcOH. The yield of gluconic acid in the solution containing 10% of glucose is 76·5%. Both II and III produce hydroxygluconic and glycuronic acids in culture solution with $CaCO_3$. CH. ABS.

Chemistry of the diphtheria bacillus. II. Aqueous extracts of the bacillus. J. HIRSCH (Z. Hyg., 1932, **114**, 195—223).—Aq. extracts of dried culture contain considerable proportions of N and P and are toxic to guinea-pigs. The toxic action is not associated with the N-constituents. The P content of the extract decreases and its toxicity increases with the age of the culture used. In older cultures the ratio of inorg. to total P rises considerably. A. G. P.

Composition of the diphtheria bacillus. A. LEULIER, P. SÉDALLIAN, and A. FINCK (Compt. rend. Soc. Biol., 1931, **107**, 1135—1136; Chem. Zentr., 1932, ii, 1927).

Paratyphoid-*A*-inhibiting properties of paraphoid cultures. A. ROCHAIX, P. SEDALLIAN, and (MME.) CLAVEL (Compt. rend., 1932, **195**, 1111—1112).—The filtrate of 24-hr. mixed cultures of paratyphoid-*A* and -*B* inhibits the growth of *A*, but not of *B*. Blood cultures from a guinea-pig injected subcutaneously with *A* and *B* are positive with respect to *B* only. The inhibitory power of the filtrate is transmissible in series of cultures, is destroyed at 60°, and considerably weakened by incubation at 37° for 24 hr. A. C.

Chemistry of bacteria. III. Lipin content of various types of tubercle bacillus. E. CHARGAFF and J. DIERYCK (Biochem. Z., 1932, **255**, 319—329).—Tables summarise the fat, phosphatide, wax, and polysaccharide contents of 28 strains of tubercle bacillus. The strains may be divided into three groups with total lipin contents of 24, 16, and 11% (dry wt.), the groups containing strains of Calmette-Guérin, of the bovine, and of the human tubercle bacillus, respectively. P. W. C.

***B. paratuberculosis* of Moeller and Grassberger.** E. DARZINE (Ann. Inst. Pasteur, 1932, **49**, 743—749).—Moeller's bacillus (*A*) is strongly acid-resisting and Grassberger's strain (*B*) but feebly so. *A* withstands the action of 10·5% H_2SO_4 for 24 hr., whilst *B* is killed in 5 min. When *A* is fixed and stained with Ziehl's fuchsin it is not decolorised in 24 hr. by 2% aq. Na_2SO_3, whilst under similar treatment *B* is decolorised in 5 min. These differences are due to the nature of the fatty envelopes. The fat from *A*, extracted by $CHCl_3$, has m.p. 45—46°, that from *B* has m.p. 30°. The staining properties of *A* and *B* correspond with those of free palmitic and oleic acids, respectively, *i.e.*, the more saturated the fat of the envelope the more permanently it will stain and the more acid-resisting will be the strain. P. G. M.

Occurrence of a specific carbohydrate in *Bacterium perfringens*. M. E. JIMENEZ (Compt. rend. Soc. Biol., 1931, **106**, 140—141; Chem. Zentr., 1932, ii, 724).—Extraction of cultures of *B. perfringens* with salt solution and pptn. with EtOH+1·3% NaOAc gives a ppt. containing a sp. carbohydrate. L. S. T.

Bacteria fermenting urea. E. N. MISCHOUSTIN (Zentr. Bakt. Par., 1932, II, **87**, 150—166).—Soil organisms fermenting urea may be differentiated according to the nature of C compounds which they are able to assimilate. The organism examined (? nov. sp.) utilises salts of org. acids far more readily than carbohydrates, and in general shows a preferential assimilation inversely related to the no. of constituent C atoms linked to O. NH_4 salts are more readily utilised than urea, asparagine, or peptone, which are taken up after preliminary hydrolysis. No evidence of the formation of MeCHO from acetates was obtained. A. G. P.

Factors influencing the reduction of nitrates and nitrites by bacteria in semi-solid media. C. E. ZOBELL (J. Bact., 1932, **24**, 273—281).—Many strains of organisms are examined. In a no. of cases, NO_2' produced is further reduced by the same organism, notably those of the *Brucella* and *Salmonella* groups. A. G. P.

Metabolism in the *Brucella* group. III. Viability in aqueous solutions. C. E. ZOBELL and M. H. ZOBELL. **IV. Bacteriostatic action of dyes. V. Production of hydrogen sulphide. VI. Nitrate and nitrite reduction. VII. Glucose utilisation.** K. F. MEYER and C. E. ZOBELL (J. Infect. Dis., 1932, **50**, 538—541; **51**, 72—90, 91—98, 99—108, 109—116).—V. The test can be used in conjunction with the dye tolerance test.

VI. Differences in the effects of different strains are recorded; they may be used for characterisation.

VIII. Various strains show no significant differences in glucose utilisation or in terminal reactions after growth in glucose media. CH. ABS.

Fermentation of α-methyl-*d*-glucoside by members of the *coli-aerogenes* group. S. A. KOSER and F. SAUNDERS (J. Bact., 1932, **24**, 267—271).—*B. aerogenes* but not fæcal *B. coli* can ferment α-methyl-*d*-glucoside with the production of acid and gas. A. G. P.

Influence of aeration and of sodium chloride on the growth curve of bacteria in various media. C. E. A. WINSLOW, H. H. WALKER, and M. SUTERMEISTER (J. Bact., 1932, **24**, 185—208).—Aeration of cultures of *E. coli* prolongs the "lag period" of the growth curves and subsequently accelerates and prolongs the period of logarithmic increase. 0·1*M*-NaCl has a stimulating and 0·5*M*-NaCl a toxic action during the period of increase. Both concns. are toxic during the "lag period." A. G. P.

Metabolic activity of the bacterial cell at various phases of the population cycle. H. H. WALKER and C. E. A. WINSLOW (J. Bact., 1932, **24**, 209—241).—In a stable culture of *E. coli* addition of lactose to a peptone medium decreased the NH_3 produced by the organisms without affecting CO_2 production. Effects of sub-toxic quantities of NaCl are recorded. A. G. P.

Factors determining the rate of mortality of bacteria exposed to alkalinity and heat. J. H.

WATKINS and C. E. A. WINSLOW (J. Bact., 1932, **24**, 243—265).—Effects on the toxicity of NaOH to *E. coli* of variations in age of culture, concn. of bacteria and of NaOH, and of temp. are examined. A. G. P.

Multiplication and respiration of soil bacteria in presence of protozoa. L. VON T. KOVACS (Mezog. Kutat., 1932, 5, 203—214; Chem. Zentr., 1932, ii, 1641).—In presence of protozoa (I) the CO_2 evolution was increased, particularly with mixed cultures; it was higher with glucose–$(NH_4)_2SO_4$ than with peptone–$(NH_4)_2SO_4$ solutions (on sand). CO_2 evolution was diminished by excess of (I). The bacterial count and the CO_2 developed were related in peptone (but less so in glucose) solutions, particularly in presence of (I). A. A. E.

Effect of *Colpidium* on ammonia production by soil bacteria. J. MEIKLEJOHN (Ann. Appl. Biol., 1932, **19**, 584—608).—Bacterial nos. in soil are depressed in the presence of *Colpidia*, but NH_3 produced by cultures was not reduced. In general, NH_3 and CO_2 production per organism and the no. of bacteria in the colony bear an inverse linear relationship. A. G. P.

Carbohydrate metabolism of parasitic protozoa. I. Behaviour of glycogen in cysts of *Amoeba butschlii*, Prowazek. T. VON BRAND (Z. Parasitenk., 1932, 4, 753—775).—Rate of disappearance of glycogen from cysts is largely dependent on temp. and is not influenced by the O_2 supply. Glycogen probably acts as an energy source. A. G. P.

Particle size of biological units. J. H. FERGUSON (J. Physical Chem., 1932, **36**, 2849—2861).—A review of the ultramicroscopy, ultrafiltration, and sedimentation of viruses and bacteriophage. E. S. H.

Action of aliphatic and aromatic compounds on diphtheria toxin. S. SCHMIDT (Biochem. Z., 1932, **256**, 158—189).—The toxic and other effects, at const. p_H, of equimol. solutions (suspensions, mixtures) of a large no. of compounds (aliphatic, carbocyclic, heterocyclic) have been examined. Many of the compounds have pronounced toxic effects. Purified toxin should always be used in such experiments. W. McC.

Effect on solutions of diphtheria toxin and diphtheria antitoxin of contact with certain surfaces. P. J. MOLONEY and E. M. TAYLOR (Biochem. J., 1932, **26**, 1754—1761).—Diphtheria toxin or antitoxin disappears from solution in contact with a sufficiently large surface of paraffin wax, or of glass which has been first in contact with light petroleum, or of glass tubes which have been plugged with cotton wool or filter-paper and heated for 1 hr. at 180°. Glass, cleaned with chromate–H_2SO_4 and heated at 180° for 1 hr., has relatively little effect on the toxin. S. S. Z.

Purification of diphtheria toxin. A. LEULIER, P. SÉDALLIAN, and CLAVEL (Compt. rend. Soc. Biol., 1931, **107**, 1136—1137; Chem. Zentr., 1932, ii, 1927).—The whole of the active toxin fraction is obtained from a bouillon culture by centrifuging at p_H 4·7. The ppt. contains chiefly the nucleoproteins sol. in dil. alkali. A. A. E.

Action of salicylsalicylic acid on tetanus toxin. L. VELLUZ (Compt. rend. Soc. Biol., 1932, **109**, 178—179; Chem. Zentr., 1932, ii, 1926).

Oligodynamic action of distilled water and its practical significance. F. HODER (Z. Immunitats., 1932, **74**, 455—458; Chem. Zentr., 1932, ii, 724).—H_2O and NaCl solutions prepared in a Cu apparatus are useless for bacteriological purposes on account of their oligodynamic action. NaCl also has an effect on bacteria. L. S. T.

Intake of dissolved substances by bacteria. III. H. HABS (Z. Hyg., 1932, **114**, 358—370; cf. A., 1932, 1170).—Factors concerned in the absorption of disinfectants by bacteria are discussed. A. G. P.

[Antiseptic properties of] thymol. J. SILBERSTEIN (Pharm. Zentr., 1932, **73**, 727—728).—1% Thymol solution kills *Streptococcus pyogenes* in 0·5 min., whilst 1% antiformin solution requires >5 but <15 min., and 1% EtOH and 1% PhOH solutions are ineffective after 15 min. The val. of thymol, particularly as a fatty acid ester, for disinfection etc. is emphasised. R. S. C.

Mechanism of chemotherapeutic action. III. Differentiation between parasiticidal and virulence-decreasing action of arsenicals. L. REINER and C. S. LEONARD. **IV. Effect of blockade on the chemotherapeutic action of the plasma of animals treated with arsenicals.** L. REINER, C. S. LEONARD, and S. S. CHAO. **V. Rate of methylene-blue reduction and decrease in virulence of trypanosomes treated with arsenicals with and without sodium thioglycollate.** L. REINER and C. S. LEONARD. **VI. Binding of arsenicals by trypanosomes *in vitro*. VII. Binding of arsenicals by arsenic-resistant trypanosomes *in vitro*.** L. REINER, C. S. LEONARD, and S. S. CHAO. **VIII. Variation in size of the spleen following treatment with arsenicals, blockade with India-ink, and infection with *T. equiperdum*.** L. REINER and S. S. CHAO (Arch. Int. Pharm. Ther., 1932, **43**, 10—36, 37—48, 49—62, 186—198, 199—208, 209—215).—III. Tervalent arsenicals decrease the virulence of trypanosomes (I), but increase the time of infection. If the (I) are pretreated with arsenicals (II) in broth, this property cannot be demonstrated. It is suggested that, in presence of plasma, some form of (II) acts directly on the (I), possibly a combination of (II) with globulin.

IV. Blockade of the reticulo-endothelial system increases the As content and the chemotherapeutic activity of the plasma of animals treated, after blockade, with (II). It does not inhibit the formation of the active chemotherapeutic agent. Storage of (II) in the spleen and liver is not changed.

V. (I) treated *in vitro* with (II) show a decrease in virulence but no change in their capacity to reduce methylene-blue anaerobically. Na thioglycollate (III) inhibits this decrease completely.

VI. Dead (I) bind more As [of tervalent (II)] than

living ones. The relative amount bound runs parallel with the toxicity *in vitro*. The binding to living (I) corresponds with a closely-packed unimol. layer. It is inhibited by the presence of (III).

VII. As-resistant (I) bind slightly less As than normal strains, but the figure is of the same order. This indicates an increase in tolerance rather than a decrease in affinity for arsenicals. The methylene-blue reduction rate is identical with that of normal strains.

VIII. Size of the spleen increases with the duration of (I) infections. Treatment with (II) tends to decrease the size of the spleen, whilst blockade has the opposite effect. H. G. R.

Mechanism of chemotherapeutic action. IX. Role of NH_2, OH, and As:As groups in parasitotoxic action of arsphenamine derivatives. X. Toxic action of hydrogen peroxide on trypanosomes. L. REINER and C. S. LEONARD (Proc. Soc. Exp. Biol. Med., 1932, **29**, 946—950, 951—953).—IX. Hiramatsu's reaction (A., 1930, 370) is given by compounds possessing aminophenol groups (I) and the presence of As is not necessary. *p*-$NH_2 \cdot C_6H_4 \cdot OH$ is not toxic to trypanosomes, but its autoxidation product is. Reducing agents inhibit the toxic action. Various org. arsenious oxides, not capable of giving on oxidation iminoquinone structure, are more toxic than are (I) and quinone. Toxicity of arsphenamine derivatives is due chiefly to As^{III} and not to (I).

X. H_2O_2 is toxic to trypanosomes. *In vivo* the formation of traces of H_2O_2, where the catalase content is low, might be involved in the rate of the AsO-formation and be concerned indirectly with the chemotherapeutic action of arsenicals. H. G. R.

Trypanocidal action and chemical constitution. XIV. Relative velocity of oxidation of arylarsenoxides. A. COHEN, H. KING, and W. I. STRANGEWAYS.—See this vol., 130.

Properties of adrenal lipin. J. STEFL (Compt. rend. Soc. Biol., 1931, **106**, 406—409; Chem. Zentr., 1932, ii, 732).—When oxidised adrenaline, which no longer shows the chemical or physiological properties of adrenaline, is treated with an aq. emulsion of adrenal lipin adrenaline is re-formed, slowly at room temp. and quickly when heated. L. S. T.

Resynthesis of adrenaline. J. STEFL (Compt. rend. Soc. Biol., 1931, **106**, 410—412; Chem. Zentr., 1932, ii, 732).—The new synthesis of adrenaline (cf. preceding abstract) occurs when oxidised adrenaline is heated in dil. HCl solution. The adrenal lipin is also weakly acidic. L. S. T.

Effect of adrenaline on lactic acid content of blood and urine in rabbits. J. A. COLLAZO, J. PUYAL, and J. CASTELLANO (Anal. Fís. Quím., 1932, **30**, 759—763).—After injection of 0·5 mg. per kg. of adrenaline, lactic acid rises to 97·5 mg. per 100 c.c. in the blood and to 65 mg. per 100 c.c. in the urine. Blood-sugar rises to 260 mg. per 100 c.c. and glycosuria is observed. R. K. C.

Effect of adrenaline on lactic acid content of blood in normal man. J. A. COLLAZO, J. PUYAL, and J. CASTELLANO (Anal. Fís. Quím., 1932, **30**, 764—766).—After injection of 1 mg. of adrenaline the lactic acid in the blood rises to twice the normal val. A corresponding rise in blood-sugar and urinary lactic acid is observed. R. K. C.

Effect of adrenal operations on blood-calcium in man. A. JUNG and A. C. HAKKI (Compt. rend. Soc. Biol., 1931, **108**, 40—42; Chem. Zentr., 1932, ii, 1796).—Adrenalectomy or resection of a subthyroid artery diminishes abnormally high blood-Ca, but scarcely affects normal vals. A. A. E.

Function of adrenal tissue. V. Role of adrenal tissue hormones in sulphur metabolism. K. A. WINTER and M. REISS (Endokrinologie, 1932, **10**, 404—409; Chem. Zentr., 1932, ii, 732).—In rabbits removal of one or both adrenals markedly increases the S obtainable from protein-free blood. The addition of adrenal extract lowers the S level in normal animals by 25%. L. S. T.

Gastric secretion caused by insulin. E. B. BOLDYREV and J. F. STEWART (J. Pharm. Exp. Ther., 1932, **46**, 419—429).—In dogs with gastric fistulæ administration of commercial or cryst. insulin (2 units or more) stimulates gastric secretion having a high free and total acidity and high pepsin content. This action of insulin is inhibited by atropine, but not by intravenous administration of glucose. W. O. K.

Vagus control of pancreatic function. Experimental insulin resistance. E. B. BOLDYREV and J. F. STEWART (J. Pharm. Exp. Ther., 1932, **46**, 407—418).—Cryst. insulin administered to animals or man produces symptoms characteristic of vagus stimulation, and these effects as well as the hypoglycæmic action are inhibited by blockage of the vagus surgically or by administration of atropine. W. O. K.

Effect of insulin on phloridzin glycosuria in the normal dog. F. RATHERY and Y. LAURENT (Compt. rend. Soc. Biol., 1931, **108**, 643—645; Chem. Zentr., 1932, ii, 1648).—Large doses of insulin increased or diminished urinary sugar. A. A. E.

Relation of phosphorus to the metabolism of sugar in the animal body, and the action of insulin and synthalin. Z. Y. TSEN (Acad. Sinica Inst. Chem. Mem., 1930, No. 1, 1—47).—Normal human plasma contained total P 8·2, org. P 4·7, inorg. P. 2·9, whilst diabetic plasma contained, respectively, 15·9, 11·6, 1·5 mg. per 100 c.c. The total P was parallel to the sugar. Insulin and synthalin decreased org. and increased inorg. P. Experiments *in vitro* with guinea-pig plasma exhibited none of these changes. CH. ABS.

Determination of the thyroxine content of thyroid and thyroid preparations. I. ABELIN (Arch. exp. Path. Pharm., 1932, **168**, 722—725).—The material is hydrolysed by aq. NaOH, the thyroxine extracted with BuOH according to the method of Leland and Foster (A., 1932, 432), and then determined by measurement of its I content. W. O. K.

Mechanism of effect of thyroxine on tissue metabolism. T. EBINA (Tohoku J. Exp. Med., 1932, **19**, 139—154).—Injection of thyroxine (0·01 mg. per 100 g.) into rats increases the respiration and

anaerobic glycolysis of kidney tissue, but affects only the respiration of liver tissue. When added to these organs *in vitro*, it increases the respiration and anaerobic glycolysis of both. CH. ABS.

Effect of thyroxine on blood-sugar. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1931, **108**, 225—227; Chem. Zentr., 1932, ii, 1794—1795).—Hyperglycæmia (max. vals. 0·044—0·083 mg. per 100 c.c.) which occurs on injection of thyroxine into normal (chloralosed) dogs is not observed with adrenalectomised dogs, but is then replaced by hypoglycæmia. After adrenaline and other hyperglycæmic substances there is an increase in the insulin content of pancreatic venous blood. Injection of thyroxine causes an increase in insulin secretion. A. A. E.

Changes in the weight, pulse, respiration, and blood-p_H and -alkali reserve in hyperthyroidised animals treated with thyroxine or "parathormone" or with thyroid and parathyroid gland. C. I. PARHON and H. DEREVICI (Compt. rend. Soc. Biol., 1932, **107**, 386—388; Chem. Zentr., 1932, ii, 1194).

Change in blood-sugar, -cholesterol, -calcium, -potassium, and -phosphorus on treatment with thyroid or thyroxine and "parathormone" and on combined treatment. C. I. PARHON and H. DEREVICI (Compt. rend. Soc. Biol., 1932, **107**, 388—389; Chem. Zentr., 1932, ii, 1194).—In dogs, thyroid increases the blood-sugar, -K, and -P and decreases the -cholesterol and -Ca. "Parathormone" decreases the -sugar and -cholesterol, and increases the others. A. A. E.

Effect in man of the parathyroid hormone on the plasma-, corpuscle-, and cerebrospinal fluid-chlorine. C. I. PARHON and M. CAHANE (Compt. rend. Soc. Biol., 1931, **107**, 835—836; Chem. Zentr., 1932, ii, 1463—1464).—Plasma- and corpuscle-Cl are slightly, and cerebrospinal fluid-Cl is not, increased. A. A. E.

Estimation of the functional activity of the thyroid by means of urine or serum and investigation of the relationship between the thyroid and other endocrine organs. M. L. KOH (Korean Med. J., 1932, **2**, 45—48).—The function of the thyroid is determined by way of the atropine-neutralising substance (I) in the urine by adding atropine sulphate to the urine and examining its effect on the cat's eye. Feeding thyroid to rabbits increases (I) in the urine and serum; thyroidectomy decreases it. Transplantation of rabbit's thyroid gland into a thyroidectomised rabbit, or injection of thyroxine or thyroid extract before thyroidectomy, causes transitory reappearance of (I). (I) is not the thyroid hormone itself; it is sol. in H_2O, but not in EtOH or Et_2O. It is stable at $\geqslant 80°$ for 30 min., but is destroyed at 100°. In serum it is combined with albumin, from which it cannot be separated by adsorption with siliceous earth. CH. ABS.

Are the substances designated as "anterior pituitary hormone" in the urine identical with the pituitary substances having a similar action? J. FREUD (Deut. med. Woch., 1932, **58**, 974—975; Chem. Zentr., 1932, ii, 731).—The similarity is admitted, but the identity is not proved. A. A. E.

Appearance of thyroid substances in the blood after the action of the anterior lobe of the pituitary. W. GRAB (Arch. exp. Path. Pharm., 1932, **168**, 715—721).—The blood of animals which have been treated parenterally with pituitary anterior lobe when fed to tadpoles accelerates their metamorphosis, thus indicating the presence in it of thyroid secretion. W. O. K.

Equilibrium between anterior pituitary and thyroid hormones in the normal and pathological organism. M. ARON, C. VAN CAULAERT, and J. STAHL (Compt. rend. Soc. Biol., 1931, **107**, 64—66; Chem. Zentr., 1932, ii, 1317).—Administration of thyroid arrests the action of the anterior pituitary thyreotropic hormone (I). By evaluation of urine or blood with rabbit's thyroid there is determined not the abs. content of (I), but its excess over thyroid hormone. In the blood and urine of hyperthyreotics there is therefore found little, and in that in myxœdema much, (I), much thyroxine being present in the former case. A. A. E.

Presence of the luteinising factor in the guinea-pig pituitary. A. LIPSCHUTZ (Compt. rend. Soc. Biol., 1931, **108**, 646—647; Chem. Zentr., 1932, ii, 1792).—Injection of the anterior pituitary lobe of male or female guinea-pigs into infantile rats did not cause the formation of corpora lutea. Either this factor is not present, or its amount is only 10% of that in the rat pituitary. A. A. E.

Activity of the anterior pituitary gland in various animal species and in various ages by comparison of the hormone present in the organism with the morphological development of the thyroid. M. ARON (Compt. rend. Soc. Biol., 1932, **106**, 609—611; Chem. Zentr., 1932, ii, 1463).

Effect of parathyroidectomy on blood-calcium. A. G. WEISS, J. MONGUIO, and L. BERNARD (Compt. rend. Soc. Biol., 1931, **108**, 12—14; Chem. Zentr., 1932, ii, 1796).—Ligation of the sub-thyroid artery and adrenalectomy in the cat did not affect the blood-Ca. A. A. E.

Acidity and calcium content of gastric juice in thyro-parathyroidectomised animals or animals treated with parathormone. C. I. PARHON and M. CAHANE (Compt. rend. Soc. Biol., 1932, **109**, 243—245; Chem. Zentr., 1932, ii, 1795).—The acidity was little affected; parathormone slightly increased the Ca content. A. A. E.

Cardiovascular and metabolic reactions of man to the intramuscular injection of posterior pituitary liquid (pituitrin), pitressin, and pitocin. A. GROLLMAN and E. M. K. GEILING (J. Pharm. Exp. Ther., 1932, **46**, 447—460).—In man therapeutic doses of pitressin and pituitrin cause a brief fall in the O_2 consumption, pulse rate, and cardiac output followed by a more prolonged rise. Pitocin causes a slight rise in O_2 consumption only. W. O. K.

Clinical significance of pituitrin hyperglycæmia. B. ASCHNER and L. JASO-ROLDAN (Z. klin. Med., 1932, **121**, 495—503; Chem. Zentr., 1932, ii, 1793).—The effect is due partly to mobilisation of

adrenaline from the adrenals and partly to a direct mobilisation of glycogen. A. A. E.

Presence in the blood and cerebrospinal fluid, and distribution in these liquids and in urine, of the anterior pituitary hormone having an excito-secretory action on the thyroid gland. C. VAN CAULAERT, M. ARON, and J. STAHL (Compt. rend. Soc. Biol., 1932, **106**, 607—609; Chem. Zentr., 1932, ii, 1463).—Under normal and pathological conditions in guinea-pigs the urine contains half as much as the blood; the amount in the cerebrospinal fluid is variable. A. A. E.

Does the hormone of the corpus luteum affect the blood-cholesterol? M. KNELL (Arch. Gynakol., 1932, **150**, 176—185; Chem. Zentr., 1932, ii, 1928).—Injection of the hormone into rabbits did not affect the blood-cholesterol. A. A. E.

Excretion of follicular and anterior pituitary hormone at the end of pregnancy. H. RUNGE, H. HARTMANN, and K. SIEVERS (Arch. Gynakol., 1932, **149**, 608—622; Chem. Zentr., 1932, ii, 1193).—As parturition approaches the excretion of follicular hormone increases, whilst that of anterior pituitary hormone varies considerably. A. A. E.

Œstrus-producing and luteinising action of preparations of the anterior lobe of the pituitary. K. COESTER (Arch. exp. Path. Pharm., 1932, **168**, 745—752).—Details are given of the biological assay on rats of preps. from the anterior lobe of the pituitary or from urine of pregnancy in respect of their œstrus-producing and of their luteinising activities. The vals. found in the case of certain trade preps. are stated. W. O. K.

Is there a follicle-ripening hormone as well as a luteinising hormone in the anterior pituitary gland? M. ARON (Compt. rend. Soc. Biol., 1932, **108**, 1218—1220; Chem. Zentr., 1932, ii, 1645).—Differences in the effects produced in rabbits by gonadostimulin are attributed to dosage; the existence of a sp. luteinising factor is improbable. A. A. E.

Occurrence of growth-promoting substances in urine of pregnancy. E. WEHEFRITZ and E. GIERHAKE (Klin. Woch., 1932, **11**, 1106—1108; Chem. Zentr., 1932, ii, 730).—Urine of pregnancy is treated with Mg mixture to remove PO_4''', and the hormones are salted out by $(NH_4)_2SO_4$ and dissolved in 5% $(NH_4)_2HPO_4$. Fractional adsorption then separates the sexual hormones from that which produces increased growth in hypophysectomised rats and other animals. L. S. T.

Effect of follicular hormone on pregnancy. M. MAINO (Arch. Ist. Biochim. Ital., 1932, **4**, 347—360).—Administration to rabbits of 2000—2400 units of cryst. œstrin per day for 10 days, from the 1st, 10th, or 20th day of gestation, causes resorption of the fœtus. No permanent effect is produced on the reproductive organs. Urinary excretion of the hormone in pregnancy may be the result of a mechanism protecting the fœtus. R. K. C.

Pituitary sexual hormone. A. A. SCHMIDT and E. DERANKOVA (Endokrinol., 1932, **11**, 1—15; Chem. Zentr., 1932, ii, 1316).—Dog's gastric or intestinal juice did not inactivate anterior pituitary sexual hormone (from urine of pregnancy), but pancreatic juice inactivated it rapidly. A. A. E.

Rabbit as test for pituitary hormone and pregnancy hormone. T. MARTINS (Compt. rend. Soc. Biol., 1931, **107**, 180—182; Chem. Zentr., 1932, ii, 1316).—After two intravenous injections of 5 c.c. of urine the result can be observed after 24 hr. or less. Et_2O extraction of the urine, which presumably removes an inhibitor (? folliculin), is preferred. A. A. E.

Crystalline hormone from urine of pregnancy. I. A. LEJWA (Biochem. Z., 1932, **256**, 236—238).—To the urine, after treatment with 10% AcOH and filtration, $(NH_4)_2SO_4$ (40 g. to 100 c.c. of urine) is added, the ppt. is dissolved in H_2O, and the solution, adjusted to p_H 3·5—4·0 with dil. AcOH, is shaken for 2 hr. with permutit. The pure hormone is obtained by successive pptn. with aq. EtOH and $COMe_2$, extraction with EtOAc, and crystallisation at 0° from aq. EtOH after removal from the adsorbent by elution with excess of 0·125% aq. NH_3. W. McC.

Female sexual hormones. G. SANDULESCO, W. W. TCHUNG, and A. GIRARD (Compt. rend., 1933, **196**, 137—140).—The following derivatives of equilenin (I) (this vol., 98) are prepared: *Me ether*, m.p. 197—198° (corr.); *semicarbazone*, m.p. 268° (decomp.); *picrate*, m.p. 205—208° (corr.; decomp.); *styphnate*, m.p. 212—213° (decomp.); *acetate picrate*, m.p. 106—107°. (I) heated in air passes into equilenin-red; a colorimetric method for determination of the amount of (I) in mixtures of hormones involving the formation of the red compound is described. Folliculin from the urine of pregnant women does not contain (I). H. B.

Progestin. W. M. ALLEN (J. Biol. Chem., 1932, **98**, 591—605).—An improved method (cf. Amer. J. Physiol., 1930, **92**, 174) of preparing progestin is described, and the assay of progestin is discussed. A. L.

Splenic hormone and calcium metabolism. T. MIWA (Keijo J. Med., 1932, **3**, 403—444).—The blood-Ca of rabbits is decreased by withdrawal of blood and, to a greater extent, by starvation. Splenectomy is followed by a temporary rise in the serum-Ca (I) and a temporary decrease in body-wt. Subcutaneous injection of extracts from cow's spleen and, to a smaller extent, of those from liver, kidney, and muscle produces a decrease in (I), partly due, however, to the content of inorg. salts. Injection of venous blood-serum of the spleen but not that of the ear produces a decrease in (I). There exists an antagonism between the splenic and parathyroid hormones. The thymus gland appears to synergise the action of the spleen on Ca metabolism. Stimulation or blocking of the reticulo-endothelial system has no influence on (I). The splenic hormone is probably a sterol. F. O. H.

Influence of the gonads on protein metabolism. II. Effect of injections of saline suspensions of testes and testicular extracts on urinary creatinine after castration. I. SCHRIRE and H. ZWARENSTEIN (Biochem. J., 1932, **26**, 1886—1889).—The

injections cause the high urinary creatinine of castration to decrease to the normal pre-castration level. S. S. Z.

Detoxicating hormone of the liver [yakriton]. XXXII. Difference of detoxicating mechanism by yakriton in ammonia and phenol poisoning. A. Sato and S. Yoshimatsu. **XXXIII. Chloroform and detoxicating liver power.** S. Yanagawa. **XXXIV. Counteracting effect of yakriton on the anticoagulant heparin.** T. Sato. **XXXV. Effect of yakriton on milk secretion.** K. Asakura. **XXXVI. Effect of yakriton in maintaining the highest agglutinin titre.** G. Moro (Tohoku J. Exp. Med., 1932, **19**, 1—9, 10—14, 15—31, 32—35). Ch. Abs.

Physical methods in vitamin research. E. H. Reerink, A. van Wijk, and J. van Niekerk (Chem. Weekblad, 1932, **29**, 645—650).—A review. H. F. G.

Availability of vitamins in plant tissues. J. E. Richardson and H. L. Mayfield (Science, 1932, **76**, 498—500).—Changes in potency of vitamins in carrots and potatoes after boiling, storing under different conditions, and canning are recorded. L. S. T.

Carotenoids of hen's egg-yolk after carotenoid-free feeding. E. Virgin and E. Klussmann (Z. physiol. Chem., 1932, **213**, 16—20).—The egg-yolks of hens on a diet containing carotene contained more carotenoid than those of hens on a carotene-free diet owing to the presence not of carotene but of xanthophylls. On both diets xanthophylls were found in the liver. J. H. B.

Role of carotenoids in the animal body. H. von Euler and E. Klussmann (Biochem. Z., 1932, **256**, 11—17).—Birds (chicks, pigeons) utilise xanthophyll for part (in some cases perhaps for all) of their vitamin-*A* requirements and store it in their livers, whilst they very rapidly convert carotene into the vitamin. There is also a close relation between xanthophyll and vitamin-*E*. W. McC.

Hydrogenation and oxidation products of carotene as precursors of vitamin-*A*. R. Kuhn and H. Brockmann (Z. physiol. Chem., 1932, **213**, 1—7).—Hydroxy- and β-carotene show vitamin-*A* activity when fed to rats, but β-carotenone is inactive. The activity of α- and β-dihydrocarotenes is doubtful. J. H. B.

Extraction of vitamin-*A* from animal tissue. H. Simonnet, A. Busson, and Asselin (Compt. rend. Soc. Biol., 1932, **108**, 1123—1124; Chem. Zentr., 1932, ii, 1649).—The finely comminuted tissue is kept overnight at 0° in $COMe_2$; the mixture is filtered and the residue treated with dry Et_2O. After 1 hr. the extract is separated, dried with Na_2SO_4, and the Et_2O is removed. This residue is dissolved in a little abs. Et_2O, filtered, and the residue dissolved in oil. Unminced tissue can be kept for 48 hr. at 10—12° without loss of vitamin-*A*. A. A. E.

Vitamin potency of certain Lofoten (Norwegian) cod-liver oils. G. E. Éwe (J. Amer. Pharm. Assoc., 1932, **21**, 1145—1146).—23 commercial samples of this oil had vitamin-*A* and -*D* activities (determined biologically) of 800—1200 and 108—271 units per g., respectively. R. S. C.

Carotene (vitamin-*A*) and thyroxine. H. von Euler and E. Klussmann (Z. physiol. Chem., 1932, **213**, 21—34).—Carotene increases and thyroxine injections lessen the body-wt. of rats. The administration of both substances together may maintain equilibrium. J. H. B.

Cause of infections in cases of vitamin-*A* deficiency. P. Arons and M. P. J. van der Rijst (Arch. néerl. Physiol., 1932, **17**, 578—613).—These infections are not the result of diminished powers of resistance but of local changes caused by accumulation of secretion products in consequence of keratinisation of the glandular ducts and atrophy of the glands. H. G. R.

Biological testing of vitamin-*A*. J. Ueno, Y. Ota, K. Tone, and S. Yokoyama (J. Soc. Chem. Ind. Japan, 1932, **35**, 491—492B).—The use of the carp (*Cyprinus caprio*) for the assay of vitamin-*A* is recommended. The increase in wt. due to the vitamin is greater when the fish are kept in darkness than in daylight. F. O. H.

Colorimetric and biological assay of vitamin-*A*. E. C. Wise and F. W. Heyl (J. Amer. Pharm. Assoc., 1932, **21**, 1142—1145).—The $SbCl_3$ determination of vitamin-*A* in seven cod-liver oils gave results comparable with the biological activity, if the unsaponifiable fraction, but not if the crude oil, was used. R. S. C.

Antimony chloride colour reaction for vitamin-*A*. V. Evaluation of a colorimetric unit on the basis of the biological unit for vitamin-*A*. E. R. Norris and A. E. Church (J. Nutrition, 1932, **5**, 495—501).—Colorimetric and biological units are correlated. A. G. P.

Pyruvic acid and vitamin-B_1 deficiency. A. P. Meiklejohn, R. Passmore, and R. A. Peters (Biochem. J., 1932, **26**, 1872—1879).—The depressed O_2 uptake by the minced brain from deficient pigeons in the presence of pyruvate (I) is always lower than when lactate (II) is present. On the other hand, whilst the addition of vitamin-B_1 concentrates is incapable of restoring the lowered O_2 uptake with (I) as substrate, it does so in the case of (II). The change in the O_2 uptake in the presence of (I) is not due to blockage by (II). Pyruvic acid is not a stage in the oxidation of lactic acid in the pigeon's brain. S. S. Z.

Vitamin-B_1 content of the organs of white rats fed on normal and B_1-free diets. H. G. K. Westenbrink (Arch. néerl. Physiol., 1932, **17**, 560—577).—The vitamin-B_1 contents of heart, liver, kidneys, brain, muscle, lung, spleen, stomach, and intestine were examined. The heart, liver, and kidneys have the highest content, the two last-named evidently acting as vitamin reserves. All these organs, with the exception of the brain, lose their vitamin content after feeding for 5 weeks on a B_1-free diet. P. G. M.

Tissue respiration in beriberi. II. H. G. K. Westenbrink (Arch. néerl. Physiol., 1932, **17**, 549—555).—The O_2 uptake of the liver tissue of normal rats and pigeons is the same as that of animals with

beriberi, and the respiration of tissues in this disease is unaffected. P. G. M.

Antiscorbutic value of fresh lime juice. A. HASSAN and R. BASILI (Biochem. J., 1932, **26**, 1846—1850).—The protective dose for juice expressed daily from ripe Egyptian limes gathered not more than 2 days previously was 1·5 c.c. per guinea-pig daily. A daily dose of 3 c.c. of juice from West Indian limes grown in Egypt and kept during the experimental period of 2 months in a refrigerator did not protect. S. S. Z.

" Hexuronic acid " (ascorbic acid) as the anti-scorbutic factor. A. SZENT-GYORGYI and W. N. HAWORTH (Nature, 1933, **131**, 24).—The name *ascorbic acid* is suggested for the cryst. substance $C_6H_8O_6$ which prevents scurvy in guinea-pigs. L. S. T.

Vitamin-*C* and hexuronic acid. T. MOORE and S. N. RAY (Nature, 1932, **130**, 997—998).—Suprarenal glands from normal but not scorbutic guinea-pigs are blackened by 0·4% $AgNO_3$, supporting the view that hexuronic acid and vitamin-*C* are identical. Suprarenals from rats fed for long periods on diets completely deficient in vitamin-*C* always stain with $AgNO_3$ in agreement with the view that rats can synthesise this vitamin. L. S. T.

Methylnornarcotine, glycuronic acid, and vitamin-*C*. W. J. DANN (Nature, 1933, **131**, 24—25).—Contrary to the observations of Rygh (A., 1932, 1294), daily administrations of methylnornarcotine or glycuronolactone alone or in conjunction failed to prevent scurvy in guinea-pigs fed on a scurvy-producing diet. L. S. T.

Effects of feeding irradiated ergosterol to animals. G. PALLASKE (Klin. Woch., 1932, **11**, 1060—1063; Chem. Zentr., 1932, ii, 736).—Hens, cats, rabbits, and dogs did not exhibit injury. A. A. E.

Effect of irradiated ergosterol on the tetany in rabbits following parathyroidectomy. E. LESNÉ, R. DUBOIS, and H. SIMONNET (Compt. rend. Soc. Biol., 1931, **107**, 441—443; Chem. Zentr., 1932, ii, 1320).—Administration of irradiated ergosterol to parathyroidectomised rabbits does not arrest the fall in blood-Ca, but prevents tetany. A. A. E.

Effect of irradiation on the metabolism of carbohydrates and its relation to vitamin-*D*. L. PINCUSSEN (Klin. Woch., 1932, **11**, 1231; Chem. Zentr., 1932, ii, 1196).—In the organs of irradiated animals the glycogen increases and the lactic acid decreases. Similar effects are caused by administration of irradiated foods or vitamin-*D*. A. A. E.

Parathyroidectomy and vitamin-*D*. Effect on blood-calcium. A. ARTHUS and A. JEDRZEJOVSKA (Compt. rend. Soc. Biol., 1931, **107**, 105—106; Chem. Zentr., 1932, ii, 1320).—In rabbits which have received vigantol before parathyroidectomy tetany does not occur and the fall in blood-Ca is much smaller than normally. A. A. E.

Functions of radiation in the physiology of plants. I. Methods and apparatus. F. S. BRACKETT and E. S. JOHNSTON. **II. Effects of near infra-red radiation on plants.** E. S. JOHNSTON (Smithson. Miscel. Coll., 1932, **87**, Nos. 13 and 14).—I. The ways in which changes in intensity and wave-length of light may affect plant behaviour are discussed and a suitable form of apparatus for such tests is described.

II. Tomato seedlings were grown in a nutrient solution containing salts of Ca, Mg, K, Mn, together with H_3BO_3 and Fe humate, and submitted to either visible radiation alone or visible combined with near infra-red radiation. Plants grown under the latter conditions show some characteristics of shade-grown plants (long internodes), although there is also an evident destruction of chlorophyll and the H_2O requirement is less than normal. P. G. M.

Study of photosynthesis in connexion with photoperiodism. S. V. TAGEEVA (Bull. Appl. Bot., Leningrad, 1931, **27**, No. 5, 197—245).—Variation of the length of day did not affect the daily photosynthetic course or the energy of photosynthesis in oats and millet; hence photosynthesis does not determine the differences in photoperiodical response observed between short-day and long-day plants. With different daylight durations there was no correspondence between the energies of photosynthesis and of accumulation of org. substances. CH. ABS.

Influence of desiccating winds on photosynthesis. S. S. SKVORTZOV (Bull. Appl. Bot., Leningrad, 1931, **25**, No. 3, 45—66).—Dry winds in the absence of sufficient soil-H_2O lead to leaf dehydration and retardation or cessation of photosynthesis. Slight leaf injury produces decreased photosynthesis. CH. ABS.

Attenuation of chlorophyll in green parasitic plants. M. MOLLIARD (Compt. rend., 1932, **195**, 1190—1192).—The chlorophyll content of leaves of radish grown on extract of carrot tubercles is one tenth of that of leaves from a plant grown on mineral salt and sucrose medium. The CO_2 assimilation of the former plant is also proportionately lower. When grown on radish extract, the radish gives normal leaves. These results support the view that parasitic plants are derived from what were originally autotrophic plants, which have been modified by absorption of substances from other species. A. C.

Relation between starch synthesis and weight of seeds of *Pisum* hybrids. (MLLE.) C. BOURDOUIL (Compt. rend., 1932, **195**, 1317—1319; cf. A., 1932, 201).—The wt. of ripe seeds of second generation hybrids of two varieties of pea depends on the ability of the sol. carbohydrates to polymerise to starch. This ability is transmitted by the parents according to Mendelian rules. A. C.

Influence of nitrogenous and mineral nutrition on the time of heading in barley and millet with different daylight durations. I. N. BORODINA (Bull. Appl. Bot., Leningrad, 1931, **27**, No. 5, 171—193).—Lack of N accelerates the appearance of the earing stage in barley, whilst lack of P, or lack of K with long daylight duration, delays it. The effect of exclusion of nutrients is marked with a short day. The C : N ratio does not account for photoperiodism. Millet plants are not affected by lack of N or K; lack of P caused depression. CH. ABS.

Opening of stomata in severely wilted plants. W. S. Iljin (Jahrb. wiss. Bot., 1932, 77, 220—251).—Inter-relationships between humidity, respiration rates, and the transformation of sugars into starch and *vice versa* associated with the opening and closing of stomata are examined. A. G. P.

Effect of ethylene chlorohydrin vapours on dormant lilac tissues. F. E. Denny and L. P. Miller (Contr. Boyce Thompson Inst., 1932, 4, 513—528).—Treatment with $CH_2Cl{\cdot}CH_2{\cdot}OH$ increased the catalase and invertase activity of bud tissues and to a small extent that of twig bark. Amylase activity was not affected. Considerably increased respiratory activity occurred in young twigs. Corresponding chemical changes in buds included increased H_2O and sol. N contents and decreased sugars, especially sucrose. A. G. P.

Growth-promoting substances. E. Maschmann and F. Laibach (Biochem. Z., 1932, 255, 446—452).—A substance which accelerates the growth of the coleoptile of *Avena* is detected in Ringer's solution in which a slice of surviving tumour (carcinoma, sarcoma) tissue has been kept for 24 hr. at 37°, but is not present in aq. extracts of the tissue pulp. Such a growth-promoting substance is detected in liver, kidney (guinea-pig, mouse), heart-muscle, breast-muscle (hen), and blood (hen, guinea-pig) in 10-day embryo chicks, but not in egg-yolk or in brain of hen and guinea-pig. P. W. C.

Formation of growth-promoting substance by *Aspergillus niger*. T. Sakamura and T. Yanagihara (Proc. Imp. Acad. Tokyo, 1932, 8, 397—399).—The growth-promoter of *Avena* coleoptiles is formed in aerobic and anaerobic peptone cultures of *A. niger* at 30°. It is inhibited by addition to the culture of glucose (in contradiction to Boysen-Jensen, A., 1931, 1091, 1334), sucrose, fructose, maltose, galactose, or glycerol, but not by mannitol or lactose. Alanine, asparagine, aspartic and glutamic acids do not, and Na nucleate does, stimulate its production. It is also formed when peptone is incubated at p_H 4 and 35° with the pulped mycelium, and when peptone is treated with H_3PO_4 to p_H 3·8 in the prep. of agar cubes. A. C.

Occurrence of decomposition products of chlorophyll. I. Decomposition of chlorophyll in the digestive system of the cow. P. Rothemund and O. L. Inman.—See this vol., 168.

Ionic concentration as a factor in resorption. M. Gracanin (Compt. rend., 1932, 195, 1311—1313).—The velocity of adsorption of PO_4''' by young plants of *Hordeum distichum* and *Zea mays* from solutions of $CaHPO_4$ is max. in the first 24 hr. Adsorption increases with the concn. of $CaHPO_4$, and is in excess of the plant's requirements. The ratio of adsorbed to available PO_4''' falls from 100% to about 50% as the salt concn. increases from 0·001% to 0·1% (as P_2O_5). A. C.

Absorption and accumulation of solutes by living plant cells. III. Respiration of cut discs of potato tuber in air and immersed in water, surface : volume effects and salt accumulation. F. C. Steward, R. Wright, and W. E. Berry (Protoplasma, 1932, 16, 576—611; cf. A., 1922, 664).—Respiratory activity of potato discs under various conditions is examined. Absorption of KBr as measured by cell sap concn. is associated with and is probably dependent on increased metabolic activity, notably on increased aerobic respiration. A. G. P.

Mechanism of transport of organic materials in plants. T. H. van der Honert (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1104—1112).—When the surface-active substance K oleate is added at one end of a horizontal tube containing dil. HCl covered with Et_2O its rate of transport along the H_2O–Et_2O interface is about 70,000 times its rate of diffusion through the H_2O layer. It is suggested that a similar mechanism may account for the high rate of transport of sugars and other substances through the sieve tubes. A. G.

Biological detoxication of ammonia in higher plants and its relationship to the [H·] of the cell sap. M. Kultzscher (Planta [Z. wiss. Biol.], 1932, 17, 699—757).—Equilibrium between NH_3 and amide in plants is largely controlled by the [H·] of the sap. In highly acid plants detoxication of NH_3 results from neutralisation by acids present and storage as NH_4 salts ("ammonium plants," Ruhland and Wetzel, *ibid.*, 1926, 1, 558). There occur also intensive deamination and deamidation processes. In plants of $p_H > 5{\cdot}0$ the NH_3 amide equilibrium is displaced in the opposite direction and NH_3 is detoxicated as amide ("amide plants"). Intermediate classes ("mixed type") of plants are characterised by variations in the amide : NH_3 ratio associated with variations in the p_H of the sap. The ratio amide : NH_3 corresponding with a particular p_H is not const., since inherent plant characteristics and other factors may be concerned. Nutritional experiments indicate great differences in the val. of urea and asparagine for the higher plants. A. G. P.

Arginine metabolism and urea formation in higher plants. II. G. Klein and K. Tauböck (Biochem. Z., 1932, 255, 278—286; cf. A., 1932, 1179).—Arginine fed to sterile cultures of *Zea mays* and *Phaseolus vulgaris* is absorbed unchanged by the roots, but is quickly hydrolysed by the plants. A small part of the urea arising is found in the plants, but most is quickly utilised and is not converted into NH_3. P. W. C.

Nitrogen distribution in the leaves of Philippine camphor trees. J. Maranon (Philippine J. Sci., 1932, 49, 461—468).—No sp. differences were apparent between the N distribution of camphor leaves yielding a mixture of camphor and oil and those yielding a lævorotatory oil only. In old leaves showing chlorophyll degradation there was a higher proportion of NH_2-acid-N and lower humin-N than in young or full-grown leaves. Young leaves have less NH_3-N than full-grown or old leaves. A. G. P.

Distribution of nitrates and "organisation" of nitrogen in the leaves of green plants. E. Parisi and G. De Voto (Atti R. Accad. Lincei, 1932, [vi], 16, 270—274).—The leaf itself of sunflower, wheat, or beet is relatively poor in NO_3', but the

petioles and veins are rich in NO_3' and often contain more than any other organ, even than the root. Thus, the HNO_3 probably undergoes " organisation " on passing into the leaf itself. Sunlight accelerates the formation of NH_2-compounds in the green parts of plants. The petioles contain more sugar than the leaves and more in the afternoon than in the morning. T. H. P.

Relationships between tree response and internal composition of shoots of the peach. F. P. CULLINAN (Proc. Amer. Soc. Hort. Sci., 1931, 28, 1—5).—In trees subjected to varying amounts of pruning the vals. for total N and sugar increased from base to tip of shoots. Application of N fertilisers increased the N content of the new growth. CH. ABS.

Fruiting responses of the peach to applications of sodium nitrate. R. V. LOTT (Proc. Amer. Soc. Hort. Sci., 1931, 28, 23—27).—Increase in the amount of $NaNO_3$ was accompanied by an increase in the H_2O-sol. and total N, and a decrease in the total and reducing sugars, in the fruit. CH. ABS.

Vegetative responses of the peach to applications of sodium nitrate. F. E. ASHLEY (Proc. Amer. Soc. Hort. Sci., 1931, 28, 28—33).—The % and amount per unit length of both H_2O-sol. and total N in the shoots increased, whilst the starch content decreased, as the rate of application of $NaNO_3$ was increased. CH. ABS.

Seasonal variations in nitrogen concentration in twigs of peach trees under sand-hill conditions. C. F. WILLIAMS (Proc. Amer. Soc. Hort. Sci., 1931, 28, 39—44). CH. ABS.

Nitrogen intake and translocation in apple trees following autumn, winter, and spring sodium nitrate applications. W. W. ALDRICH (Proc. Amer. Soc. Hort. Sci., 1931, 28, 532—538).—Transfer of N from storage tissues to terminal growing points does not take place to any great extent until growth starts. CH. ABS.

Carbohydrate and nitrogen relationships in apple shoots as influenced by soil management. J. T. SULLIVAN and F. P. CULLINAN (Proc. Amer. Soc. Hort. Sci., 1931, 28, 519—525).—The total N in the terminal shoots was greater, and the starch less, for trees receiving tillage with cover crop than for trees in sod or lucerne. CH. ABS.

Variations in amounts of carbohydrates in maize leaves. L. F. PUHR and A. N. HUME (S. Dakota Agric. Exp. Sta. Bull., 1932, No. 270, 33 pp.).—Daily variations in the sugar and starch contents were similar in early and late maturing varieties. Insol. carbohydrates reached a max. val. later in the day than did the sugars. Non-reducing always exceeded reducing sugars in quantity and their variations were more regular. A. G. P.

Effect of nitrate applications on soluble carbohydrate in apples. E. F. HOPKINS and E. W. GREVE (Proc. Amer. Soc. Hort. Sci., 1931, 28, 501—506).—Little correlation was found. CH. ABS.

Changes in green lima beans subjected to various storage conditions. R. L. CAROLUS (Proc. Amer. Soc. Hort. Sci., 1932, 28, 367—374).—Total sugars decrease most rapidly during the first 24 hr., but do not show any significant additional losses. Total and insol. N tend to increase and sol. N to decrease during storage. However, actual loss of total N occurs. CH. ABS.

Mineral nutrition of plants. E. BOTTINI (L'Ind. Chimica, 1932, 7, 1634—1637).—Compositions of the mineral constituents of a no. of cereals, root and leguminous crops, grass, etc. are given, the functions of each constituent in vegetable biochemistry being described and the proportions in which it is absorbed by plants indicated. T. H. P.

Catalase in barleys of different origins. N. N. IVANOV and M. I. LISHKEVICH (Bull. Appl. Bot., Russia, 1929, 21, No. 4, 3—32).—Northern barley contains more catalase than southern, except that grown in a mountainous southern region. Amylase activity is also greater. The enzyme content serves as an index of maturity. CH. ABS.

New vegetable principle : uric acid. R. FOSSE, P. DE GRAEVE, and P. E. THOMAS (Compt. rend., 1932, 195, 1198—1200; cf. A., 1932, 662).—Uric acid occurs in the following seeds in the amounts given : broad bean 0·23, melitot 0·25, purple clover 0·24, aleppo 0·176, coronilla 0·13, garden cress 0·108, field maple 0·054, castor oil 0·061, white lupin 0·048, and soya bean 0·03 mg. per kg. The uric acid is the origin of allantoin in plants and also of part of their urea and NH_3. A. C.

Biochemical variability of castor seeds due to geographical factors. Z. P. PRIZEMINE (Bull. Appl. Bot., Leningrad, 1929, 21, No. 4, 391—426).—The yield of oil depends on the maturity of the seeds, but little on geographical factors. Increase in oil content is accompanied by decrease in protein. In northern climates the free fatty acid is higher, the lipase activity greater, and the amount of cellulose in the testa of immature seeds is smaller. CH. ABS.

Food value of *Phaseolus vulgaris*. P. JUNKERSDORF and K. MEYER (Biochem. Z., 1932, 256, 100—104).—The " black bean " of Central America (Mexico) has a high starch content, whilst the protein content approaches that of the soya bean. Its composition shows that it is a valuable food. W. McC.

Determination of iodine in blood, foods, and urine. E. J. BAUMANN and N. METZGER [with L. K. BALDAUF] (J. Biol. Chem., 1932, 98, 405—416).—The dried material is electrically burned in an atm. of O_2 in a closed vessel connected with absorption flasks containing aq. KOH. The aq. extract of the ash and the absorption fluids are treated with KOH and H_2O_2, taken to dryness, and the residue is again incinerated etc. as before. The I content of the final residue is determined by slight modifications of standard methods (A., 1925, i, 183; 1926, 1284). F. O. H.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1933.

General, Physical, and Inorganic Chemistry.

Dispersion and absorption of helium. J. P. Vinti (Physical Rev., 1932, [ii], **42**, 632—640).—Theoretical. The relative degrees of importance of singly excited, doubly excited, and continuous states in the dispersion and absorption spectrum are moderate, small, and very large, respectively. N. M. B.

Spectrum of Li III. H. G. Gale and J. B. Hoag (Physical Rev., 1931, [ii], **37**, 1703).—Lines required by the Bohr theory have been measured at 135·0, 113·9, 108·0, 105·5, and 104·2 Å. and at 729·1 Å. L. S. T.

Hyperfine structure of ionised lithium. S. Goudsmit and D. R. Inglis (Physical Rev., 1931, [ii], **37**, 329). L. S. T.

Structure of arc and spark lines of nitrogen. P. G. Kruger and R. C. Gibbs (Physical Rev., 1931, [ii], **37**, 1702—1703). L. S. T.

Absorption bands of atmospheric oxygen. H. D. Babcock and W. P. Hoge (Physical Rev., 1931, [ii], **37**, 227; cf. A., 1931, 1343).—Revised wave-lengths for 382 O_2 lines have been derived. L. S. T.

Diffuse bands accompanying the *D*-lines of sodium. K. Wurm (Z. Physik, 1932, **79**, 736—741).—Bands were observed due to Na_2 polarisation mols.; the heat of dissociation is estimated to be 0·1 volt. A. B. D. C.

Hyperfine structure in aluminium. R. Ritschl (Nature, 1933, **131**, 58—59).—Details of hyperfine structure observed in Al arc and spark lines are recorded. Al has a nuclear moment. L. S. T.

Nuclear spin of aluminium. R. C. Gibbs and P. G. Kruger (Physical Rev., 1931, [ii], **37**, 656—657).—The four Al lines obtained with a Schuler hollow-cathode discharge cooled by liquid air are sharp and lack structure. The lines 3944, 3961, and 4663 Å. result from transitions which should give wide hyperfine structure separations and should be observable if the nuclear moment of Al differs from 0. Al may be regarded as an exception to present theories of nuclear structure. L. S. T.

Aluminium may have a nuclear spin. H. E. White (Physical Rev., 1931, [ii], **37**, 1175).—Previous evidence (cf. preceding abstract) is inconclusive and Al is predicted to have a nuclear spin. L. S. T.

Band spectrum, predissociation, and structure of the P_2 molecule. G. Herzberg (Ann. Physik, 1932, [v], **15**, 677—706).—The ultra-violet band spectrum of the P_2 mol. has been measured and the vibrational structure analysed. Predissociation sets in at the vibrational quantum no. $v'=11$. The heat of dissociation of the P_2 mol. is 5·008 volts=115·45 kg.-cal. In this predissociation it is a question of a radiationless intercombination. The at. separation in the ground state is remarkably large in comparison with the at. separations of neighbours of P_2 in the periodic table. Abnormal vals. for the vibration quantum nos. and for the heat of dissociation are found also for this mol. W. R. A.

Band spectrum of sulphur. P. Huber (Physical Rev., 1931, [ii], **37**, 471).—The effect of predissociation is especially evident in emission, the $n' \longrightarrow 0$ progression breaking off suddenly after the 8—0 band. The heat of dissociation of S_2 is therefore $< 4{\cdot}39$ volts. Five emission bands between 2828 and 2980 Å. have been photographed. L. S. T.

Iron spectrum in the hydrogen flame. (Miss) M. Adam (Ann. Physik, 1932, [v], **15**, 613—618).—The Fe spectrum in the H_2 flame shows that the *a* lines, in comparison with the *b* lines and the lines of the Fe arc, are considerably intensified. The *b* lines gradually appear stronger than the *a* lines in proceeding through the series H_2 flame, mantle of illuminating gas, H_2–O_2 flame, arc. W. R. A.

Hyperfine structure in the copper spectrum. A. G. Shenstone (Physical Rev., 1931, [ii], **37**, 1023).—The nuclear moment of Cu is probably $1\frac{1}{2}$. Ag shows no hyperfine structure. L. S. T.

Effect of hydrogen on the intensities of the spectra of zinc, cadmium, and mercury. J. G. Black and W. G. Nash (Physical Rev., 1931, [ii], **37**, 468).—H_2 mixed with Cd or Hg in a low-voltage arc has a similar effect as with Zn (A., 1930, 2). Hg has more than enough energy to dissociate H_2, Zn just enough, but Cd has insufficient. In spectroscopic analysis the absence of a "raie ultime" apparently does not prove the absence of an element when H_2 is present. L. S. T.

Series in the spectrum of germanium II. C. W. Gartlein (Physical Rev., 1931, [ii], **37**, 1704).—Two series have been obtained from the spectrum of Ge II in the region 500—9000 Å. The second ionisation potential of Ge is approx. 15·86 volts. L. S. T.

First spark spectrum of arsenic. A. S. Rao (Current Sci., 1932, **1**, 42—43).—Terms of the As II spectrum due to the 4*d* electron and to the configur-

ation $4s4p^3$ have been detected. Tolansky's val. (3/2) for the nuclear moment of As is confirmed. Ch. Abs.

Sixth spectrum of arsenic. D. Borg and J. E. Mack (Physical Rev., 1931, [ii], **37**, 470).—The lines of the transition $3d^9 4s \leftarrow\!\!- 3d^9 4p$ have been identified in As VI. L. S. T.

Deviations from the sum rule in the spectrum of strontium. W. Kast (Z. Physik, 1932, **79**, 731—735). A. B. D. C.

Wave-lengths of silver, molybdenum, copper, iron, and chromium $K\alpha_1$ lines. J. A. Bearden (Physical Rev., 1933, [ii], **43**, 92—97).—Data obtained by the double-crystal spectrometer agree for Ag and Mo, but differ for Cu, Fe, and Cr from the results of photographic methods. N. M. B.

Interferential comparison of the red and other radiations emitted by a new cadmium lamp and the Michelson lamp. J. E. Sears and H. Barrell (Proc. Roy. Soc., 1933, **A**, **139**, 202—218).—The new Cd lamp (Osram), when excited with a current of 1 amp., is a safe substitute for the Michelson lamp as a standard source of monochromatic red radiation. When the current is increased to 2 amp. the Osram lamp becomes unsuitable. L. L. B.

Line fluorescence of cadmium vapour. (Mlle.) E. Kalinowska (Compt. rend., 1933, **196**, 168—170).—The intensities of the lines of the triplet 4678, 4800, 5086 Å. of the fluorescence spectrum excited in saturated Cd vapour at 600—900° by light of Al and Cd sparks show that the excitation of the Cd atom to the state 2^3S is mainly due to a single act of absorption of the photons, but at low pressures also to excitation of loosely-bound mols. C. A. S.

Nuclear moment of indium. D. A. Jackson (Z. Physik, 1933, **80**, 59—66).—The nuclear moment of In is most probably 9/2 (cf. A., 1930, 1075). A. B. D. C.

Molecular fluorescence of antimony. J. Genard (Nature, 1933, **131**, 132). L. S. T.

Arc spectrum of iodine. S. C. Deb (Proc. Roy. Soc., 1933, **A**, **139**, 380—397).—The spectrum of I has been photographed in the region 3200—9113 Å. in emission and 2300—1800 Å. in absorption, and 160 out of the total of 437 recorded lines have been classified. The ionisation potential is 10·548 volts. L. L. B.

Dissociation of excited iodine molecules by collisions with argon atoms. L. A. Turner and E. W. Samson (Physical Rev., 1931, [ii], **37**, 1684).—I atoms are produced by illumination of an I–A mixture (0·3 mm. I, 5 cm. A) with continuous light of wave-length > 5100 Å. from a C arc. The excited mols. appear to dissociate on collision with A atoms. L. S. T.

Monochromatic excitation of fluorescence of iodine. I. I. Agarbiceanu (Compt. rend., 1933, **196**, 166—168; cf. A., 1931, 7; 1932, 891).—Hg lines 5461, 5769, and 5790 Å. excite in I vapour, provided it is free from any other gas, respectively 5, 9, and 9 lines. C. A. S.

First spectrum of xenon. C. J. Humphreys and W. F. Meggers (Bur. Stand. J. Res., 1933, **10**, 139—149).—538 lines of Xe I between 3340 and 11,140 Å. were measured and classified. H. J. E.

Stark effect for xenon. H. W. Harkness and J. F. Heard (Proc. Roy. Soc., 1933, **A**, **139**, 416—435).—The Stark effect for Xe has been examined in the region 3500—8400 Å. Displacements have been observed for 98 lines. The results support the quantum-mechanical explanation of the origin of Stark displacements. Lines belonging to the second spectrum of Xe have been observed, none showing displacement in the electric field. L. L. B.

Absorption of light in cæsium vapour. H. J. J. Braddick and R. W. Ditchburn (Nature, 1933, **131**, 132—133).—The absorption of light in Cs vapour at 0·15—0·6 mm. and 270° has been measured from 3184 to 1935 Å. Absorption at a given wave-length is directly proportional to pressure, and a preliminary val. for total absorption at 3130 Å. is $1{\cdot}92\ (\pm 0{\cdot}1) \times 10^{-19}$ cm.$^{-1}$ Agreement with photo-ionisation measurements indicates that absorption at this wave-length is photo-electric. L. S. T.

Extension of the first spark spectrum of cæsium (Cs II). J. Olthoff and R. A. Sawyer (Physical Rev., 1932, [ii], **42**, 766—776; cf. A., 1932, 439).—Intensities, wave-lengths, frequencies, and classifications are tabulated for about 260 lines in the range 2300—10,000 Å. N. M. B.

Activation of nitrogen–mercury mixtures by illumination with light from a quartz–mercury arc. B. L. Snavely and L. A. Turner (Physical Rev., 1931, [ii], **37**, 1684).—Illumination of a N_2–Hg mixture (5 mm. N_2, 0·001 mm. Hg) in quartz lowers the resistance of the W filament if this is originally at 400°. The excited Hg atoms appear to activate the N_2, but only with the H_2O-cooled arc, showing that the 2537 line is involved. L. S. T.

Hyperfine structure and polarisation of mercury resonance radiation. A. Ellett (Physical Rev., 1931, [ii], **37**, 216—217).—A reply to criticism. L. S. T.

Bluish-green fluorescence of mercury vapour. P. D. Foote, A. E. Ruark, and R. L. Chenault (Physical Rev., 1931, [ii], **37**, 1685).—At 21° and 33° the green glow is invisible in the absence of a foreign gas. Addition of a few mm. of N_2 renders it bright. L. S. T.

Intensities in the ultra-violet spectrum of mercury. E. D. McAlister (Physical Rev., 1931, [ii], **37**, 1021—1022).—Intensities of the major lines in the region 2000—4000 Å. of a Hg arc have been measured. L. S. T.

Band spectra which appear near visible triplet lines of mercury. E. Matuyama (Nature, 1933, **131**, 58).—Details of bands emitted near to the visible triplet lines $2^3P_{0,1,2}$—2^3S_1 in electrodeless excitation of the vapour are recorded. L. S. T.

Origin of the mercury bands at 2480 A. J. G. Winans (Physical Rev., 1932, [ii], **42**, 800—806).—Evidence that the S bands near 2480 Å.,

photographed under varied excitation conditions, have as origin the Hg_2^- or Hg_2 mol. is discussed. N. M. B.

Absolute intensities in the visible and ultra-violet spectrum of a quartz mercury arc. E. D. McAlister (Smithsonian Miscell. Coll., 1933, **87**, 1—18).—Abs. intensity measurements, accurate to ±3%, were made on 32 lines. Four arcs showed intensity divergences to a max. of 10%. N. M. B.

Zeeman effect of the hyperfine structure in thallium II and III. R. F. Bacher (Physical Rev., 1931, [ii], **37**, 226).—The positions and intensities of the Zeeman components of several lines in the first and second spark spectra of Tl now calc. agree with experimental results (A., 1930, 1330). L. S. T.

Paschen–Back effect and hyperfine structure of Bi II. J. B. Green (Physical Rev., 1931, [ii], **37**, 1687; cf. A., 1932, 208).—The Zeeman effect in Bi II has been studied in a field of 34,000 gauss. L. S. T.

Width of spectral lines in gases. V. Weisskopf (Physikal. Z., 1933, **34**, 1—24).—A summary dealing mainly with the theory. A. J. M.

Pressure broadening of spectral lines. II. H. Margenau (Physical Rev., 1933, [ii], **43**, 129—134; cf. A., 1932, 668).—Mathematical. N. M. B.

True and apparent intensity distribution in spectral lines. H. C. Burger and P. H. van Cittert (Z. Physik, 1932, **79**, 722—730).—A method is given for evaluating the integral relating true to apparent intensity distributions in spectral lines.

Multiplet separations in the spectra of atoms with two optical electrons. H. C. Brinkman (Z. Physik, 1932, **79**, 753—775).—Matrix elements are given for interaction of two electrons and for spin-orbital coupling. A. B. D. C.

Spectroscopic applications of the electrodeless discharge. G. Dejardin (Canad. J. Res., 1932, **7**, 556—570).—Spectroscopic study of the electrodeless discharge furnishes one of the best methods of separating the spectra corresponding with different degrees of ionisation of the atom. The empirical classification obtained from the change of line intensity with intensity of excitation agrees well with theory. Results for Ne, A, Kr, Xe, Hg, and P are discussed in detail. J. W. S.

Electrical discharge in gases at normal temperatures and pressures. J. D. Stephenson (Proc. Physical Soc., 1933, **45**, 20—40).—Experiments on corona and spark discharges show that there is a definite val. which can be called the true breakdown strength of the gas. C. W. G.

Method of extending the frequency range of the cathode-ray tube. H. Hartridge (Nature, 1933, **131**, 95—96). L. S. T.

Atomic scattering factor for X-rays in the region of anomalous dispersion. D. Coster and K. S. Knol (Proc. Roy. Soc., 1933, **A**, **139**, 459—466).—Theoretical. A method of calculating the at. factor for *X*-rays in the region of anomalous dispersion, especially in the neighbourhood of the *K*-edge of the scattering element, is described. L. L. B.

Quadrupole lines in X-ray spectra. II. E. Segrè (Atti R. Accad. Lincei, 1932, [vi], **16**, 442; cf. A., 1932, 316).—Results obtained by other workers confirm the author's views attributing the forbidden lines of *X*-ray spectra to quadrupole radiation.

Structure of $K\alpha$ of carbon. A. Hautot (Compt. rend., 1932, **195**, 1383—1384; cf. this vol., 108).—The ray of greater wave-length is itself double, so that $K\alpha$ of C consists of at least three lines, those of shorter λ being separated from that of greatest by 0·2 and 0·7 Å., as in $K\alpha$ of the heavier elements (cf. A., 1927, 491). C. A. S.

Absolute measurement of the Cu $L\alpha$ line. C. E. Howe and M. Allen (Physical Rev., 1931, [ii], **37**, 1694).—60 determinations indicate a val. of 13·326 Å. ±0·01 for the $L\alpha$ line of Cu. L. S. T.

Relative intensities of the $L\alpha_1$, β_1, β_2, and γ_1 lines in tantalum, tungsten, iridium, and platinum. V. J. Andrew (Physical Rev., 1932, [ii], **42**, 591—608; cf. A., 1931, 1114).—The respective corrected intensities at 30 kv. of $L\alpha_2$, β_1, β_2, γ_1 are: Ta, 100, 49·5, 18·8, 9·0; W, 100, 49·4, 20·2, 10·0; Ir, 100, 48·0, 21·2, 10·2; Pt, 100, 46·1, 21·0, 9·7. N. M. B.

Are the wave-lengths of X-ray satellites affected by chemical combination? F. K. Richmyer (Physical Rev., 1931, [ii], **37**, 457).—The two-electron jump theory of the origin of satellites requires that one jump should be affected by chemical combination. In comparing the $K\alpha_{3,4}$ satellites of Si and Na_2SiO_3 the difference in wave-length between satellite and parent line for the latter is in the case of $K\alpha_3$, 3·9% and in that of $K\alpha_4$ 2·8% > for Si. L. S. T.

Upper atomic limit of the satellites of the X-ray line $L\alpha_1$. E. Ramberg (Physical Rev., 1931, [ii], **37**, 457). L. S. T.

***X*-Ray absorption coefficients of the light elements and their relations to the various absorption formulæ.** S. J. M. Allen (Physical Rev., 1931, [ii], **37**, 456).—More accurate measurements at 1·539 and 1·934 Å. have been obtained for O, C, B, Be, Li, and H and corrections applied for impurities present. The vals. of μ/ρ have been compared with those given by existing formulæ, and a new formula is put forward. L. S. T.

Measurement of X-ray emission wave-lengths by means of the ruled grating. R. B. Witmer and J. M. Cork (Physical Rev., 1932, [ii], **42**, 743—748).—Data are recorded for the *L* series of the elements V to Zn, and the *K* series of C to Si. Except in the case of the $K\alpha$ lines of C, F, and O the wave-lengths are longer than those found for the corresponding lines by the crystal method. N. M. B.

Multiplex-echelon gratings. E. Lau (Z. Physik, 1933, **80**, 100—104).—An echelon with steps of two different thicknesses gives greater resolving power than that so far obtained. A. B. D. C.

Theory of the multiplex-echelon grating. P. GORLICH (Z. Physik, 1933, **80**, 105—106; cf. preceding abstract). A. B. D. C.

Oxygen atom in various states of ionisation. D. R. HARTREE and (MISS) M. M. BLACK (Proc. Roy. Soc., 1933, **A**, **139**, 311—335).—Theoretical. One-electron wave functions for the normal electron arrangements of O^{+++}, O^{++}, O^{+}, and neutral O have been calc., and the results have been used to calculate the total energies of the various stationary states arising from the normal electron arrangements, and hence the ionisation energies of these states, using Slater's theory of complex spectra (A., 1930, 126). L. L. B.

Relation between ionisation and ionisation current in gases at high pressures. W. R. HARPER (Proc. Camb. Phil. Soc., 1933, **29**, 149—155)—The phenomena which limit saturation in a high-pressure ionisation chamber are examined with particular reference to the part played by preferential recombination. N. M. B.

Relation between ionic radius and higher ionisation potential. J. A. M. VAN LIEMPT (Rec. trav. chim., 1933, **52**, 85—87; cf. this vol., 5).—Tables are given showing that the product (ionic radius × second ionisation potential) is const. for elements of any one group of the periodic classification. F. L. U.

Ionisation of hydrogen by positive ion impacts. M. E. HUFFORD (Physical Rev., 1931, [ii], **37**, 468).—Ionisation by positive ions is indicated when positive ions of Li, Na, and H are accelerated in an atm. of H_2 at low pressures. L. S. T.

New ultra-ionisation potentials of mercury vapour. W. M. NIELSEN (Physical Rev., 1931, [ii], **37**, 87—88).—Crit. ultra-ionisation potentials have been observed at 10·40, 10·66, 11·00, 11·41, 11·72, 12·06, 12·40, 12·80, and 13·25 volts. L. S. T.

Electronic energy levels of neutral and ionised oxygen. R. S. MULLIKEN (Physical Rev., 1931, [ii], **37**, 1711—1712).—Theoretical. Existing data on O_2 and O_2^+ bands indicate 11·7 volts as the most probable val. for the min. ionising potential of O_2. L. S. T.

Photo-electric effect of electric spark radiation. J. MEIKLEJOHN (Phil. Mag., 1933, [vii], **15**, 146—163). H. J. E.

Photo-electric emission from different metals. H. C. RENTSCHLER, D. E. HENRY, and K. O. SMITH (Rev. Sci. Instr., 1932, [ii], **3**, 794—802).—Sensitivity–wave-length curves are given for U, Co, Mg, Th, Zr, Ti, Ta, Zn, Cd, Al, Cu, Ag, W, Ca, Ba, and electrodes coated with BaO. C. W. G.

Optical and photo-electric experiments with thin metallic layers. R. SCHULZE (Physikal. Z., 1933, **34**, 24—38).—The theory of optical phenomena at thin layers is extended to cover the cases of inner multiple reflexion and interference. A new method of obtaining thin layers is described. For layers up to a thickness of 2 mμ the index of refraction and extinction coeff. are const. Photo-electric determinations allow the absorption coeff., β, and the free wave-length, λ, of the emitted electrons to be calc. β and λ were independent of wave-length for the Au layers used. A. J. M.

Photo-electric currents in gases between parallel plate electrodes. L. A. YOUNG and N. E. BRADBURY (Physical Rev., 1933, [ii], **43**, 34—37).—The dependence on accelerating field strength, pressure, and nature of the gas is investigated. The physical phenomenon of importance is the Ramsauer scattering in the vicinity of the emitter. N. M. B.

Oblique initial emission of electrons from glowing rough crystalline metal surfaces. H. SEEMAN (Z. Physik, 1932, **79**, 742—752). A. B. D. C.

Efficiency of secondary electron emission. S. R. RAO (Proc. Roy. Soc., 1933, **A**, **139**, 436—447; cf. A., 1930, 1080, 1081).—The efficiencies of the secondary electron emission from Cu, Fe, Ni, and Ag faces, calc. from Farnsworth's data (A., 1928, 453) for various primary potentials, show a strong resemblance to similar efficiencies of soft *X*-rays. For polycryst. and single-crystal faces of Ni, the efficiencies calc. from the author's data are nearly the same at potentials < 150 volts. The observed tendency to saturation in the soft *X*-ray intensity curves at about 3000 volts might be due to the photo-electric methods of measurement. L. L. B.

Radiation from slow electrons. L. NEDELSKY (Physical Rev., 1932, [ii], **42**, 641—665).—Mathematical. N. M. B.

Elastic scattering of electrons by mercury atoms. E. B. JORDAN and R. B. BRODE (Physical Rev., 1933, [ii], **43**, 112—115).—The angular distributions for electrons of 10—800 volts energy, and an angle range 5—172°, were investigated. N. M. B.

Secondary electrons from molybdenum. L. J. HAWORTH (Physical Rev., 1931, [ii], **37**, 93—94).—A continuation of previous work (A., 1931, 11). L. S. T.

Collision of slow electrons with atoms. II. General theory and inelastic collisions. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1933, **A**, **139**, 187—201; cf. A., 1931, 1107).—Mathematical. The theory of the collisions of slow electrons with atoms is extended to allow for the distortion of the scattered wave by the field of the excited atom and for the effect of electron exchange. The excitation probabilities of the 2^1P and 2^3P states of He are calc. L. L. B.

Electron scattering in helium. Absolute measurements at 90° and 45°. S. WERNER (Proc. Roy. Soc., 1933, **A**, **139**, 113—129).—The scattered intensity is measured at velocities corresponding with 30—400 volts and at scattering angles of 90° and 45°. The experimental results are compared with the nuclear scattering calc. from Rutherford's formula and with that calc. from Mott and Bethe's formula (A., 1930, 972, 974). Agreement is found above 150 volts, but at low velocities the scattering is much $<$ nuclear scattering. L. L. B.

Technique of ion counting. H. T. GRAZIADEI (Physikal. Z., 1933, **34**, 82—88).—The use of an arrangement due to Swann for the removal of the

external opposing field which occurs in the charge method is considered, and it is shown that the modified method gives results as good as those obtained by the discharge method. The observation by Sheppard (Nature, 1932, **129**, 169) of the existence of periodic oscillations of the ionic content of air was not verified. A. J. M.

Multiply-charged large ions. J. J. Nolan and J. G. O'Keeffe (Proc. Roy. Irish Acad., 1933, **41**, A, No. 4, 26—40).—The Aitken counter was used to investigate the charges carried by nuclei from various sources. Large ions produced by spraying H_2O have charges varying from 30 to 250 units. Atm. nuclei can be charged to several thousand electronic charges, whilst those produced by flames can carry some hundreds of charges. It was found that the ions fell into well-defined groups, especially ions produced by spraying H_2O. A. J. M.

Equilibrium of atoms and ions adsorbed on a metal surface. R. C. Evans (Proc. Camb. Phil. Soc., 1933, **29**, 161—164).—Mathematical. The rate of attainment of equilibrium, in order to interpret data on the rate of evaporation of the alkali metals adsorbed on hot W, is investigated. N. M. B.

Effect of ammonia on positive ion emissivity of iron, nickel, and platinum. A. K. Brewer (J. Amer. Chem. Soc., 1932, **54**, 4588—4597; cf. A., 1932, 669).—Thermionic emission of positive ions was investigated with gas pressures between 100 and 10^{-6} mm. At low temp., a pure Fe filament in NH_3 emits positive ions more copiously than a K–Al_2O_3–Fe emitter in vac. Ni is almost as efficient as Fe, but the emission from Pt is not greatly increased by NH_3. H_2, however, enhances the emission of positive and negative ions from Pt and Ni, but has little effect on Fe. N_2 has only very small effects on Fe and Ni, and none on Pt. Work function vals. indicate that ions before being emitted reside on the surface in a completely dissociated state. The relation of the results to adsorption and surface catalysis is discussed. J. G. A. G.

Mobilities of gaseous ions in $MeNO_2$–H_2 and MeCN–H_2 mixtures. E. A. Higley and C. C. Thorsen (J. Franklin Inst., 1933, **215**, 69—80).—Measurements are recorded. In H_2, $MeNO_2$ forms stable complexes with positive ions and, less readily, with negative ions; MeCN forms complexes with positive ions and possibly also with negative ions. H. J. E.

Neutralisation and ionisation of high-velocity ions of neon, argon, and krypton by collision with similar atoms. H. F. Batho (Physical Rev., 1932, [ii], **42**, 753—765; cf. Rudnick, A., 1931, 1347).—The free paths for neutralisation of the ion and ionisation of the atom were measured over low pressure ranges and the velocity range corresponding with accelerating potentials of 10,000—22,000 volts for Ne, A, and Kr. In each case, the free path for ionisation, reduced to 760 mm., was approx. $6{\cdot}5\times10^{-4}$ cm.; the free paths for neutralisation $\times10^4$ were 0·95, 0·45, and 0·35 for Ne, A, and Kr, respectively. Both free paths decrease with increasing velocity. N. M. B.

Properties of H-rays. C. Pawlowski (Acta phys. Polon., 1932, **1**, 177—207; Chem. Zentr., 1932, ii, 2010—2011).—A discussion of the authors' results (A., 1931, 1348) for H rays expelled from paraffin, cellophane, collodion, and H_2 by means of Po α-rays. Ch. Abs.

Application of the Fermi–Thomas model to positive ions. E. Guth and R. Peierls (Physical Rev., 1931, [ii], **37**, 217). L. S. T.

Scattering of molecular rays by gases. I. F. Knauer (Z. Physik, 1933, **80**, 80—99).—The scattering of mol. rays of H_2, He, H_2O, and O_2 by the gases themselves and by Hg was studied for scattering angles between 22° and 124°; the observations are explained by classical mechanics assuming appropriate force fields. A. B. D. C.

Reflexion of metallic atoms from alkali halide crystals. R. R. Hancox (Physical Rev., 1932, [ii], **42**, 864—881; cf. Zahl, A., 1931, 1207).—The scattering of mol. beams of Hg from crystals of LiF, LiCl, NaF, and KI, and of a mol. beam of Cd from NaCl, has been investigated as a function of crystal and beam temp. N. M. B.

Effective cross-sections of molecules on the basis of gas theory. II. Its dependence on other magnitudes. H. E. Binkele (Ann. Physik, 1932, [v], **15**, 729; cf. A., 1931, 890).—The exact comparison of mol. dimensions obtained by means of consideration of the van der Waals b, the viscosity cross-section, and the at. radii deduced from crystallographic or spectroscopic data is discussed. W. R. A.

Effective cross-sections of atoms compared with slow and fast electrons. R. L. Rosenberg (Ann. Physik, 1932, [v], **15**, 757—786).—Theoretical. W. R. A.

Action cross-section for collisions of the second kind between atoms and ions. O. S. Duffendack and K. Thomson (Physical Rev., 1933, [ii], **43**, 106—111).—The relative probability of excitation of terms in the spark spectra of Cu, Au, Al, and Ag by impacts of the second kind with ions of He and Ne was determined as a function of the resonance discrepancy. N. M. B.

Third report of the at. wt. commission of the International Union for Chemistry. G. P. Baxter, P. Curie, O. Honigschmid, P. Lebeau, and R. J. Meyer (Ber., 1933, **66**, [A], 21—30).—The report follows the lines of its precursors. Recent work on the at. wts. of C, N, F, Kr, Xe, K, La, Tl, Se, Te, and I is criticised in detail. The following alterations are recommended: I, 126·92 instead of 126·932; La, 138·92 instead of 138·90. H. W.

Physical at. wts. F. W. Aston (J.C.S., 1932, 2888—2894).—A lecture. A. J. M.

Comparison of the masses of He and H^1 on a mass-spectrograph. K. T. Bainbridge (Physical Rev., 1933, [ii], **43**, 103—105).—Results give He : H^1 = 3·971283±0·000042. If He=4·00216±0·00013 on the O^{16} scale, H^1=1·007775±0·000035 in agreement with Aston. N. M. B.

Precision determination of the mass ratio of O^{18} and O^{16}. H. D. Babcock and R. T. Birge (Physical Rev., 1931, [ii], **37**, 233; cf. following abstract).—The vibrational isotope effect gives O^{18}

18·0065±0·0001, whilst the rotational isotope effect gives 18·0064 and 18·0074. L. S. T.

Relative abundance of the oxygen isotopes, and the basis of the at. wt. system. R. T. BIRGE and D. H. MENZEL (Physical Rev., 1931, [ii], **37**, 1669—1671).—A discussion. Mecke and Childs' val. of 630 : 1 (A., 1931, 543) for the abundance ratio of of O^{16} : O^{18} is preferred to other vals. (A., 1929, 971; 1930, 1232). Owing to the uncertainty of the connecting factor, it is desirable not to convert the results obtained by one system for the measurement of at. masses to those obtained by the other. L. S. T.

Precision determination of atomic mass ratios from band spectra. R. T. BIRGE (Physical Rev., 1931, [ii], **37**, 227).—Theoretical. L. S. T.

Vibrational isotope effects in polyatomic molecules. E. O. SALANT and (MISS) J. E. ROSENTHAL (Physical Rev., 1932, [ii], **42**, 812—822).—Mathematical. N. M. B.

Intensity ratio for the boron isotopes B^{10} and B^{11}. L. S. ORNSTEIN and J. A. VREESWIJK, jun. (Z. Physik, 1933, **80**, 57—58).—The intensity ratio for B^{10} : B^{11} is 1 : 4·43, giving the at. wt. 10·816 (cf. this vol., 207). A. B. D. C.

Evidence against the existence of a chlorine isotope of mass 39. M. ASHLEY and F. A. JENKINS (Physical Rev., 1931, [ii], **37**, 712).—The ultra-violet absorption bands of AgCl give no band corresponding with Cl^{39}, which cannot be present to an extent $>0·001$ of Cl^{37}. No heavier isotopes could be detected from a similar investigation of AgBr and AgI bands. L. S. T.

Lead isotopes. (MISS) E. R. BISHOP, (MISS) M. LAWRENZ, and C. B. DOLLINS (Physical Rev., 1933, [ii], **43**, 43—46; cf. A., 1932, 554).—The magneto-optic method shows 16 isotopes of probable mass and order of abundance : 208, 206, 207, 205, 212, 210, 204, 202, 203, 211, 201, 209, 216, 215, 214, and 213. In U salts 206, 210, 202, and 214, and in Th salts 208, 216, 204, and 212, predominate. N. M. B.

Bismuth isotopes. F. ALLISON and (MISS) E. R. BISHOP (Physical Rev., 1933, [ii], **43**, 47).—The magneto-optic method shows 14 isotopes of probable mass and order of abundance : 211, 210, 209, 212, 215, 214, 213, 216, 207, 205, 206, 208, 219, 217. N. M. B.

Radium isotopes. (MISS) E. R. BISHOP and C. B. DOLLINS (Physical Rev., 1933, [ii], **43**, 48).—The magneto-optic method shows 4 isotopes of probable mass and order of abundance : 226, 228, 230, and 232. N. M. B.

Isotopes of uranium, thorium, and thallium. R. GOSLIN and F. ALLISON (Physical Rev., 1933, [ii], **43**, 49—50).—The magneto-optic method shows isotopes of probable mass and order of abundance : U, 238, 239, 240, 234, 237, 235, 233, 236; Th, 232, 230, 234, 235, 236, 229, 233, 231; Tl, 207, 205, 211, 203, 201, 209, 215, 213. N. M. B.

Isotopes of uranium, thorium, and lead, and their geophysical significance. C. S. PIGGOT (Physical Rev., 1933, [ii], **43**, 51—59).—A determination, by the magneto-optic method, of the isotopes of the elements involved in the radioactive disintegrations (at. nos. 81—92) indicates 4 radioactive series beginning with 8 isotopes of U (2 to each), and ending with 16 isotopes of Pb (4 to each). Calculations on U^{238} and Pb^{206} would give the most accurate age determinations. N. M. B.

Nuclear moments of the two rubidium isotopes. H. KOPFERMANN (Naturwiss., 1933, **21**, 24).—Investigation of the visible spectrum of neutral and simply ionised Rb as regards hyperfine structure shows that if the moment of Rb^{85} is taken as 5/2, and that of Rb^{87} as 5/2 or 3/2, and the magnetic moment of Rb^{87} is 2·3 times that of Rb^{85}, a term scheme can be drawn up. No isotopic displacement is shown by the lines studied. The results are not in agreement with those of Jackson (A., 1931, 887). A. J. M.

Mass defects of C^{13}, O^{18}, N^{15}, from band spectra, and the relativity relation of mass and energy. R. T. BIRGE (Physical Rev., 1931, [ii], **37**, 841—842).—The mass defects of C^{13}, O^{18}, and N^{15}, 10·7, 17·7, and 27·0, respectively, obtained from band spectra data are satisfactorily located on the "mass defect" curve of Chadwick and co-workers (A., 1931, 783). L. S. T.

Corpuscular *X*-ray spectra of the radio-elements. C. D. ELLIS (Proc. Roy. Soc., 1933, **A**, **139**, 336—342).—Direct comparison of the β-ray spectra of Ra-(B+C) and Th-(B+C) shows that certain lines are common to each. These must represent the corpuscular *X*-ray spectrum of an atom of at. no. 83, since the electronic structure of an atom of this at. no. is the only common feature in the two sources. L. L. B.

Radioactive families. (MISS) E. R. BISHOP (Physical Rev., 1933, [ii], **43**, 38—42).—Available data are interpreted in terms of radioactive transformation diagrams. N. M. B.

Radioactivity of lanthanum, neodymium, and samarium. W. F. LIBBY and W. M. LATIMER (J. Amer. Chem. Soc., 1933, **55**, 433—434; cf. this vol., 4).—The radiation emitted by La and Nd is of the β-ray type. The activities of La, Nd, and Sm are approx. 8, 2·5, and 3 times, respectively, that of K per mol. Gd gave negative results. The activity is probably due to unstable isotopes, but traces of Ac may be present in the La and Nd. J. G. A. G.

Upper limit of energy in the β-ray spectrum of actinium-*B*. B. W. SARGENT (Proc. Camb. Phil. Soc., 1933, **29**, 156—160).—Absorption curves in paper and Al for the β-rays of Ac-(B+C) and Ac-C'' gave 0·08±0·02 g. per sq. cm. for the range of the β-rays of Ac-B; the energy required for this range is 300,000±50,000 volts, which must be the end-point of the continuous spectrum. N. M. B.

Mechanism of γ-excitation by β-disintegration. G. GAMOW (Nature, 1933, **131**, 57—58).—A theory of electronic emission and excitation of the nucleus concerned is outlined. L. S. T.

Internal conversion of the γ-rays and nuclear level systems of the thorium-*B* and -*C* bodies. C. D. ELLIS and N. F. MOTT (Proc. Roy. Soc., 1933, **A**, **139**, 369—379).—The vals. calc. for the internal

conversion coeffs. (this vol., 111) are compared with experimental data from Th-*B* and Th-*C*. The level schemes of Th-*C.C''*, Th-*B.C*, and Th-*C''*.Pb are discussed. Quadrupole transitions are more common than dipole. The long-range α-particles from Ra-*C.C'* and Th-*C.C'* are compared. L. L. B.

New coupling effect between γ-rays and sheath electrons ? E. STAHEL (Naturwiss., 1933, **21**, 43).—A method of investigating experimentally the coupling effect between excited at. nuclei and sheath electrons is described. A. J. M.

Heights of nuclear potential barriers. E. C. POLLARD (Nature, 1933, **131**, 97).—The heights of the nuclear barriers of the light elements, calc. from scattering experiments with α-particles and from min. energy methods involving the range of α-particle of least velocity which enters a nucleus and causes emission, appear to be proportional to the at. nos. This indicates that the protons produced from P by α-particles from Po and from K by Ra-*C* are due to resonance with a virtual α-particle level, since the α-particle will have insufficient energy to surmount the barrier. L. S. T.

Disintegration of lithium by protons of high energy. M. C. HENDERSON (Physical Rev., 1933, [ii], **43**, 98—102).—The results of Lawrence (cf. A., 1932, 554) are extended to protons of 1,125,000 electron-volts energy. The probability of disintegration of the individual nucleus is independent of the proton energy above 4×10^5 volts. N. M. B.

Atomic disintegration at low potentials. H. R. VON TRAUBENBERG, A. ECKARDT, and R. GEBAUER (Naturwiss., 1933, **21**, 26).—An apparatus for bringing about the disintegration of atoms by protons at low potentials is described. Li still shows disintegration with a potential of 29 kv., giving proton velocity of 13 kv. A. J. M.

Measurements with liquid helium. XX. Attempt to show the presence of neutrons in the atmosphere. W. MEISSNER and K. STEINER (Z. Physik, 1933, **80**, 1—3).—An upper limit for the neutron content of the atm. is $1\cdot6\times10^{-11}$ by vol. A. B. D. C.

Excitation of neutron emission from beryllium. G. KIRSCH and W. SLONEK (Naturwiss., 1933, **21**, 62).—A Geiger counter was used to obtain the excitation curve of neutron emission from Be. The form of the curve shows the resonance positions, which are displaced somewhat to higher absorption vals. than those obtained when the Wilson method was used. The relative distance between the resonance positions remains the same. A. J. M.

Diffusion of neutrons: inelastic collisions with nuclei. P. AUGER (Compt. rend., 1933, **196**, 170—172; cf. A., 1932, 895).—Observations with the bombarded Be source (*a*) isolated in the centre of the chamber, (*b*) with a paraffin screen around it, and (*c*) backed against a diffuser of Cu, Al, Fe, or Pb and surrounded by the paraffin screen, give varying relative nos. of long and short paths. It is concluded that short paths are due to slow neutrons, produced by diffusion of rapid neutrons in matter, accompanied by loss of some 90% of their energy. Collisions between neutrons and nuclei would frequently be inelastic, when the excited nuclei in returning to the normal state might emit γ-rays, or be disintegrated with emission of corpuscular rays (cf. *ibid.*, 443). C. A. S.

Nature of the dark modification of active nitrogen. J. OKUBO and H. HAMADA (Phil. Mag., 1933, [vii], **15**, 103—113).—On destroying the glow of active N by a second weak discharge the issuing gas is inactive if the N_2 is pure, but active if it is contaminated (cf. A., 1928, 3). The effect of heating to 600—650° on the spectrum of active N, and its ability to excite the *D* lines of Na, is described. Modifications of Cario and Kaplan's theory (A., 1930, 124) are suggested. H. J. E.

Apparent fatigue and ageing phenomena in the active nitrogen afterglow. C. T. KNIPP and L. N. SCHEUERMAN (Physical Rev., 1931, [ii], **37**, 475).—The duration of the N afterglow decreases with an increase in time of energising by high frequency. This appears to be a fatigue effect. When the N_2 is kept for some months, an increase in the duration of the afterglow on flash results. This appears to be an ageing effect favourable to the formation of the active aggregates. L. S. T.

Metastable molecules and active nitrogen. J. KAPLAN (Physical Rev., 1931, [ii], **37**, 226).—Strong, uncondensed discharges through mixtures of N_2 and Hg vapour at 5 cm. yield spectra of the first positive group with an intensity distribution similar to that of the N_2 afterglow. The possible modes of formation of the metastable N mols. are discussed. L. S. T.

Active nitrogen. J. OKUBO and H. HAMADA (Physical Rev., 1932, [ii], **42**, 795—799).—Two assumptions on the vibrational state, by which the observed results on active N can be explained, are discussed. N. M. B.

New source of active nitrogen. J. KAPLAN (Physical Rev., 1931, [ii], **37**, 1004—1005).—The afterglow of active N has been obtained in the uncondensed discharge produced by a 25,000-volt 1-kw. transformer at 0·1 mm. to approx. 5 mm., but only after long running of the tubes at approx. 0·001 mm. L. S. T.

Occurrence of O III in stellar spectra. R. K. MARSHALL (Astrophys. J., 1932, **76**, 316). L. S. T.

Excitation of helium in the chromosphere. P. C. KEENAN (Astrophys. J., 1932, **76**, 139—143).—The turbulent motion of the chromospheric gases may give the Ca atoms sufficient velocity to excite normal He atoms by collision. L. S. T.

Normal state of helium molecule-ions He_2^+ and He_2^{++}. L. PAULING (J. Chem. Physics, 1933, **1**, 56—59).—A theoretical treatment based on Schrodinger's equation. F. L. U.

Auroral spectrum. J. KAPLAN (Physical Rev., 1932, [ii], **42**, 807—811).—The first negative bands of N have been excited under conditions closely resembling those in the aurora; the probable origin of the bands is discussed. N. M. B.

Energy of cosmic rays. E. REGENER (Nature, 1933, **131**, 130; cf. A., 1932, 1072). L. S. T.

Pressure and temperature dependence of ionisation by cosmic rays. B. GROSS (Z. Physik, 1933, **80**, 125—133). A. B. D. C.

Electromagnetic fields due to variable electric charges and the intensities of spectrum lines according to the quantum theory. G. A. SCHOTT (Proc. Roy. Soc., 1933, **A**, **139**, 37—56).—Mathematical. The numerical vals. calc. from the expressions derived for the intensities of the lines of the Lyman, Balmer, and Paschen series show that the usual method of determining the electric moment of a distribution by means of Schrodinger's integrals, and then applying the classical expression for the radiation from a dipole of equal moment, is liable to gross errors. L. L. B.

Energies and wave-functions of the state $(1s)(2s)'S$ in helium-like atoms. J. P. VINTI (Physical Rev., 1931, [ii], **37**, 448—449).—Theoretical. L. S. T.

Extrapolation of atomic structure factor curves. M. MUSKAT (Physical Rev., 1931, [ii], **37**, 656).—Froman's formula (A., 1931, 18) can be obtained without invoking a sp. theory of the electron distribution causing the at. structure factor, and is independent of wave-mechanical interpretations of electron distribution. L. S. T.

Interaction between atoms with s-electrons. N. ROSEN and S. IKEHARA (Physical Rev., 1933, [ii], **43**, 5—8).—Formulæ previously obtained (cf. A., 1932, 211) are evaluated, and illustrated by curves. Calc. vals. for H and the alkali metal mols. are in good agreement with experiment. N. M. B.

Polarisabilities and intra-atomic energies of hydrogen and helium. J. G. KIRKWOOD (Physical Rev., 1931, [ii], **37**, 459—460).—A method of calculating polarisabilities and intra-at. energies has been developed and applied to He and H_2. L. S. T.

Van der Waals forces of helium and the stability of a small energy helium molecule. H. MARGENAU (Physical Rev., 1931, [ii], **37**, 1014; cf. A., 1932, 328).—Theoretical evidence for the existence of a He mol. of low energy of linking is given. L. S. T.

Pauli's principle and the structure of the atomic nucleus. III. Mechanical moment of atomic nuclei. E. N. GAPON (J. Gen. Chem. Russ., 1932, **2**, 707—709).—Theoretical. E. T.

Theory of interchange of vibrational and translational energy. C. ZENER (Proc. Camb. Phil. Soc., 1933, **29**, 136—141).

Relation of empirical atomic and ionic radii to the Thomas–Fermi charge distribution in atoms. W. BRAUNBEK (Z. Physik, 1932, **79**, 701—710).—The radius of an atom is defined as that of a sphere outside which there is a const. amount of charge of the Thomas–Fermi distribution. This gives radii comparable with empirical vals. for any one column of the periodic table. The column under Li and the corresponding singly-charged positive ions are considered in detail, and the const. amount of charge is approx. that of one electron. A. B. D. C.

Radiation from glowing oxides and oxide mixtures in the visible spectrum. H. HOPPE (Ann. Physik, 1932, [v], **15**, 709—728).—The radiation from glowing CeO_2, Nd_2O_3, SnO_2, ZrO_2, ZnO, Al_2O_3–Cr_2O_3, CeO_2–ThO_2 and MgO–ZnO has been studied at different temp. The influence of temp. and particle size has been considered. Single crystals of white sapphire and ruby have also been examined. W. R. A.

Crystal radiation and grain-boundary radiation of non-metallic bodies [oxides]. F. SKAUPY and H. HOPPE (Z. tech. Physik, 1932, **13**, 226—228; Chem. Zentr., 1932, ii, 667).—A single crystal of white sapphire shows practically no radiation in the visible region up to 1500° abs., but polycryst. Al_2O_3 shows high emissivity especially in the blue region of the spectrum. The spectral distribution of the radiations from Al_2O_3–Cr_2O_3 mixtures shows that the addition of Cr_2O_3 modifies the grain-boundary properties of the Al_2O_3. L. S. T.

Reflexion of light at a surface covered by a unimolecular film. C. STRACHAN (Proc. Camb. Phil. Soc., 1933, **29**, 116—130).—Mathematical.

Asymptotic expansions of the expressions for the partition function and the rotational specific heat of a rigid polyatomic molecule for high temperatures. (MISS) I. E. VINEY (Proc. Camb. Phil. Soc., 1933, **29**, 142—148).—Mathematical. N. M. B.

Repulsion exponents for alkali hydrides. A. KREBS (Z. Physik, 1933, **80**, 134—136).—The known band spectra of LiH and NaH give estimates of the repulsion exponents for these mols. in the gaseous phase; the vals. are 3·9 for LiH and 4·8 for NaH, agreeing closely with the vals. 4·1 and 4·9 for the mols. in crystal form. A. B. D. C.

Highly-attenuated flames of potassium vapour with halogens. M. KROCSÁK and G. SCHAY (Z. physikal. Chem., 1932, **B**, **19**, 344—365; cf. A., 1931, 282).—The light emission of the flames consists principally of (*a*) the red resonance doublet of K, (*b*) the second violet resonance doublet, and (*c*) a continuum which extends over almost all the visible spectrum. (*a*) originates in the gas space, chiefly by the primary reaction (1) $K+X_2=KX+X$ (X=Cl or Br), and to a much smaller extent by the secondary gas reaction (2) $K_2+X=KX+K$. In (1) every collision leads to reaction, the effective cross-section exceeding the val. deduced from the gas theory. (*b*) results partly from (2) and partly, it is probable, from double excitations. (*a*) originates on the wall as a consequence of the secondary wall reaction K+X=KX. The flames have a relatively high conductivity, due to electrons which, together with K ions, are released from an adsorbed K film on the wall by a kind of chemical photo-effect. R. C.

Total radiation from heated carbon dioxide. T. DREISCH (Z. Physik, 1932, **79**, 710—721).—Between 300° and 900° the total radiation from CO_2 is 7·41% that of black-body radiation. A. B. D. C.

Emission spectrum of CO_2. H. D. Smyth and T. C. Chow (Physical Rev., 1931, [ii], **37**, 1710).—An extension of previous work (A., 1932, 107). L. S. T.

Structure of the third positive group of CO bands. G. H. Dieke and J. W. Mauchly (Physical Rev., 1933, [ii], **43**, 12—30; cf. A., 1932, 444).—Full data for the $0\longrightarrow0$ (λ 2833), $0\longrightarrow1$ (2977), $0\longrightarrow2$ (3134), and $0\longrightarrow3$ (3305) bands are tabulated. N. M. B.

Band spectrum of CO^+. D. Coster, H. H. Brons, and H. Bulthuis (Z. Physik, 1932, **79**, 787—822).—Measurements of rotation lines in some CO^+ bands are tabulated and discussed. A. B. D. C.

CO bands in the region 2220—3300 Å. H. P. Knauss (Physical Rev., 1931, [ii], **37**, 471; cf. A., 1931, 1350).—Bands obtained in the electrodeless ring discharge at 2925, 3028, 3138, and 3253 Å. have been identified with a new system corresponding with transitions $C(^1\Sigma)$ to $a'(^3\Sigma)$. L. S. T.

Band spectra of MgO, CaO, and SrO. P. C. Mahanti (Physical Rev., 1932, [ii], **42**, 609—621).—Wave-lengths of band heads, intensities, and vibrational quantum analysis are tabulated for the red and green bands of MgO, and the blue and ultra-violet bands of CaO and SrO. N. M. B.

Barium hydride band spectra in the near infra-red. W. W. Watson (Physical Rev., 1933, [ii], **43**, 9—11; cf. A., 1932, 439).—Quantum assignments of frequencies and combination differences are tabulated for the 8924 Å. band system. N. M. B.

Distribution of intensity within the β and γ bands of nitric oxide. O. R. Wulf and E. J. Jones (Physical Rev., 1931, [ii], **37**, 471).—Variations in the distribution of intensity within these bands occurs when the products from an O_2 discharge tube interact with those from an active N tube. Conditions suggest that the excitation of band spectra may depend on chemiluminescent processes, and that intensity distributions will therefore frequently be abnormal. L. S. T.

Absorption spectra of some higher oxides. A. K. Dutta and P. K. Sen Gupta (Proc. Roy. Soc., 1933, **A**, **139**, 397—405).—The absorption spectra of N_2O_5, TeO_3, and MoO_3 have been studied. All showed the same type of absorption as SO_3 (A., 1932, 981): first absorption on the long wave-length side, corresponding with dissociation into N_2O_4, TeO_2, and MoO_2, respectively, and normal O atom; then a patch of re-transmitted light; and finally a second region of absorption denoting dissociation into N_2O_4, TeO_2, and MoO_2, respectively, and O excited to the $^1D_2$ state. The heat of dissociation of O_2 is calc. to be 128 kg.-cal. from data for N_2O_5. L. L. B.

OH bands and the ultra-violet line spectrum of the Wehnelt interrupter. R. W. Shaw (Physical Rev., 1931, [ii], **37**, 1548). L. S. T.

OH band, 3064 Å., and the solar spectrum. R. W. Shaw (Astrophys. J., 1932, **76**, 202—209).—New assignments of lines of the P and Q branches of OH bands 3064 and 3122 Å. have been made. L. S. T.

Water-vapour absorption spectrum in the near infra-red. E. D. McAlister and J. H. Unger (Physical Rev., 1931, [ii], **37**, 1012).—Fine structure of the 1·13 and 1·45 μ bands has been revealed, and new lines have been added to the 1·38 μ band. L. S. T.

Ultra-violet absorption spectra of phosphine, arsine, and stibine. G. H. Cheesman and H. J. Emeléus (J.C.S., 1932, 2847—2848).—Two diffuse absorption bands were observed for PH_3 at approx. 2315 and 2290 Å. (cf. Melville, A., 1932, 479). Below 2270 Å. absorption is continuous. These bands have been shown to be due to PH_3 and not to any secondary product. AsH_3 gave an absorption limit at 2390 Å. SbH_3 gave no definite val. for the absorption limit owing to the rapid surface decomp. of SbH_3. There seems to be a definite gradation in the absorption spectra of the hydrides of N, P, As, and Sb, NH_3 having well-defined predissociation bands, PH_3 weak ones, and AsH_3 and SbH_3 showing only continuous absorption. A. J. M.

3360 Å. band of NH. R. W. B. Pearse (Physical Rev., 1931, [ii] **37**, 1712—1713).—The band shows the three P, three Q, and three R branches appropriate to a $^3\Pi\longrightarrow{}^3\Sigma$ transition where the $^3\Pi$ state is near Hund's case b. L. S. T.

Boron hydride bands. R. F. Paton and G. M. Almy (Physical Rev., 1931, [ii], **37**, 1710).—Bands due to BH and the same as those previously reported (A., 1931, 403, 996) have been obtained in a 110-volt direct-current arc in H_2 with B contained on a Ni or Cu electrode. The isotope band due to $B^{10}H$ has also been identified. The abundance ratio of B^{11} to B^{10} is $4{\cdot}86\pm0{\cdot}15$, indicating an at. wt. of $10{\cdot}841\pm0\,005$ (cf. this vol., 204). L. S. T.

Vibrational quantum analysis of the ultra-violet SO_2 and CS_2 absorption bands. W. W. Watson and A. E. Parker (Physical Rev., 1931, [ii], **37**, 1013).—Formulæ for these bands are given. L. S. T.

Band spectrum of bismuth chloride. P. G. Saper (Physical Rev., 1931, [ii], **37**, 1710).—A band system due to BiCl has been obtained in the region 4300—5500 Å. by introducing vapour from heated $BiCl_3$ into active N. A vibrational analysis has been made and equations for the wave-nos. of $BiCl^{35}$ and $BiCl^{37}$ heads are given. L. S. T.

Zeeman effect in the $^2\Sigma$—$^2\Sigma$ cyanogen bands. E. L. Hill (Physical Rev., 1931, [ii], **37**, 1709).—Theoretical. L. S. T.

Dependence on p_H of the ultra-violet absorption of hydroxyazo-compounds. T. Uemura (Arch. Phys. biol. Chem.-Phys., 1931, **9**, 29—72; Chem. Zentr., 1932, ii, 2290).—Changes in the mol. other than the dissociation of OH with increasing p_H are indicated. A. A. E.

Ultra-violet absorption of binary liquid mixtures. I. System acetone–chloroform. R. Kremann, M. Pestemer, and P. Bernstein (Monatsh., 1932, **61**, 351—360).—Ultra-violet absorption curves for mixtures of $COMe_2$ and $CHCl_3$ of various compositions show that the max. is displaced in the direction of shorter wave-lengths as the proportion of

$COMe_2$ is increased. The max. displacement occurs at about 70 mol.-% $COMe_2$, whilst viscosity data indicate compound formation in equimol. proportion. E. S. H.

Absorption of light and constitution. VII. Mode of action of positive groups. A. Burawoy (Ber., 1933, **66**, [*B*], 228—233).—Positive groups (NR_2, OR, SR) have in general a bathochromic action only as terminal members of the conjugated system causing the band. The action of NR_2 is more pronounced than that of OH. In homopolar and heteropolar compounds the effect depends mainly on the increased polarity of the chromophoric, conjugated system. In the branches of conjugated systems positive groups are strongly hypsochromic if substitution is direct, almost inactive or feebly hypsochromic if it is indirect (*i.e.*, through an aromatic substituent). In conjugated systems of homopolar compounds, the corresponding *K* band is displaced towards the red in the sequence of terminal groups, C:NH, C:O, C:S, which in cations are replaced by $C{:}NH_2^+$, $C{:}OH^+$, $C{:}SH^+$. Numerous examples are cited. Reply is made to Dilthey and Wizinger (A., 1932, 1127). H. W.

Infra-red absorption spectrum and molecular structure of ozone. S. L. Gerhard (Physical Rev., 1932, [ii], **42**, 622—631).—Curves are plotted for the 4·7, 7·39, 9·6, and 11·38 μ bands. The last-named is attributed to N_2O_5 as an impurity. Fundamental vibrational frequencies are at 528, 1033, and 1355 cm.$^{-1}$ The mol. is probably an isosceles triangle with the apex angle $< 60°$. N. M. B.

Infra-red absorption bands of ammonia. H. J. Unger (Physical Rev., 1933, [ii], **43**, 123—128).—Fine structure data are tabulated for 8 bands at 1·028, 1·18, 1·219, 1·223, 1·258, 1·304, 1·5, and 1·66 μ. N. M. B.

Transmission of gases from 20 to 33 μ. J. Strong (Physical Rev., 1931, [ii], **37**, 1003; cf. A., 1931, 996).—Data for SO_2, NH_3, H_2S, N_2O, and C_2H_2 at atm. pressure are recorded. L. S. T.

Infra-red absorption spectrum of hydrogen cyanide. K. N. Choi and E. F. Barker (Physical Rev., 1932, [ii], **42**, 777—785).—Bands at 14, 7, 4·7, 3·6, and 3 μ in the range 3—15 μ were investigated for fine structure. The mol. is linear, with fundamental frequencies 712, 3289, and (approx.) 2100 cm.$^{-1}$; the moment of inertia from the fine structure of the 14 μ band is $18{\cdot}68\times10^{-40}$ g.-cm.^{2} It is not possible to state from the data whether the mol. is HCN or HNC. N. M. B.

Infra-red absorption by hydrogen sulphide at 8 μ. H. H. Nielsen and A. D. Sprague (Physical Rev., 1931, [ii], **37**, 1183—1184).—The band at 8·0 μ previously reported (A., 1929, 1215; 1931, 283) is due to H_2O vapour as impurity. L. S. T.

Infra-red band system of iodine bromide. R. M. Badger and D. M. Yost (Physical Rev., 1931, [ii], **37**, 1548—1549).—Five new absorption bands of moderate intensity have been observed in the region 6850—8060 Å. in IBr at 50° and 90 mm. The estimated energy of dissociation of IBr into normal atoms is $1{\cdot}801\pm0{\cdot}007$ volts ($41{,}520\pm150$ g.-cal.). L. S. T.

Chemical aspects of infra-red absorption spectra of ethyl halides. P. C. Cross and F. Daniels (J. Chem. Physics, 1933, **1**, 48—55).—The infra-red absorption spectra of EtCl, EtBr, and EtI have been determined between 1·5 and 15 μ. The entire spectrum is accounted for by eight observed fundamental frequencies and their first harmonics and simple combinations. The types of vibration between the atom pairs are discussed in relation to problems in chemical kinetics. F. L. U.

Preparation of reststrahlen plates and the reflexion power of powders. R. B. Barnes (Physical Rev., 1933, [ii], **43**, 31—33).—The wave-lengths of reflexion max. from plates of natural crystal surfaces, fused and then recryst. substances, and pressed crystal powders were the same. The reflexion power of the pressed powders depended inversely on the size of the particles. NaCl, KCl, and TlCl were used. N. M. B.

Raman effect. A. Ganguli (Phil. Mag., 1933, [vii], **15**, 193—196; cf. A., 1932, 320).—Mathematical. H. J. E.

Rotational fine structure in Raman spectra. E. F. Barker (Physical Rev., 1931, [ii], **37**, 330). L. S. T.

Raman effects with liquid and solid carbon dioxide. J. C. McLennan and H. D. Smith (Canad. J. Res., 1932, **1**, 551—555).—Procedure is described for obtaining CO_2 as a clear liquid and a clear solid in a form suitable for light-scattering experiments. A spiral form of Hg arc convenient for this work is described. The frequency shifts and intensities observed are almost identical for the three states of aggregation of CO_2, supporting the view that the CO_2 mol. undergoes no change in form throughout the temp. range −92° to 20°. J. W. S.

Raman spectrum of carbon dioxide. A. Langseth and J. R. Nielsen (Z. physikal. Chem., 1932, **B**, **19**, 427—433).—Six new weak bands, interpreted as max. of positive and negative rotation branches, have been observed. Corrections are made in the energy diagram of the CO_2 mol. previously proposed (A., 1932, 1188). R. C.

Molecular scattering of light from ammonia solutions. A. Hollaender and J. W. Williams (Physical Rev., 1931, [ii], **37**, 1367—1368).—In 16*N*-aq. NH_3 lines corresponding with frequency differences 1073, 1615, 3219, 3311, and 3394 are observed. It is difficult to determine from the data whether there is a change in the characteristic frequencies when NH_3 is dissolved in H_2O. L. S. T.

Raman spectrum of SO_4'' in gypsum. J. Cabannes (Compt. rend., 1932, **195**, 1353—1355; cf. A., 1932, 792).—Of the six lines due to internal oscillations of SO_4'' 1009 (cm.$^{-1}$), 414, and 495 are symmetrical, and 671 is anti-symmetrical. 620 and 1136 are compound as required by theory, namely that 620 should consist of a symmetrical and an anti-symmetrical line, and 1136 of one symmetrical and two anti-symmetrical lines. SO_4'' is nearly a regular tetrahedron, the symmetry being probably D_3. C. A. S.

Raman spectra and a slight asymmetry of the carbon and nitrogen atoms. R. T. DUFFORD (Physical Rev., 1931, [ii], **37**, 1013).—A discussion of the Raman spectra of the simpler org. halides and related compounds indicates a slight lack of equality of the valencies of the C and N. L. S. T.

Raman effect. XIX. Raman spectrum of organic substances (isomeric paraffin derivatives. I.) A. DADIEU, A. PONGRATZ, and K. W. F. KOHLRAUSCH. **XX. Theory of valency force system with three mass points.** F. LECHNER. **XXI. Raman spectrum of organic substances (isomeric paraffin derivatives. II.)** H. KOPPER, R. SEKA, and K. W. F. KOHLRAUSCH. **XXII. (Isomeric paraffin derivatives. III.) XXIII. (Polysubstituted benzenes. II.)** A. DADIEU, A. PONGRATZ, and K. W. F. KOHLRAUSCH (Monatsh., 1932, **61**, 369—384, 385—396, 397—408, 409—425, 426—441).—XIX. Data are given for NH_2Pr^{β}, $Pr^{\beta}OH$, $Pr^{\beta}SH$, $Pr^{\beta}Cl$, $Pr^{\beta}Br$, $Pr^{\beta}I$, *tert.*-amyl alcohol, chloride, and bromide, $Bu^{\gamma}OH$, $Bu^{\gamma}Cl$, $Bu^{\gamma}Br$, and $Bu^{\gamma}I$.

XX. Theoretical. Mol. consts. are derived for MeCN, MeNC, HCN, CH_2Cl_2, CH_2Br_2, and CH_2I_2.

XXI. Data are given for *iso*pentane, $Bu^{\beta}OH$, NH_2Bu^{β}, $Bu^{\beta}SH$, $Bu^{\beta}Cl$, $Bu^{\beta}Br$, $Bu^{\beta}I$, $Bu^{\beta}NO_2$, $Bu^{\beta}NO_3$, *iso*butyric acid, *sec.*-BuOH, and *tert.*-amyl iodide.

XXII. Data are given for *iso*- and *N*-amyl alcohol, -amine, -thiol, chloride, bromide, iodide, *sec.*-Bu chloride, bromide, and iodide.

XXIII. Data are given for PhCl, *o*-, *m*-, and *p*-$C_6H_4Cl_2$, 1 : 2 : 3-, 1 : 3 : 5-, and 1 : 2 : 4-$C_6H_3Cl_3$, 1 : 2 : 3 : 4-, 1 : 2 : 3 : 5-, and 1 : 2 : 4 : 5-$C_6H_2Cl_4$, C_6HCl_5, and C_6Cl_6. E. S. H.

Raman effect in organic sulphides and some thio-compounds. V. N. THATTE and A. S. GANESAN (Phil. Mag., 1933, [vii], **15**, 51—64; cf. A., 1931, 409).—Measurements on Et, Pr, Bu^{β}, allyl, and benzyl sulphides, *iso*amyl hydrogen sulphide, thioglycollic acid, and thioacetic acid are recorded. The variation of the C–H and C–S–C frequencies is discussed. H. J. E.

Lustre and refraction of transparent substances. W. HARTWIG and A. JOHNSEN (Z. Krist., 1932, **84**, 14—19). C. A. S.

Permanent changes in the fluorescence of hæmatoporphyrin. S. RAFALOWSKI (Spraw. Prace Polsk. Towarz. Fizycz., 1931, **5**, 299—309; Chem. Zentr., 1932, ii, 2291).—Changes similar to those observed by Harasimiu (*ibid.*, 1929, **4**, 211) are produced by treatment with O_2, light and heat being developed. The dilution effect is attributed to introduction of O_2 with the glycerol. A. A. E.

Triboluminescence. S. S. BHATNAGAR, K. G. MATHUR, and K. L. BUDHIRAJA (Z. physikal. Chem., 1932, **163**, 8—16).—The triboluminescence of As_2O_3, saccharin, and $UO_2(NO_3)_2$ has been investigated. Large crystals exhibit a stronger luminescence than smaller crystals. The change of the crystals into the non-luminescent form is the more rapid the smaller is the viscosity of the liquid phase and the higher the temp. Irradiation with *X*-rays or ultraviolet light promotes the change. Addition of gelatin weakens the luminescence. All these observations are accounted for if it is supposed that the luminescence is the accompaniment of the micro-crystallisation of inclusions within the crystals of mother-liquor in the sol state. R. C.

Ionisation of water vapour by electron impact. H. D. SMYTH and D. W. MUELLER (Physical Rev., 1933, [ii], **43**, 116—120).—Ionisation potentials found for H_2O^+ were 12·7 and 16·0 volts. The following ions were observed: H^+ and OH^+ at 18·9, H_3O^+ with H_2O^+, O^+ at 18·5, H_2^+ at 33·5, and O_2^+ (very weak). The probable processes are discussed. Traces of negative ions were noted. N. M. B.

Ionisation of sulphur dioxide by electron impact. H. D. SMYTH and D. W. MUELLER (Physical Rev., 1933, [ii], **43**, 121—122; cf. preceding abstract).—Ions observed were SO_2^+ at 13·1±0·3, SO^+ at 16·5±0·5, either S^+ or O_2^+ at 16·0±0·7 volts. Probable formation processes are discussed. N. M. B.

Reversal of the current from a cuprous oxide photo-cell in red light. H. H. POOLE and W. R. G. ATKINS (Nature, 1933, **131**, 133).—Serpidox and Auger cells, but not a Siemens cell, show a small reverse current in red light. L. S. T.

Theory of the crystal-photo-effect. H. TEICHMANN (Proc. Roy. Soc., 1933, **A**, **139**, 105—113).—It is shown that the existence of a difference in the electron concn. between different parts of a crystal in connexion with the quantum-mechanical model of a semi-conductor developed by Wilson postulates the existence of the crystal-photo-effect in single crystals and explains the experimental facts satisfactorily. L. L. B.

Occurrence and explanation of selective photo-electric electron emission from composite alkali cathodes. W. KLUGE (Physikal. Z., 1933, **34**, 115—126).—Photo-electric cells with layers of the type Ag–M_2O–M, where M is Na, K, Rb, or Cs, were investigated. Two sharing max. were found in each case, the short-wave max. being const. and independent of M, at about 410 mμ. The long-wave max. increased in wave-length with increasing at. wt. of M. An explanation is given. A. J. M.

Dipole rotation in crystalline solids. C. P. SMYTH and C. S. HITCHCOCK (J. Amer. Chem. Soc., 1932, **54**, 4631—4647).—Dielectric consts. and sp. conductances of solid and liquid $PhNO_2$, ethylene chloride, NH_2Ph, PhOH, H_2O, C_6H_6, Me_2SO_4, Et_2SO_4, and certain solutions have been determined at temp. between −90° and 40° with frequencies between 300 and 60,000. No sudden increase of mol. aggregates occurs in liquids as the f.p. is approached. Traces of impurities have very marked effects on the dielectric const. of a solid determined at low frequencies. In solids, neither large polar mols. nor small polar groups in the mols. rotate, although Me_2SO_4 mols. may rotate about certain axes, and in this mol. the MeO group gives dipole orientation down to a transition point at −70°. J. G. A. G.

Dipole moment of nitric oxide. C. P. SMYTH and K. B. MCALPINE (J. Chem. Physics, 1933, **1**, 60—61).—Measurement of the dielectric const. shows

that the dipole moment of NO is indistinguishable from zero. F. L. U.

Dielectric constant of solid hydrogen sulphide. J. D. KEMP and G. H. DENISON (J. Amer. Chem. Soc., 1933, **55**, 251).—A discontinuous change of dielectric const., ε, from 2·9 to 9 occurs at the transition point 103·5° abs., whilst at the upper transition point, 126·3° abs., there is no marked change. At the m.p. 187·6° abs., ε=9·4. Thus, at 103·5° abs., the mols. pass from a state of little or no rotation of electric moment to one of almost complete rotational freedom of the electric moment. J. G. A. G.

Dielectric polarisation. II—IV. E. C. E. HUNTER and J. R. PARTINGTON (J.C.S., 1932, 2812—2819, 2819—2824, 2825—2829; cf. A., 1931, 1113).—II. The dielectric consts. and densities of dil. solutions of PrSH, BuSH, PhSH, and MeCN in C_6H_6, and the mol. refractions of the pure compounds have been determined. The dipole moments of EtSH, PrSH, BuSH, and PhSH are approx. const., and > for H_2S. Taking the val. for H_2S valency angle (90°), and assuming that it is the same in the mercaptans and sulphides, the group moments H–S, MeS–, and EtS– can be calc. from the experimental data. From these the vals. for MeSH and EtSH can be calc. The moment of MeSH lies between that of H_2S and EtSH. Induction effects are probable. The moment of MeCN agrees with Werner's (A., 1929, 1217), and not Williams' (A., 1928, 229, 355) vals. The differences in physical and chemical properties between the alcohols and mercaptans are discussed, and are explained by different deformabilities of the S and the O atom. The relative insolubility of the mercaptans in H_2O as compared with that of the alcohols can be due to the higher internal pressure of the latter, which is influenced by dipole moments.

III. The dielectric consts. and densities of dil. solutions of Me_2S, Pr_2S, and Bu_2S in C_6H_6 have been determined, together with the mol. refractions of the pure compounds. From a comparison of the moments of the aliphatic and aromatic ethers and sulphides it is shown that the valency angles of O and S in these compounds are different for the aliphatic and aromatic series. The calculation of valency angles from dipole moments leads only to approx. results.

IV. The dielectric consts. and densities of dil. solutions of MeSCN (I), EtSCN (II), Me, Et, and allyl *iso*thiocyanate (III) in C_6H_6, and the mol. refractions of the pure compounds have been found. An increase in moment from (I) to (II) indicates induction along the hydrocarbon chain in these compounds. The moment of (III) is not greatly different from that of EtNCS, and hence the presence of a double linking in the β-position does not affect the moment. It is probable that the configuration of the ·NCS group is not V-shaped but linear. (I) and (II) have moments almost identical with that of PhSCN. The moments of *p*-substituted PhSCN indicate that the SCN group is inclined to the nucleus, and this holds also for alkyl compounds. The approx. angle for the S valencies calc. for these compounds is 120°. A. J. M.

Dielectric polarisation. V. Benzene solutions of pyrones, thiopyrones, and thioketones. Dioxan solutions of ureas and thioureas. E. C. E. HUNTER and J. R. PARTINGTON (J.C.S., 1933, 87—90).—The electric moments of dimethyl-, diphenyl-, and dimethylthio-γ-pyrone, thiobenzophenone, dioxan, $CO(NHMe)_2$, $CS(NHMe)_2$ carb- and thiocarb-anilide have been measured. The chemistry of these compounds and the mechanism of the formation of oxonium salts are discussed. W. R. A.

Electric moments of *cyclo*hexane derivatives. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1932, **B**, **19**, 434—442).—Measurements have been made with alcohols, acetates, ketones, and chloro-*cyclo*hexane. R. C.

Dipole moments of some organometallic compounds. E. BERGMANN and W. SCHÜTZ (Z. physikal. Chem., 1932, **B**, **19**, 401—404).—The following vals. have been obtained: NPh_3, 0·26; PPh_3, 1·45; $AsPh_3$, 1·07; $SbPh_3$, 0·57; $HgEt_2$, $0·39\times10^{-18}$ e.s.u.; $BiPh_3$ and $HgPh_2$, 0. It is concluded that the mols. of PPh_3, $AsPh_3$, and $SbPh_3$ are triangular pyramids, the heights of which decrease in this order, whilst with $BiPh_3$ the mol. is a triangle with the central atom at its centre of gravity. R. C.

Dipole moments of some derivatives of ethylene oxide. E. BERGMANN and W. SCHÜTZ (Z. physikal. Chem., 1932, **B**, **19**, 395—400).—Configurations have been arrived at by means of dipole moment determinations. R. C.

Dipole moment of some compounds with a cumulated unsaturated system. E. BERGMANN and W. SCHÜTZ (Z. physikal. Chem., 1932, **B**, **19**, 389—394).—Dipole moment measurements with *p*-substituted Ph azides suggest that the N atoms form an open chain. PhN:C:NPh and its di-*p*-Me derivative have finite moments, indicating that the system N:C:N has a finite moment. R. C.

Measurement of electrical dipole moments by a molecular ray method. M. WOHLWILL (Z. Physik, 1933, **80**, 67—79).—Measurements of the intensity distribution in a mol. beam after passage through an intensely inhomogeneous electrical field give the dipole moment of p-$NH_2\cdot C_6H_4\cdot NO_2$ as $5·6\times10^{-18}$ c.g.s. unit with a possible error of 10%. A. B. D. C.

[Molecular] volumes of oxides and chlorides, and atomic volume curves. I. ZASLAVSKI, A. ASTASCHEVA, and I. SAKOV (J. Gen. Chem. Russ., 1932, **2**, 590—592).—The max. of the at. vol.–at. no. curve correspond with the min. of the same curve, in which the at. vols. are derived from the mol. vol. of chlorides and oxides. R. T.

Photographic method for deriving the optical constants of the metals. S. E. WILLIAMS (Proc. Physical Soc., 1933, **45**, 49—66).—The relative intensities of diffraction spectra from gratings consisting of alternate strips of glass and metal have been photographed with light plane-polarised in the plane of incidence and perpendicular to it. The optical consts. are calc. by the approx. Drude formula. C. W. G.

Optical dispersion of helium. H. MARGENAU (Physical Rev., 1931, [ii], **37**, 1021).—Theoretical. L. S. T.

Refractive indices of potassium chlorate crystals, and the structure of the ClO_3 group. W. H. ZACHARIASEN (Physical Rev., 1931, [ii], **37**, 1693).—Vals. of n of $KClO_3$ crystals calc. from at. arrangement agree with observed vals. if the height of the Cl^{+5} dipole above the O atoms is 0·99 Å. The two valency electrons of Cl^{+5} are probably displaced with respect to the core in a direction away from the O plane. L. S. T.

Relation of the anisotropy of optical polarisability to geometrical structure of molecules. H. A. STUART and H. VOLKMANN (Z. Physik, 1933, **80**, 107—124).—The Kerr const. was determined for a no. of C_6H_6 derivatives with known geometrical structures, and from the const. was determined the anisotropy of the optical polarisability and its ellipsoid. The ellipsoid of optical polarisability is shown to be quantitatively related to the geometrical structure, and measurement of the Kerr const. is therefore a possible method of determining the structure of complicated mols. A. B. D. C.

Photo-electric polarimetry. Measurement of rotatory dispersion of sugars. G. BRUHAT and P CHATELAIN (J Phys. Radium, 1932, [vii], **3**, 501—511).—An improved apparatus is described. Data recorded in the ultra-violet for sucrose to 3021 Å., and for glucose, fructose, and invert-sugar to 3657 Å., are in good agreement with those calc. from the formulæ for simple dispersion. The apparatus was used to follow the mutarotation of glucose, and showed that the α- and β-forms have the same dispersion. N. M. B.

Significance of so-called specific exaltations of molecular refraction and molecular dispersion. E. HÜCKEL (Z. physikal. Chem., 1932, **163**, 67—69).—It is the exaltations themselves, and not their quotients by the mol. wt, which are of significance in connexion with the investigation of constitutive influences. R. C.

Rules of optical activity and their application to the elucidation of constitution and configuration. K. FREUDENBERG (Ber., 1933, **66**, [*B*], 177—194).—A lecture dealing with the magnitude and sign of optical activity, the vicinal rule, the law of displacement, and optical superposition. G. W.

Simplest principles and laws of optical activity. W. KUHN (Ber., 1933, **66**, [*B*], 166—176).—The problem of optical activity can be referred to the behaviour of the individual absorption bands, since the total activity is invariably the sum of the contributions of individual bands. Activity of a band is due to the passage of the optical oscillatory process from the respective chromophoric group to its neighbourhood in the mol. The contribution to the activity of an absorption band is generally particularly great when the chromophoric part of the mol. which causes the band is close to the asymmetric centre. Particular importance, so far as activity in the visible region is concerned, is attached to chromophoric parts which cause absorption bands in the visible and near ultra-violet. The changes in the optical behaviour of a band due to chemical action is greatest when the action occurs in closest proximity to the chromophoric part affecting that band, and hence is at a max. when the chromophoric part is itself changed chemically. H. W.

Rotatory dispersion in the visible and ultra-violet range of configuratively correlated carbinols, halides, and acids. P. A. LEVENE and A. ROTHEN (J. Amer. Chem. Soc., 1933, **55**, 429—430).—Dispersion curves down to 2300 Å. for β-methylbutanol, α-bromo-β-methylbutane, α-iodo-β-methylnonane, and β-methyl-*n*-valeric acid are expressed by two-term Drude formulæ. The contribution of the functional group is + and that of the rest of the mol. —. Contrary to Kuhn (A., 1930, 276) the rotation, in the visible, of the two halides is opposite to the sign of the contributions of Br and of I. For β-methyl-*n*-valeric acid in heptane, $[M]^{25}=8{\cdot}088/(\lambda^2-0{\cdot}042)-11{\cdot}68/(\lambda^2-0{\cdot}034)$. J. G. A. G.

Magnetic rotatory power of gaseous chlorine and hydrochloric acid. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1933, **196**, 106—107).—Using the yellow, green, and blue Hg lines $[A]_{Cl}=10{\cdot}4\times10^{-5}$ (radians) compared with 9·0—9·5$\times10^{-5}$ deduced from MeCl, EtCl, etc.; dispersion $\alpha_g/\alpha_y=1{\cdot}16$ (absorption prevents observation with the blue line). $[A]_{HCl}=13{\cdot}1\times10^{-5}$ compared with $[A]_{Cl}+[A]_H=12{\cdot}4\times10^{-5}$; dispersion $\alpha_g/\alpha_y=1{\cdot}12$; $\alpha_b/\alpha_y=1{\cdot}80$. C. A. S.

Faraday effect in ionised gases for 4-cm. waves. P. KECK (Ann. Physik, 1932, [v], **15**, 903—925).—The magnetic rotation of waves of length about 4 cm. on passing through ionised gases has been measured, together with the refractive index and absorption coeff. A. J. M.

Dependence on temperature of the polarisation and association of ethyl ether. M. WOLFKE and J. MAZUR (Spraw. Prace Polsk. Towarz. Ficyz., 1931, **5**, 357—364; Chem. Zentr., 1932, ii, 2034).—The transition which occurs at —105·4° is reflected in the polarisation. Association exists between 35° and —105·4°; it increases with fall of temp. to a max. val. of 29%. A. A. E.

Theory of nucleus formation. V. BAYERL and H. FLOOD (Naturwiss., 1933, **21**, 27).—The commencement of drop formation in the adiabatic expansion of saturated H_2O vapour in air under various conditions of temp. has been investigated, the results being in agreement with the theory of nucleus formation of Volmer, Weber, and Farkas. A. J. M.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1932, [v], **18**, 888—898; cf. A., 1930, 277, 853; 1931, 685, 1106, 1127, 1215, 1356; 1932, 1078). —Mathematical. A. J. M.

Compact molecules. H. J. BACKER (Chem. Weekblad, 1932, **29**, 666—671).—A reply to van Laar (this vol., 11). H. F. G.

Linear relationships between the radii of molecules. T. S. WHEELER (Rec. trav. chim., 1932, **51**, 1204—1206).—Data for 22 gases and vapours indicate that linear relationships exist between mol. radii as calc. by four different methods. J. W. S.

The chemical bond. G. N. LEWIS (J. Chem. Physics, 1933, **1**, 17—28).—Theoretical. F. L. U.

Constitution of complex salts of metal halides and amines and dependence of their stability on the anion. W. HIEBER and E. LEVY (Z. Elektrochem., 1933, **39**, 26—34).—Consideration of all available data leads to the conclusion that in the tetrammine complex compounds of the halides of bivalent metals of the transitional groups (where the amine=NH_3, en, C_5H_5N, NH_2Ph, or N_2H_4) the halogen atoms are linked directly with the central atom. In the majority of such compounds the stability increases in the order chloride>bromide>iodide. Deviations from this behaviour are discussed. F. L. U.

Formula of hypophosphoric acid. F. BELL and S. SUGDEN (J.C.S., 1933, 48—49).—If the formula of hypophosphoric acid is H_2PO_3 instead of $H_4P_2O_6$ then hypophosphates should be paramagnetic. The Na (hydrated and anhyd.), the Ag, and guanidine hypophosphates are diamagnetic, suggesting that the parent acid is $H_4P_2O_6$. The attempts of Arbusov and Arbusov to prepare alkyl hypophosphates by the action of an alkyl halide on $Ag_4P_2O_6$ were repeated; the products obtained did not give the reactions of true hypophosphates and were all diamagnetic. W. R. A.

Symmetry of the benzene molecule. V. DEITZ and D. H. ANDREWS (J. Chem. Physics, 1933, **1**, 62—67).—Symmetry nos. for C_6H_6 and *cyclo*hexene have been calc. on the basis of Fowler's v.-p. equation for a crystal to be 6 and 2, respectively. Consequently either the C_6H_6 ring is puckered or the H atoms are staggered. In the series C_6H_6, *cyclo*hexadiene, *cyclo*hexene, *cyclo*hexane, the m.p. is closely parallel with the symmetry of the mol. F. L. U.

Unknown property of compounds of certain elements. J. ŠTERBA-BOHM and A. DORABIALSKA (Rocz. Chem., 1932, **12**, 875—879).—A const. evolution of heat is observed in the following compounds, in the order of intensity: Sc_2O_3>Pr_4O_7>Y_2O_3>Nb_2O_5>$(HCO_2)_3La$>Sb_2O_3>Bi_2O_3>As_2O_3>Ta_2O_5. Compounds of Ce, Nd, Sm, Gd, Yb, V, Ca, Co, Be, Al, Ti, Cs, and Tl do not give this effect, which is ascribed to disintegration of the at. nucleus. The thermogenic elements all possess odd at. nos. R. T.

Heteropoly-compounds. III. Crystal hydrate regions of phosphotungstates and phosphomolybdates. A. V. RAKOVSKI and E. A. NIKITINA (J. Gen. Chem. Russ., 1932, **2**, 681—690; cf. A., 1931, 1382).—Tensimetric measurements of solutions of the salts $3Na_2O,P_2O_5,24WO_3,aH_2O$; $2Na_2O,P_2O_5,24WO_3,bH_2O$; $P_2O_5,24WO_3,cH_2O$; $3Na_2O,P_2O_5,24MoO_3,dH_2O$, and $P_2O_5,24MoO_3,eH_2O$ give a=12·18—32·62, b=16·76—33·09, c=19·05—56·99, d=17·47—73·84, and e=19·78—60·30. These results indicate a lower H_2O content than would follow from Pauling's theory of the constitution of such salts (A., 1929, 1367). It is concluded that further condensation with elimination of H_2O takes place, as follows: $2nH_3[PO_4{\cdot}W_{12}O_{18}(OH)_{36}] \longrightarrow H_{6n}[(PO_4,W_{12}O_{18})_{2n}O_n(OH)_{72-n}]+nH_2O$. R. T.

Homogeneously distorted cubic ferromagnetic lattices. F. BITTER (Physical Rev., 1932, [ii], **42**, 697—708).—Mathematical. The work of Becker and Kersten (cf. A., 1930, 1355) is corrected for crystallographic symmetry. N. M. B.

Magnetic and catalytic properties of wood ashes. E. WEDEKIND (Naturwiss., 1933, **21**, 24—25).—Wood ashes possess a small magnetic power due to the presence of Fe_3O_4. They also possess catalytic properties varying with the type of wood, and dependent not only on the Fe_3O_4, but also on very small concns. of other substances. A. J. M.

Magnetic investigations on the oxides of chromium. W. H. ALBRECHT and E. WEDEKIND (Z. anorg. Chem., 1933, **210**, 105—112).—Cr_2O_3 obtained by igniting the hydrolysis product of $Cr(OEt)_3$ has magnetic susceptibility $\chi\times10^6=19\pm1$; that obtained by pptg. $Cr^{...}$ salts with aq. NH_3 and igniting the ppt. has $\chi\times10^6=30\pm3$. These vals. are independent of the field strength or temp. By igniting Cr_2O_3 in H_2 at 800—1200° a product of increased susceptibility and ferromagnetic properties is obtained, but the original properties are recovered after subsequent ignition in O_2. E. S. H.

Magnetochemical investigations. VIII. Constitution of some simple cobalt and nickel compounds in the light of their magnetic behaviour. W. KLEMM and W. SCHUTH (Z. anorg. Chem., 1932, **210**, 33—56; cf. A., 1932, 1191).—Measurements of magnetic susceptibility of oxides, sulphites, halides, and some complex compounds of Co and Ni have been made. CoO and NiO are regarded as occupying a transitional region between para- and ferro-magnetic substances. NiS and CoS resemble CuS in having a low susceptibility and temp. coeff.; they are regarded as the metallic type of compound. Among the halides, the metallic type is shown only by NiI_2 at low temp. The tendency to form metallic compounds increases with the polarisability of the anion and the ionisation potential of the cation. Compounds of low complexity occupy an intermediate region with regard to magnetic properties between the highly complex compounds and simple salts. E. S. H.

Ferromagnetism of dilute solid solutions. F. BITTER (Physical Rev., 1931, [ii], **37**, 1015).—Theoretical. L. S. T.

Paramagnetism of the dissolved cobaltous ion. R. MERCIER (Compt. rend., 1933, **196**, 164—166).—Using solutions in MeOH of $CoCl_2,6H_2O$ 1—$20\times10^{-3}N$ the magnetic moment (in Weiss magnetons) of Co^{++} varies linearly with temp. from 23·9 at 293° abs. to 18·1 at 177°, which, assuming the state of the Co^{++} ion to be $^4F_{9/2}$, is in conformity with the Van Vleck–Stoner theory. C. A. S.

Influence of crystalline fields on the susceptibilities of salts of paramagnetic ions. II. The iron group, especially Ni, Cr, and Co. R. SCHLAPP and W. G. PENNEY (Physical Rev., 1932, [ii], **42**, 666—686).—Mathematical. N. M. B.

Diamagnetism of water at different temperatures. A. P. WILLS and G. F. BOEKER (Physical Rev., 1932, [ii], **42**, 687—696).—In view of widely divergent available data a new and highly-sensitive manometric balance method is described. Preliminary investigations on H_2O freshly boiled, and the same

after keeping several days in contact with He indicate, respectively, less and greater diamagnetism at temp. above 23·5°; the change in sp. susceptibility was $<1\%$. N. M. B.

Magnetic moments of potassium and lithium with regard to their magnetic nuclear moments. I. W. Meissner and H. Scheffers (Physikal. Z., 1933, **34**, 48—53).—The val. of the Bohr magneton is $0{\cdot}916\times10^{-20}$ gauss cm. The nuclear moment of Li for the cases of uncoupling and coupling of the nuclear and valency electrons is at the most 5% and 0·5% of the magneton, respectively. The heats of dissociation of K and Li obtained agree with those of Lewis (A., 1931, 1107). A. J. M.

Magnetic rotatory dispersion of a coloured diamagnetic substance : thiobenzophenone. A. Cotton and M. Scherer (Compt. rend., 1932, **195**, 1342—1345; cf. this vol., 10).—The diamagnetic liquid $CSPh_2$ exhibits anomalous magnetic rotatory dispersion, and $d\rho/d\lambda$ has opposite signs on the two sides of the absorption band—positive on the short-wave side. C. A. S.

Surface tension of liquids. M. Seta (L'Ind. Chimica, 1932, **7**, 1488—1496).—A general account of surface tension and some of its consequences. The theory of the capillary electrometer, the determination of association in liquids, and the influence of the form of a liquid surface on the v.p. are outlined. H. F. G.

Structure of interference lines obtained by the powder method. I. Levin and E. Ott (Z. Krist., 1932, **84**, 166—169).—The doubling of diffraction lines predicted by Möller and Reis (cf. A., 1929, 246, 492) as likely to occur under certain conditions in Debye–Scherrer diagrams has been verified in powder diagrams of high-temp. cristobalite (cf. A., 1932, 451). C. A. S.

Application of Blair–Leighton equation to X-rays. J. A. Lester and J. M. Blair (J. Physical Chem., 1933, **37**, 17—20).—Theoretical (cf. A., 1932, 1006). E. S. H.

New representation of geometrical crystallography. I. B. Delaunay (Z. Krist., 1932, **84**, 109—149). C. A. S.

Binding energies in growth of crystal nuclei from metallic atoms. H. S. Taylor, H. Eyring, and A. Sherman (J. Chem. Physics, 1933, **1**, 68—76).—Binding energies for various geometrical configurations of 3—8 atoms of Na, 4—5 atoms of Cu, and 4 and 6 atoms of H have been calc. The data obtained indicate the manner in which a unit cell would grow from the vapour phase in the absence of surfaces. The unit cell is shown to be unstable. F. L. U.

Surface motion of sputtered particles. R. W. Ditchburn (Proc. Camb. Phil. Soc., 1933, **29**, 131—135).—Using glass and metal targets evidence of surface motion for particles of sputtered Cd, as with vaporised Cd, was obtained. N. M. B.

Measurement of X-ray absorption coefficients by the use of the FP–54 pliotron. L. M. Heil and J. E. Edwards (Physical Rev., 1933, [ii], **43**, 1—4).—Ionisation currents of the order 3×10^{-15} amp. were measured by the pliotron (cf. Du Bridge, *ibid.*, 1931, [ii], **37**, 392) in the determination of *X*-ray absorption coeffs. in the range 0·25—0·6 Å. N. M. B.

Forces of linkings in the lattice and X-ray spectrum. R. Glocker (Naturwiss., 1933, **21**, 27).—An addition to a previous paper (A., 1932, 892). A. J. M.

Laue patterns from thick crystals at rest and oscillating piezoelectrically. J. M. Cork (Physical Rev., 1932, [ii], **42**, 749—752; cf. Barrett, A., 1932, 563).—The multiple structure of Laue spots was investigated for quartz and Na K tartrate oscillating piezoelectrically and for the same crystals and calcite, rock-salt, and other materials at rest, the surfaces being either polished or etched. N. M. B.

Graphical method of interpreting Weissenberg photographs. W. A. Wooster and N. Wooster (Z. Krist., 1933, **84**, 327—331). C. A. S.

Arrangement of atoms in crystals. M. L. Huggins (Physical Rev., 1931, [ii], **37**, 447—448).—A criticism (cf. A., 1931, 897). L. S. T.

Structure of groups in crystals. W. H. Zachariasen (Physical Rev., 1931, [ii], **37**, 775—777).—A reply to criticism (cf. preceding abstract). L. S. T.

Accurate determination of lattice constants by the Debye–Scherrer method. K. Moeller (Naturwiss., 1933, **21**, 61—62).—Deviations from Bragg's relationship affect the Debye–Scherrer method for symmetrical as well as unsymmetrical reflexion. The amount of the deviation is calc. for NaCl and Ag. The deviation is so great for fine crystals as to demand correction, especially with pairs of substances of very different electron density and nuclear form. A. J. M.

Atomic radius of carbon in diamond. V. Posejpal (Compt. rend., 1933, **196**, 337—339).—The at. diameter of C in diamond deduced from the authors' equations (cf. A., 1932, 1187) using n_D, n_F, and n_G is respectively 1·44, 1·50, and 1·54 Å., compared with 1·54 determined by *X*-rays. This agreement confirms the rule that photons penetrate an atom only so far as the level the energy of which, eV, equals $h\nu$ of the photon. C. A. S.

Complex magnetic structure of ferromagnetic single crystals. N. Akulov and M. Degtiar (Ann. Physik, 1932, [v], **15**, 750—756).—Finely-powdered Fe_2O_3 forms characteristic patterns on the surface of single crystals of Fe, showing slip lines similar to those produced by etching; there are also two systems of lines parallel to the axis of least magnetisation which are not detectable in the etching patterns. W. R. A.

Accurate determination of lattice constants of non-cubic substances. W. Stenzel and J. Weerts (Z. Krist., 1932, **84**, 20—44).—A method, accurate to $\pm0{\cdot}01\%$, for this purpose is described, resulting in the following revised vals.: Cd a 2·9736, c 5·6058; Zn, a 2·6590, c 4·9351; Mg a 3·2022, c 5·1991; Re a 2·7553, c 4·4493; β-Sn a 5·8194, c 3·1753 Å. C. A. S.

Orientation of crystals of organic substances on minerals of ionic structure. L. Royer (Compt. rend., 1933, **196**, 282—284; cf. A., 1932, 326, 451).—

Only ionically constructed org. substances orient themselves on minerals of ionic structure and on these only when the spacings are suitably related, *e.g.*, hexagonal quinol on calcite (but on no carbonate isomorphous therewith) or KNO_3, and $CS(NH_2)_2$ on blende. Non-ionic substances, *e.g.*, $C_{10}H_8$, anthracene, phenanthrene, fluorene, camphor, never show such epitaxy. C. A. S.

Orientation of crystals of organic substances on minerals of ionic structure. G. FRIEDEL (Compt. rend., 1933, **196**, 284—285; see preceding abstract).—Apart from the necessary relation between the spacings, epitaxy has never been observed save between substances both of which have heteropolar linkings. It therefore provides a means of recognising this type of linking. C. A. S.

Structural and morphological relationships of minerals of type ABC_2. Structures of wolfsbergite and emplectite, and their relation to stibnite. W. HOFMANN (Z. Krist., 1933, **84**, 177—203).—Wolfsbergite, $CuSbS_2$, has a 6·01, b 3·78, c 14·46 Å., 4 mols. in the unit cell, space-group V_h^{16}; each Cu is surrounded tetrahedrally by 4S, Cu–S=2·25—2·33 Å.; each Sb octahedrally (distorted) by 6S, Sb–S=2·44—3·66 Å.; both Sb and S and Cu and S form also zigzag chains. The connexion between structure and cleavage and twinning is demonstrated. Emplectite, $CuBiS_2$, is isomorphous, with a 6·12, b 3·89, c 14·51. The holohedry (space-group V_h^{16}) of stibnite is confirmed by etch figures, and the probable similarity of its structure to that of wolfsbergite inferred. C. A. S.

***K*-*X*-Ray absorption spectra of some chlorine compounds in aqueous solution. I.** O. STELLING [with F. NORLING] (Z. physikal. Chem., 1932, **B**, **19**, 462—470).—1, 2, and 4*N*-NaCl give the same absorption edge, which is softer than that of solid NaCl. For 1·75*N*-KCl the edge is the same as for solid KCl, but for 3·3*N*-KCl it is harder. Apparatus suitable for such absorption measurements is described. R. C.

***X*-Ray studies on the hydrous oxides. I. Alumina. II. Stannic oxide. III. Stannous oxide.** H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1932, **36**, 3010—3029, 3030—3038, 3039—3045).—I. Published data for v.p. and *X*-ray analysis of pptd. Al_2O_3 and $Al_2O_3,3H_2O$ are tabulated. An *X*-ray investigation of Al_2O_3 pptd. under widely varying conditions gives only two hydrates, viz., gibbsite, $Al_2O_3,3H_2O$, both natural and artificial, and diaspore, Al_2O_3,H_2O. Pptd. Al_2O_3 aged at 100° is a new form, termed δ-Al_2O_3, containing adsorbed H_2O. Samples prepared by Hüttig's method are either δ-Al_2O_3 or mixtures of δ-Al_2O_3 and gibbsite. Samples prepared by Willstätter's method are not definite hydrates, but δ-Al_2O_3 or amorphous Al_2O_3 with adsorbed H_2O. δ-Al_2O_3 is formed by dehydrating gibbsite below 250° and by the thermal decomp. of $AlCl_3,6H_2O$. The existence of ζ-Al_2O_3 (cf. Barlett, A., 1932, 904) has been confirmed.

II. SnO_2,xH_2O has been prepared by hydrolysis of $Sn(OEt)_4$ and composition–temp. curves have been obtained under equilibrium conditions. The absence of breaks in the curves indicates that definite hydrates are not formed. The breaks reported by Thiessen and Koerner (A., 1931, 323) are due to lack of equilibrium. *X*-Ray analysis confirms the absence of definite hydrates and shows that the products consist of SnO_2 with varying amounts of adsorbed H_2O.

III. SnO exists in an α-form (bluish-black) and a β-form (greyish-green). The transition temp. (α⟶β) is approx. 550°. The crystal structure of α-SnO is tetragonal, of the PbO type, a_0 3·78, c_0 4·79 Å. The temp.–composition isobar and *X*-ray analysis of the ppt. formed by interaction of solutions of $SnCl_2$ and aq. NH_3 indicate the composition $2SnO,H_2O$. The hemihydrate is dehydrated into α-SnO by (*a*) excess of alkali, (*b*) the action of light, especially in absence of free ammonia, and (*c*) heating at 120—550°. E. S. H.

Structure of α-zinc hydroxide. W. FEITKNECHT (Z. Krist., 1932, **84**, 173—176).—α-$Zn(OH)_2$ (cf. A., 1930, 700), prepared by lixiviation of ZnI_2, has a 3·14 Å., $c:a$ approx. 1·63, space-group of $C6$ type. The polymorphism of $Zn(OH)_2$ is due to the strong polarising influence of Zn^{++} on $(OH)^-$. C. A. S.

Active oxides. LIX. Variation of magnetic and *X*-ray spectroscopic properties during the conversion of a mixture of zinc and iron oxides into spinel. H. KITTEL and G. F. HUTTIG [with Z. HERRMANN] (Z. anorg. Chem., 1933, **210**, 26—32; cf. A., 1932, 1211).—When mixtures of ZnO and Fe_2O_3 are heated below 620° no marked change in magnetic properties or *X*-ray diagram occurs. Products which have been heated at 620—670° show a considerably higher magnetic susceptibility, whilst those heated at 670—770° are ferromagnetic. *X*-Ray data indicate that these changes are accompanied by a change of structure. E. S. H.

***X*-Ray study of wüstite (FeO) solid solutions.** E. R. JETTE and F. FOOTE (J. Chem. Physics, 1933, **1**, 29—36; cf. A., 1931, 1369).—A series of Fe oxides with 76·08—76·72% Fe has been prepared. The NaCl structure of FeO was recognised in all specimens. Contrary to earlier results, the size of the unit cell decreases as the Fe content decreases. The results are discussed. F. L. U.

Relation of atomic sizes to interatomic distances in homopolar crystals. G. W. BRINDLEY (Z. Krist., 1932, **84**, 169—172).—The at. radii of a no. of elements have been calc. by Slater's method (cf. A., 1930, 1234) and the sum, R, of these radii has been compared with the interat. distances, D, as deduced from compounds of the form $X^{+n}Y^{-n}$, *e.g.*, SiC, AlN, BeO, CuBr, etc. The mean vals. of R/D when n=4, 3, 2, and 1 are 0·99, 1·09, 1·21, and 1·46, respectively; the increased contraction is attributed to increasing electrostatic attraction, the linkings being regarded as of the homopolar tetrahedral type (cf. A., 1931, 548, 670). C. A. S.

Structure of trifluorides of transition metals. N. WOOSTER (Z. Krist., 1933, **84**, 320—321).—The unit cell of FeF_3 and similar fluorides is triclinic (cf. A., 1931, 549, 1359), although approximating to cubic, and isomorphous with that of WO_3 (cf. *ibid.*, 1115); the ratio (vol. of F)/(vol. of FeF_3)=(vol. of O)/(vol. of WO_3)=0·77. C. A. S.

Tetrahedral representation of the carbonate and nitrate groups. R. REINECKE (Z. Krist., 1932, **84**, 159—166).—The spatial arrangements of the CO_3'' and NO_3' groups are discussed in the light of the author's views (cf. A., 1931, 1001; 1932, 796), and also the bearing of these on the relations between carbonates and nitrates. Relations between the calcite and perovskite types are established. C. A. S.

Crystal structure of rubidium nitrate. L. PAULING and J. SHERMAN (Z. Krist., 1933, **84**, 213—216; cf. A., 1929, 1131).—$RbNO_3$, regarded as hexagonal, has a 10·45, c 7·38 Å., with 9 mols. in the unit cell, space-group C_{3v}^5 ($H3m$); regarded as rhombic, it has a 18·08, b 10·45, c 7·38 Å., with 18 mols. in the unit cell. C. A. S.

Crystal structure of lithium sulphate. J. G. ALBRIGHT (Z. Krist., 1932, **84**, 150—158).—The unit cell of $LiSO_4$ has a 8·24, b 4·95, c 8·44 Å., β 107° 54′, and contains 4 mols., space-group C_{2h}^5 ($P2_{1/a}$). The SO_4 groups form tetrahedra, S—O=1·50, O—O 2·45 Å.; each Li is surrounded, approx. tetrahedrally, by 4 O atoms, one from each of 4 SO_4 groups, Li—O 1·97, O—O (average) 3·20. The co-ordination no. of Li with respect to O is therefore 4. C. A. S.

Structures of ammonium and potassium perchlorates. C. GOTTFRIED and C. SCHUSTERIUS (Z. Krist., 1932, **84**, 65—73).—The unit cells of $KClO_4$ and NH_4ClO_4 have respectively a 8·834, 9·202, b 5·650, 5·816, c 7·240, 7·449 Å.; both contain 4 mols., space-group V_h^{16}. Each K (NH_4) is surrounded by 12 O, average distance K (NH_4)—O=3·02 (3·12) Å.; each Cl, slightly irregularly tetrahedrally, by 4 O, average distances O—O 2·36 (2·42), Cl—O 1·44 (1·49) Å. C. A. S.

Crystal structure of lead bromide. W. NIEUWENKAMP and J. M. BIJVOET (Z. Krist., 1932, **84**, 49—61).—The unit cell of $PbBr_2$ has a $4{\cdot}71_5$, b 8·02, c $9{\cdot}48_5$ Å., and contains 4 mols., space-group V_h^6. The structure is a new one for compounds of the type AB_2. Pb has co-ordination no. 9, and Br half 4 and half 5, and the Pb ions are polarised. C. A. S.

Crystal structure of lead fluoride. J. A. A. KETELAAR (Z. Krist., 1932, **84**, 62—64).—The unit cell of rhombic PbF_2 has a 3·80, b 6·41, c 7·61 Å., and contains 4 mols., d 8·24 (that of cubic PbF_2 being 7·66). The structure resembles that of $PbBr_2$ (see preceding abstract), with which it is isomorphous. C. A. S.

Crystal structure of potassium silver cyanide. J. L. HOARD (Z. Krist., 1933, **84**, 231—255).—$KAg(CN)_2$, d 2·32, is hexagonal, a 7·384, c 17·55 Å., 6 mols. in unit cell, space-group (probably) D_{3d}^2; it is not pyroelectric. The structural units are K^+ and $[Ag(CN)_2]^-$ ions, the latter being nearly linear. Each K is surrounded octahedrally (distorted) by 6N, K—N=2·56, 2·97, and 3·05, Ag—N=3·29 Å.; the CN groups form close-packed parallel layers. C. A. S.

Structure of rubidium ferricyanide. W. BUSSEM and C. GOTTFRIED (Z. Krist., 1933, **84**, 317—318).—$Rb_3Fe(CN)_6$ is isomorphous with the K and not with the Cs salt (cf. A., 1931, 27). The unit cell has a 13·74, b 10·66, c 8·63 Å., β 90° 3′ ±20′. Space-group but showing a pseudo-structure according with V_h^{14}. C. A. S.

X-Ray investigation of 12-molybdophosphates and related compounds. J. L. HOARD (Z. Krist., 1933, **84**, 217—230).—$XPMo_{12}O_{40}30H_2O$ [X= (*a*) H_3, (*b*) Nd, (*c*) Sm, (*d*) Gd]; $Y_2SiMo_{12}O_{40},31H_2O$ [Y= (*e*) Mg, (*f*) Ni], and (*g*) $Be_2SiW_{12}O_{40},31H_2O$ have been examined. The *salts* (*b*), (*c*), and (*d*) crystallise in yellow octahedra (cf. A., 1918, ii, 77). All seven are cubic, space-group probably O_h^1, with 8 mols. in the unit cell; the following vals. of a and d are given: (*a*) 23·1, 2·52; (*b*) 23·1, 2·62; (*c*) 23·1, 2·60; (*d*) 23·1, ?; (*e*) 23·04, 2·56; (*f*) 23·0, ?; (*g*) 23·3, 3·66. A possible structure on the lines proposed for the silicotungstates (cf. A., 1929, 1367) is discussed. C. A. S.

Crystal structure of cerussite. M. Y. COLBY and L. J. B. LACOSTE (Z. Krist., 1933, **84**, 299—309; cf. A., 1929, 1131).—Cerussite has a $5{\cdot}16_6$, b $8{\cdot}46_8$, c $6{\cdot}14_6$ Å., with 4 mols. in unit cell, space-group V_h^{16}. The structure is the same as that of aragonite and KNO_3 (cf. A., 1925, ii, 484; 1931, 1359). C. A. S.

Crystal structure of sodium ferrite. S. GOLDSZTAUB (Compt. rend., 1933, **196**, 280—282).—$NaFeO_2$ (cf. A., 1893, ii, 169) is obtained in large crystals by more prolonged heating. These are rhombohedral, d 4·23, with a 5·59 Å., α 35° 20′, and 1 mol. in the unit cell; space-group D_{3d}^5 ($R\bar{3}m$). C. A. S.

X-Ray spectroscopy of monazite from Bortschowotschny, Transbaikalia. C. MATVEEV (Neues Jahrb. Min., 1932, *A*, **65**, Bl.-Bd., 223—232; Chem. Zentr., 1932, ii, 2163).—Three varieties are characterised. A. A. E.

Lattice constants and axial ratios of stibnite. J. G. ALBRIGHT (Physical Rev., 1931, [ii], **37**, 458).—*X*-Ray examination gives a 11·29, b 11·45, and c 3·87 Å., whence the $a:b:c$=0·986 : 1 : 0·339, confirming Gottfried's (A., 1928, 350) and not Dana's data. L. S. T.

Structure of afwillite, $3CaO,2SiO_2,3H_2O$. C. GOTTFRIED (Z. Krist., 1932, **84**, 172—173).—The unit cell of afwillite (cf. A., 1925, ii, 429) has a 11·39, b 5·47, c 13·09 Å., β 98° 26′, and contains $3[3CaO,2SiO_2,3H_2O]$, space-group C_2^2. C. A. S.

Crystal structure of sulvanite. L. PAULING and R. HULTGREN (Z. Krist., 1933, **84**, 204—212; cf. A., 1929, 989).—Sulvanite, Cu_3VS_4, is cubic, a 5·370 Å., with 1 mol. in the unit cell, space-group T'_d ($P\bar{4}3m$). Each Cu and each V is surrounded tetrahedrally by 4S, Cu—S=2·285, V—S=2·186 Å.; each S by 3 Cu at three corners of a tetrahedron with one V in the midst of the 3Cu—a new structure. Cu probably resonates between Cu^I and Cu^{II}, and V between V^V and lower states. C. A. S.

***X*-Ray analysis of vesuvianite.** B. E. WARREN (Physical Rev., 1931, [ii], **37**, 1697; cf. A., 1931, 1116).—Vesuvianite, $H_2Ca_{10}Al_6Si_9O_{38}$, has a 15·60, c 11·83 Å., 4 mols. per unit cell, which contains 260 atoms and involves 44 parameters; space-group D_{4h}^{14}. The structure closely resembles the garnet $Ca_3Al_2Si_3O_{12}$

and contains SiO_4 and Si_2O_7 groups. The co-ordination nos. are Si 4, Al 6, and Ca 8. L. S. T.

Crystal structure of potassium hydrogen tartrate. A. FERRARI and R. CURTI (Z. Krist., 1932, **84**, 8—13).—Good crystals of this salt of a new habit were obtained by slow addition of AcOH to aq. $NaKC_4H_4O_6$. The unit cell has a 7·614, b 10·70, c 7·80 Å., and contains 4 mols.; the length of the C chain probably coincides with the b axis. C. A. S.

Crystal structure of β-arabinose. E. G. COX (Z. Krist., 1932, **84**, 45—48).—Arguments based on both chemical and X-ray investigations are stated in support of the author's deduction (cf. A., 1931, 1275) of a ring structure for β-arabinose, as opposed to the long-chain structure proposed by Andress and Reinhardt (cf. *ibid.*, 1116). C. A. S.

***p*-Chlorobromobenzene and its congeners: variate equivalent points in molecular lattices.** S. B. HENDRICKS (Z. Krist., 1932, **84**, 85—96).—The following data are given (in this order), a (d_{100}), b, c (in Å.), γ, no. of mols. in unit cell: p-$C_6H_4Cl_2$, 14·83 (13·70), 4·10, 5·88, 112° 30′, 2; p-$C_6H_4Br_2$, 15·46 (14·29), 4·11, 5·80, 112° 38′, 2; p-C_6H_4ClBr, 15·15 (13·95), 4·13, 5·81, 113° 0′, 2; all are monoclinic prismatic. p-$C_6H_4Cl_2$ and p-$C_6H_4Br_2$, although apparently isomorphous, have different structures, but the lattice of an equimolal solid solution of the two and that of p-C_6H_4ClBr as regards the positions of the halogens are closely similar, so that it is concluded that in the last named (space-group C_{2h}^5—$P2_1a$), the Cl and Br atoms both occupy the same set of equiv. positions (cf. A., 1931, 530; 1932, 830). C. A. S.

Structure of some naphthalene and stilbene derivatives. J. NOVAK (Z. Krist., 1933, **84**, 310—316; cf. A., 1926, 58, 392; 1929, 1288).—The following data are recorded: Et 2 : 4-dinitro-α-naphthylmalonate, d^{25} 1·406, monoclinic prismatic, $a : b : c$—0·5372 : 1 : 0·6208, β 112° 14′. Et 2 : 4-dinitro-α-naphthylacetate, m.p. 131°, d^{25} 1·368, monoclinic prismatic, $a : b : c$=1·2545 : 1 : 1·2604, β 112° 24′. 5-Nitro-8-acetamido-1-methylnaphthalene, d^{26} 1·333; monoclinic prismatic, $a : b : c$=9·0454 : 1 : 5·7005, β 118° 48′. *s*-2 : 4 : 6-Trinitro-4′-methyldiphenylethylene, d^{26} 1·4908, triclinic, $a : b : c$=1·5416 : 1 : 0·6812, α 96° 20·5′, β 110° 18·5′, γ 90° 59′. *s*-2 : 4-Dinitro-3′ : 4′-methylenedioxydiphenylethylene, d^{26} 1·5494; monoclinic prismatic, $a : b : c$=0·8419 : 1 : 1·6681, β 95° 24′. C. A. S.

Crystal structure of anthracene. J. M. ROBERTSON (Z. Krist., 1933, **84**, 321—322; cf. A., 1929, 1367; 1930, 528, 1097).—Previous results are confirmed and amplified, showing that the C atoms lie accurately at the corners of three regular plane hexagons, the distance from centre to centre of the atoms being 1·41 Å.; the mol. is, however, inclined at varying angles to all the crystallographic axes. The smallest distance between C atoms of neighbouring mols. is 3·67 Å. Co-ordinates of all C atoms have been determined. C. A. S.

Problems in the X-ray analysis of the structure of animal hairs and other protein fibres. W. T. ASTBURY (Trans. Faraday Soc., 1933, **29**, 193—205).—The unit spacing along protein chains is 3·5 Å. In animal hairs this val. is nearly attained (3·4 Å.) in the stretched, β-keratin, form. In the unstretched, α-keratin, state the chain is folded and the spacing reduced owing to the interaction of side-chains. The side spacings of about 5 and 10 Å. in two directions at right angles can be reasonably explained as due to the thickness of the chain and to the space occupied by side groups, respectively. The existence of sharply defined micelles is less probable than that of numerous crystallisation faults. A. G.

Physical structure of coal, cellulose fibre, and wood as shown by the Spierer lens. R. THIESSEN (Ind. Eng. Chem., 1932, **24**, 1032—1041).—An attempt is made to correlate the physical structures of cellulose fibre, wood, and coal, as revealed by use of the Spierer lens, with the results of X-ray analysis. Further evidence is thus adduced for the colloidal nature of coal. Fibres of wood or cellulose are produced by characteristic arrangements of micelles, as postulated by X-ray analysis. H. E. B.

Structural variations in the cellulose nitrates. M. MATHIEU (Trans. Faraday Soc., 1933, **29**, 122—131).—X-Ray diagrams show that in cellulose nitrate (I) from cotton the chains of glucose residues are separated at well-defined distances, dependent slightly on the % N, but that the nitrate groups are arranged at random. When films of (I) are treated with solvents the latter act first as swelling agents, and then as dispersing agents. The dispersion increases with increasing solubility and dilution of (I). Heating with H_2O under pressure causes scission of the glucose chains. A. G.

Change in the lattice of cellulose nitrate. J. J. TRILLAT (Trans. Faraday Soc., 1933, **29**, 85—89).—When solutions of cellulose nitrate (12·95% N) are evaporated, the film first gives a no. of Debye–Scherrer rings in the X-ray diagram. As drying proceeds these rings progressively disappear until the diagram becomes similar to that of the original nitrate. It is assumed that the solvents form cryst. additive compounds. Cellulose nitrate with 10—12% N give amorphous X-ray diagrams. A. G.

Hall e.m.f. and intensity of magnetisation. E. M. PUGH and T. W. LIPPERT (Physical Rev., 1932, [ii], **42**, 709—713; cf. A., 1931, 29).—Further evidence that the Hall e.m.f. is a function of the intensity of magnetisation alone is adduced. N. M. B.

Mono-crystal Barkhausen effects in rotating fields. F. J. BECK, jun., and L. W. MCKEEHAN (Physical Rev., 1932, [ii], **42**, 714—720).—Directions of Barkhausen effects in a stationary single-crystal Si-steel disc in a magnetic field, slowly rotating in the plane of the disc, were determined. N. M. B.

Propagation of large Barkhausen discontinuities. III. Effect of a circular field with torsion. L. TONKS and K. J. SIXTUS (Physical Rev., 1933, [ii], **43**, 70—80; cf. this vol., 15).—A large circular field caused by a current in the Ni–Fe wire has negligible effect if the wire is under tension alone; the considerable effect if the wire is twisted is investigated. N. M. B.

Effect of tension on the electrical resistance of single bismuth crystals. (MISS) M. ALLEN

(Physical Rev., 1932, [ii], **42**, 848—857).—The dependence of the tension coeff. of resistance (at 30°) on the orientations of the principal and secondary cleavage planes with respect to the tension was investigated. N. M. B.

Effect of homogeneous mechanical stress on the electrical resistance of crystals. P. W. BRIDGMAN (Physical Rev., 1932, [ii], **42**, 858—863).—Mathematical. The effect can be expressed in terms of a set of consts. for Bi. N. M. B.

Ferromagnetic anisotropy of single crystals. R. M. BOZORTH (Physical Rev., 1932, [ii], **42**, 882—892; cf. A., 1932, 987).—Mathematical. N. M. B.

Magnetic susceptibility of silicon-rich ferrosilicons. C. BEDEL (Compt. rend., 1933, **196**, 262—264).—The magnetic susceptibility, χ, of ferrosilicons containing 34·64—99·66% Si, the Fe containing only 0·03% C, has been determined. All are paramagnetic (cf. A., 1923, ii, 25); χ shows large max. near 34·64 and 49·8% and a small one near 56·86% Si, indicating the probable existence of $FeSi_2$ (cf. A., 1901, ii, 317), although χ for the percentage corresponding with this compound may vary greatly for different heat treatments. C. A. S.

Resistance–temperature relation of beryllium oxide and zinc oxide. J. A. OSTEEN (Physics, 1932, **3**, 81—89).—For BeO, $(1/\rho)(d\rho/dT)=Q/RT^2-a$ gives a straight line with transition at 750°; ZnO gives two straight lines of different slopes, with transition between 250° and 500°. The effect on the slope of successive heatings is described. CH. ABS.

Velocity of sound in an absorptive gas. D. G. BOURGIN (Physical Rev., 1932, [ii], **42**, 721—730; cf. A., 1929, 1136).—Mathematical. The theory of velocity propagation as conditioned by internal energy exchanges is considered with special reference to CO_2. N. M. B.

Optical method for measuring the absorption of ultrasonic waves in liquids. P. BIQUARD (Compt. rend., 1933, **196**, 257—259; cf. A., 1932, 900).—The variation of the quantity of light diffracted with variation in intensity of the ultrasonic waves causing such diffraction is investigated. C. A. S.

Dispersion of sound in nitrogen tetroxide and its interpretation in terms of dissociation rate. W. T. RICHARDS and J. A. REID (J. Chem. Physics, 1933, **1**, 114—128).—A full account of work previously published (A., 1932, 916). F. L. U.

Heat of expansion of a gas of varying mass. L. J. GILLESPIE and J. R. COE, jun. (J. Chem. Physics, 1933, **1**, 103—113).—An expression for the heat of expansion of a gas in an open system has been developed with the help of the Beattie–Bridgeman equation of state, and verified by results for the slow expansion of CO_2 and of NH_3. The rapid expansion of CO_2 gave vals. lower than those calc., the difference increasing with the rate of expansion. F. L. U.

Low-temperature specific heats. III. Molecular rotation in crystalline primary *n*-amylamine hydrochloride. J. C. SOUTHARD, R. T. MILNER, and S. B. HENDRICKS (J. Chem. Physics, 1933, **1**, 95—102).—If cryst. n-$C_5H_{11}\cdot NH_3Cl$ is quenched to 90° abs. a metastable form is obtained which is slowly converted into a stable form on heating above 165° abs. Regions of gradual transition occur at 210—230° and 242—252° abs. Results of determinations of heat capacity and *X*-ray structure are interpreted on the basis of rotation of $C_5H_{11}\cdot NH_3^+$ groups in the crystals. F. L. U.

Maximum rate of evaporation of water. T. ALTY (Phil. Mag., 1933, [vii], **15**, 82—103).—The max. rate of evaporation has been measured between 4° and −8°. It is only 4% of the val. deduced from the Knudsen equation (Ann. Physik, 1915, [v], **47**, 697). H. J. E.

Vaporisation of water. A. REYCHLER (Bull. Soc. chim. Belg., 1932, **41**, 521—524).—Vals. of the latent heat of H_2O at 0—180° as calc. from the equation $\lambda=RT(d\ln f/dT)/(f/T)$ (where f is the v.p. at T° abs.) are in close agreement with experimental data. J. W. S.

Behaviour of water in the critical region. W. KOCH (Forsch. Gebiet Ingenieurw., 1932, **A**, **3**, 189—192; Chem. Zentr., 1932, ii, 1137).—The heat content of H_2O at 240 kg. per sq. cm. increases regularly with rise of temp., but there is an inflexion at 379·6°, where c_p is max. at 36 g.-cal. per g. (cf. Callendar, A., 1928, 1179). A. A. E.

Saturation pressures of steam (107—374°). A. EGERTON and G. S. CALLENDAR (Phil. Trans., 1932, **A**, **231**, 147—205).—The v.p. have been determined at 5° intervals by a dynamic method, and can be represented by $\log_{10} p_{atm.}=-2010\cdot97/T+5\cdot43733$, with a probable accuracy of 1 in 6000. T_c is between 374° and 374·5°. C. W. G.

Specific heat of Monel metal between −183° and 25°. W. F. HAMPTON and J. H. MENNIE (Canad. J. Res., 1932, **7**, 677—679).—The heat capacity of Monel metal over the range −183° to 25°, measured in an adiabatic calorimeter, is $-2\cdot503+0\cdot09948t+0\cdot00001684t^2-0\cdot00000041651t^3$. It varies from 0·0997 at 20° to 0·0621 at −160°. J. W. S.

Physico-chemical constants of dioxan. W. A. ROTH and I. MEYER (Z. Elektrochem., 1933, **39**, 35—37).—The following consts. for highly purified dioxan have been determined: heat of fusion 33·8 g.-cal. per g.; heat of combustion $6\cdot370\pm0\cdot010$ kg.-cal. per g.; d $1\cdot05565(1-0\cdot001063t)$; coeff. of thermal expansion 0·00109 between 13° and 25°. F. L. U.

Calorimetric determination of the intrinsic energy of gases as a function of the pressure. Data on oxygen and its mixtures with carbon dioxide to 40 atmospheres at 28°. F. D. ROSSINI and M. FRANDSEN (Bur. Stand. J. Res., 1932, **9**, 733—747).—The internal energy of air, O_2, and mixtures of O_2 with up to 37 mol.-% CO_2 has been determined. $(\partial U/\partial P)_T$ is const. over the range studied: air −6·08, O_2 −6·51, mixtures of O_2 and CO_2 $-6\cdot51-11\cdot0x-11\cdot0x^2$, x being the mol. fraction of CO_2. C. W. G.

Thermal diffusivity of zinc. R. H. FRAZIER (Physical Rev., 1933, [ii], **43**, 135—136; cf. A., 1932, 442, 799). N. M. B.

Natural convection of heat in air for small differences of temperature. Comparison of

limit value of convection with conductivity of medium. P. VERNOTTE (Compt. rend., 1932, **195**, 1245—1247). C. A. S.

Density and molecular state of rhenium tetrachloride and rhenium hexachloride in the gaseous state. D. M. YOST and G. O. SHULL (J. Amer. Chem. Soc., 1932, **54**, 4657—4661; cf. A., 1931, 1255).—Re combines slowly with excess of Cl_2 at temp. below 650°. On cooling to room temp. the product is mainly $ReCl_4$. Vapour density data for the range 558—670° are consistent with the coexistence of $ReCl_4$ and Re_2Cl_8, and in the presence of excess Cl_2, of $ReCl_6$, and free Cl_2 in addition. J. G. A. G.

Joule–Thomson effect in helium. J. R. ROEBUCK and H. OSTERBERG (Physical Rev., 1933, [ii], **43**, 60—69).—The effect of air as an impurity up to 10% is negligible. With improved apparatus the porous plug coeff. μ for He was measured from −190° to 300° and from 1 to 200 atm. N. M. B.

Joule–Thomson effect in helium. J. R. ROEBUCK and H. OSTERBERG (Physical Rev., 1931, [ii], **37**, 110—111).—The isenthalpic curves for pure He between −100° and 100° are linear with negative slope. L. S. T.

Empirical equation of state. H. S. FRANK and F S. LEI (Physical Rev., 1932, [ii], **42**, 893—899).—The law of Ramsay and Young holds for Et_2O both as a gas and as a highly compressed liquid, and leads to an equation of state for these conditions. A microcryst. structure in the liquid at high pressures is indicated. The calc. molal vol. at 0° abs. and zero external pressure is 79·46 c.c. N. M. B.

Dependence on temperature of the density of ethyl ether. J. MAZUR (Spraw. Prace Polsk. Towarz. Ficyz., 1931, **5**, 349—356; Chem. Zentr., 1932, ii, 2034).—Change in d of Et_2O is almost linear from 0·6964 at 34·978° to 0·8595 at −105·42° and is thereafter slower. At −105·42° interconversion of liquid forms takes place. A. A. E.

Density of ammonia at reduced pressures and its relation to the at. wt. of nitrogen, the gas constant, R, and the limiting molal volume, V_0. G. DIETRICHSON, C. W. ORLEMAN, and C. RUBIN (J. Amer. Chem. Soc., 1933, **55**, 14—21).—The density at 2/3 and 1/3 atm. is 0·51161 and 0·25458 ±0·00001, respectively. The gas density method is not as trustworthy as gravimetric analyses for the determination of at. wt. owing to uncertainties in R and V_0. J. G. A. G.

Normal density of ammonia. G. DIETRICHSON, L. J. BIRCHER, and J. J. O'BRIEN (J. Amer. Chem. Soc., 1933, **55**, 1—13).—The normal density of NH_3 is found to be 0·77126±0·00001 by a method in which adsorption effects are eliminated. J. G. A. G.

Entropy of polyatomic molecules and the symmetry number. J. E. MAYER, S. BRUNAUER, and M. G. MAYER (J. Amer. Chem. Soc., 1933, **55**, 37—53).—Mathematical. The additive terms in the entropy expression for polyat. mols. with two or more identical atoms are considered and expressions for computing the molal entropy of diat. rigid linear and non-linear polyat. and C_2H_6-like mols. are developed, on certain assumptions. The calc. molar entropies (neglecting nuclear spin which cancels in chemical reactions) of C_2H_6, C_2H_2, and C_6H_6 gases at 1 atm. and 298° abs. are 55·5, 47·2, and 65·1 e.u., respectively. J. G. A. G.

Entropy of hydrogen. W. D. RODEBUSH (Physical Rev., 1931, [ii], **37**, 221). L. S. T.

Viscosity of water. M. GOLAZ (Compt. rend., 1932, **195**, 1371—1373).—Mathematical. C. A. S.

Effect of a magnetic field on the heat conductivity and viscosity of gases. H. SENFTLEBEN (Physikal. Z., 1933, **34**, 141—142).—For the same pressures and field strengths the relative change of viscosity is < that of heat conductivity. A. J. M.

Viscosity and molecular weights of polymeric materials. E. O. KRAEMER and F. J. VAN NATTA (J. Physical Chem., 1932, **36**, 3175—3186).—Measurements of the viscosities of solutions of polymeric hydroxydecoic acids, having mol. wts. of 780—25,200, indicate a simple relation between viscosity and mol. wt. over a wide range. The relation breaks down for mol. wts. > 15,000 in the polymeric ω-hydroxydecoic acids; hence Staudinger's vals. for the mol. wt. of rubber, cellulose, etc. are untrustworthy. E. S. H.

Permeability of palladium to hydrogen. V. LOMBARD and C. EICHNER (Bull. Soc. chim., 1932, [iv], **51**, 1462—1486; cf. A., 1932, 685, 906).—A long time is required to produce a steady state of diffusion at low temp. (275—300°) unless the Pd wall is heated previously to a higher temp. in an atm. of H_2. The rate of diffusion is a function of the rate at which H_2 is supplied to the Pd diaphragm, and to obtain comparable results at different temp. a certain min. rate must be maintained. M. S. B.

***X*-Ray studies on the diffusion of copper into nickel.** C. MATANO (Mem. Coll. Sci. Kyoto, 1932, **15**, 351—353).—The rate of diffusion of Ni plated on Cu is $3·5\times10^{-7}$ sq. cm. per day at 650° and $1·9\times10^{-5}$ sq. cm. per day at 890°. A. R. P.

Sodium–lead alloys. Structure of the compound known as Na_4Pb. C. W. STILLWELL and W. K. ROBINSON (J. Amer. Chem. Soc., 1933, **55**, 127—129).—*X*-Ray data indicate a face-centred cube with a_0 13·27±0·035 Å. The unit cell contains 78 atoms. The exact formula is $Na_{31}Pb_8$. J. G. A. G.

Hardenable lead alloys. B. GARRE and F. VOLLMERT (Z. anorg. Chem., 1933, **210**, 77—80).—Small amounts of Ag_3Sn, $AgCd_4$, or Ag_2Cd_3 form mixed crystals with Pb. Addition of these compounds up to 2% increases the Brinell hardness of Pb, the increase in alloys quenched in cold H_2O from 250° being > in those cooled slowly. In the case of Ag_2Cd_3 the hardness of the product decreases with time, and addition of > 2% results in atm. oxidation. A solution recommended for etching all alloys of Pb contains conc. HCl (120 c.c.), H_2O (100 c.c.), and cryst. $CuCl_2$ (90 g.). E. S. H.

System gold–manganese. H. MOSER, E. RAUB, and E. VINCKE (Z. anorg. Chem., 1933, **210**, 67—76).

—Thermal and microscopical analyses of this system are described. The existence of AuMn is recognised. Three transformations in the solid state have been observed. The first, in alloys of high Mn content, is connected with the presence of impurities; the second is accompanied by increase of vol. and is connected with the α—— transformation of Mn, the β-Mn having a low solvent power for Au; the third corresponds with a $\gamma \longrightarrow \delta$ transformation of the mixed crystals and is most marked in alloys containing 10—12% Mn, when annealed at 530°. The $\gamma \longrightarrow \delta$ transformation is accompanied by a great increase of hardness. E. S. H.

Alloys of platinum with copper. N. S. KURNAKOV and V. A. NEMILOV (Z. anorg. Chem., 1933, 210, 1—12).—Thermal analysis indicates a transformation at 700—800° in alloys containing 40—60 at.-% Pt, which is most pronounced at 50 at.-% Pt. Brinell hardness curves have been constructed for the series of alloys, both annealed and quenched. The microstructure of alloys containing < 35 at.-% Pt is homogeneous and suggests a series of solid solutions in this region. Alloys containing 35—40 at.-% Pt tend to develop after annealing a needle-like structure, which is pronounced in alloys containing 50 at.-% Pt. With > 60 at.-% Pt this structure disappears and another homogeneous structure is formed. These changes are due to the formation of PtCu. Measurements of electrical resistance and its temp. coeff. give data in conformity with these results. E. S. H.

Alloys of platinum with nickel. N. S. KURNAKOV and V. A. NEMILOV (Z. anorg. Chem., 1933, 210, 13—20).—Thermal analysis gives no indication of a transformation in this series. Measurements of hardness and observations of microstructure for alloys of different composition suggest the formation of a series of solid solutions. A discontinuity in the hardness curve at about 20 at.-% Pt corresponds with the appearance of a fine net structure in place of a homogeneous mass, but it is unlikely that a compound is formed. These deductions are confirmed by measurements of electrical resistance and its temp. coeff. E. S. H.

Is there a compound Al_2Zn_3? E. SCHMID and G. WASSERMANN (Mitt. Materialprüf., 1932, 218—219).—Al–Zn alloys (79% Zn) have a face-centred cubic lattice at high temp. and this structure is retained at room temp. if a little Mg is added and the alloy quenched. The lattice consts. of β-alloys are reduced, compared with pure Al, to an extent which is the same as that observed in the γ-solid-solution phase, *i.e.*, 0·0085 Å. for every 10 at.-% Zn, and no superstructure lines attributable to a regular distribution of the atoms in the lattice can be observed. On decomp. β forms a very fine-grained mixture of α-Zn-rich and γ-Al-rich solid solutions. These observations indicate that the compound Al_2Zn_3 does not exist and that the β- and γ-phases in Al–Zn alloys are identical, being separated from one another by a gap of immiscibility. A. R. P.

Does a compound Al_2Zn_3 exist? M. VON SCHWARZ and O. SUMMA (Metall-Wirt., 1932, 11, 369—371; Chem. Zentr., 1932, ii, 2361).—For alloys containing about 21·3% Al, Mg (0·1%) or Cd (0·5%) has no great effect on the transformation velocity of the β-phase. Heating curves for 10—50% Al, independently of the addition of Mg or Cd, show an arrest at 290°. The cooling curve shows the decomp. of the β-phase into the α- and γ-phases. Addition of Mg or Cd, or a high Al content, lowers the transition temp. by 5—20° (256—235°). An alloy containing 21·3% Al and 0·1% Mg (hexagonal) after heating at 350° and quenching to 0°, is face-centred cubic, a 3·978 Å. Pure Al (face-centred cubic) has a 4·043 Å. An alloy with 25 or 50% Zn, quenched from 350° to 0°, had a 4·030 Å. The β-phase cannot have the composition Al_2Zn_3. A. A. E.

Improvement of zinc–aluminium alloy, Al_2Zn_3. H. MEYER (Z. Physik, 1932, 78, 854).—Structures deduced from *X*-ray diagrams (cf. preceding abstract) are consistent with the electrical properties discussed by Meyer (cf. A., 1932, 799). A. B. D. C.

Does a compound Al_2Zn_3 exist? E. SCHMID and G. WASSERMANN (Metall-Wirt., 1932, 11, 386—387; Chem. Zentr., 1932, ii, 2361—2362; cf. preceding abstracts).—*X*-Ray results are in accord with those of Schwarz and Summa, but it is possible that the β- and γ-phases are identical. A. A. E.

Diagram of state of magnesium–zinc alloys. A. A. BOTSCHVAR and I. P. VELITSCHKO (Z. anorg. Chem., 1933, 210, 164—165).—Contrary to the statement of Hume-Rothery and Rounsefell (A., 1929, 398), only one cryst. species is present in Mg–Zn alloys with 33—42 at.-% Mg. F. L. U.

Lattice parameters of solid solutions of silicon in copper. H. F. KAISER and C. S. BARRETT (Physical Rev., 1931, [ii], 37, 1697).—Measurements of a_0 for α-Cu–Si alloys containing < 0·06% impurity have been made. The parameters at 20° are 3·6103, 3·6128, 3·6150, 3·6151, and 3·6157 Å. for alloys with 1·09, 3·01, 5·02, 5·91, and 6·36% Si, respectively. Calc. and observed d indicate that the solid solution is of the simple substitution type. L. S. T.

System phosphorus–selenium. P. L. ROBINSON and W. E. SCOTT (Z. anorg. Chem., 1933, 210, 57—66).—Se dissolves in molten P below 50°, giving rise to solid solutions. At about 130° reaction takes place slowly with formation of P_4Se_3. This compound, isolated by extraction with CS_2 and sublimation, has m.p. 242°. At higher temp., free yellow P in the prep. is converted into red and the m.p. varies. The transformation of yellow to red P is accelerated by the presence of Se. E. S. H.

Thermo-electric power in the systems tellurium–sulphur and tellurium–selenium. A. PETRIKALN and K. JACOBY (Z. anorg. Chem., 1933, 210, 195—202).—Addition of S to Te increases the thermo-electric power up to the miscibility limit at 1·6% S, beyond which it is progressively diminished. Addition of Se causes a steady rise, initially very rapid F. L. U.

Recrystallisation of mixed crystals rich in tin. A. A. BOTSCHVAR and N. E. MERKURJEV (Z. anorg. Chem., 1933, 210, 161—162).—Sn containing small amounts of Sb, Pb, Bi, Cu, or Al, with which it forms

mixed crystals, yields on cooling smaller crystals than does the pure metal. The depression of crystal size is the greater the smaller is the solubility of the added metal, except in the case of Bi. F. L. U.

Segregate structures in copper–tin and silver–zinc alloys. D. W. SMITH (Amer. Inst. Min. Met. Eng., 1932).—In both systems the α-phase segregates from the β-phases as needles parallel to (111) in the β-phases; in the Cu–Sn system the α-phase is oriented so that a (111) plane is parallel to a (110) plane in the β-phase of the parent solid solution. In the Cu–Sn system a pseudomorphic segregation of the α-phase takes place in the form of plates in positions originally occupied by twins in the β-matrix; the twinning plane in the β-phase is probably a (133) plane. CH. ABS.

Many-component systems containing iron. V. Rontgenographic data for the systems Cr–C and Fe–Si–P. F. SAUERWALD, W. TESKE, and G. LEMPERT (Z. anorg. Chem., 1933, **210**, 21—25).—The only phases in the Cr–C system (up to 8·5% C) recognised by *X*-ray analysis are Cr, Cr_4C, and a hexagonal carbide. In the Fe–Si–P alloys the existence of Fe_3P, Fe_2P, Fe, Fe_3Si_2, and FeSi is shown. E. S. H.

Structure of ternary eutectics. A. A. BOTSCHVAR and K. V. GOREV (Z. anorg. Chem., 1933, **210**, 171—172).—In ternary eutectics the three cryst. species need not be distributed irregularly. In the systems Cd–Pb–Bi, Cd–Pb–Sn, and Cd–Sn–Bi, crystals of the first-named metal are surrounded by those of the second, and the latter by those of the third. F. L. U.

Structure of hyper- and hypo-eutectic alloys. A. A. BOTSCHWAR and K. W. GOREW (Z. anorg. Chem., 1933, **210**, 166—167; cf. A., 1929, 388).—From the microscopical examination of binary alloys containing 5% of one component above or below the eutectic composition it appears that in either case, but not in both, "halos" of the second component may surround primary crystals of the first, separating these from the eutectic. Such halos are readily formed around Bi and Sb. The metals studied were Bi, Sb, Cd, Pb, and Sn. F. L. U.

Alcohol hydrates. G. G. S. GALLART (Anal. Fís. Quím., 1932, **30**, 815—826).—The densities of 0—100% solutions of PrOH at 25°, 30°, and 35° are recorded. The mol. susceptibilities of aq. EtOH and aq. PrOH indicate the existence of hydrates containing 6, 3, and 1, and 16, 6, 3, and 1 mols. of H_2O, respectively, but it is necessary to assume freedom of movement of the groups in these compounds. H. F. G.

Heat of evaporation of mixtures of ethyl alcohol and water. A. V. FROST (J. Gen. Chem. Russ., 1932, **2**, 597—600).—The experimental data are in agreement with Bose and Muller's calc. vals. (A., 1907, ii, 332). R. T.

System ethyl alcohol–*n*-heptane at 30°. J. B. FERGUSON, M. FREED, and A. C. MORRIS (J. Physical Chem., 1933, **37**, 87—91).—Neither the composition of the co-existent phases nor the total and partial pressures afford support for the peculiar partial pressure curves reported by previous investigators. E. S. H.

Internal friction of liquid mixtures of limited miscibility. System olive oil–water. R. KREMANN, F. GRIENGL, and H. SCHREINER (Kolloid-Z., 1933, **62**, 61—66).—Measurements of the viscosity of mixtures of olive oil with H_2O, dil. HCl, and dil. NaOH show that a max. is attained at about 24% of olive oil over the region between 0·1*N*-HCl and 0·01*N*-NaOH. The max. is displaced in the direction of increasing amount of olive oil as the concn. of NaOH is increased, and reaches 75% of olive oil in presence of 0·1*N*-NaOH. The max. viscosity falls with increasing HCl content, but rises with increasing NaOH concn. up to 0·01*N*, after which it falls. E. S. H.

Relation between solubility and diffusion coefficient of gases in liquids. J. HORIUTI (Z. Elektrochem., 1933, **39**, 22—24).—Theoretical. F. L. U.

Solubility of polythionates. I. Solubility of potassium polythionates. A. KURTENACKER and W. FLUSS (Z. anorg. Chem., 1933, **210**, 125—134; cf. A., 1931, 52).—The following solubilities (wt.-%) have been determined: $K_2S_3O_6$ 8·14 at 0°, 18·43 at 20°; $K_2S_4O_6$ 12·60 at 0°, 23·18 at 20°; $K_2S_5O_6$ 15·50 at 0°, 24·78 at 20°. The solubility of binary mixtures of the salts has also been studied, and data are given for the composition of the solution in equilibrium with different solid phases. The K polythionates form neither double salts nor mixed crystals. F. L. U.

Solubility isotherms of complex metal thiocyanates. II. System sodium thiocyanate–cobalt thiocyanate–water, in relation to julienite. A. DE SWEEMER (Natuurwetensch. Tijds., 1933, **15**, 14—17).—The only compound existing at 25°, viz., $Na_2Co(CNS)_4,8H_2O$, is less sol. than the corresponding K salt, and is stable over a very wide concn. range. It separates from saturated aq. $Co(CNS)_2$ on addition of 5% of NaCNS, and from a saturated aq. NaCNS on addition of 0·5% of $Co(CNS)_2$. Julienite exhibits similar solubility relationships. The other solid phases at 25° are $NaCNS,2H_2O$ and $Co(CNS)_2,3H_2O$. H. F. G.

Solubility of lithium in liquid ammonia at low temperatures. W. C. JOHNSON and M. M. PISKUR (J. Physical Chem., 1933, **37**, 93—99).—V.p. of solutions of Li in liquid NH_3 have been determined at 0°, −32·7°, −33·2°, and −63·5°. Different, high concns. of Li were used, and the composition of the saturated solution at each temp. was obtained by extrapolation. Between −63·5° and 0° the solubility increases from 10·698 to 11·319 g. Li per 100 g. NH_3. E. S. H.

Solubility of ammonium and sodium sulphates in aqueous ammonia solutions. A. P. BELOPOLSKI and N. P. ALEKSANDROV (J. Appl. Chem., Russia, 1932, **5**, 293—298).—The yield of $(NH_4)_2SO_4$ at 0° from a solution containing 80 g. NH_3 per 100 g. H_2O is 95·5%. CH. ABS.

Raising the solubility of dyes by neutral salts. W. OSTWALD (Trans. Faraday Soc., 1933, **29**, 347—351).—The solubility of benzopurpurin 4B is increased

five-fold by the presence of 0·00001 mol. Na_2SO_4 per litre. A. G.

Supersaturation and crystallisation by the dilation method. M. R. NAYAR (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 100—103).—The supersaturation of salt solutions has been investigated by a dilatometric method. Unless the solubility varies considerably with the temp. there is no tendency to form supersaturated solutions. J. W. S.

Extraction of solutions. A. F. HOLLEMAN (Chem. Weekblad, 1932, **29**, 762).—A brief mathematical treatment. H. F. G.

Hydration of various electrolytes, determined by the partition of an aliphatic acid between benzene and water. E. ANGELESCU and O. DUTCHIEVICI (Bul. Soc. Chim. Romania, 1932, **14**, 46—52).—The degrees of hydration of Na and K chlorides, bromides, and nitrates, calc. from the partition of $PrCO_2H$ between C_6H_6 and *N* aq. solutions, are in close agreement with the results obtained by other methods. H. F. G.

Distribution of silver and sodium between glass and nitrate or bromide melts at equilibrium. A. GUNTHER-SCHULZE and O. MOHR (Z. tech. Physik, 1932, **13**, 356—358; Chem. Zentr., 1932, ii, 2139).—By repeated treatment of the glass with $AgNO_3$ all the Na in the glass can be replaced by Ag. $NaNO_3$ melts containing moderate amounts of Ag can be almost completely freed from Ag by a single treatment with glass powder. With bromide melts the passage of Ag into glass can be almost completely suppressed by small quantities of NaBr. In electrolysis, only Na passes into the glass until this process is complete, transference of Ag commencing thereafter. A. A. E.

Absorption of gases and vapours by active carbon and silica gel. P. DEMOUGIN (Mém. Poudres, 1932—1933, **25**, 18—90).—Comparative vals. are given for the adsorption of various gases and vapours by SiO_2 gel and by C activated by various methods. The activation of C appears to depend in all cases on the entrainment of tarry matter by H_2O vapour evolved during the process; continuous evolution of H_2O may be effected by oxidation of part of the C, by injection of H_2O vapour, or by impregnating the C before heating with $ZnCl_2$, H_3PO_4, etc. Theories of adsorption are discussed. H. F. G.

Tensimetric investigations of the behaviour of some charcoals towards sulphur. R. JUZA and W. BLANKE (Z. anorg. Chem., 1933, **210**, 81—92).—The behaviour of several forms of C towards S vapour under different conditions of temp. and pressure indicates that in the case of graphite and gas C the main effect is capillary condensation; surface adsorption is predominant with technical active C, whilst both these processes as well as chemosorption and dissolution occur with sugar C. E. S. H.

Determination of adsorptive power of activated charcoal for methylene-blue and iodine from aqueous solutions. E. ERDHEIM (Rocz. Chem., 1932, **12**, 888—895).—A standard method and apparatus are described. R. T.

Sorption of water vapour by glass. E. P. BARRETT and A. W. GAUGER (J. Physical Chem., 1933, **37**, 47—51).—A test of the rectilinear character of the logarithmic form of the sorption isotherm for the system H_2O vapour–glass with R.H.$=10^{-3}$ to 3×10^{-2} gave results agreeing with those of Frank (A., 1929, 1000). The isotherm may be extrapolated to include pressures of the next higher order of magnitude. E. S. H.

Determination of [sorption] isothermals by the retentivity technique. L. J. BURRAGE (J. Physical Chem., 1933, **37**, 33—39).—Improved technique is described. Good agreement with the static technique is obtained, the chief difference being the rate of attainment of equilibrium. When disturbing factors are absent, the isothermals consist of a series of rectangular steps. E. S. H.

Discontinuities in the sorption process. L. J. BURRAGE (J. Physical Chem., 1933, **37**, 41—45; cf. preceding abstract).—Experiments with C show that the sorption isothermals consist of series of rectangular steps similar to the desorption isothermals. E. S. H.

Thermodynamics of adsorption at the surface of solutions. E. A. GUGGENHEIM and N. K. ADAM (Proc. Roy. Soc., 1933, **A**, **139**, 218—236).—The usual convention adopted in fixing Gibbs' geometrical dividing surface, in which the surface excess $\Gamma_1^{(1)}$ of one of the components is arbitrarily taken as zero, is criticised as being inconvenient in forming a physical conception of the surface. A no. of other conventions have been examined and the relations between the vals. of Γ obtained from these are derived from Gibbs' general equations. The structure of the surface of H_2O–EtOH mixtures is calc. on the assumption that the inhomogeneous layer does not extend beyond the first layer of mols. L. L. B.

Separation of traces of substances on precipitates during crystallisation. R. MUMBRAUER (Z. physikal. Chem., 1933, **163**, 142—154).—The coppttn. of Th-*B* and Th-*X* with Ag_2SO_4, $Ag_2C_2O_4$, Ag_2CrO_4, and $PbCrO_4$ has been investigated. The adsorption of foreign ions largely turns on the case of their displacement by the legitimate ions of the lattice. This is determined by the rate of crystallisation, the solubility of the adsorption compound, the sizes of the ions, and the polarising influence of the foreign ions on the oppositely-charged ions of the lattice. If the adsorption compound has a very small solubility, foreign polarising ions may be adsorbed, despite Hahn's adsorption rule, even when their charge has the same sign as that of the lattice. R. C.

Effect of adsorption layers on disperse systems. III. Effect of surface-active substances on crystallisation processes in Liesegang rings. N. SERB-SERBINA (Kolloid-Z., 1933, **62**, 79—85; cf. A., 1931, 34).—The secondary periodicity frequently noticed in the formation of Liesegang rings by the usual method is attributed to the pptn. of Ag_2CrO_4 in place of $Ag_2Cr_2O_7$ under certain conditions. Further experiments are described on the formation of periodic structures of PbI_2 and Ag salts of fatty acids. Surface-active substances of simple mol. type (alcohols, amines,

phenols) or hydrophilic colloids (gelatin, saponin) alter the dispersity of the ppt., the cryst. form, and the velocity of crystallisation, and reduce the distance between the rings. These effects are attributed to changes in the degree of supersaturation. E. S. H.

Passage of substances undergoing adsorption through the adsorbent layer. M. M. DUBININ, V. ANDREEV, O. MILEKHINA, G. PETROV, and S. TOROPOV (J. Appl. Chem., Russia, 1932, **5**, 413—424).—The use of various indicators for determining the saturation of adsorbents is described. CH. ABS.

Adsorption and moistening phenomena in technology and biology. E. BERL and B. SCHMITT (Naturwiss., 1932, **20**, 943—944).—The nature of flotation in its application to biological processes is discussed. Biologically active substances may be hydrophilic or hydrophobic. Poisons, narcotics, hormones, and vitamins possess a definite arrangement of hydrophilic and hydrophobic groups, and can be taken up only by certain parts of the organism. A. J. M.

Interfacial activity and orientation of polar molecules. IX. Applicability of Antonov's rule, especially to adsorption layers. A. TAUBMANN (Kolloid-Z., 1933, **62**, 76—77; cf. A., 1932, 992).—Data for the surface tensions and interfacial tensions of *iso*amyl alcohol, oleic acid, vaseline oil, and solutions of *p*-toluidine in C_6H_6 or hexane against H_2O are not in accordance with Antonov's rule. Addition of KOH (2—4%) raises the interfacial tension at a C_6H_6–H_2O boundary. E. S. H.

Instability of thick films of insoluble oils on water. C. G. P. FEACHEM and E. K. RIDEAL (Trans. Faraday Soc., 1933, **29**, 409—415).—The breaking up into drops of a thick film of oleic acid on H_2O is described. By counting and measurement it is found that each drop contains the excess oil in the area of the film which it occupies, that large drops increase at the expense of small drops which have a larger spreading pressure, and that the smallest drops observed are about 10 times as large as the smallest deduced theoretically from potential energy considerations. It is also shown, however, that, if the latter were formed, they would have a life of about 0·33 sec. M. S. B.

Surface films of cellulose derivatives on aqueous solutions. N. K. ADAM (Trans. Faraday Soc., 1933, **29**, 90—106).—Measurements are recorded of the surface pressure and area of films of the Me, Et, and Bz ethers of cellulose and of cellulose nitrates, acetates, and esters of other fatty acids containing up to 18 C atoms on H_2O and on 2*N*-NaOH; the ultramicroscopic appearance of the films is also described. The esters spread incompletely on H_2O, but completely on 2*N*-NaOH, but the nitrates containing $>12{\cdot}6\%$ N are exceptional. In other cases spreading occurs until the films are one glucose unit thick, from which it appears that the chains lie flat on the surface. The pressure–area curves are generally similar, with slight variations due to the size of substituent groups. At low pressures there is a gradual or rapid approach to the line of zero pressure. The chains may be vibrating vigorously in the plane of the surface. Chains of different derivatives differ in their adhesion to H_2O and in the adhesion between chains. The areas occupied by films of common plasticisers are greatly reduced by the addition of cellulose CH_2Ph ether or nitrate which impede the movement of the mols. of the plasticiser. A. G.

Electrical and mechanical properties of protein films. A. H. HUGHES (Trans. Faraday Soc., 1933, **29**, 211—216).—Films of gliadin, glutenin, and ovalbumin gelatinise at surface concns. of $1{\cdot}4\times10^{-7}$ g. per sq. cm. The surface potentials indicate that gliadin contains a larger proportion of polar side-chains than the other two. Surfaces of gelatin sols become rigid 2—3° above the setting point of the bulk of the sol. A. G.

Surface potentials of unimolecular films of ergosterol. Photochemical formation of vitamin-*D*. R. J. FOSBINDER.—See this vol., 325.

Spreading of liquids on solid surfaces. Anomalous behaviour of fatty oils and fatty acids with experiments leading to a tentative explanation. R. BULKLEY and G. H. S. SNYDER (J. Amer. Chem. Soc., 1933, **55**, 194—208).—The interfacial tension between metals and fatty oils and fatty acids is $<$ that between metals and petroleum oils. It is found, however, that fatty oils and fatty acids spread little or not at all, whilst mineral oils spread apparently without limit on clean polished steel, Cd, Pt, and mica. The higher fatty acids do not "wet" the surfaces, but roll about freely, depositing on the surface an adsorbed film which reduces the surface energy to a low val. Thin layers of mineral oil containing fatty acids rupture spontaneously on metal surfaces owing to the formation of an underlying film of low surface energy on which the thin layers are unstable. The fact that fatty oils and acids do not spread on metal surfaces is due to the decrease in surface energy of the metal in advance of the spreading layer as a result of the breaking away of an expanding ring or by the condensation of vapours. J. G. A. G.

Linear phenomena. I. Linear wetting and linear adsorption. Micellar weight and micellar dimensions of lyophilic colloids. D. L. TALMUD, B. A. TALMUD, and S. E. BRESLER (Z. physikal. Chem., 1933, **163**, 91—106; cf. A., 1931, 1228).—The conditions for linear wetting, *i.e.*, the spreading of an added substance along the boundary line between three phases, have been theoretically deduced. Quant. determinations of linear adsorption have been made by adding the linear active substance to the surface of a solution of a lyophilic colloid or to an unsaturated film of an insol. surface-active colloid, when it forms a unimol. adsorbed thread along the micelle–H_2O–air boundary line and thus renders the micelles insol., so that they exert a surface pressure which may be measured by Langmuir's trough apparatus. The linear adsorption of cetyl alcohol and $C_{30}H_{62}$ on the surface of tannin solutions, of cetyl alcohol on agar-agar solutions, and of myristic acid and cetyl alcohol on unsaturated films of ethylcellulose has been examined. The adsorption data may be used to calculate the mean diameter and wt. of the micelles

of lyophilic colloids. The mol. wt. of tannin micelles is found to be about 500, and mean diameter 9·5 Å. R. C.

Dependence of wettability of solid substances on the time of contact. A. POCKELS (Kolloid-Z., 1933, **62**, 1—2).—Many org. substances, glass, porcelain, Ag, Sn, and Pt, which are not normally wetted by H_2O, are wetted when left in contact with H_2O for several days. After exposure to air for an equal time this property is lost. An orientation of surface mols. in the org. compounds is inferred, whilst the behaviour of metals is attributed to the formation of an adsorption layer in air, which is removed slowly by H_2O. E. S. H.

Bubble formation in glass tubes. W. B. MANN and R. W. B. STEPHENS (Phil. Mag., 1933, [vii], **15**, 143—146).—The production of bubbles with Fleuss oil, soap, and saponin films is described. H. J. E.

Influence of disturbing factors and temperature on liquid droplets formed at the surface of the same liquid. L. D. MAHAJAN (Z. Physik, 1932, **79**, 389—393).—The factors considered are: impurities at the surface of the mother liquid, impurities in this liquid, impurities in the surrounding medium, electric charge, and temp. A. B. D. C.

Dried collodion membranes. L. MICHAELIS (Kolloid-Z., 1933, **62**, 2—10).—A lecture, describing the determination of the porosity of collodion membranes by measuring the p.d. between two solutions separated by the membrane. E. S. H.

Properties of collodion membranes from different cellulose nitrates. W. LINNHOFF (Kolloid-Z., 1933, **62**, 10—13).—Directions are given for the prep. of collodion membranes which are impermeable to proteins, but permeable to H_2O and simple electrolytes, and thus suitable for osmotic pressure measurements. E. S. H.

Harmonic concentration differences at a membrane. J. STAUB (Kolloid-Z., 1933, **62**, 13—15).—Examples are given and speculations are advanced. E. S. H.

Appearance of stationary concentrations between two membranes. J. P. WERRE (Kolloid-Z., 1933, **62**, 16—20).—Theoretical. E. S. H.

Properties of Becquerel membranes. J. J. BIKERMAN (Kolloid-Z., 1933, **62**, 26—31).—When a cracked test-tube, containing conc. $AgNO_3$ solution, is immersed in aq. Na_2S diffusion occurs through the crack and a film of Ag is formed, polysulphide being produced in the Na_2S solution. The explanation is that an electric current flows between the solutions through the primarily formed Ag_2S membrane. The membrane has unidirectional properties; it is permeable to cations in one direction and to anions in the other. E. S. H.

Explanation of membrane processes (Becquerel phenomenon, negative osmosis, abnormal permeability, etc.). K. SOLLNER (Kolloid-Z., 1933, **62**, 31—37).—A lecture. E. S. H.

Simple test for streaming in the porons diaphragm diffusion cell. C. R. DAWSON (J. Amer. Chem. Soc., 1933, **55**, 432—433).—If the pores are coarse, the diffusion is increased several fold by tilting the cell. J. G. A. G.

Depression of m.p. of *r-iso*borneol, *l*-borneol, *d*-camphoroxime [and bornyl methylxanthate] by various substances. T. S. PATTERSON, (MISS) J. H. BLACKWOOD, and J. M. STEWART (J.C.S., 1933, 93—95).—*r-iso*Borneol has m.p. 212°, K 462. *l*-Borneol has m.p. 207·8°, K 355. K for *d*-camphoroxime, m.p. 119·6°, falls from 1000 for c=0·5 to 170 for c=10%. Bornyl methylxanthate shows no appreciable depression when 10% of o-$C_6H_4Cl{\cdot}CO_2H$ or NHAcPh is added. D. R. D.

Cryoscopic study of paraldehyde, ether, and acetone in solutions of sodium acetate. (MLLE.) O. HUN (Compt. rend., 1933, **196**, 177—178; cf. A., 1932, 804).—Further f.-p. data are recorded. Paraldehyde shows a tendency to polymerisation. C. A. S.

Motion of suspended particles in glycerol and in water. J. H. SMITH (Phil. Mag., 1933, [vii], **15**, 15—19; cf. A., 1930, 697).—The cloud effects which are observed when suspended particles are illuminated have been previously attributed to photophoresis, but are now shown to be due to slow eddy currents. Similar boundaries are produced by transversely heating pure glycerol. H. J. E.

Sedimentation equilibrium in the ultracentrifuge. Types obtained with soap solutions. J. W. MCBAIN and M. E. L. MCBAIN (Proc. Roy. Soc., 1933, **A**, **139**, 26—37).—The sedimentation equilibrium of charged colloids and of electrolytes is discussed. Experiments with soap solutions in Svedberg's oil turbine ultra-centrifuge have led to the observation of a new type of sedimentation equilibrium ("snowfall equilibrium"), in which a dynamic balance is maintained between the rapid sedimentation of neutral micelle and its continued formation in the more dil. regions, and its continued resolution into simpler forms in the more conc. regions. Cases are described in which sedimentation is: (1) wholly downwards (with $0{\cdot}5N_w$-$C_{11}H_{23}{\cdot}CO_2K$), (2) wholly upwards (with $0{\cdot}25N_w$-$C_{17}H_{33}{\cdot}CO_2Na$), and (3) both upwards and downwards (with $0{\cdot}5N_w$-$C_{11}H_{23}{\cdot}SO_3H$, and also with $0{\cdot}5N_w$-$C_{11}H_{23}{\cdot}CO_2K$ containing $1{\cdot}0N_w$-KCl). The results of the third type confirm the independent existence of neutral micelle and ionic micelle in soap solutions, the former rising to the top and the latter sinking to the bottom. L. L. B.

Measurement of migration velocity of colloid particles. W. HACKER (Kolloid-Z., 1933, **62**, 37—42).—Difficulties in the existing methods of studying electrophoresis by macro-methods are discussed. In a procedure designed to eliminate these, the sol is covered by an overlayer liquid, which contains the electrolyte which is also present in the intermicellar liquid. E. S. H.

Measurement of migration velocity of gold micellar ions by observation of the moving bondary. W. HACKER (Kolloid-Z., 1933, **62**, 66—76).—A method is devised by which the electrophoresis of Au sols can be measured simultaneously by observing the rate of movement of the boundary

and by determining the amount of Au transported. The results of the two methods are in agreement. The moving-boundary method gives correct vals. when the intermicellar liquid is used as the overlayer. E. S. H.

Photophoresis of silver particles. A. LUSTIG and A. SOLLNER (Z. Physik, 1932, **79**, 823—842).—Ag particles which are mechanically equiv. according to Karman's criterion show positive, negative, or zero photophoretic activity. A. B. D. C.

Electrophoretic effect of the concentration effect. J. SCHIELE (Physikal. Z., 1933, **34**, 61—64).—Quant. experiments are described to show the connexion between the potential effect and the Debye–Onsager concn. effect. For all the salts investigated the relaxation and the electrophoresis are increased by the potential effect. The theoretical concn. effect was never quite reached, as the limiting vals. could not be measured for any of the electrolytes used. A. J. M.

Electrokinetic phenomena in liquid carbon dioxide. A. CUKIERMAN (Spraw. Prace Polsk. Towarz. Ficyz., 1930, **5**, 1—15; Chem. Zentr., 1932, ii, 2302).—With liquid CO_2, streaming potentials are observed only at pressures which give rise to turbulence; with PhMe no effect is observed. Perrin's theory is supported. A. A. E.

Rhythmic crystallisation due to diffusion of alkali carbonates in gelatin. (MLLE.) S. VÉIL (Compt. rend., 1933, **196**, 109—110).—A drop of conc. aq. Na_2CO_3 or K_2CO_3 placed on a film of gelatin on glass diffuses outwards with the formation first of microscopic and then of visible concentric layers. Li_2CO_3 behaves similarly but less distinctly; $(NH_4)_2CO_3$ gives only a blurred effect (cf. A., 1920, ii, 169). C. A. S.

Periodic structures. Liesegang phenomenon. M. F. TABOURY and SALVINIEN (Bull. Soc. chim., 1932, [iv], **51**, 1340—1345).—In the system aq. $AgNO_3$–$K_2Cr_2O_7$ in gelatin, no rings are formed if the gelatin is pure or contains only SO_4'', but if ions are present which form insol. Ag salts (Cl′, Br′, I′, CN′) rings are produced. The influence of an electric current on the form and spacing of the rings is such as would be expected from its effect on the velocity of diffusion of the ions and the fact that the Ag_2CrO_4 bears a positive charge. A magnetic field produces no appreciable deformation. The formation of spirals is due to foreign bodies (*e.g.*, air bubbles). D. R. D.

Periodic precipitation of mercuric iodide. (MLLE.) S. VEIL (Compt. rend., 1933, **196**, 266—268).—When a drop of aq. KI is placed on gelatin impregnated with $HgCl_2$, microscopic rings, first yellow, then red, are formed which increase in width with increasing distance from the centre; there is a clear space between the drop and the first ring. C. A. S.

Effect of Brownian motion on viscosity of suspensions. R. EISENSCHITZ (Z. physikal. Chem., 1933, **163**, 133—141).—An equation for the viscosity of a suspension of ellipsoidal particles, which takes into account the Brownian motion, has been derived from hydrodynamical considerations. R. C.

Method for determining diffusion constants of colloids which show mechanical birefringence. P. BOEDER (J. Rheology, 1932. **3**, 494—500).—The statistical equilibrium between the orientation of non-spherical particles due to flow and the disorienting effect of the Brownian movement is determined by an optical method and leads to a val. for the diffusion const. Experiments with solutions of cotton-yellow yield results in accordance with theory. E. S. H.

Theory of the structure of colloidal systems. H. KALLMANN and M. WILLSTATTER (Naturwiss., 1932, **20**, 952—953).—Under certain conditions the coagulated particles are not in direct contact, but are separated by a layer of H_2O some hundreds of a mol. thick. The forces then acting between the colloidal particles are van der Waals forces. A. J. M.

Prussian-blue hydrosols. E. L. LEDERER [with O. HARTLEB] (Kolloid-Z., 1933, **62**, 42—46).—Sols of Prussian-blue are decolorised and coagulated by heating and by irradiation with visible or ultra-violet light, or β-particles, but not with α-particles, γ- or *X*-rays. The absorption spectrum has been measured between 460 and 226 mμ; Beer's law holds at concns. $< 0{\cdot}02\%$. The time required for coagulation by light is proportional to the concn. and the thickness of the layer of sol, and is reduced by the presence of electrolytes. An optimum effect is exerted by light of wave-length 420 mμ. E. S. H.

Preparation of colloids by ultrasonic dispersion. N. MARINESCO (Compt. rend., 1933, **196**, 346—348; cf. A., 1932, 693).—Sols of gamboge, mastic, or white P in H_2O, of low m.-p. alloys or Hg in H_2O, an alcohol, or glycerol, and of Na, K, or Cs in petrol or vaseline oil, are obtainable at room temp. by exposing the surface in contact with H_2O etc. to ultrasonic waves. With metals of high m.p., *e.g.*, Pb, Sn, Zn, or Cu, particles of ionic dimensions are formed. Photomicrographs of many such sols are given. C. A. S.

Determination of colloid osmotic pressure in small quantities of fluid. R. M. HILL (J. Biol. Chem., 1933, **99**, 323—325).—The Krogh and Nakagawa osmometer (A., 1927, 1104) has been adapted to measure the colloid osmotic pressure of 0·3 c.c. of fluid. H. G. R.

Physical properties of concentrated hydroxide sols. N. R. DHAR and R. N. MITTRA (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 60—64).—Conc. sols of $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$ have been prepared. The first two only are coagulated by KCl. The coagulation concn. of the KCl increases with dilution of the sols. The former shows periodicity in coagulation. The viscosities of the conc. sols are very high and vary logarithmically with the concn. The sols can be dried and again peptised in cold H_2O. Thus their behaviour is more like that of lyophilic than of lyophobic sols. J. W. S.

Structural properties of anisotropic solutions of soap as determined by a new centrifugal falling ball method. J. W. MCBAIN and O. O. WATTS (J. Rheology, 1932, **3**, 437—460).—A centrifugal ball

plastometer is described. The viscosities of the conical anisotropic liquid phases, middle soap and neat soap, have been determined. Relative viscosities of 10^6 to 10^{10} are recorded. E. S. H.

New conception of certain colloidal [aluminium] oxides. A. H. THOMAS (J. Amer. Leather Chem. Assoc., 1933, **28**, 2—24).—The diminished solubility in dil. acid of $Al(OH)_3$ after it has been heated or left for some time is explained by "olation" and "oxolation." Oxyiodide sols and also $Al(OH)Cl_2$ sols show differences in behaviour on the addition of KCl. The p_H of $AlCl_3$ solutions is increased by K_2SO_4, the effect increasing with the basicity of the $AlCl_3$ solution. The order of the anions when arranged according to the readiness with which they enter the Al complex is the same as for Cr complexes. Evidence for this is afforded by conductimetric titrations of $Al(OH)I_2$ sols to which varying amounts of $AgNO_3$, Ag_2SO_4, AgOAc, and Ag tartrate have been added. A two-dimensional structural formula for $Al_2O_3,4H_2O$ is suggested. D. W.

Dye sols. IV. Colour change of Congo acid sol on heating. R. TANAKA (J. Soc. Chem. Ind. Japan, 1932, **35**, 547B; cf. A., 1931, 37, 426).—The change from blue to red is more marked in less conc. solutions, but the return of the blue colour on cooling occurs most rapidly in conc. solution. On evaporating and drying the sol a red to bluish-black residue remains which can be peptised by H_2O, giving a red solution. The phenomena are explained by the increased dispersion of the colloidal particles on heating, the formation of polydisperse systems, and by the increased activity of the heated particles. A colour change from violet to reddish-violet is also observed when a dil. aq. solution of sulphocyanin 5R is heated. J. W. S.

Flocculation values for arsenic sulphide sol. D. N. GHOSH (J. Indian Chem. Soc., 1932, **9**, 591—597).—Flocculation vals. for an As_2S_3 sol have been determined for the earlier stages of coagulation by measurement of the rate of change of the intensity of scattered light which is assumed to be proportional to the rate of growth of the particles. A. S. C. L.

Cause of thixotropy. P. BARY (Compt. rend., 1933, **196**, 183—184).—The Fe_2O_3 in a ferric oxide sol occurs partly in the form of hydrophobic granules and partly as a hydrated hydrophilic colloid which forms filaments on evaporation (cf. A., 1928, 705, 1186). It is suggested that the latter consist of Fe_2O_3 polymerised in polar chains the poles of which attach themselves to the granules, thus immobilising the solution and causing thixotropy. Calculation shows this to be at least qualitatively possible. C. A. S.

Sensitisation of stannic hydroxide sol by silicic acid sol. S. GHOSH and N. R. DHAR (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 39—42).—The p_H vals. of mixtures of $Sn(OH)_4$ and SiO_2 sols have been studied with reference to the coagulation of their mixtures. $Sn(OH)_4$ sol is acid (p_H 4·95) and SiO_2 sol alkaline (p_H 8·8) and max. sensitisation occurs at about p_H 7·10. The sensitisation of one sol by another of the same charge is said to be due to the removal of the stabilising ions by mutual reaction. J. W. S.

Movements and precipitations of an amphoteric colloid due to an electric field and slight electrolysis. Modified Hardy's experiment suitable for demonstration purposes. W. J. PENFOLD and J. SUTHERLAND (Biochem. J., 1932, **26**, 1839—1842).—The gelatin-protected Ag colloid is introduced between two chemically clean lantern slides kept 0·03 mm. apart by the insertion of Pt foil electrodes at the opposite sides of the cell. S. S. Z.

Measurements on the concentration and dispersity of suspensions by the photo-electric cell. I, II. M. MATSUI, T. NODA, S. KAMBARA, and S. OYAMADA (J. Soc. Chem. Ind. Japan, 1932, **35**, 569—574B, 575—577B).—I. Dispersions of $CaCO_3$, kaolin, $MgCO_3$, $Mg(OH)_2$, Al_2O_3, and Fe_2O_3 show a linear relation between the concn. and the extinction coeff.

II. The extinction method can be applied to the determination of insol. matter in commercial NaCl, Na_2CO_3, etc. An apparatus suitable for commercial use is described. J. W. S.

Hysteresis in the sol–gel transformation of agar sols. S. GHOSH (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 12—18; cf. A., 1931, 166).—With increase of concn. the hysteresis in the sol–gel transition of agar first decreases, passes through a min., and then increases, the effect being much > with gelatin. The change of viscosity with time is also much slower with agar sol than with gelatin. Inoculation of agar sols with gels of the same temp. and concn. accelerates gelation, the process being analogous to the seeding of a supersaturated solution. The extinction coeff. of 1% agar sol at 6000 Å. remains unchanged during gelation and there appears to be very little change in the no., size, or structure of the colloidal particles during setting. A mechanism of gelation brought about by slow orientation is suggested. J. W. S.

Dependence of osmotic pressure and micellar weight of gelatin solutions on the temperature and previous history of the solution. J. EGGERT and H. BINGER (Biochem. Z., 1932, **256**, 239—240; cf. Frankel, A., 1932, 995).—Frankel's views are criticised on the ground that no account is taken of the influence of temp. on solvation pressure and no distinction made between the phenomena of solvation and those of aggregation. W. McC.

Influence of the amount of impurity in gelatin on the density of Liesegang's rings. Jablczinsky's relation. M. F. TABOURY and R. ECHARD (Bull. Soc. chim., 1932, [iv], **51**, 1377—1381).—After removal of all sol. impurities from gelatin and subsequent addition of 1, 2, and 3 g., respectively, of KBr per litre, Ag_2CrO_4 rings were allowed to form and the diameters of the rings obtained in each case were measured. The no. of rings of diameter < any given val., *i.e.*, the density of the rings, increases with the concn. of KBr. The results are in agreement with Jablczinsky's relation expressed in its

general form $(R_n - R_0) = q^{n-1}$, R_n being the radius of the nth ring counting from the centre. M. S. B.

Ageing phenomenon in gelatin layers and its prevention. R. O. Herzog and F. Koref (Kolloid-Z., 1933, **62**, 91—92).—Thin films of gelatin on cellulose nitrate acquire a horny surface on keeping and lose their power to swell in H_2O. The original properties are restored by soaking the film in 3—5% pancreatin solution for 15—30 min. E. S. H.

Influence of lyotropic substances on the mutarotation and gelatinisation of gelatin–water mixtures. J. R. Katz and J. F. Wienhoven (Rec. trav. chim., 1933, **52**, 36—46).—The influence of CNS′, I′, NO_3′, Br′, Cl′, SO_4'', and F′, and of a no. of org. compounds on the mutarotation of 3% aq. gelatin has been studied. Reduction of the ratio $[\alpha]_D^t/[\alpha]_D$ from its normal val. is closely parallel with reduction of gelatinising power. Among non-electrolytes the most effective are those which most strongly reduce the surface tension of water, and among electrolytes those which are most strongly adsorbed at a solution–Hg interface. The observations are discussed theoretically. F. L. U.

Inhibition of the alcoholic precipitation of proteins by alkalis. L. Nasch (Kolloid-Z., 1933, **62**, 93—97).—Experiments on the addition of EtOH to protein sols in presence of 0·2*N*-NaOH indicate that a definite amount of NaOH is required to protect a given amount of protein from coagulation by the EtOH. This is shown very clearly by the albumins, whilst the globulins conform only in dil. solution and when the EtOH concn. is < 33%. E. S. H.

Soya-bean paste as an emulsifying agent. A. M. Field, B. H. Alexander, and E. B. Sylvanus (Science, 1933, **77**, 91).—The proteins of the soya-bean and not the lecithin appear to be the chief stabilising factor. L. S. T.

Physico-chemical properties of the crystallised hæmocyanin of the snail. J. Roche (Compt. rend. Soc. Biol., 1931, **107**, 1146—1148; Chem. Zentr., 1932, ii, 2325).—Hæmocyanin of *Limulus* has a higher isoelectric point and a greater acid-combining power than that of the snail or jellyfish, which have the same isoelectric point and solubility but are distinguished by their neutralisation curves. A. A. E.

Union of biocolloids. XIII. Two- and three-component systems. S. J. von Pryzlecki and M. L. Grynberg (Biochem. Z., 1932, **256**, 75—99).—The influence of p_H, polysaccharides, nucleosides, and salts on the combination between ovalbumin gel and various protein sols (hæmoglobin, serum-albumin, ovalbumin, glutin) has been studied. H. W. D.

Physico-chemical studies of lipins in their relations to salts, drugs, and proteins. M. Spiegel-Adolf (Biochem. J., 1932, **26**, 2183—2190).—In an electrolyte-free medium the addition of lecithin (I) to proteins does not produce flocculation. If there is an excess of salt no changes can be detected by the interferometer. Between the two extremes there are salt concns. at which additions of (I) cause a decrease of the refractive index of the mixture. For sols of (I) of a given age, different concns. of neutral salts are required to avoid flocculation by the same amount of serum-albumin (II) or pseudoglobulin (III). In mixtures containing both kinds of proteins with just sufficient salt to prevent flocculation by (II), the (II)–neutral salt compound inhibits to some degree the flocculating power of (III), the final effect depending on the (II)/(III) ratio. S. S. Z.

Viscosity investigations for the examination of the constitution of natural products of high molecular weight and of rubber and cellulose. H. Staudinger (Trans. Faraday Soc., 1933, **29**, 18—32).—Measurements of the viscosities of solutions sufficiently dil. to allow each long-chain mol. room for free rotation give the following vals. for the nos. of structural units per mol.: caoutchouc 1800, balata 750, cellulose 750, cellulose triacetate 360. A. G.

Shaking effect in cellulose solutions and other sols detected by means of Tyndall light. R. O. Herzog, O. Kratky, and E. Petertil (Trans. Faraday Soc., 1933, **29**, 60—64).—The angle of depolarisation of Tyndall light from solutions of cellulose acetate, ethylcellulose, polystyrenes, polyvinyl acetate, and other colloids increases when these are shaken with air, and decreases asymptotically to its initial val. on keeping. The effect depends on the concn. and mol. wt. of the solute and on the nature of the solvent; for the upper layers of the solution it is > for the lower layers. A. G.

Structure of xerogels of cellulose and derivatives. S. E. Sheppard (Trans. Faraday Soc., 1933, **29**, 77—85).—Probably about 5% H_2O can combine with the OH groups on the surface of cellulose micelles, the rest of the H_2O being in capillary spaces. Sorption of H_2O by combination with OH is diminished by esterification or etherification of the OH, and sorption in capillaries is diminished by incorporating non-solvent liquids and by esterifying with acids of high mol. wt. Molar sorption of primary alcohols falls with increasing mol. wt. to a const. val. for alcohols with > 3 C atoms, and it is assumed that the mols. of such alcohols are too large to penetrate capillaries. Diffusion of H_2O vapour into films of cellulose esters obeys Fick's law after an initial period of 1—1·5 hr. Isotropic films of cellulose esters can be obtained by evaporating the solutions on a Hg surface. When dried on a solid surface the film is uniaxial, and if it is then swollen and dried while stretched in one direction it is biaxial. A. G.

Protein structure and protein hydration. D. J. Lloyd and H. Philips (Trans. Faraday Soc., 1933, **29**, 132—146).—Hydration of proteins in H_2O is due to co-ordination of H_2O with OH, CO_2H, NH_2, $CO{\cdot}NH_2$, NH, and CO groups. The side-chains of sol. proteins contain large proportions of these groups. Acid-sol. proteins contain lysine, arginine, and histidine, and alkali-sol. proteins contain aspartic and glutamic acids. In acids, alkalis, and, to a smaller extent, in neutral salts hydration is increased owing to the great difference in size and valency of the ions. If the protein ions are not freely diffusible, hydration is also affected by the Donnan equilibrium. The closeness of packing of protein chains depends on the

nature of the side groups, and this affects the solubility and hydration. Generally the more hydrated and biologically active proteins contain larger proportions of side groups with an affinity for H_2O. A. G.

Constitution of the keratin molecule. J. B. SPEAKMAN and M. C. HIRST (Trans. Faraday Soc., 1933, **29**, 148—165).—The work required to stretch a wet wool fibre is const. between p_H 4 and 8 but diminishes at lower and higher p_H. At the same p_H weak acids have more effect than strong acids owing to the increased swelling due to the Donnan equilibrium effect. Swelling is not the primary cause of increased ease of extension, as this is unaffected when the swelling is reduced by the addition of NaCl. In presence of NaCl the p_H inside the fibre is nearly the same as that outside, and the stability (isoelectric) region is reduced to p_H 5—7. Diazotising diminishes the work of extension. The max. amount of acid absorbed by wool is 80 m.-equiv. per 100 g. at p_H 1, and this is approx. equiv. to the free NH_2 groups in arginine, lysine, and histidine. In the normal keratin mol. these form cross linkings of the type $R{\cdot}NH_3{\cdot}CO_2R'_2$ with the CO_2H groups of glutamic and aspartic acids, and the action of acids and alkalis is to break these linkings. Each combination of basic and acid groups has its own isoelectric point, and the resultant of these six points constitutes the isoelectric region of p_H 5—7. A. G.

Laws of swelling. J. R. KATZ (Trans. Faraday Soc., 1933, **29**, 279—297).—A review. A. G.

Swelling of silk. W. S. DENHAM and E. DICKINSON (Trans. Faraday Soc., 1933, **29**, 300—305).—Measurements of the swelling of silk filaments in various buffered and unbuffered solutions showed min. at p_H 1·4, 2·8, 3·8, and 4·7. The diameter in air increases with increasing R.H., and when hairs are taken through a cyclic change hysteresis is observed.

Application of the van 't Hoff–Le Chatelier–Braun principle to chemical equilibria. K. POSTHUMUS (Rec. trav. chim., 1933, **52**, 25—35).—The conditions under which the principle is valid for the addition of one of the components of a system in homogeneous equilibrium are deduced from the second law of thermodynamics. When the system N_2–H_2–NH_3 contains (at equilibrium) $>$ 50% N_2, further addition of the latter causes a decrease in the total amount of NH_3. F. L. U.

Thermodynamic treatment of chemical equilibria in systems composed of real gases. II. Relation for the heat of reaction applied to the ammonia synthesis reaction. Energy and entropy constants of ammonia. A correction. L. J. GILLESPIE and J. A. BEATTIE (Physical Rev., 1931, [ii], **37**, 655).—Cf. A., 1930, 1508. L. S. T.

Dissociation of oxygen to 5000° abs. Free energy of atomic oxygen. H. L. JOHNSTON and M. K. WALKER (J. Amer. Chem. Soc., 1933, **55**, 187—193).—From spectroscopic data, the "free energy" of at. O and the degree of dissociation of mol. O_2 are computed for the range 298—5000° abs. Dissociation is about 1% at 2500—2600° abs. and 96·6% at 5000° abs. J. G. A. G.

Equilibrium constants of the component reactions in the decomposition of hydrogen sulphide by steam in the interval 350—900°. E. TERRES and H. WESEMANN (Angew. Chem., 1932, **45**, 795—802).—The reaction $CO_2+H_2S \rightleftharpoons COS+H_2O$ at a kaolin surface has been investigated at 350—600°; the equilibrium const. rises from $5{\cdot}61\times10^{-3}$ at 400° to $23{\cdot}1\times10^{-3}$ at 600°, the mean heat effect being 8522 g.-cal. At higher temp. decomp. of the COS into CO and S becomes marked, and increasing quantities of CS_2 are formed. The equilibrium const. of the reaction $COS+H_2S \rightleftharpoons CS_2+H_2O$ rises from $3{\cdot}98\times10^{-3}$ at 700° to $10{\cdot}8\times10^{-3}$ at 900°, the heat effect being 13·9 kg.-cal. The equilibrium const. of the reaction $2H_2O+CS_2 \rightleftharpoons 2H_2S+CO_2$ is calc. for the interval 20—1000°. If steam and CS_2 react at about 800°, H_2S and CO_2 are formed, but with an excess of CS_2, COS and CO also are formed. Excess of H_2O yields an excess of CO_2 among the products. The equilibrium data for H_2O–CS_2 mixtures containing initially 10—80% CS_2 are given. H. F. G.

Equilibrium dehydrogenation of ethane, propane, and the butanes. F. E. FREY and W. F. HUPPKE (Ind. Eng. Chem., 1933, **25**, 54—59).—Equilibrium consts. for the reaction $C_nH_{2n+2} \rightleftharpoons C_nH_{2n}+H_2$ have been determined at 760 mm. and 400°, 450°, and 500° for C_2H_6 and at 350°, 400°, and 450° for C_3H_8 and *n*- and *iso*-C_4H_{10}. The dehydrogenation catalyst employed was air-dried Cr_2O_3 gel. There is very little interference by side reactions. The degree of dissociation increases with the no. of alkyl substituents attached to the ethylene group in the product. *n*-C_4H_{10} yields all the three known forms of C_4H_8. The free energies of dehydrogenation have been calc. at 400°. M. S. B.

Equilibrium law for strong electrolytes. Alkali metal bromides and iodides. K. JABŁCZYNSKI and A. BAŁCZEWSKI (Rocz. Chem., 1932, **12**, 880—887).—The expression $n^{4/3}/n_0=K$ (n_0 is the concn. of undissociated salt and n of one of its ions) is verified cryoscopically for Li, Na, K, NH_4, and H bromide and iodide, a const. val. being obtained for K if the hydration of the ions is taken into consideration ($Li^{\cdot}$ 10·3, $Na^{\cdot}$ 3, $K^{\cdot}$ 0, $NH_4^{\cdot}$ 0, $H^{\cdot}$ 9, Br' 1, and I' 2 mols. H_2O). The vals. of K for LiBr in presence of HBr, and of KI in presence of HI, are the same as for the bromides alone, indicating that only a part of the salt undergoes ionic dissociation. The degree of hydration of ions can be determined from cryoscopic measurements of the apparent mol. wt. of mannitol in presence of increasing concn. of salt; the vals. thus obtained diminish with the concn. and degree of hydration of the ions present. R. T.

Equilibrium constants of the first and second stages of dissociation of carbonic acid. Y. KAUKO (Suomen Kem., 1932, **5**, 53—54B).—The recorded vals. for the first-stage const. are confirmed. H. F. G.

Mathematical treatment of equilibrium in the system base–carbon dioxide–water in the liquid and gas phases. Y. KAUKO (Suomen Kem., 1932, **5**, 52B).—A series of equations of general application is derived. H. F. G.

Graphical representation of equilibrium relationships in the system base–carbon dioxide–water in the liquid and gaseous phases. Y. KAUKO (Suomen Kem., 1932, 5, 53B).—The p_H is plotted against the sum of the molar concns. of CO_2, H_2CO_3, HCO_3', and CO_3''. H. F. G.

Constitution of hydrochloric acid solutions of cobalt salts. P. JOB (Compt. rend., 1933, **196**, 181—183).—Measurements of the coeff. of absorption for λ 4500—7000 Å. show that the change in colour from red to blue is connected with the conversion of $[CoCl]^+$ into $[CoCl_3]^-$. C. A. S.

Physico-chemical studies of complex formation involving weak acids. IX. Alkaline solutions of thorium tartrate. H. T. S. BRITTON and W. E. BATTRICK (J.C.S., 1933, 5—9).—Conductivity and p_H data for mixtures of aq. $ThCl_4$ and $Na_2C_4H_4O_6$, alone and with added NaOH and HCl, indicate that the solutions contain a basic Th tartrate, $Th(OH)_{2x}(C_4H_4O_6)_{2-x}$, where x is variable. D. R. D.

Physical chemistry of the adenosinetriphosphoric acids. F. EIRICH and W. FILZ (Biochem. Z., 1932, **256**, 115—126; cf. A., 1932, 1287, 1288):—Conductometric, potentiometric, and titrimetric examination of the two adenosinetriphosphoric acids and of their Ag and Na salts shows that the acids are respectively hexabasic (Ag_4 salt) and pentabasic (Ag_3 salt). Determination of the dissociation consts. of the acidic groups and comparison of these with the consts. of adenylic and inosic acids and of the mono- and di-carbohydratephosphoric esters make it possible to suggest ways of distributing the consts. amongst the groups. Support is given to Barrenscheen's view that the difference between the two acids consists in an ester-like combination between a phosphoric acid group and an alcoholic group in the sugar residue. W. McC.

Spatial interpretation of state of indicators, and the analytical significance of the apparent dissociation constants of indicators. V. N. SKVORTZOV (J. Gen. Chem. Russ., 1932, **2**, 576—584).—Theoretical. The dissociation coeff. of an indicator is a function of the concn. of unchanged indicator and of the ions of its *aci*-form. R. T.

Reciprocal reactions and mixed halides among elements of the inner groups of the periodic system. M. G. RAEDER (Z. anorg. Chem., 1933, **210**, 145—160).—Cryoscopic and ebullioscopic measurements indicate that the halides of P, As, Sb, Ti, and Sn readily undergo reciprocal interaction with exchange of halogen atoms, and that mixed halides can be formed. M.-p. and f.-p. curves are, however, all of the eutectic and/or mixed crystal type, without max. corresponding with compound formation. Mixed halides cannot be isolated. F. L. U.

Equilibria in the melted state between alkali and alkaline-earth metals and their salts. E. RINCK (Ann. chim., 1932, [x], **18**, 395—531).—The equilibria represented by $Na+KX \rightleftharpoons K+NaX$ (X=OH, F, Cl, Br, I) agree with the requirements of the law of mass action. The two liquid phases are in all cases homogeneous. For Na $d'_4=0{\cdot}9385-0{\cdot}000260(t-96{\cdot}5)$ and for K $d'_4=0{\cdot}826-0{\cdot}000222(t-62{\cdot}5)$. Isotherms for the system $2Na+CaCl_2 \rightleftharpoons Ca+2NaCl$ between 712° and 1100° have three branches, two of which represent bivariant systems, salt+homogeneous metal, whilst the third represents the univariant system salt+two metal phases. Na and Ca have a limited miscibility, the crit. solution temp. being (by slight extrapolation) about 1180°. Solid Ca and Ba show a transition at 450° and 375°, with a heat effect of 7 and 1 g.-cal. per g., respectively. This is confirmed by measurements of their electrical resistances at different temp. F. L. U.

System ammonia–water at temperatures up to 150° and at pressures up to 20 atmospheres. I. L. CLIFFORD and E. HUNTER (J. Physical Chem., 1933, **37**, 101—118).—The composition of the vapours in equilibrium with aq. NH_3 has been determined at 60°, 80°, 90°, and 100° for solutions with total v.p. up to 1·5 atm. Total v.p. and composition of vapours have also been determined between 100° and 150° at 1—20 atm. Isotherms for the range 60—150°, and isobars for 0·02—10 atm. are given. E. S. H.

Diagram of state of fused salts of lithium. A. A. BOTSCHVAR (Z. anorg. Chem., 1933, **210**, 163).—M.-p. curves for LiCl–LiBr, LiF–LiBr, and LiF–LiCl are given. F. L. U.

System CaO–B_2O_3. E. T. CARLSON (Bur. Stand. J. Res., 1932, **9**, 825—832).—The compounds $CaO,2B_2O_3$, m.p. 986±5°, CaO,B_2O_3, m.p. 1154±5°, $2CaO,B_2O_3$, m.p. 1298±5°, and $3CaO,B_2O_3$, m.p. 1470°, are formed. Their optical properties are described. Mixtures containing < 23% CaO separate on fusion into two layers. C. W. G.

M.p. of mixtures of potassium nitrate and sodium nitrite. M. Y. KAGAN and N. KAMUISHAN (J. Appl. Chem., Russia, 1932, **5**, 347—349). CH. ABS.

Behaviour of mixtures of zinc oxide and anhydrous zinc chloride at high temperatures. A. FERRARI and G. TRAMPETTI (Atti R. Accad. Lincei, 1932, [vi], **16**, 343—345).—The solubility of ZnO in fused $ZnCl_2$ is < 5 mol.-%, and the existence of anhyd. oxychlorides of Zn is improbable. Hydrated Zn oxychlorides decompose on fusion into oxide and chloride. O. J. W.

Binary systems. II. F. E. C. SCHEFFER and J. SMITTENBERG (Rec. trav. chim., 1933, **52**, 1—8; cf. A., 1932, 1204).—Data for the systems o-$C_6H_4Cl{\cdot}NO_2$–CO_2, m-$C_6H_4Cl{\cdot}NO_2$–CO_2, and o-$C_6H_4(OH){\cdot}NO_2$–CO_2 are given. The first two show a quadruple point (solid, two liquids, vapour), which is not found in the third. F. L. U.

Systems (I) diphenyl–diphenylamine, (II) diphenyl–benzophenone, and (III) benzophenone–diphenylamine. H. H. LEE and J. C. WARNER (J. Amer. Chem. Soc., 1933, **55**, 209—214).—F.-p. data are recorded. The eutectics for Ph_2–$NHPh_2$ (29·5°), and Ph_2–$COPh_2$ (25·2°), contain 41·7 and 39·3 mol.-% of Ph_2, respectively. The *compound* $NHPh_2,COPh_2$, m.p. 40·2°, exists in a metastable form, m.p. 30·8°. J. G. A. G.

Chemical equilibria of reactions between hydrocarbons. III. A. A. VEDENSKI and A. V.

FROST (J. Gen. Chem. Russ., 1932, **2**, 715—725).—The empirical relation $\log K = -3348/T - 5{\cdot}957 \log T + 0{\cdot}00186T - 1{\cdot}095 \times 10^{-7}T^2 + 11{\cdot}79$ is found for the reaction C (graphite) $+ 2H_2 \rightleftarrows CH_4$, over the range 26·9—1726·9°. The val. of the entropy of graphite calc. from K by the application of the third law of thermodynamics differs from that calc. from sp. heat data. R. T.

Double sulphate of aluminium and sodium. M. MOUSSERON and P. GRAVIER (Bull. Soc. chim., 1932, [iv], **51**, 1382—1387).—Solubility, density, viscosity, and dilatometric measurements indicate that Na alum is stable between 11° and 39° only. The heat of formation from $Al_2(SO_4)_3,18H_2O$ and $Na_2SO_4,10H_2O$ is −3980 g.-cal. and the heat of dissolution in H_2O is −8500 g.-cal. A stable hydrate containing $4H_2O$ has also been obtained at 15° in vac. M. S. B.

Tensimetric analysis of the systems manganous sulphate–water and alkali alumino-oxalates–water. N. K. VOSKRESENSKAYA (J. Gen. Chem. Russ., 1932, **2**, 630—636).—The existence of the following hydrates is indicated by composition–v.-p. curves: $MnSO_4$,1 and $5H_2O$; $Na_3Al(C_2O_4)_3$,1—1·5, 2·5, and $4{\cdot}5H_2O$; $K_3Al(C_2O_4)_3$,0·5, 2, and $3H_2O$; $(NH_4)_3Al(C_2O_4)_3,H_2O$. No solid solutions are formed in the first three systems, but the fourth consists of an unbroken series of solid solutions of anhyd. salt, monohydrate, and H_2O. R. T.

Physical chemistry of the alumina–silica refractories. I. "Physical chemistry" of a system of refractory components. R. B. SOSMAN. **II. The clay minerals.** C. S. ROSS and P. F. KERR. **III. Minerals with the composition Al_2O_3,SiO_2.** H. INSLEY. **IV. Equilibria in the system alumina–silica.** R. B. SOSMAN. **V. Behaviour of unstable or monotropic forms in the system Al_2O_3–SiO_2 and related systems.** A. B. PECK (J. Amer. Ceram. Soc., 1933, **16**, 54—57, 57—58, 58—60, 60—68, 68—75).—I. Introduction to a phase-rule study.

II. A brief description is given of kaolinite, nacrite, dickite, beidellite, nontronite, montmorillonite, saponite, and of a K-bearing clay of the composition $5H_2O,3Al_2O_3,5(MgO,CaO,K_2O),15SiO_2$. The initial H_2O appears to be H_2O of crystallisation (or zeolitic); the second is high-temp. H_2O of constitution, and the final is variable H_2O of adsorption.

III. The nature, occurrence, and relationship of andalusite, cyanite, and sillimanite (Al_2O_3,SiO_2) are described.

IV. The development of the phase-rule study of the Al_2O_3–SiO_2 system and the mechanism of the dehydration of kaolin are described.

V. The action of heat on the various Al_2O_3–SiO_2 minerals and the interrelationship of the effects of temp., time, and grain-size are discussed. J. A. S.

Equilibrium cyanide–cyanamide. A. PERRET and R. PERROT (Compt. rend., 1933, **196**, 268—271; cf. A., 1932, 1098).—The production of $CN{\cdot}NH_2$ when $NaCN + Fe$ is heated with various chlorides has been examined. C. A. S.

Reduction of tricalcium phosphate. W. JANSEN (Z. anorg. Chem., 1933, **210**, 113—124).—The reduction of $Ca_3P_2O_8$ by H_2 becomes measurable at 900—1000°, by CO at 1300°, and by graphite below 1100°. In presence of Fe these temp. are lowered, to 700—750° for graphite, and to 600° for H_2. The results are discussed in relation to the production of Fe in the blast furnace. From the point of view of contamination with P the most favourable reducing agent is CO. F. L. U.

Solubilities in the system potassium chloride–sodium chloride–magnesium chloride–water at 0°. A. P. PALKIN and E. N. VARASOVA (J. Appl. Chem., Russia, 1932, **5**, 316—324). CH. ABS.

Equilibria in the interaction of sodium carbonate, sodium hydroxide, calcium hydroxide, and trisodium phosphate with calcium and magnesium sulphates. J. LEICK (Z. anorg. Chem., 1933, **210**, 203—209).—Data relating to reactions occurring during the purification of boiler-feed water are given. F. L. U.

Heat-capacity curves of the simpler gases. I. Heat capacity, entropy, and free energy of gaseous nitric oxide from near 0° abs. to 5000° abs. H. L. JOHNSTON and A. T. CHAPMAN. **II. Heat capacity, entropy, and free energy of gaseous oxygen from near 0° abs. to 5000° abs.** H. J. JOHNSTON and M. K. WALKER (J. Amer. Chem. Soc., 1933, **55**, 153—172, 172—186).—I. From spectroscopic data (A., 1930, 24) it is found that the calc. heat-capacity curve has a sharp rise between 1° and 5° abs. corresponding with attainment of rotational equipartition, a max. at about 75° abs. which results from excitation to the upper level of the normal $^2\Pi$ electronic state, and a vibrational component which starts about 300° abs., reaching equipartition val. at 3000° abs. At high temp. effects due to centrifugal stretching of the mol. and the anharmonic character of the oscillations are produced. The entropy and "free energy" have been calc. for the range 1—5000° abs. The degree of dissociation into atoms is approx. $1{\cdot}5 \times 10^{-5}$ at 2000° abs. and 0·35 at 5000° abs.

II. The heat-capacity curve for mol. O_2 calc. from spectroscopic data (A., 1929, 1137) has two max. below 2° abs. owing to transformations between closely related electronic forms. The increments in the ranges 3—10° abs. and 200—2500° abs. correspond with the attainment of rotational and vibrational equipartition, respectively. At 2500° abs., an additional electronic component of the sp. heat appears. At high temp., effects due to mol. stretching and anharmonic vibration are produced. Entropy and "free energy" vals. for the range 1—5000° abs. are recorded. J. G. A. G.

Vapour pressure and heat of vaporisation of graphite. A. L. MARSHALL and F. J. NORTON (J. Amer. Chem. Soc., 1933, **55**, 431—432).—The rate of loss in wt. of C rings heated at 2350—2800° abs. by high-frequency induction in a vac. leads to $C_{(s)} \longrightarrow C_{(monat.\ g.)}$, $\Delta H = 177$ kg.-cal., $C_2 \longrightarrow 2C$, $\Delta H = 150$ kg.-cal. J. G. A. G.

Determination of heat of dissolution of gases. H. HORIUTI (Z. Elektrochem., 1933, **39**, 20—22).—Theoretical. Heats of dissolution of gases at const. pressure and at const. vol. are derived thermo-

dynamically, taking into account the thermal expansion of the solution. F. L. U.

Heat of dissolution of gases, particularly carbon dioxide. Y. KAUKO (Suomen Kem., 1932, **5**, 54B).—The latent heats of evaporation of CO_2 and NH_3, and the mean heat of dissolution, L, of CO_2 in H_2O, are approx. linear functions of the v.p. At const. pressure L varies rapidly with temp., and is largely dependent on the degree of association of the H_2O. The vals. previously recorded for the heat of dissociation are not compatible with the heat of dissolution. If Henry's law is applicable, CO_2 is not associated in solution. H. F. G.

Heat capacity, heat of sublimation, and heat of dissolution of phosphorus pentoxide. M. FRANDSEN (Bur. Stand. J. Res., 1933, **10**, 35—58).—The heat capacity C_v of P_2O_5 vapour between 360° and 1100°, measured by condensing the vapour in H_2O in a calorimeter and deducting the heat of dissolution, is 36·8±1·0 g.-cal. per mol. The heat capacity of solid P_2O_5 between 25° and 350° is given by $C_v=22{\cdot}17+0{\cdot}0780t-8{\cdot}45\times10^{-5}t^2$ g.-cal. per mol. The heat of sublimation is 8·8±1·3 kg.-cal. per mol. at 358°. The heat of dissolution with formation of HPO_3 is 42·0±2·1 kg.-cal. per mol., and with formation of H_3PO_4 is 54·4±2·1 kg.-cal. per mol. H. J. E.

Carbon rings. XXII. Heats of combustion of high-membered ring compounds. L. RUZICKA and P. SCHLAPFER (Helv. Chim. Acta, 1933, **16**, 162—168).—The following corr. mol. heats of combustion (kg.-cal.) at const. vol. are recorded: *cyclo*octane 1262; *cyclo*octanone 1161; *cyclo*pentadecane 2356; *cyclo*pentadecanone 2260; *cyclo*heptadecane 2673; *cyclo*heptadecanone 2573; *cyclo*heptadecenone (civetone) 2517; *cyclo*triacontane 4665; *cyclo*triacontanedione 4590. The mean val. for CH_2 is 156—157 kg.-cal. The results show that the compounds are strainless. H. B.

Electrolytic transport of water in sodium iodide solutions. Role of parchment paper membrane in electrolysis of aqueous solutions of alkali and alkaline-earth halides. G. BABOROVSKY and A. WAGNER (Z. physikal. Chem., 1933, **163**, 122—132).—By the method previously described (A., 1928, 954) the true transport no., N, of $Na^{\cdot}$ has been found to be 0·455 in M-NaI and 0·528 in 0·1M-NaI at 22—25°; the amounts of H_2O transported electrolytically, Z, are 2·25 and 0·77 mol., respectively. From the data for the M solution the hydration of I′ is 2·55 if the hydration of $Na^{\cdot}$ is assumed to be 8, whilst if that of I′ is 2, the hydration of $Na^{\cdot}$ is 7·33. The discrepancy between the vals. of N and Z for alkali and alkaline-earth halides and halogen acids calc. from analysis of the anode and cathode solutions seems to be due to adsorption of the anions by the parchment membrane and to the swelling of the latter. R. C.

Conductivity and viscosity of aqueous glycerol solutions of sulphuric acid. L. E. SABININA (J. Gen. Chem. Russ., 1932, **2**, 637—644).—With increasing concn. of H_2SO_4 and of glycerol the viscosity diminishes more rapidly than the mol. conductivity; this is attributed to desolvation of the ions in the more conc. solutions. The temp. coeff. of the conductivity falls with rise of temp. R. T.

Electrical conductivity of mixed salt solutions. A. K. SMITH and R. A. GORTNER (J. Physical Chem., 1933, **37**, 79—86).—Binary combinations of aq. NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $CuSO_4$, $ZnSO_4$, KCl, and HCl were examined at 30·17°. The differences between the observed conductivities and those calc. from the additive rule are sometimes positive and sometimes negative. No generalisation can be made, but the importance of the reaction between solute and solvent is emphasised. E. S. H.

Electrical conductivities of mixtures of sulphuric acid, acetic acid, and water [at 25°]. N. F. HALL and H. H. VOGE (J. Amer. Chem. Soc., 1933, **55**, 239—246).—H_2SO_4 at low concns. in AcOH behaves as a typical weak electrolyte with dissociation const. of 10^{-9} approx. The sp. conductance of the system AcOH–H_2SO_4 has a strong max. at 0·8—0·9 mol. fraction of H_2SO_4. A conductance diagram for the system H_2SO_4–AcOH–H_2O is given. J. G. A. G.

Electrolytic solutions. I. Conductance as influenced by the dielectric constant of the solvent medium. C. A. KRAUS and R. M. FUOSS (J. Amer. Chem. Soc., 1933, **55**, 21—36).—The conductances of 0·00001—0·2N solutions of tetra*iso*amylammonium nitrate and thiocyanate and tri*iso*amylammonium picrate in dioxan, H_2O, $C_2H_4Cl_2$, C_6H_6, and mixtures of these have been determined at 25°. Temp. coeffs. are recorded. At sufficiently low concns., the equiv. conductivity, Λ, increases with dilution, even in solvents of very low dielectric const., and sp. effects, viscosity excepted, due to the solvent medium are absent. With increasing dielectric const. of the medium, the min. val. of Λ is displaced towards regions of higher concn. J. G. A. G.

Conductivity of solutions of zinc oxide in sodium hydroxide solution. F. R. SNELL (J. Indian Chem. Soc., 1932, **9**, 583—587).—Conductivity measurements afford no evidence of the formation of complexes when the ratio ZnO : NaOH is varied from 1 : 2·5 to 1 : 7. A. S. C. L.

Transference and conductivity studies on solutions of certain proteins and amino-acids with special reference to the formation of complex ions between the alkaline earths and certain proteins. S. MIYAMOTO and C. L. A. SCHMIDT (J. Biol. Chem., 1933, **99**, 335—358).—Na salts of caseinogen (I), dephosphorised caseinogen (II), aspartic (III) and glutamic (IV) acids, and Ba salts of (III) and (IV) do not appear to form complex ions, but such ions are produced by Ca salts of (I) and (II). Since the no. of complex ions in solution of Ca–(II) is 10% < Ca–(I), the phosphoric acid in (I) would seem to be responsible for this difference. H. G. R.

Electrochemical investigation of cadmium–silver alloys. A. OLANDER (Z. physikal. Chem., 1933, **163**, 107—121).—The e.m.f. of $Cd_{liquid}|(Li, Rb, Cd)Cl|(Cd, Ag)_{solid}$ for various Cd–Ag alloys has been measured at 330—555°. The data are used to derive the equilibrium diagram. R. C.

Voltaic cell Ag|fused $AgNO_3$|C. A. Sconzo (Annali Chim. Appl., 1932, **22**, 794—802).—As the temp. of this cell is raised gradually to 350°, its e.m.f. rises regularly up to 240° and subsequently falls, rises, falls, and rises. The behaviour is attributed to changes in the velocity of reaction of the C with the fused $AgNO_3$. T. H. P.

Galvanic cells containing potassium triphenylmethyl. H. E. Bent and E. S. Gilfillan, jun. (J. Amer. Chem. Soc., 1933, **55**, 247—249).—Solutions of CPh_3K and related compounds in Et_2O behave as normal electrolytes in cells containing K amalgam electrodes, but the compounds undergo a slow irreversible reaction when in contact with K, and this precludes their use in cells containing K metal. The following were prepared: *diphenyldiphenylylmethyl Me ether*, m.p. 94—95°, *diphenyl-α-naphthylmethyl Me ether*, m.p. 142°, and *phenyl-α-naphthyldiphenylyl Me ether*, m.p. 190—191°. J. G. A. G.

Effect of carbamide on quinhydrone electrodes. T. Sasaki (J. Chosen Med. Assoc., 1931, **21**, 797—800).—The slight effect depends on the buffers present. When $CO(NH_2)_2$ is added to OAc′ or PO_4''' buffers, [H·] determined with the H_2 electrode tends to shift to the acid side, whilst with the quinhydrone electrode, or in either case when more $CO(NH_2)_2$ is used, it shifts towards the alkaline side. Ch. Abs.

Influence of acid concentration on the oxidation–reduction potential of mixtures of ferric and ferrous sulphates in sulphuric acid solution. T. J. Glover (J.C.S., 1933, 10—15).—E.m.f. data are given for cells of the type $Pt|FeSO_4$, $Fe_2(SO_4)_3$, 0·1—10N-$H_2SO_4|N$-HgCl or Hg_2SO_4 electrode at 20° and 60°. There is a logarithmic relation between e.m.f. and the ratio $[Fe''']/[Fe'']$. On increasing $[H_2SO_4]$ there is no change in $[Fe''']/[Fe'']$ at 20°, but at 60° there is an apparent rise in the val. of this ratio, which is probably due to the formation of complex ions of different oxidation–reduction potential. The potential of the N-Hg_2SO_4 electrode is 0·9551 volt at 18° and the temp. coeff. $2{\cdot}83\times10^{-4}$. D. R. D.

Electrochemical behaviour of thallium in sodium hydroxide solution. I. Kühn (Bul. Soc. Chim. Romania, 1932, **14**, 80—88).—The current–voltage curve of Tl in 2N-NaOH exhibits three breaks. Between about −0·32 and +0·39 volt, Tl· enters the solution, whilst between 0·39 and 1·4 volts, Tl·· ions are formed. Müller's conclusion, that the process is $Tl\longrightarrow 2Tl''\longrightarrow Tl^{\cdot}+Tl'''$, is not confirmed. The deposit formed on a Pt anode in a TlOH solution consists of Tl_2O_3 containing 4—6% of Tl_2O. The normal potential of Tl in TlOH solution is −0·320 volt. H. F. G.

Influence of high-frequency currents on polarised electrodes. II. S. Glasstone and G. D. Reynolds (Trans. Faraday Soc., 1933, **29**, 399—409).—The H.F. effect (cf. A., 1932, 915) is not due to any influence on the chemical reaction at the electrode, but is related to an increase in the rate of diffusion of the depolariser. The H.F. effect on the limiting current (for 100% efficiency) is independent of the surface tension of the electrolyte, but increases as the viscosity increases and decreases with stirring or with rise of temp. Addition of neutral salt increases conduction and decreases the H.F. effect. Under a wide variety of conditions the relative H.F. effect is proportional to the square root of the power expended in the solution per unit area of electrode surface. The H.F. effect is probably due to a mechanical disturbance in the electrolyte which may have its origin in the oscillatory rotation of the mol. dipoles of the H_2O used as solvent. M. S. B.

Potential effect with strong and weak bases. J. Schiele (Physikal. Z., 1933, **34**, 60—61).—For strong bases the magnitude of the Wien effect is small. The behaviour of weak bases corresponds completely with that of weak acids (cf. A., 1932, 813). The potential effect in agar-agar solutions has been examined. A. J. M.

Application of quantum mechanics to chemical kinetics. R. P. Bell (Proc. Roy. Soc., 1933, **A, 139**, 466—474).—Mathematical. Consideration of a simple system typical of the transits involved in a chemical reaction leads to the conclusion that a quantum-mechanical treatment is necessary for a reaction involving the motion of a proton or H atom, but heavier atoms behave classically. Departure from classical behaviour may in some cases lead to discrepancies between the experimental data and modern theories of reaction kinetics. L. L. B.

Relation between energy of activation and the constant S of Arrhenius' equation. II. E. N. Gapon (J. Gen. Chem. Russ., 1932, **2**, 710—714).—The expression $RT'_i-Nh\nu$ is derived, in which T'_i is the temp. at which the velocity coeffs. of a given group of reactions possess the same val., N is the no. of mols., and ν is the frequency of vibration between two atoms. The relations previously found (A., 1931, 313) between S and energy of activation have only a limited application to bimol. reactions. R. T.

Streaming kinetics. Photolysis model. E. Abel and H. Schmid (Monatsh., 1932, **61**, 361—364).—Theoretical. E. S. H.

Critical ignition of explosive hydrogen mixtures. J. H. Maas and C. Ewing (J. Physical Chem., 1933, **37**, 13—15).—"Stepped" ignition of H_2–O_2 mixtures depends on the presence of N_2. A smooth curve is obtained with pure H_2 and O_2 or in presence of A. E. S. H.

Gaseous combustion at high pressures. XIV. Explosions of hydrogen–air and carbon monoxide–air mixtures at initial pressures up to 1000 atmospheres. W. A. Bone, D. M. Newitt, and D. T. A. Townend. **XV. Formation of nitric oxide in carbon monoxide–oxygen–nitrogen explosions.** D. T. A. Townend and L. E. Outridge. **XVI. Nitric oxide formation in continuous high-pressure flames of carbon monoxide in oxygen–nitrogen atmospheres.** D. M. Newitt and F. G. Lamont (Proc. Roy. Soc., 1933, **A, 139**, 57—74, 74—83, 83—93).—XIV. A bomb capable of withstanding explosion pressures up to 10,000 atm. is described. Mixtures of $2H_2+O_2+3{\cdot}76N_2$ (I), $2CO+O_2+3{\cdot}76$ CO (II), and $2CO+O_2+3{\cdot}76N_2$ (III) have been exploded at initial

pressures up to 500 atm. in the first and second and 1000 atm. in the third case. With explosions of (I) there was a definite increase in the "explosion times" with d at initial pressures above 250 atm. In the explosions of (III) the characteristic lag in the "explosion time" reached a max. at a d corresponding with P_i between 350 and 500 atm., and afterwards remained const. In the explosions of (II) the "explosion times" began to increase with further increase in d above P_i =250 atm. and at the same time slight C deposition began to take place.

XV. A study has been made of the NO formation in $2CO+3O_2+2N_2$ explosions at P_i=50—90 atm., under conditions such as would ensure a much more rapid cooling of the explosion products from T_m and therefore a greater NO survival. The NO yields greatly exceed any previously obtained in such explosions, and the experimental results support the view that there is a primary N_2 activation followed by a secondary NO formation.

XVI. An apparatus is described in which CO flames can be steadily maintained in selected O_2–N_2 atm. at all pressures up to 100 atm. The NO formation depends more on the N_2/CO_2 ratio than mean temp. in the flame, and is favoured by increase of pressure. N_2 activation is undoubtedly prominent in steady CO–O_2–N_2 flames as well as in such explosions at high pressures. L. L. B.

Rates of detonation in carbon monoxide–oxygen mixtures. C. Campbell, C. Whitworth, and D. W. Woodhead (J.C.S., 1933, 59—62).—The rate of detonation increases almost linearly with [CO] from 50 to about 75% CO, after which it falls. There is no sharp peak at 75% CO (cf. A., 1931, 436). D. R. D.

Radiation in gaseous explosions. W. T. David and R. M. Parkinson (Phil. Mag., 1933, [vii], **15**, 177—192; cf. A., 1920, ii, 73).—The total radiation during the explosion and subsequent cooling of CO–air mixtures is > for H_2–air mixtures of comparable composition. With CO and H_2 in varying proportions the radiation decreases as the % H_2 is increased. This is attributed to the slower explosion and cooling for CO. CH_4–, C_2H_2–, or C_2H_4–air mixtures behaved similarly to mixtures of CO and H_2 with air, the rate of emission of radiation depending on the C : H ratio. H. J. E.

Atomic chlorine and its reaction with hydrogen. W. H. Rodebush and W. C. Klingelhoefer, jun. (J. Amer. Chem. Soc., 1933, **55**, 130—142; cf. A., 1932, 1000).—The prep. of at. Cl is described and its recombination at various surfaces has been investigated. When Cl atoms are admitted to a stream of H_2 and Cl_2 at 0·3—0·5 mm. a chain reaction is started which, in general, proceeds until one of the gases has reacted completely. The reaction is not retarded by Pyrex glass owing to its small effect on the recombination of Cl atoms. The simple Nernst mechanism is adequate to account for the results, and the probability of the reaction $Cl+H_2=HCl+H$ is approx. $1·4\times10^{-5}$ per collision at 0° and $3·3\times10^{-5}$ at 25°. From the temp. coeff. a heat of activation of 6100± 1000 g.-cal. is calc. J. G. A. G.

Influence of ionisation on ignition temperature of combustible gases. B. Lewis and C. D. Kreutz (J. Chem. Physics, 1933, **1**, 89—94; cf. A., 1931, 689).—The ignition temp. of mixtures of CH_4 with "air" (*i.e.*, 1 vol. O_2+4 vols. N_2, A, or He) has been determined in a flow system in which one of the constituents could be sparked before mixing. When the constituents thus sparked were A, He, N_2, and O_2, a reduction of the normal ignition temp. by 28°, 83°, 115°, and 233°, respectively, was observed. The effect could in some cases be delayed for 2·5 min. after sparking had ceased. It is concluded that the responsible agents are gaseous ions. F. L. U.

Explosive conditions in saturated alcohol vapour–air mixtures. K. Fricke (Angew. Chem., 1933, **46**, 87—90).—Air saturated with the vapour of an EtOH–H_2O mixture becomes explosive between certain limits of temp. which depend on the concn. of the mixture and on the pressure. These limits have been determined for 12 mixtures (3·8%—99·8% EtOH) in an apparatus described. Curves are plotted showing dependence of explosion pressure on temp., change of upper and lower limiting explosion temp. and also inflammation temp., which is just above the latter, with concn. of liquid mixture, change of max. pressure with concn., and dependence of temp. of max. pressure on concn. M. S. B.

Kinetics of thermal decomposition of trichloromethyl chloroformate. H. C. Ramsperger and G. Waddington (J. Amer. Chem. Soc., 1933, **55**, 214—220).—$COCl_2$ is the sole decomp. product of 4—17 mm. of $ClCO_2CCl_3$ at 260—310°. The reaction is of first order and largely homogeneous, the rate coeff. being $k=1·4\times10^{13}e^{-14,500/RT}$. The maintenance of the high-pressure rate in the range studied is accounted for if the mol. is 8×10^{-8} cm. in diameter and contains 14 classical oscillators. J. G. A. G.

Influence of various alkalis and of the solvent on the rate of iodometric oxidation of thiocyanate. E. Angelescu and V. D. Popescu (Bul. Soc. Chim. Romania, 1932, **14**, 25—45; cf. A., 1931, 1372).—Previous work has been extended by using $NaHCO_3$ at various concns., $Na_2B_4O_7$ with various KCNS concns., Na_2HPO_4, Na and K tartrates, and NaOAc, and by experiments with EtOH solutions. The influence of the added alkali is governed primarily by the concn. of the OH ions formed, and by buffer action. The reaction velocity varies with the initial concn. of HOI, and NH_4 salts accelerate the reaction by increasing the HOI concn. The unimol. equation is applicable only to strongly buffered solutions. The results confirm the view of the mechanism previously suggested. H. F. G.

Autoxidation of stannous chloride. II. Survey of certain factors. R. C. Haring and J. H. Walton (J. Physical Chem., 1933, **37**, 133—145; cf. A., 1932, 476).—The rate of autoxidation increases with rising temp., but the true temp. coeff. is marked by other changes. Ultra-violet light below 3070 Å. accelerates the reaction, but visible light has no effect. A peroxide (not isolated) was detected in the fresh, partly oxidised $SnCl_2$; this disappears by reaction with further $SnCl_2$. Many org. substances, partic-

ularly NO_2-compounds, inhibit the reaction, whilst $CS(NH_2)_2$ acts as a strong positive catalyst. The reaction is catalysed by powdered C, especially when $Cu^{\cdot\cdot}$ salts are added as promoters. Induced oxidation was observed in the cases of aq. allyl alcohol and butaldehyde in presence of $SnCl_2$ and also in solutions of $SnCl_2$ in some alcohols, acids, esters, and ketones. E. S. H.

Autoxidation. C. NEUBERG and M. KOBEL (Naturwiss., 1932, **20**, 953—954).—Glyoxal, in the form of its H sulphite compound, is readily oxidised by atm. O_2, in presence of phosphates, to glyoxylic acid. The process is more rapid than with methylglyoxal. There is no oxidation in the absence of Na_2SO_3. A. J. M.

Velocity of decomposition of diazo-compounds in aqueous solution. IX. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1932, **36**, 564—567B; cf. A., 1932, 1002).—The decomp. velocities at various temp. and the temp. coeff. of the velocities are recorded for *o*-$OMe{\cdot}C_6H_4{\cdot}N_2Cl$, *o*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$, and *o*-$OMe{\cdot}C_6H_3(p\text{-}NO_2){\cdot}N_2Cl$. J. W. S.

Kinetics of formation of sulphuric acid. E. ABEL (Z. Elektrochem., 1933, **39**, 34—35).—Preliminary. A mechanism of the Pb chamber process in which the primary reaction is $SO_2+HNO_2 \longrightarrow SO_3+HNO$ is suggested. F. L. U.

Velocity of absorption of gases by liquids. III. Theoretical considerations of gas absorption due to chemical reactions. IV. Absorption of carbon dioxide by potassium carbonate solutions. I. S. HATTA (J. Soc. Chem. Ind. Japan, 1932, **35**, 559—561B, 561—563B).—III. Formulæ are derived for the velocity of absorption of gas by a liquid (*a*) in the absence of chemical reaction; (*b*) when an instantaneous reaction occurs; (*c*) when a reaction of moderate velocity occurs.

IV. The absorption of CO_2 by aq. K_2CO_3 follows a course in agreement with the equations deduced, suggesting that three reactions occur, viz., $CO_2+CO_3^{\cdot\cdot}+H_2O=2HCO_3'$; $CO_2+OH'=HCO_3'$; $CO_3^{\cdot\cdot}+H_2O=HCO_3'+OH'$. J. W. S.

Velocity of absorption of gases by liquids. V. Absorption of carbon dioxide by potassium carbonate solutions. II. S. HATTA (J. Soc. Chem. Ind. Japan, 1933, **35**, 9—11B).—The velocity of absorption increases by about 30% per 10° rise in temp. The velocity of stirring has little influence, although with KOH it has a considerable effect. When the film of liquid is thin, the velocity is inversely proportional to the thickness and almost independent of change in composition of the liquid. With thick films the converse is true. D. R. D.

Theory of the dissolution of gas in liquid. II. Rate of dissolution of gas in liquid containing a reacting substance; kinetic derivation of the distribution law. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1932, **7**, 388—398).—The rates of dissolution of O_2 into Na_2SO_3 solution and of CO_2 into NaOH solution are better explained on the basis of the author's theory (A., 1932, 345) than by the diffusion theory; the determining factor, viz., the threshold normal velocity of the gas mols. entering the solution, depends on the nature of the liquid phase, and decreases with increase of solute concn. The threshold velocities are calc. for the case of O_2 dissolving in H_2O. The distribution law is derived from purely kinetic considerations. H. F. G.

Absorption of silicon fluoride by sodium fluoride. V. S. YATLOV and I. G. RUISS (J. Appl. Chem., Russia, 1932, **5**, 332—343).—The rate of the reaction $2NaF(s)+SiF_4(g)=Na_2SiF_6(s)$ is: 275°, 0·48; 350°, −1·0; 400°, −4·8; 470°, −20·1. At 470°, NaF containing 45·83% Na_2SiF_6 was converted into 92·2% Na_2SiF_6 in 3·5 hr. CH. ABS.

Dissolution of magnesium in aqueous salt solutions. I. Effect of impurities. L. WHITBY (Trans. Faraday Soc., 1933, **29**, 415—425).—The rate of dissolution of four samples of Mg of $<99{\cdot}90\%$ purity has been measured in 0·1, 1, and 3*N*-NaCl and 0·05*N*-HCl by measurement of H_2 evolution. Large variations are observed in NaCl and duplication of results is impossible except by employing very pure Mg. The variations are caused by changes in the type of film formed at the cathodic parts of the surface. The rate in HCl is the same for all samples because the acid prevents film formation. Little difference in behaviour is shown by hard-worked and fully annealed metal. The presence of about 0·02% Mn causes an acceleration of attack with time, although quantities up to 2% are normally added to Mg to reduce corrosion. In most other cases the action slows off with time. The mechanism of attack is discussed. M. S. B.

Active oxides. LVII. Rate of decomposition of zinc oxalate into zinc oxide, carbon dioxide, and carbon monoxide. G. F. HUTTIG and E. LEHMANN (Z. physikal. Chem., 1932, **B**, **19**, 420—426; cf. A., 1932, 1211).—In the decomp. in a vac. at 325°, 360°, and 405° there is a period of induction, after which $dn/d\tau=kn^{2/3}$, where n is the no. of mols. of C_2O_3 per mol. of total ZnO in the solid phase at time τ. The explanation offered is that decomp. sets in at the crystal surfaces, then progresses linearly inwards with uniform velocity. Cr_2O_3 accelerates the decomp. by activation of the ZnC_2O_4 mols. MeOH vapour reduces the rate of decomp. to a val. which is almost const., independent of n. R. C.

Determination of the linear speed of transformation of austenite into pearlite. A. A. BOTSCHVAR (Z. anorg. Chem., 1933, **210**, 168—170).—In a 0·9% C steel the linear rate of transformation of austenite on cooling was practically zero for the first 30° of supercooling below the transition temp., and for a greater degree of supercooling was much lower than that found by Tammann and Siebel. F. L. U.

Kinetics of oil drying. N. FUCHS.—See B., 1933, 114.

Rate of burning of colloidal propellants. F. R. W. HUNT and G. H. HINDS.—See B., 1933, 125.

Interaction of carbon monoxide and nitric oxide. F. F. MUSGRAVE and C. N. HINSHELWOOD (J.C.S., 1933, 56—59).—H_2O catalyses the reaction between CO and NO at 920°, the mechanism being apparently $CO+H_2O=CO_2+H_2$, $2NO+2H_2=N_2+$

$2H_2O$. The reaction velocity $\propto [NO]^2$. Br inhibits reaction, probably by combining with the H_2.
D. R. D.

Catalysis of hydrogen peroxide. F. HABER and J. WEISS (Naturwiss., 1932, **20**, 948—950).—The reaction between a Fe^{II} salt and H_2O_2 in neutral solution has been studied. The explanations previously put forward by Manchot and Lehmann (A., 1928, 261) are criticised, and two new methods are described for investigating the reaction. The reaction can be explained by means of a chain mechanism: (1) $Fe^{II}+H_2O_2=Fe^{III}(OH)+OH$; (2) $OH+H_2O_2=H_2O+O_2H$; (3) $O_2H+H_2O_2=O_2+H_2O+OH$; (4) $Fe^{II}+OH=Fe^{III}(OH)$. A. J. M.

Hydrolysis of salts of halogen-substituted aliphatic acids in aqueous solution. H. M. DAWSON and N. B. DYSON (J.C.S., 1933, 49—56).—The rate of formation of Br′ by hydrolysis of $CH_2Br{\cdot}CO_2Na$ may be represented by $v=v_1+v_2=k_1c+k_2c^2$, where $c=[CH_2Br{\cdot}CO_2']$, the Na salt being considered as completely ionised. v_1 is the velocity of the unimol. reaction (1) $CH_2Br{\cdot}CO_2'+H_2O=OH{\cdot}CH_2{\cdot}CO_2H+Br'$, and v_2 of the bimol. reaction (2) $2CH_2Br{\cdot}CO_2'=CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2'+Br'$, which is followed by $CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2'+H_2O=CH_2Br{\cdot}CO_2'+OH{\cdot}CH_2{\cdot}CO_2H$. In presence of a catalyst (concn. c'), $=k_1c+k_2c^2+k_3cc'$. The catalysts act by means of reactions analogous to (2): $CH_2Br{\cdot}CO_2'+X'=X{\cdot}CH_2{\cdot}CO_2'+Br'$, $X{\cdot}CH_2{\cdot}CO_2'+H_2O=X'+OH{\cdot}CH_2{\cdot}CO_2H$. The following have catalytic action: $OH'>OAc'=HCO_2'>OH{\cdot}CH_2{\cdot}CO_2'>CH_2Br{\cdot}CO_2'$ [reaction (2)] $>CH_2Cl{\cdot}CO_2'$. With OH′, k_3 is so large that $v=k_3cc'$, approx. Allowance must in all cases be made for the effect of the inert salt concn. and the catalytic action of the reaction products.
D. R. D.

Oxidation of sulphites. I—III. S. I. VOLFKOVICH and A. P. BELOPOLSKI (J. Appl. Chem., Russia, 1932, **5**, 509—528, 529—551, 552—556).—I. At a const. rate of O_2 flow, increase in concn. of K_2SO_3 retards oxidation; at const. K_2SO_3 concn., increase in the rate of O_2 flow increases the rate of oxidation up to a max. val. At the max. the reaction is unimol., but when 94% of the K_2SO_3 is oxidised the velocity coeff. falls. The rate of reaction is approx. doubled by raising the temp. from 0° to 10° at the limiting O_2 rate.

II. The reaction is very slow when p_H is high or low. $CoSO_4$ is an effective catalyst. At p_H 7·6 other catalysts are (diminishingly) effective in the order: $FeSO_4$, $CuSO_4$, $NiSO_4$, $MnSO_4$; at p_H 9·9: $CuSO_4$, $NiSO_4$, $MnSO_4$, $FeSO_4$; in highly alkaline medium: $NiSO_4$, $CoSO_4$, $CuSO_4$, $FeSO_4$, $MnSO_4$.

III. Solid K_2SO_3 is not oxidised by dry O_2 at 25—80°, but the reaction proceeds if the O_2 is moist. $CaSO_3$ is not oxidised at 25—110° even when suspended in H_2O, but the reaction proceeds in presence of $CoSO_4$, $MnSO_4$, or $CuSO_4$. CH. ABS.

Retarding action of glass on Landolt's reaction. A. JULIARD (Compt. rend., 1933, **196**, 179—181).—Liebreich's "dead space" phenomenon (cf. A., 1890, 1207) as exemplified by localised delay in appearance of I_2 in Landolt's reaction (cf. A., 1922, ii, 488) is due to adsorption of I′ ions on glass. The delay is intensified by the presence of glass wool, but not if this has been previously impregnated with aq. KI. C. A. S.

Ozone as oxidising catalyst. IV. Ozonation of benzaldehyde at a low temperature. E. BRINER and H. BIEDERMANN (Helv. Chim. Acta, 1933, **16**, 213—216; cf. A., 1932, 1212).—In studying the effect of O_3 on PhCHO, both the action of ozonised O_2 on the solvent and autoxidation of PhCHO by O_2 have been shown to be negligible at −30°. The most suitable solvent is EtCl. The yield of BzOH and BzO_2H is, in general, much > that calc. from the chemical equation, and increases as the concn. of O_3 decreases. It is decreased when the concn. of O_2 in the gas is diminished by admixture of N_2.
F. L. U.

Logarithmic relation between constants of Arrhenius' equation. Activation energy of dehydrogenation of *cyclo*hexane in presence of nickel catalysts prepared in various ways. A. A. BALANDIN (Z. physikal. Chem., 1932, B, **19**, 451—461; cf. A., 1930, 1377).—A review of available data for dehydrogenation reactions and new determinations confirm the relation $\log_e k_0=aQ+b$ between the consts. of $k=k_0e^{-Q/RT}$. It is a consequence of this relation that catalysts with high vals. of Q are the most active. In the dehydrogenation of *cyclo*hexane catalysed by Ni supported on Al_2O_3 Q=16,230 kg.-cal. per mol., comparison of which with Q=9850 kg.-cal. for ordinary Ni catalysts shows that the effect of the support is to be traced to its qualitatively influencing the Ni surface, not merely to an increase in surface area (cf. A., 1923, ii, 551). Similar observations have been made with TiO_2 as the support, and neither catalyst is able to effect the decomp. of CH_4. The $Ni-Al_2O_3$ catalyst approximates to Pd supported on asbestos. R. C.

Catalysts for the production of hydrogen by means of the water-gas reaction. VII—VIII. *X*-Ray examination and coexistence of the two oxides in Fe_2O_3–Cr_2O_3 catalysts. II. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1933, **36**, 14—16B, 16—18B; cf. A., 1932, 235, 578).—VII. The temp. at which Fe_2O_3 loses its activity is not affected by addition of Cr_2O_3, but the fall in activity becomes less pronounced.

VIII. When the catalyst is in use, the Fe_2O_3 is completely reduced to Fe_3O_4 within 19 hr., after which it suffers no further change. D. R. D.

Catalytic properties of bright platinum and iridium deposits in the activation of hydrogen. L. P. HAMMETT and A. E. LORCH (J. Amer. Chem. Soc., 1933, **55**, 70—80).—Bright deposits of Pt and Ir, produced by electrolysis of chloroplatinous and chloroiridous acids, respectively, have reproducible catalytic activity as determined by means of the reaction $H_2 \rightleftharpoons 2H^+ + 2e$. Exposure to pure H_2 at room temp. causes decay of catalytic activity, and this is related to the "sintering" which occurs at higher temp. (350°). The catalytic life increases with thickness of metallic deposit, and it is concluded that the apparently smooth deposits have internal surfaces of which the catalytic activity persists owing to low

accessibility to H_2. Activation of H_2 probably causes the decay (cf. A., 1932, 1004). J. G. A. G.

Present position of the theory of ammonia catalysis. I. Chemical mechanism of the catalysis. W. FRANKENBURGER (Z. Elektrochem., 1933, **39**, 45—50). F. L. U.

Poisoning of platinum catalysts in the oxidation of ammonia. W. HENNEL (Przemysl Chem., 1932, **16**, 258—265).—Synthetically prepared NH_3 contains traces of org. substances, which are probably responsible for the poisoning of Pt catalysts used in the process of oxidation to HNO_3. This effect is not obtained by adding NH_2Me, C_5H_5N, C_6H_6, or C_2H_2 to the reaction mixture. Decarriere's finding that C_2H_2 poisons Pt catalysts (A., 1922, ii, 284) is ascribed to the presence of P in the C_2H_2 used in his experiments. R. T.

Action of catalysts on the dehydration of Kato kaolin. T. Ao (J. Soc. Chem. Ind. Japan, 1932, **35**, 567—568B).—The dehydration of Kato kaolin commences at about 400°, proceeds very rapidly at 400—500°, and ends practically at 1300°. In presence of 1—2% of Na_2WO_4 the first and last temp. are lowered to 300° and 1000°, respectively. Thermal balance measurements indicate that the dehydration in absence of catalyst takes place at about 400°, proceeds rapidly at 450—600°, and ends practically at 850°. In presence of Na_2WO_4 or of $(NH_4)_2MoO_4$ the dehydration proceeds more smoothly and perfectly (cf. change of α-quartz to α-tridymite in the presence of the same catalysts). J. W. S.

Manufacture of formaldehyde by catalytic oxidation and dehydrogenation of methyl alcohol. I. G. NATTA.—See B., 1933, 100.

Catalytic dehydrogenation of ethyl alcohol. M. Y. KAGAN and O. M. PODUROVSKAYA (J. Appl. Chem., Russia, 1932, **5**, 378—388).—CuO, obtained by pptg. aq. $CuSO_4$ or $Cu(NO_3)_2$ with NaOH, and reduced with H_2, EtOH, or CO, is a satisfactory catalyst; CuO heated at 900—950° before reduction is better. The ratio MeCHO : H_2 is 87% at 260° and 86% at 320°, whilst the EtOH decomposed is, respectively, 17·8 and 48·4%. Time does not appreciably affect the ratio, but affects the % EtOH decomposed. Presence of H_2O increases the yield of AcOH. The use of mixed catalysts was investigated. CH. ABS.

Catalytic oxidation of propyl alcohol. I. G. LAKOMKIN, O. S. URBANSKAYA, and E. D. OLSHEVSKAYA (J. Appl. Chem., Russia, 1932, **5**, 581—603).—Equimol. quantities of PrOH and H_2O are passed over a Cu–CuO catalyst (max. yield, Cu 400—420°, CuO 340°). Slow passage of the vapours through the reaction tube decomposes the EtCHO formed. CHEt:CMe·CHO is also formed. Pyrocatalytic oxidation of EtCHO to $EtCO_2H$ results in low yields. CH. ABS.

Test of "tunnel" theory of heterogeneous catalysis on hydrogenation of styrene. E. CREMER and M. PÓLÁNYI (Z. physikal. Chem., 1932, **B**, **19**, 443—450).—If the hydrogenation occurs through the "tunnel effect" (A., 1931, 318, 576) the velocity should be much smaller for the heavier than for the lighter H isotope, and when almost all the H has reacted the heavier isotope should be conc. in the residue. Experiment has failed to reveal such concn. Measurement of the displacement of the isotopic ratio in such experiments would make it possible to decide whether the motion of the atoms in chemical reactions could be represented by the equations of motion of classical mechanics or there were appreciable quantum-mechanical deviations. R. C.

Kinetics of electrode processes. II. Reversible reduction and oxidation processes. J. A. V. BUTLER and G. ARMSTRONG (Proc. Roy. Soc., 1933, **A**, **139**, 406—416).—The cathodic reduction of methylene-blue solutions and the cathodic and anodic behaviour of solutions of quinhydrone at Pt electrodes have been studied. A transition phenomenon is observed over the whole range of currents and of concn., which is ascribed to the depletion of the depolariser in the neighbourhood of the electrode. L. L. B.

Electrolysis of dry liquid ammonia. R. COUSTAL and H. SPINDLER (Compt. rend., 1932, **195**, 1263—1264).—Dry liquid NH_3 electrolysed with p.d. of 2—8000 volts shows no definite contra-e.m.f. and does not obey Ohm's law, current increasing less rapidly than p.d. With a current of a few milliamp., anodes of Cu, Au, or Ag are rapidly reduced to powder which when heated evolves NH_3 leaving the metal; graphite behaves similarly. Sb, Fe, Mo, Ni–Cr, Pt, Te, and W are more resistant, but become covered with a yellow film; Ni affords a white substance turning violet on hydration, converted by HNO_3 into a yellow plastic product which is unattacked by HCl or H_2SO_4, but sol. in aqua regia, and leaving Ni when heated above 300° (cf. A., 1900, ii, 474). C. A. S.

Electrolytic deposition of zinc from acid solutions. H. KIYOTA (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 301—310).—Zn cannot be deposited quantitatively with safety on a Classen electrode from H_2SO_4 solutions, but good smooth deposition can be obtained from AcOH solutions. Optimum c.d., acid concn., and times of electrolysis for varying concn. of Zn are tabulated. Concns. of Na_2SO_4, $(NH_4)_2SO_4$, etc. $< 0{\cdot}15N$ do not interfere, but NO_3' and Cl' must be absent. J. W. S.

Anodic phenomena in cadmium-plating solutions. G. SODERBERG.—See B., 1933, 110.

Deposition of copper on aluminium. H. GINSBERG.—See B., 1933, 153.

Electrodeposition of nickel and chromium. J. W. CUTHBERTSON.—See B., 1933, 153.

Electrochemical behaviour of platinum. III. G. GRUBE and D. BEISCHER (Z. Elektrochem., 1933, **39**, 38—45).—The electrolytic deposition of Pt from various baths has been studied. The most satisfactory for separation of bright Pt are those containing $[Pt(NH_3)_2(NO_2)_2]$ or a mixture of H_2PtCl_6 with $Na_2NH_4PO_4$. From these baths H_2 is evolved at the cathode even at the lowest c.d. Under no conditions did Pt separate from $K_2Pt(CN)_4$, although reduction to an unidentified compound took place at a Hg cathode. F. L. U.

Spectroscopic study of decomposition and synthesis of organic compounds by electrical discharges: electrodeless and glow discharges. W. D. HARKINS and J. M. JACKSON (J. Chem. Physics, 1933, **1**, 37—47; cf. A., 1930, 1171).—In both types of discharge the nature of the products is largely determined by the initial decomp. of the mols. into fragments such as OH, CH, NH, C_2, CN, N_2, CO, CO^+, H_2O, CS, S_2, C, C^+, H, and S, which form the starting point for the subsequent syntheses. CH_4, n-C_7H_{16}, C_6H_6, $C_6H_4Me_2$, $C_6H_3Me_3$, PhCHO, PhOH, C_4H_4S, and C_5H_5N have been examined. The effects are due mainly to electron impacts. The phenomena are too complicated to enable a definite mechanism to be postulated. F. L. U.

Influence of pressure on photographic sensitivity to light of various wave-lengths. N. T. ZE and C. L. CHAO (Compt. rend., 1933, **196**, 107—108; cf. A., 1932, 581).—E being the illumination which produces in the emulsion under pressure p the same density as E_0 does under normal pressure, E/E_0 increases with p, but the amount of this increase decreases rapidly, as λ decreases, from 1·77 for 81·3 kg. per sq. cm. to 2·64 for 1224 kg. for λ 5770, but is practically unchanged for $\lambda < 3650$. C. A. S.

Photochemical nitrification in sea-water. C. E. ZOBELL (Science, 1933, **77**, 27—28).—Irradiation of sea-water by sunlight or ultra-violet light with max. intensity at 2950 Å. oxidises NH_4 salts to NO_2', and it appears that part, at least, of the nitrification of sea-water is photochemically activated. L. S. T.

Temperature coefficient of the photosensitised hydrogen–oxygen reaction. H. S. TAYLOR and D. J. SALLEY (J. Amer. Chem. Soc., 1933, **55**, 96—109).—The velocity of H_2O formation in 600 mm. of $2H_2 : O_2$ mixture at 280—535° photosensitised by 0·0004—0·02 mm. Hg has been determined. The length of reaction chain does not increase markedly below 490°, and as the temp. coeff. of the Hg-sensitised and the direct photochemical reactions of H_2 and O_2 are similar over the whole temp. range (cf. A., 1929, 659), it is suggested that the chain mechanism of the reaction is the same whether initiated by H or O atoms. However, with 1·3—97·5 mm. of NH_3 as photosensitiser in place of Hg, the rate of H_2O formation above 300° increases more rapidly than is required by the Arrhenius equation, and for each temp. there is a concn. of NH_3 which gives a max. velocity, showing that at high concns. a chain-breaking effect of NH_3 becomes predominant. Sensitisation by NH_3, in addition to initiating the reaction by H atoms, involves assistance in propagating the chains, possibly by means of NH_2 and its oxidation products. J. G. A. G.

Combination of hydrogen and oxygen photosensitised by nitrogen peroxide. R. G. W. NORRISH and J. G. A. GRIFFITHS (Proc. Roy. Soc., 1933, **A, 139**, 147—162).—The general results of Thompson and Hinshelwood (A., 1929, 657) for the reaction H_2–O_2 catalysed by NO_2 between 300° and 500° have been confirmed. The reaction is photochemically sensitive, and where measurable velocities were obtained, exposure of the reaction vessel to a Hg-vapour lamp increased the thermal effect fourfold at 300° and twofold at 360°, the photochemical effect disappearing at 450°. As the photochemical effect was subject to the same wave-length threshold as the photochemical decomp. $NO_2+h\nu=NO+O$, it is concluded that O atoms are the genesis of the reaction chains for the photosensitised reaction. Also, as the photochemical effect is subject to the same limits of pressure of NO_2 as the purely thermal effect, it is inferred that the NO_2 provides atoms of O which start the reaction. A kinetic mechanism is developed to explain the results. L. L. B.

Production of hydrogen peroxide in the mercury-sensitised hydrogen–oxygen reaction. J. R. BATES and D. J. SALLEY (J. Amer. Chem. Soc., 1933, **55**, 110—123; cf. this vol., 34).—With dry H_2–O_2 mixtures yields of $H_2O_2 > 85\%$ have been obtained and the H_2O formed is ascribed largely to the secondary decomp. of H_2O_2. Added H_2O vapour has no effect on the yield of H_2O_2 and therefore the reaction $H+O_2+H_2O \longrightarrow H_2O_2+OH$ is not important. The Haber mechanism for reaction between H atoms and O_2 mols. is not the only course of reaction at room temp. H_2O_2 formation occurs not only by combination of OH radicals, but also by some other reaction, the nature of which is discussed. J. G. A. G.

Kinetics of mercury-sensitised reaction between hydrogen and oxygen. J. R. BATES (J. Amer. Chem. Soc., 1933, **55**, 426—427).—Almost all existing data are correlated if the following reactions are assumed: $Hg+h\nu \longrightarrow Hg'$, $Hg'+H_2 \longrightarrow 2H+Hg$, $Hg'+O_2 \longrightarrow O_2'+Hg$, $H+O_2 \longrightarrow HO_2$, $HO_2+H_2 \longrightarrow H_2O_2+H$, $2HO_2 \longrightarrow H_2O_2+O_2$. In agreement with experiment, this mechanism requires a higher quantum efficiency at lower light intensities. J. G. A. G.

Photo-dissociation of hydrogen peroxide in the presence of hydrogen and carbon monoxide and the recombination of OH radicals. G. VON ELBE (J. Amer. Chem. Soc., 1933, **55**, 62—69).—The rate of reaction in the vapour phase of 1·7—5·1 mm. H_2O_2 with O_2 and CO at 28° and 40° in the light of the Zn spark has been investigated by a flow method. The results do not accord with the scheme of Frankenburger and Klinkhardt (A., 1932, 348) involving the reaction $OH+OH+X=H_2O_2+X$. J. G. A. G.

Effect of the walls of the container on the photochemical reaction H_2+Cl_2. A. TRIFONOV (Trans. State Phys.-Tech. Lab., Moscow, 1930, No. 14, 26—33).—At pressures > 30 mm., disruption of the reaction chains takes place in the gaseous space; at < 10 mm., the disruption takes place chiefly at the wall surface. CH. ABS.

Relation between light intensity and the velocity of photochemical reactions. A. K. BHATTACHARYA (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 33—38).—The mechanisms of the photochemical reactions between H_2 and the halogens are discussed with respect to the relation between intensity of illumination and velocity of reaction (cf. A., 1930, 175, 555, 1384). J. W. S.

Relation between intensity and velocity of a photochemical reaction. W. V. BHAGWAT (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 54—59).—Theoretical. J. W. S.

Anomalous decomposition of ozone in presence of chlorine. L. J. HEIDT, G. B. KISTIAKOWSKY, and G. S. FORBES (J. Amer. Chem. Soc., 1933, **55**, 223—231; cf. A., 1932, 348, 815).—The thermal and photo-decomp. of O_3 alone and in presence of Cl_2 has been investigated at temp. between 2° and 50° in SiO_2 and Pyrex vessels. Very erratic results were obtained, especially when the reaction system was very carefully purified. In general, a fast reaction succeeded a slow reaction, the duration of which was curtailed by rise of temp. or absorption of light. Temp. coeffs. as high as 14·6 and quantum efficiencies between 3 and 0·8 were observed. Conc. H_2SO_4 or H_2O in the reaction system did not eliminate the anomalies, which were minimised when greased stopcocks were used in the gas train. J. G. A. G.

Bromine-sensitised photo-decomposition of chlorine dioxide. J. W. T. SPINKS (J. Amer. Chem. Soc., 1933, **55**, 428—429).—The quantum efficiency of the direct decomp. by light of wave-length 4360 Å. is only slightly less than by light of λ 3650, although predissociation does not extend beyond 3750 Å. In presence of Br_2, light of λ 5460 Å. causes decomp. with a similar quantum efficiency. J. G. A. G.

Photochemistry of mixtures of chlorine, oxygen, and carbon monoxide. G. K. ROLLEFSON (J. Amer. Chem. Soc., 1933, **55**, 148—152; cf. A., 1931, 1137; 1930, 433).—In accordance with the view that CO_2 and $COCl_2$ are formed by the reaction of the photochemically produced intermediate compound COCl with O_2 and Cl_2, respectively, it is found that at const. temp. the ratio of CO_2 to $COCl_2$ produced is a function solely of the $O_2 : Cl_2$ ratio. Experiments at 20°, 89°, and 130° show that the heat of activation of reaction (1) $COCl+Cl_2=COCl_2+Cl$ exceeds that of (2) $COCl+O_2=CO_2+ClO$ by 3000 g.-cal., and the probability of (1) is 20 times that of (2). J. G. A. G.

Photochemical decomposition of carbonyl chloride vapour. F. ALMASY and T. WAGNER-JAUREGG (Z. physikal. Chem., 1932, **B**, **19**, 405—419).—An amplification of a preliminary note (A., 1931, 578). Decomp. requires $\geq$ 100 kg.-cal. Decomp. in radiation of wave-length 2750—3050 Å. is largely or wholly due to predissociation. R. C.

Photochemical oxidation of carbonyl chloride. G. K. ROLLEFSON and C. W. MONTGOMERY (J. Amer. Chem. Soc., 1933, **55**, 142—147).—The rate of direct photochemical oxidation of $COCl_2$ to CO_2 and Cl_2 at temp. between 20° and 200° is given by $d[CO_2]/dt = kI_0[COCl_2]/(1+k'[Cl_2]/[O_2])$. A mechanism based on the primary process $COCl_2+h\nu=COCl+Cl$ leads to the above relation. J. G. A. G.

Photo-oxidation of gaseous hydrogen iodide. J. R. BATES and G. I. LAVIN (J. Amer. Chem. Soc., 1933, **55**, 81—89).—The photo-decomp. of 50—112 mm. of HI in presence of 101—611 mm. of O_2 leads ultimately to the formation of H_2O. The reactions $HI+h\nu \longrightarrow H+I$, $H+HI \longrightarrow H_2+I$, $H+O_2 \longrightarrow HO_2$, $HO_2+HI \longrightarrow H_2O_2+I$, $HO_2 \longrightarrow H+O_2$ lead to an expression consistent with the data, and a life of 10^{-8} to 10^{-9} sec. for the quasi-mol. HO_2. J. G. A. G.

Photochemical kinetics of iodine–oxalate reaction. I. E. ABEL, H. SCHMID, and K. RETTER (Z. physikal. Chem., 1932, **163**, 53—66).—In the reaction at 25° in the light of a Hg-vapour lamp, either unfiltered or filtered (3660 and 4050 Å.), at very low [I′] and under conditions of practically total absorption of the incident radiation and const. radiation intensity, the rate, k, at const. [I′], is independent of $[I_2]$ and $[I_3']$. It is proportional to $[C_2O_4'']$ and $[HC_2O_4']$, the proportionality factors being in the ratio 1 : 0·03. When $[I'] < 0{\cdot}001N$, k increases with $1/[I']$ less rapidly than corresponds with proportionality. No reaction of I with $H_2C_2O_4$ could be detected. R. C.

Photo-reactions of oxalates with bromine and iodine. I, II. R. O. GRIFFITH, A. MCKEOWN, and A. G. WINN (Trans. Faraday Soc., 1933, **29**, 369—386, 386—395).—I. The influence of light of wave-length 579—313 mμ on the action of Br on neutral oxalate and $H_2C_2O_4$ has been studied at 6·5°, 11·5°, and 16·5°. For an absorption range up to 85%, $\gamma\sqrt{E}$, where γ is the quantum yield and E the rate of absorption of radiant energy (quantum per c.c. of beam per min.), is independent of the initial concn. of Br, the extent of reaction, the incident energy, and the dimensions of the reaction cell. For absorptions $>$ 85% $\gamma\sqrt{E}$ falls progressively, and its variation with absorption can be accounted for quantitatively on the basis of a reaction mechanism involving a Br atom chain. Two independent processes occur and are differently retarded by Br′; one involves C_2O_4'' and the other HC_2O_4'. In 0·25M-KBr the intrinsic rate of the C_2O_4'' reaction is 100 times that of the other, and in 0·03125M-KBr the ratio is 34. For both reactions the retarding influence of Br′ increases with decreasing wave-length. The temp. coeffs. of the two reactions are 2·07 and 2·16, respectively. Expressions for $\gamma\sqrt{E}$ are given in terms of concns. of C_2O_4'' or HC_2O_4', Br′, Br_2, and Br_3' and also of the extinction coeffs. of Br_2 and Br_3'. These reproduce the experimental results quantitatively. The photochemical reaction of I with neutral oxalate at 25° for light of wave-length 579, 546, and 436 mμ in presence of KI conforms to a similar expression for $\gamma\sqrt{E}$. The rate of reaction with $K_2C_2O_4$ is slightly $>$ with $Na_2C_2O_4$.

II. Theoretical. The above experimental data are interpreted by reaction mechanisms according to which: (1) The effective primary process is a photo-dissociation of the trihalide ion, the free halogen acting as an internal light filter. (2) Most of the halogen atoms (X) formed by the primary process are transformed into X_2', *i.e.*, $X+X' \quad X_2'$. (3) The rate-determining reactions are: (*a*) $HC_2O_4'+Br \longrightarrow C_2O_4'+H^{\cdot}+Br'$; (*b*) $C_2O_4''+Br \longrightarrow C_2O_4'+Br'$, and $C_2O_4''+Br_2' \longrightarrow C_2O_4'+2Br'$; (*c*) $C_2O_4''+I \longrightarrow C_2O_4'+I'$, followed by reaction of C_2O_4' with Br_2 (and Br_3') or I_2 (and I_3') with regeneration of Br or I atoms. The effective chain-breaking mechanism is $X_2'+X_2' \longrightarrow X_3'+X'$. M. S. B.

Photolysis of aqueous ammonia. L. GION (Compt. rend., 1933, **196**, 344—345; cf. A., 1932, 1006).—In absence of O_2 ultra-violet light produces hyponitrite and photolysis of NH_3: $4NH_4OH=$

$(NH_4)_2N_2O_2+4H_2+2H_2O$, and $2NH_3=N_2+3H_2$, although it was not possible to isolate hyponitrite owing to the great dilution. In presence of O_2 hyponitrite is also formed, but immediately oxidised to nitrite, the concn. of which is limited by its photochemical destruction, the formation of N_2 being proportional to the period of illumination (cf. A., 1912, ii, 750). C. A. S.

Photochemical action of complex light. C. WINTHER (Z. wiss. Phot., 1933, **31**, 251—264).—The abnormal results obtained by Padoa and Vita (A., 1926, 808, 1014; 1928, 378) for the photochemical action of white light compared with the sum of the actions of component spectral portions are criticised on the following grounds: (1) A $NiSO_4$ filter passing light between 567 and 480 mμ has (from extinction coeff. measurements) a transparency of 94·5%, not 9%, as stated. (2) Induction periods for the reactions investigated have not been considered. (3) The results of the measurement of the oxidation of HI by titration with $Na_2S_2O_3$ will, in strongly acid solution, vary with the time of titration. Corrected results show that the time and intensity of exposures are proportional in the normal manner. New apparatus and methods, free from previous defects, are described, and careful measurements of the rate of oxidation of HI show results in conformity with theoretical expectations. The difficulty of obtaining reproducible results is discussed. J. L.

Influence of the condition of grains [in a photographic emulsion] on their sensitivity to exposure to α-particles. M. BLAU and H. WAMBACHER (Z. wiss. Phot., 1933, **31**, 243—250).—Cf. A., 1932, 1215.

Action of developer on latent images of different ages. C. JAUSSERAN (Compt. rend., 1932, **195**, 1260—1262; cf. B., 1929, 340; 1932, 129).—The probable error in photometric measurements by comparing the densities of negatives which have lain undeveloped for varying periods with a prepared scale is less as the period of development, and consequently the coeff. of contrast, is greater. Two plates exposed differently and developed after different intervals may give negatives of the same density for one period of development, and different densities for another period. Differences in negatives due to development after different intervals of time after exposure are very small with quinol, but considerable with metol. C. A. S.

Evolution of the latent image. C. JAUSSERAN (Compt. rend., 1933, **196**, 341—343).—Ilford Panchromatic plates show a decrease in density as the interval between exposure and development increases; this is due to some substance removed from the plate by thorough washing with H_2O or EtOH before exposure. Negatives of equal density but developed after different intervals after exposure are differently affected by a $K_4Fe(CN)_6$ reducer. Those of greater density undergo greater reduction when developed after a shorter interval; the reverse is the case for weaker negatives. Density alone therefore does not completely characterise a negative. C. A. S.

Photochemical hydrolysis of sucrose. A. K. BHATTACHARYA (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 45—47; cf. A., 1930, 555; 1931, 1019).—A discussion of results previously reported. J. W. S.

Possible action of short electromagnetic waves on definite chemical compounds. L. AMATI (Annali Chim. Appl., 1932, **22**, 803—811).—Glucose solution undergoes change in rotation and heating under the action of short electromagnetic waves (cf. Lakhovsky, "L'oscillation cellulaire," Paris, 1931). Slight chemical changes are similarly produced in solutions of methyl- and phenyl-glyoxal, and glyceric acid. T. H. P.

New relations in photographic effects of α-rays. T. R. WILKINS and R. WOLFE (Physical Rev., 1931, [ii], **37**, 1688).—Equations connecting the no. of grains per c.c. of emulsion have been obtained, and provided that a reciprocity correction for each emulsion is determined, the photographic plate is a good quant. means for counting α-rays. L. S. T.

Effect of gaseous impurities on the radiochemical combination of carbon monoxide and oxygen. C. ROSENBLUM (J. Amer. Chem. Soc., 1933, **55**, 220—223; cf. A., 1932, 822).—H_2O vapour slightly retards the reaction, whilst HCO_2H has no real effect. The results indicate transfer of ionisation by the highly efficient catalyst, N_2, not only to reactants but also to the less efficient catalyst CO_2. J. G. A. G.

Efficiency of carbon dioxide as a radiochemical catalyst. C. ROSENBLUM (J. Physical Chem., 1932, **37**, 53—58).—In the oxidation of H_2 or CO the catalytic efficiency of CO_2 is only 14·5%. In the polymerisation of C_2H_2 only about 30% of the CO_2 ionisation is used to promote the reaction. It is suggested that the inefficiency of a radiochemical catalyst is governed by the tendency of the inert gas to cluster about gaseous ions and crowd out reactant mols. E. S. H.

Radiochemical decomposition and synthesis of hydrogen iodide; radiochemical decomposition of hydrogen chloride. J. VANDAMME (Bull. Soc. chim. Belg., 1932, **41**, 597—606).—The ratio $M:I$ (mols. decomposed per ion pair) in the decomp. of HI by α-particles at 20° and at various pressures is 8·2 approx., and for HCl 3·3. In the synthesis of HI by the action of α-particles on a mixture of I and H_2 at 100° there is a max. velocity at an I concn $<12\%$. The ratio $M:I$ in the equimol. mixture is 1·25. O. J. W.

Purification of radon. R. LIVINGSTON (Rev. Sci. Instr., 1933, [ii], **4**, 15—17).—The gas is heated in contact with CuO containing La_2O_3. C. W. G.

Carbonyls of lithium, rubidium, and cæsium [calcium ?]. T. G. PEARSON (Nature, 1933, **131**, 166—167).—Li, Rb, and Ca carbonyls have been prepared by the action of CO on the NH_3 solution of corresponding metal ammoniate. LiCO darkens on keeping owing presumably to the separation of small amounts of C and decomposes at 300° in a vac. with liberation of C. At 500° decomp. to Li_2CO_3, Li_2O, and C is rapid. H_2O vapour is quietly absorbed forming a dirty-brown liquid, but H_2O detonates the

carbonyl with instantaneous ignition of the gaseous products (86% H_2 and 14% CO). A cloud of C is formed and a residue of Li_2CO_3 and C is left. RbCO is readily sol. in H_2O (pale yellow solution). Decomp. occurs in a vac. at 350° and rapidly increases with a rise in temp., C, oxide, and carbonate being produced. $Ca(CO)_2$ darkens in colour when treated with H_2O, and partly dissolves with evolution of heat but with no detonation. Decomp. commences at approx. 200° in vac., and $CaCO_3$, CaO, and C are the final products. L. S. T.

Polyiodides of cæsium. H. W. Foote, W. M. Bradley, and M. Fleischer (J. Physical Chem., 1933, **37**, 21—27).—The existence of CsI_3 and CsI_4 in the system CsI–I–PhMe at 6° and 25° has been confirmed. These compounds also exist in C_6H_6 in addition to a ternary compound (probably $2CsI,9I_2,4C_6H_6$). E. S. H.

Silver iodomercurate. F. Gallais (Compt. rend., 1932, **195**, 1390—1392; cf. this vol., 37).—The conductivity curve of 0·1*M*-2KI+HgI_2 in EtOH to which varying amounts of 0·1*M*-$AgNO_3$ are added indicates the formation of Ag_2HgI_4 as the only definite compound, a result confirmed by comparison of the coeffs. of magnetisation of HgI_2, AgI, and Ag_2HgI_4. *X*-Ray examination of the heated (red) form shows the same structure as that of the unheated (yellow) form (cf. A., 1930, 1359). The phototropic properties appear to be due to presence of H_2O (cf. A., 1895, ii, 146). C. A. S.

Comparison of the intermetallic compound $AuCd_3$ obtained from the melt and from solution. P. A. Thiessen and J. Heumann (Z. anorg. Chem., 1932, **209**, 325—327).—The ppt. obtained by placing Cd in very dil. $HAuCl_4$ is identical in composition and by *X*-ray analysis with the compound $AuCd_3$ obtained from the molten metals. E. S. H.

Preparation of metallic cyanamides, and their transformation into cyanides. G. Bernheim (Bull. Soc. chim., 1932, [iv], **51**, 1388—1415).—In the prep. of the cyanamides of Ca, Sr, Ba, Zn, Cd, Mg, and Be by passing $(CN)_2$ over the oxide at a high temp., Ca, Ba, *Zn*, and *Cd* cyanamides are obtained practically pure. $BeCN_2$ is the most unstable. The range of temp. through which a good yield is obtained is very narrow. Zn, Cd, Mg, and Be cyanamides are very sol. in H_2O. There is an equilibrium between CN_2'', CN′, and C although it is masked by other reactions due to the instability of the cyanides at high temp. A detailed study has been made with $BaCN_2$. The curve showing yield of $Ba(CN)_2$ as a function of temp. gives first a max. and then a min. Similar curves were obtained for the transformation of $SrCN_2$ and $CdCN_2$ into cyanides, but a max. only was obtained for $CaCN_2$ and $MgCN_2$. A min. might have been reached at a still higher temp. $Zn(CN)_2$ is too unstable for its formation to be observed. M. S. B.

"Chloride of lime." N. Tarugi (Boll. Chim. farm., 1932, **71**, 797—802, 837—847, 877—886, 917—922).—Previous work on the formation, composition, analysis, and decomp. by light and air of "chloride of lime" and on phase relationships in the system $Ca(OCl)_2$–$CaCl_2$–H_2O are reviewed at length. The primary reaction between $Ca(OCl)_2$ and Hg results in the formation of, probably, $Ca(OHgCl)_2$. It appears that the principal constituent of "chloride of lime" is $Ca(OCl)_2$, and that this is associated with other, secondary, constituents such as $Ca(OH)_2$, H_2O, etc., to form various stable systems of which the composition is dependent on the temp. H. F. G.

Hydrated dicalcium aluminate. H. Lafuma (Compt. rend., 1932, **195**, 1276—1278; cf. A., 1931, 1370; B., 1930, 907; 1932, 772).—The existence of $2CaO,Al_2O_3,8H_2O$ and its formation on hydration of aluminous cement is confirmed by the analysis of a cement calcined at 600° (a higher temp. causes recombination of Al_2O_3 with the aluminate), at which temp. free Al_2O_3 becomes insol. in cold 0·1*N*-HCl, whilst the aluminate remains readily sol. Ppts. of composition (1—4)CaO,Al_2O_3,aq. obtained by the interaction of aq. $Ca(OH)_2$ and aq. CaO,Al_2O_3 when calcined at 600° contain free Al_2O_3 unless the proportion of CaO is $>2CaO:Al_2O_3$. C. A. S.

Sublimation of magnesium in a vacuum, and pouring it in argon. J. Hérenguel and G. Chaudron (Compt. rend., 1932, **195**, 1272—1274; cf. A., 1931, 1380).—An arrangement is figured for subliming considerable quantities of Mg in a vac. of 0·01 mm. (of A), and its subsequent fusion under a pressure of 1 kg. of A, the fused metal being then siphoned into the mould. Ingots of 25 kg. of pure Mg are thus obtainable, of hardness 29 Brinell. The method is applicable to the prep. of many alloys of Mg. C. A. S.

Brick-red form of zinc oxide. H. Berg (Z. anorg. Chem., 1932, **209**, 328).—The modification described by Kutzelnigg (A., 1932, 1099) was known previously (cf. A., 1895, ii, 390). E. S. H.

Atmospheric oxidation of mercury. A. Stock, F. Gerstner, and H. Kohle (Naturwiss., 1932, **20**, 954—955).—Quant. experiments are described on the oxidation of Hg by air and H_2O, KOH, and KCl. In the last case, HgCl is formed. Hg under KCl solution, in presence of air, becomes coated with a layer of white crystals of a complex Hg^I salt. The vapour of HgO is partly dissociated into its elements at room temp. A. J. M.

[Metallic] mercuribromoiodides. A. C. Vournazos (J. pr. Chem., 1933, [ii], **136**, 41—48).—The following *compounds* have been prepared by interaction of $HgBr_2$ with the appropriate iodide either alone or in a suitable solvent ($COMe_2$, aq. $COMe_2$, or C_6H_6); $KI,2HgBr_2$ (I), $ZnI_2,4HgBr_2$, $PbI_2,4HgBr_2$, $HgI_2,2HgBr_2$, $AsI_3,6HgBr_2$, $SbI_3,6HgBr_2$, $BiI_3,6HgBr_2$, $SnI_2,4HgBr_2$, and $SnI_4,8HgBr_2$. The corresponding free *acid*, $HI,2HgBr_2$, is prepared cryst. from (I) and HCl in $COMe_2$; unlike many of the salts, it is readily decomposed by H_2O. Interaction of (I) with Cu or $CuCl_2$ in $COMe_2$ gives $KI,2CuBr_2$ and Hg or $HgCl_2$, respectively. H. A. P.

Drying agent which contains aluminium sulphate as principal constituent. N. Taketomi and S. Sakata (J. Soc. Chem. Ind. Japan, 1933, **36**, 18B).—Anhyd. $Al_2(SO_4)_3$ is an efficient drying agent which does not become sticky and may be reactivated by

heating. Addition of a little starch or kaolin is recommended. D. R. D.

Thermal and chemical changes of Kato kaolin and their application. K. HISHIYAMA and S. TABEI (J. Soc. Chem. Ind. Japan, 1933, **36**, 12—13B).—The influence of preliminary ignition at various temp. from 300° to 1200° on the solubility in HCl of the Al_2O_3 in Kato kaolin has been studied. Dissolution occurs most readily after ignition at 800°. Above 1000° the solubility is decreased suddenly. Previous addition of Na_2WO_4 lowers the first temp. to 600° and the second to 900°. At 600° the kaolin decomposes into Al_2O_3, SiO_2, and H_2O. A 37% yield of mullite is obtained on ignition at 1400°. A 43% yield may be obtained by means of a hydrothermal synthesis. D. R. D.

Action of aluminium salts on alkali tartrates. YEU-KI-HENG (Compt. rend., 1933, **196**, 259—261; cf. A., 1910, ii, 372; 1927, 856).—By comparing the curves relating rotation to x for solutions containing $x/2$ c.c. of 0·25*N*-$Al_2(SO_4)_3$, $(20-x)$ c.c. of 0·5*N*-$Na_2C_4H_4O_6$, and $x/2$ of 1·5*N*-NaOH, and for solutions containing similar vols. of solutions of double the foregoing concns., it is inferred that the compounds $Al[Al(C_4H_4O_6)_3]$ and $Na_3[Al(C_4H_4O_6)_3]$ are formed, the Al in the Al salt being only partly pptd. by aq. Na_2HPO_4, and that in the Na salt not at all. C. A. S.

Preparation of germanium tetrahalides. H. BAUER and K. BURSCHKIES (Ber., 1933, **66**, [*B*], 277—278).—$GeCl_4$, b.p. 85·5°/759 mm., $GeBr_4$, b.p. 183°, and GeI_4, m.p. 145—146°, are prepared by heating GeO_2 in a pressure flask until dissolution is complete with HCl (*d* 1·19) at 170—180°, HBr (*d* 1·78) at 180°, and HI (*d* 1·7) at 148—150°, respectively. H. W.

Germanium. XI. Germanium chloroform and germanium oxychloride. R. SCHWARZ and F. HEINRICH (Z. anorg. Chem., 1932, **209**, 273—276; cf. A., 1931, 446).—No evidence of the existence of the supposed compound GeH was obtained by passing $GeHCl_3$ vapour over Na or Na–K alloy. When Ag was used, an unidentified bright red substance, stable only at low temp., was formed. *$GeOCl_2$* is formed by reaction of $GeHCl_3$ vapour with Ag_2O. The liquid has m.p. −56° and decomposes into GeO and Cl_2 at 110°. By treating $GeOCl_2$ with NH_3 a *modification* of GeO, d_4^{21} 1·825, is produced. E. S. H.

Double compounds of zirconium sulphate. H. TRAPP (Z. anorg. Chem., 1932, **209**, 335—336).—On evaporation of ZrO_2,SO_3,H_2O, treated with 1 mol. of $FeSO_4$ or $ZnSO_4$ in 30% H_2SO_4, crystals of $ZrO_2,XO,(SO_3)_3,6H_2O$ (X=Fe or Zn) are obtained. The substances are decomposed by excess of H_2O or H_2SO_4. E. S. H.

Separation of cerium from the other cerium earths. H. BJØRN-ANDERSEN (Z. anorg. Chem., 1933, **210**, 93—99).—Ce is pptd. as cryst. $Ce(CrO_4)_2,2H_2O$ by means of $K_2Cr_2O_7$. The purity of the product can be ascertained by dissolving in acid, pptg. with $K_2C_2O_4$, igniting to CeO_2, and noting the colour. This procedure may be developed into a fractionation process. E. S. H.

Precipitation of basic lead salts and metallic phosphates. L. CLOUTIER (Ann. Chim., 1933, [x], **19**, 5—77; cf. A., 1932, 38).—Mixtures of aq. $Pb(NO_3)_2$, H_2O_2, and NaOH give ppts. varying in composition from $PbO_{1·36}$ to $PbO_{1·61}$. Over a large range of concn. the composition is $PbO_{1·45}$. No definite basic phosphates were obtained on mixing aq. Pb″, Cu″, Fe‴, UO_2″, Al‴, Zn″, Ag′, Mn″, or Cr‴ salts with H_3PO_4 and NaOH. H_3PO_4 gives with aq. $UO_2(NO_3)_2$ a ppt. of UO_2HPO_4, and with $Pb(NO_3)_2$ one of $Pb_3(PO_4)_2$, but the phosphates of Cu, Al, Zn, Ag, Mn, and Cr are pptd. only by Na_2HPO_4. NaH_2PO_4 and Na_2HPO_4 ppt. $FePO_4$ from aq. $FeCl_3$, but Na_3PO_4 gives rise to a colloidal solution. D. R. D.

Solid ammonium polyiodide. H. W. FOOTE and W. M. BRADLEY (J. Physical Chem., 1933, **37**, 29—31).—In solutions of NH_4I and I in C_6H_6 and PhMe, the only binary periodide which forms above 6° is NH_4I_3. No solvated compound exists. NH_4I_3 is a convenient source of a const., low concn. of I vapour, which can be controlled by variation of temp. E. S. H.

Reactions and properties of nitric oxide and its compounds. III. Reaction between nitric oxide and alkali nitrosodisulphonates. H. GEHLEN (Ber., 1933, **66**, [*B*], 292—297).—NO is rapidly absorbed by K nitrosodisulphonate in alkaline solution: $ON(SO_3K)_2+NO+NaOH=NaNO_2+OH·N(SO_3K)_2$. If the solution is warmed, NO and N_2O are evolved, the latter being due to reaction between HNO_2 and $OH·NH·SO_3H$. If NaOH is replaced by NH_3, an initial rapid absorption of NO soon ceases, probably owing to decomp. of the NH_4NO_2 produced. For the gas-analytical absorption of NO, $FeSO_4$ can be advantageously replaced by $ON(SO_3K)_2+NaOH$, which reacts more rapidly, does not suffer from being a balanced change, and indicates exhaustion of the reagent by becoming decolorised. H. W.

"Blue acid." W. MANCHOT [with H. SCHMID] (Z. anorg. Chem., 1933, **210**, 135—144).—Experiments are described indicating that "blue acid" is formed by the direct attachment of NO, not to H_2SO_4, but to $OH·SO_2·NO_2$. In the experiments of Berl and others (A., 1932, 1219) NO_2 was formed by reduction of H_2SO_4 by NO at high pressures. The acid cannot have the formula SO_5NH_2. F. L. U.

Indicator reactions of nitrogen sulphide. V. N. SKVORTZOV (J. Gen. Chem. Russ., 1932, **2**, 569—575).—Very similar vals. are obtained for the titration of EtOH, CCl_4, C_6H_6, and PhMe solutions of $H_2C_2O_4$ and of $(CH_2·CO_2H)_2$ with EtOH–NaOH, using N_2S_4 as indicator. It follows that the transformation of the colourless to the blue form of N_2S_4 is due, not to structural rearrangement, but to formation of a complex of the type mN_2S_4,nNaOEt. R. T.

Identity of the properties of ozone produced by different methods of ozonising oxygen; b.p. of pure ozone. E. BRINER and H. BIEDERMANN (Helv. Chim. Acta, 1933, **16**, 207—213).—Products formed by ozonising O_2 (*a*) in the usual manner, (*b*) in an "octozone" apparatus, and (*c*) with a high-frequency discharge, have been liquefied and fractionated. In every case the b.p. of the "tail" fraction

was the same, viz., −111·5°/760 mm. The chemical activity of the three products, as judged by oxidation of PhCHO, was identical. It is concluded that no polymeride other than O_3 was present. F. L. U.

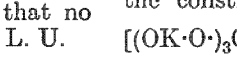
Theory of the [lead] chamber reaction. II. Hydrolysis of nitrosylsulphuric acid. W. J. Muller, D. M. Forbes, and R. Fort (Angew. Chem., 1932, **45**, 782—785).—Determination of the product obtained by diluting a solution of HSO_5N in 80% H_2SO_4 with dil. H_2SO_4 to a final H_2SO_4 concn. of 60% shows that the primary hydrolysis, which occurs rapidly, is $HSO_5N+H_2O\longrightarrow H_2SO_4+HNO_2$. In a NO atm. the reaction $3HNO_2 \rightleftharpoons HNO_3+H_2O+2NO$ takes place to only a slight extent, but if air or N_2 is blown through the acid it proceeds slowly, to the extent of about 60%; on prolonged blowing the remaining HNO_2 is removed completely but without decomp. A complete scheme is given of the reactions occurring at each stage of the chamber process. H. F. G.

Lead chamber process. III. Synthesis of nitrosylsulphuric acid from silver hydrogen sulphate and nitrosyl bromide. E. Berl, F. Becker, and W. Begerow (Z. anorg. Chem., 1932, **209**, 264—266; cf. A., 1932, 1219).—Analysis of the reaction between $AgHSO_4$ and NOBr in presence of CCl_4 indicates that nitrosylsulphuric acid is $OH{\cdot}SO_2{\cdot}ONO$. E. S. H.

Formation of sodium thiosulphate from oxidation of sodium sulphides by means of an aromatic nitro-compound. J. L. Bullock and G. S. Forbes (J. Amer. Chem. Soc., 1933, **55**, 232—238).—The first products of the oxidation of sulphide ion by means of 0·1*M*-*m*-$NO_2{\cdot}C_6H_4{\cdot}SO_3Na$ at 25° are free S, which may be pptd., and OH′; the subsequent formation of thiosulphate, according to the reaction $6OH'+4S=S_2O_3''+2S''+3H_2O$, can be entirely suppressed by a suitable choice of p_H. The velocity of oxidation is greatest with *p*- and least with *o*-substituted NO_2-compounds. The velocity decreases with fall in temp. J. G. A. G.

Decomposition of thiosulphuric acid in dilute boiling solution. E. Carrière and (Mlle.) Carlini (Compt. rend., 1933, **196**, 111—112).—The $H_2S_2O_3$ first formed by the interaction of equiv. amounts of boiling dil. aq. $Na_2S_2O_3$ and HCl decomposes thus: $21H_2S_2O_3=17SO_2+19S+H_2SO_4+H_2S_5O_6+19H_2O$; the decomp. is unimol. and autocatalytic during the first 15 min., during which about 80% of the acid is decomposed (cf. A., 1926, 482). C. A. S.

Reactivity of thiol group. II. N. Hellstrom. —See this vol., 259.

Constitution of perchromates. R. Schwarz and H. Giese (Ber., 1933, **66**, [*B*], 310—315).—Degradation of K perchromate in a tensimeter at 0° shows no stoicheiometric relationship between loss of H_2O and O, thus excluding the formula $KCrO_5,H_2O_2$. Prep. and analyses of the very unstable *Tl perchromate* show it to have the formula $TlCrO_6$, whence $KCrO_6,H_2O$ for the K salt. Addition of the blue perchromate (I) to excess of acid $KMnO_4$ containing a trace of $(NH_4)_2MoO_4$ and titration of the excess shows the presence of 5 O·O groups in the mol. Similar treatment of the red perchromates (II) shows that 3·5 O·O groups are present for each Cr atom, thus leading to the constitutions  for (I) and $[(OK{\cdot}O{\cdot})_3Cr(O){\cdot}O{\cdot}]_2$ for (II). H. W.

Selenium sulphur protochloride. A. Baroni (Atti R. Accad. Lincei, 1932, [vi], **16**, 514—520).—By fractional distillation of mixtures of S_2Cl_2 and Se, which have been heated for 4 hr. at > 250° in sealed tubes, a dark red *liquid*, $SeSCl_2$, b.p. 60—62°/20 mm., has been isolated. A max. yield of 13·2% was obtained with mixtures which had been heated at 200°, but with a mixture kept for 4 months before distillation the yield was 22%. Measurements of *n* of mixtures of S_2Cl_2 and Se before and after ageing for 4 months show that equilibrium is established slowly. $SeSCl_2$ immediately coagulates oils and rubber. The action on piperidine indicates that the substance is Se:S:Cl$_2$. O. J. W.

Hexachloroselenates. W. Petzold (Z. anorg. Chem., 1932, **209**, 267—272).—*Compounds* of the type R_2SeCl_6, where R is NH_4, K, NH_3Me, NH_2Me_2, NH_3Et, $C_2H_4(NH_3)_2$, or $C_5H_5NH_2$, have been prepared by treating the solution of RCl in conc. HCl with $SeCl_4$ or with a solution of SeO_2 in conc. HCl. Their general properties are similar to those of the hexachloroplatinates. E. S. H.

Polonium acetylacetonate. Servigne (Compt. rend., 1933, **196**, 264—266).—Po hydroxide dissolves to the extent of > 90% in acetylacetone (I); the evaporated product is sol. in $CHCl_3$, C_6H_6, EtOH, $COMe_2$, and (I), and in $CHCl_3$ at least is not ionised. On fractional crystallisation of the mixed acetylacetonates of Th, Al, and Po, the Po is conc. with the Th; hence Po is quadrivalent in this compound (cf. A., 1931, 591). C. A. S.

Decomposition reactions of oxides of chlorine. H. J. Schumacher (Z. Elektrochem., 1933, **39**, 7—13). —A lecture. F. L. U.

Detection of element 85 in certain substances. F. Allison, E. J. Murphy, E. R. Bishop, and A. L. Sommer (Physical Rev., 1931, [ii], **37**, 1178—1180).—The magneto-optic method of analysis indicates the presence of element 85 in sea-water, fluorite, apatite, monazite sand (Brazilian), kainite (Stassfurt), KBr, HF, and HBr. The greatest abundance is of the order of 1 in 10^9. L. S. T.

Oxidation of metals under the influence of friction. M. Fink and U. Hofmann (Z. anorg. Chem., 1933, **210**, 100—104).—Oxidation occurs at surfaces of pure Fe, Ni, or Cu under rolling friction in dry air at room temp. The possibility of mechanical activation of a chemical reaction is discussed. E. S. H.

Supposed isomerism in compounds of the non-electrolyte type MX_2A_4. W. Hieber and E. Levy (Z. Elektrochem., 1933, **39**, 24—26).—The supposed β-isomeride of $[Fe(C_5H_5N)_4(CNS)_2]$ reported by Spacu (A., 1914, i, 1089) and considered by Rosenheim, Roehrich, and Trewendt (A., 1932, 1009) to contain Fe^{III}, is shown by analysis to be $Fe(C_5H_5N)_3(CNS)_2,3H_2O$. No case of isomerism of this type now remains established. F. L. U.

Decomposition by heat of complex platinum salts. P. VALLET (Compt. rend., 1932, **195**, 1074—1076).—The temp. of commencement and completion of the decomp. by heat of $(NH_4)_2PtCl_6$ are 250° and 430°, of reduction by H_2 of H_2PtCl_6 100° and < 200°; of K_2PtCl_6 160° and 300°, and of $(NH_4)_2PtCl_6$ 120° and 200°. C. A. S.

Double-decomposition reaction. E. A. WILDMAN (Proc. Indiana Acad. Sci., 1932, **41**, 259—261).—A discussion based on modern views of valency. CH. ABS.

Effect of particle size on intensity in *X*-ray spectroscopic analysis. G. R. FONDA (J. Amer. Chem. Soc., 1933, **55**, 123—127).—The intensity of a diffracted *X*-ray beam is decreased by surface irregularities of the target in proportion to their magnitude and to the absorption coeff. of the target material for the wave-length involved. The importance of using finely-powdered samples in quant. chemical *X*-ray analysis is emphasised. J. G. A. G.

Qualitative analysis by electrolysis and spectrography. A. SCHLEICHER (Z. Elektrochem., 1933, **39**, 2—7).—Qual. spectrographic microanalysis can be applied to mixtures of metals after a preliminary concn. and separation by electrolysis. Procedure is described. The method is at least as sensitive as are chemical " spot " reactions. F. L. U.

Polarographic method in chemical analysis. E. KOSTUK (Bull. Assoc. Chim. Sucr., 1932, **49**, 444—451).—The apparatus and the general character of its applications in analysis are briefly described, with diagrams and graphs (cf. A., 1927, 1159; 1928, 136; 1931, 816; B., 1931, 218). J. H. L.

Volumetric analysis with fluorescent indicators. W. HOLTHOF (Z. anal. Chem., 1933, **91**, 263—266).—As a source of ultra-violet light for this work a 200-watt Osram-Nitraphot lamp may be employed with a Cellophane filter to cut out the visible part of the spectrum. A. R. P.

Improvements in the hydrogen electrode for determination of p_H. P. L. DU NOUY (Compt. rend., 1932, **195**, 1265—1267; cf. A., 1932, 135).—The necessity of frequently replatinising the Pt electrode due to its being " poisoned " by the solution examined is completely avoided by adding to that solution (in amount about 0·4 c.c.) about 0·05 c.c. of Bredig's colloidal Pd and a small bubble of H_2. Equilibrium takes a little longer (10—20 min.) to be established, but in all other respects the electrode acts normally. C. A. S.

Conductimetric analysis. I. Acids and acid mixtures. E. C. RIGHELLATO and C. W. DAVIES (Trans. Faraday Soc., 1933, **29**, 429—437).—An apparatus for general use in conductimetric analysis is described. The modifications necessary in applying the method to acids and alkalis of varying strength, or to mixtures of them, are discussed. M. S. B.

Electrometric studies of the precipitation of hydroxides. VIII. Standardisation of acid solutions by means of mercuric oxide. H. T. S. BRITTON and (MISS) B. M. WILSON (J.C.S., 1933, 9—10).—The reaction $HgO+4KX+H_2O=K_2HgX_4+2KOH$, which occurs when HgO is dissolved in aq. KI, KBr, KCl, or KCN, has been investigated by glass-electrode titration with HCl. KI forms the most stable complex. For the standardisation of acids, Me-orange should be used as indicator. D. R. D.

Detection of chlorine in presence of bromine; a microchemical reaction for silver. K. SCHERINGA (Chem. Weekblad, 1933, **30**, 92—93).—AgBr is much more sol. in 5% KCNS solution than is AgCl; this fact may be applied to detect 5% of AgCl in AgBr. Traces of Ag may be detected by the pptn. of AgCNS when a solution of AgCl in KCNS is diluted. H. F. G.

Detection of chloride and bromide in potassium ferro- and ferri-cyanide. G. BUMMING.—See B., 1933, 145.

Simplified Karns technique for the microdetermination of iodine. H. VON KOLNITZ and R. E. REMINGTON (Ind. Eng. Chem. [Anal.], 1933, **5**, 38—39).—A modification (cf. A., 1932, 1227). E. S. H.

Determination of fluorine in apatite, phosphorite, and superphosphate. I. TANANAEV (J. Appl. Chem., Russia, 1932, **5**, 834—842).—F is distilled as SiF_4 in glass vessels. CH. ABS.

Determination of fluorine in cryolite. F. J. FRERE (Ind. Eng. Chem. [Anal.], 1933, **5**, 17—18).—The sample is fused with Na_2CO_3 and K_2CO_3 in a Pt dish, and the sol. fluoride neutralised with dil. HNO_3 and titrated directly with $Y(NO_3)_3$, using Me-red as indicator. Excess of alkali causes error, and the method is unsuitable when the amount of F′ is < 0·025 g. per 100 c.c. The use of $Ce(NO_3)_3$ leads to satisfactory results in determining F′ in glasses, but the PbClF method gives low results. E. S. H.

Volumetric determination of fluorine. H. H. WILLARD and O. B. WINTER (Ind. Eng. Chem. [Anal.], 1933, **5**, 7—10).—Solutions containing F′ or SiF_6'' are titrated with standard $Zr(NO_3)_4$, using Zr–alizarin mixture in EtOH as indicator. When interfering elements are present, F′ is separated as H_2SiF_6 by adding $HClO_4$ or H_2SO_4, H_2O, and pieces of glass and distilling. Substances which cannot be decomposed by $HClO_4$ must be fused with Na_2CO_3 before volatilising the H_2SiF_6. The presence of a large amount of gelatinous SiO_2 interferes with the volatilisation of H_2SiF_6, and a method for removing the SiO_2 is described. Removal of F′ by volatilisation as SiF_4 and subsequent determination by titration with $Th(NO_3)_4$ gives unsatisfactory results in presence of plant ash. Inconsistent results were obtained by converting F′ into HBF_4, distilling, and titrating F′ in the distillate. E. S. H.

Potentiometric titration method for fluorine. N. ALLEN and N. H. FURMAN (J. Amer. Chem. Soc., 1933, **55**, 90—95).—0·1—50 mg. of F in 25—80 c.c. of 50% aq. EtOH at 70° is determined by electrometric titration in neutral solution with $Ce(NO_3)_3$ in presence of 0·25 c.c. of 0·1*M*-$K_3Fe(CN)_6$ and 10 mg. of $CeKFe(CN)_6$ in suspension. The end-point is masked by large quantities of foreign salts, and ions which ppt. Ce''' must be absent. J. G. A. G.

Determination of a small quantity of oxygen in gases. M. MUGDAN and J. SIXT (Angew. Chem., 1933, **46**, 90—91).—The O_2 in a known vol. of gas is absorbed in NH_3–$Cu^{\cdot}$ solution and the blue colour obtained compared with that of an NH_3–$Cu^{\cdot\cdot}$ solution of known composition. M. S. B.

Potentiometric titration of hydrogen peroxide and peroxides. R. MULLER and H. BRENNEIS (Berg. Huttenm. Jahrb. mont. Hochsch. Leoben, 1932, **80**, 101—102; Chem. Zentr., 1932, ii, 2689).—0·1*N*-$KMnO_4$, but not $FeSO_4$, quinol, $SnCl_2$, H_2CrO_4, or $HClO_3$, is suitable for 3% H_2O_2. A. A. E.

Detection of free sulphur, viscose silk, and the cyanide ion. A. CASTIGLIONI (Z. anal. Chem., 1933, **91**, 346—349).—The method depends on the conversion of NaCN into NaCNS by boiling with a $COMe_2$ solution of S. As all viscose silk contains S, it can be distinguished from silks made by other processes by boiling it with NaCN and $COMe_2$ and testing the solution with HNO_3 and $Fe(NO_3)_3$ for the presence of NaCNS. A. R. P.

Iodometric determination of hydrogen sulphide. M. A. PETROVA and A. K. YAKOVTZEVSKAYA (J. Appl. Chem., Russia, 1932, **5**, 671—675).—The aq. NaOH used for absorption must be diluted to 0·002—0·05*N*-NaOH before titration. CH. ABS.

Determination of titre of sodium thiosulphate solutions, using Mohr's salt. A. V. FILOSOFOV (J. Gen. Chem. Russ., 1932, **2**, 553—554).—Acid 0·1*M*-$Fe(NH_4)_2(SO_4)_3,6H_2O$ solution is oxidised by $KMnO_4$, excess of KI is added, and I is titrated with the unknown $Na_2S_2O_3$ solution. The results so obtained are more accurate and are about 1% < those obtained by direct titration with I. R. T.

Volumetric determination of dithionates. S. GLASSTONE and A. HICKLING (J.C.S., 1933, 5).—S_2O_6'' is oxidised quantitatively to SO_4'' on boiling for 1 hr. with aq. $K_2Cr_2O_7$ strongly acidified with H_2SO_4. The unchanged $K_2Cr_2O_7$ may be determined iodometrically. If SO_3'' is present, it should first be removed by boiling with 0·5*N*-AcOH for 15 min. The SO_3'' may be determined by adding standard $K_2Cr_2O_7$ to acidified KI, adding the solution to be analysed, and titrating the excess of I with $Na_2S_2O_3$. D. R. D.

Colour reaction of nitrites. A. CASTIGLIONI (Gazzetta, 1932, **62**, 1065—1067).—Nitrites may be detected in dilution up to 1 in 10^6 by the colour developed on treatment with a few mg. of Na 2 : 6-diiodophenolsulphonate and boiling (orange-yellow), or of pyrocatechol, followed by boiling and addition of NaOH (wine-red). E. W. W.

Determination of nitrous acid. E. VON MIGRAY (Chem.-Ztg., 1933, **57**, 48).—The sample (0·04—0·2 g. N_2O_3) is shaken in a stoppered flask with 20—50 c.c. of acidified 0·1*N*-$KBrO_3$; after 2—3 min., 1—2 g. of KI are added and the liberated I, *i.e.*, the excess of $KBrO_3$, is titrated with 0·1*N*-$Na_2S_2O_3$. A large excess of $KBrO_3$ should be avoided. Standardised NaOCl solution may be used in place of $KBrO_3$. H. F. G.

Detecting traces of nitrous acid with indigosols. E. VON MIGRAY (Chem.-Ztg., 1933, **57**, 94).—A dark blue colour is obtained when 100 c.c. of a solution containing 1 mg. N_2O_3 per litre are shaken with 5 drops of 10% indigosol 04B solution and 5 c.c. of H_2SO_4 (1 : 4). Smaller concns. give the colour on keeping and some other indigosols may be used. Fe^{III} salts and CrO_4'' give the colour, but NO_3' and ClO_3' do not interfere. A. G.

Applications of the polarographic method. G. SEMERANO (Giorn. Chim. Ind. Appl., 1932, **14**, 608—614).—Polarographic examination of acidified nitrite solutions reveals an increase of current at a potential of −0·77 volt from the normal Hg_2Cl_2 electrode (cf. A., 1931, 451; 1932, 1221). With $10^{-4}M$-nitrite, a diffusion wave of 21×10^{-7} amp. is obtained and it is possible to determine amounts of HNO_2 of the order 2×10^{-8} in 0·2 c.c. of liquid. With an explosive, 1 part of HNO_2 in 5×10^7 is determinable and about 0·1 of this detectable. From a study of the electrolytic reduction of nicotine and its salts in aq. solution at the dropping Hg cathode, conditions are established for the determination of the base, even in presence of C_5H_5N and NH_4 bases. Applied to tobacco, the method will detect 1 part of nicotine in 10^7 (cf. A., 1932, 1093). T. H. P.

Interference of pyridine derivatives in arsenic determination. C. R. GROSS (Ind. Eng. Chem. [Anal.], 1933, **5**, 58—60).—The presence of C_5H_5N and its derivatives, such as nicotine, retards the evolution of H_2 and AsH_3. The residue, after the wet combustion of the sample with H_2SO_4 and HNO_3, is diluted with H_2O and neutralised with aq. 3% NH_3. H_3PO_4 (1·6%) and, more slowly, Mg mixture, are added, and finally more aq. NH_3 to ppt. $MgNH_4PO_4$. The As is pptd. at the same time and is determined in the ppt. in the usual manner. T. McL.

Determination of hydrocyanic acid in air and in air–carbon dioxide mixtures. H. L. CUPPLES (Ind. Eng. Chem. [Anal.], 1933, **5**, 50—52).—Apparatus and procedure for making analyses during field fumigations with HCN are described. The vol. of gas is determined by the duration and rate of flow as measured by a capillary tube flow-meter, and the HCN is determined by absorption in NaOH or Na_2CO_3 and titration with $AgNO_3$ or I_2. The latter method gives satisfactory results in presence of CO_2. E. S. H.

Gas-volumetric analysis of carbonic acid in solutions and solids. S. HATTA (J. Soc. Chem. Ind. Japan, 1933, **36**, 8—9B).—When the CO_2 evolved during a reaction is measured by means of a gas burette, a correction ΔV must be added to the observed vol. on account of the solubility of CO_2. Theoretically, if only displaced air and no CO_2 enters the burette, $\Delta V=(1-e^{-V/(v-v_1)})Hv_1$, where V=observed vol., v=capacity of reaction vessel, v_1=vol. of liquid, and H=solubility coeff. of CO_2 in c.c. (at actual temp. and 1 atm.) per atm. per c.c. of liquid. If complete diffusion occurs, $\Delta V=VHv_1/(V+v-v_1)$. The mean of these two calc. vals. of ΔV is the correction to be applied. Curves are given indicating the variation of ΔV with temp. D. R. D.

Official test for carbonate in sodium and potassium hydrogen carbonates. C. MORTON.—See B., 1933, 145.

Gasometric determination of potassium. A. M. VASILIEV (Uchen. Zapiski Kazan. Gosud. Univ., 1930, 90, 977—988).—$K_2NaCo(NO_2)_6$ is decomposed, *e.g.*, by acid $FeSO_4$ in CO_2, and the NO_2 liberated is measured. CH. ABS.

Titrimetric determination of small quantities of potassium. W. SELKE (Landw. Versuchs-Stat., 1932, **114**, 321—342).—In the cobaltinitrite–$KMnO_4$ method, pptn. of K cobaltinitrite is carried out in a conc. solution and without cooling. The K equiv. of the 0·02*N*-$KMnO_4$ used rises with increasing concn. of K in the test solution, approaching the steady val. 1 c.c.=0·1595 mg. K. The $H_2C_2O_4$ titre of 0·02*N*-$KMnO_4$ in presence of H_2SO_4 varies with the method, time, and temp. of heating. With the technique described, sufficiently accurate results are obtainable for determinations of K in HCO_3' soil extracts (Dirks and Scheffer). A. G. P.

Rapid detection of sodium and potassium in presence of ammonium and magnesium salts. C. CANDEA and L. I. SAUCIUC (Bul. Soc. Chim. Romania, 1932, **14**, 76—79).—The solution, which should contain only chlorides, is evaporated to dryness, and the residue is heated over a Teclu burner for $\leqslant$ 10 min. to remove NH_3 and decompose the $MgCl_2$. K and Na are detected in the usual way in the aq. extract of the residue. H. F. G.

Quantitative spectrum analysis. V. Determination of rubidium in an artificial carnallite. VI. Attempt to determine the gold in natural ores. VII. Determination of the gold : silver ratio in mixtures. VIII. Determination of each salt in a mixture of two salts with the same anion or of two oxides in a mixture. A. IWAMURA (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 355—358, 359—363, 365—370, 371—372; cf. A., 1932, 826).—V. The carnallite is briquetted with HCl and ZnO and the intensity of the Rb line at 4201·8 Å. in the spark spectrum compared with that of a standard. The results are accurate to 0·012%. Carnallite prepared from bittern from the Inland Sea, Japan, was found to contain 0·042—0·015% Rb.

VI. Electrodes were made by carbonising a mixture of ore (10 g.), C (3·5 g.), and sucrose (9·5 g.). Amounts of Au $>$ 0·0004% can be determined from the intensity of the line 2428 Å. in the spark spectrum.

VII. The intensities of the Au lines at 2676 and 2428 Å. are compared with those of the Ag lines at 3383 and 3281 Å.

VIII. The two elements are determined by weighing them in the form of a salt with a common anion, and the ratio of concn. in the mixture is then determined spectrographically; from these figures the composition of the mixture can be calc. A. R. P.

Analysis of alkali bromides. L. W. WINKLER.—See B., 1933, 145.

Separation of alkaline-earth and alkali ions. J. KUNZ (Helv. Chim. Acta, 1933, **16**, 3—6).—From a solution of the chlorides, acidified with AcOH, Ba, Sr, Ca, and Mg are successively pptd. by $(NH_4)_2CrO_4$, $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$, and $(NH_4)_3AsO_4$, respectively. In the filtrate $K^{\cdot}$ is separated as KH tartrate or as $K_3Co(NO_2)_6$ by means of the corresponding Mg salts. F. L. U.

Volumetric determination of calcium fluoride. I. TANANAEV (J. Appl. Chem., Russia, 1932, **5**, 445—447).—The method is based on the solubility of CaF_2 in $AlCl_3$ solution. CH. ABS.

Volumetric determination of barium. A. ROMEO (Annali Chim. Appl., 1932, **22**, 783—786).—The Ba is pptd. as $BaCrO_4$ in presence of AcOH, washed, dissolved in HCl, treated with KI, and titrated with $Na_2S_2O_3$. Alternatively or as a control, the excess of standard $K_2Cr_2O_7$ used for the pptn. is similarly titrated. T. H. P.

Determination of barium in ferriferous minerals. E. CHAUVENET and AVRARD.—See B., 1933, 151.

Colour reaction for magnesium. L. LA ROSA (Annali Chim. Appl., 1932, **22**, 725—728).—In presence of salts of NH_4 and other cations, 0·01% of Mg gives, with 0·5% aq. *p*-$C_6H_4(NH_2)_2$ and conc. KOH, a violet-red or purplish-violet ppt., dissolved and decolorised by dil. acid but reappearing more intensely on subsequent addition of KOH.

Analysis of natural magnesium silicates. M. BICHOVSKY and J. GINGOLD [with M. BRISCHKE] (Angew. Chem., 1932, **45**, 785—787).—The rapid method is based on the thermal decomp. of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ at 750°, $MgSO_4$ being completely stable at this temp. The sample is evaporated with HF, and then treated with H_2SO_4. The filtered solution of the sulphates is evaporated and the residue is heated at 750—800° for 1 hr. The insol. residue contains all the Al and Fe as oxides, and the solution the $MgSO_4$ and any Ca present. Fe_2O_3 is determined by the $TiCl_3$ method, and Ca as oxalate, the Mg being calc. from the SO_4'' content of the solution and the SiO_2 by difference. H. F. G.

Volumetric determination of zinc. A. HECQUET (Ann. Chim. Analyt., 1933, [ii], **15**, 10—11).—A solution of a Zn salt, slightly acidified with HCl, is titrated at the b.p. with 4% $K_4Fe(CN)_6$ which has been previously standardised against chemically pure Zn, until one drop gives a clear yellowish colour. Any org. matter is first oxidised by boiling with excess of Br, and Fe and Al are removed with aq. NH_3 and NH_4Cl at the b.p. P. G. M.

Reagent for determination of zinc. A. J. QUICK (Ind. Eng. Chem. [Anal.], 1933, **5**, 26).—$Zn^{\cdot\cdot}$ is pptd. from acid or neutral solutions by borneol-glycuronic acid. The ppt. may be weighed directly, or hydrolysed by *N*-HCl and the free glycuronic acid determined by the common sugar methods. $Zn^{\cdot\cdot}$ may thus be separated from all the common cations, except $Cd^{\cdot\cdot}$. E. S. H.

Determination of certain metals with anthranilic acid. I. Determination of zinc and cadmium and their separation from the alkaline earths. H. FUNK and M. DITT (Z. anal. Chem., 1933, **91**, 332—340).—From hot neutral or feebly acid (AcOH) solutions Zn and Cd are pptd. completely by 3% aq. Na anthranilate as anhyd. crystals which can be weighed after drying at 105°. The Zn salt

contains 19·37% Zn and the Cd salt 29·23% Cd. Alkaline earths give no ppt. under the same conditions; the sensitivity of the test is 1 p.p.m. The metals can be determined volumetrically by dissolving the ppt. in HCl and titrating the anthranilic acid with KBr–$KBrO_3$ solution, using indigocarmine–styphnic acid as indicator. A. R. P.

Determination of cadmium. Evrard method. L. C. Hurd and R. W. Evans (Ind. Eng. Chem. [Anal.], 1933, **5**, 16—17).—Evrard's method (A., 1930, 182) is not suitable for determining $Cd^{\cdot\cdot}$. Adsorption and solubility errors are encountered, and ppts. are also produced by $Sb^{\cdot\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, and $As^{\cdot\cdot\cdot}$. E. S. H.

Colorimetric determination of lead, especially in water. O. Liebknecht and L. Gerb.—See B., 1933, 126.

Thallous thiocarbonate: a specific reaction for thallium. Picon (Compt. rend., 1932, **195**, 1274—1276).—Tl_2CS_3 is formed when CS_2 is added to Tl_2S pptd. in an alkaline medium as a vermilion ppt. insol. in H_2O, and capable of indicating 1 part of Tl in 50,000 parts. It is stable at room temp. and in presence of alkalis, but loses all the CS_2 at 100° in vac., the residual Tl_2S beginning to volatilise at 300°. Mineral acids and halogens attack it readily; with salts of Cd, Ag, Pb, or Cu, it forms the corresponding $Tl^{\cdot}$ salt and metallic thiocarbonate. It is readily oxidised by $KMnO_4$, $K_3Fe(CN)_6$, $Fe(NO_3)_3$, $AuCl_3$, and (at 100°) by O_2, but not by aq. H_2O_2; SO_2 at 300° forms Tl_2SO_4. C. A. S.

Iodometric determination of copper. T. H. Whitehead and H. S. Miller (Ind. Eng. Chem. [Anal.], 1933, **5**, 15—16).—In the standard method it is not necessary to evaporate the mineral acids completely if a small amount of H_2SO_4 is present. Time is saved and the danger of forming insol. basic $Cu^{\cdot\cdot}$ salts obviated. E. S. H.

Test for phenols and copper. C. C. Fulton (Amer. J. Pharm., 1933, **105**, 25—29).—The supposed phenol is dissolved in a few drops of EtOH; 3 drops of 3% aq. H_2O_2 and 5 drops of 5*N* aq. NH_3 are added, and the mixture is stirred with a piece of Cu. A red to salmon-pink colour is produced. α- and β-Naphthol are exceptions in that they give a green colour, whilst some others, such as tyrosine etc., give a brown colour. A 1% solution of $CuSO_4$ may be used in place of the Cu. Morphine sulphate may be used in this way to detect 1 part of Cu in 3×10^6. P. G. M.

Colorimetric analysis. E. Canals and A. Hortala (Bull. Soc. Chim. biol., 1932, **14**, 1273—1278).—The colorimetric determination of $CuSO_4$, I, and $KMnO_4$ using the Toussaint photo-electric cell colorimeter is described. The apparatus, although eliminating eye fatigue, gives results not more accurate than those obtained with the ordinary colorimeter. A. L.

Micro-determination of traces of mercury. A. Stock, H. Lux, F. Cucuel, and H. Kohle (Angew. Chem., 1933, **46**, 62—65).—Sources of error in the method previously described (A., 1931, 588) are discussed, and means of obviating them are given. Most of the reagents employed contain appreciable quantities of Hg, *e.g.*, the purest HCl available contained 3×10^{-8} g. per 100 c.c., and a blank determination is necessary when $>10^{-6}$ g. Hg is to be determined. The laboratory atm. may contain from 0·2 to 200×10^{-6} g. Hg per cu. m. Very dil. $HgCl_2$ solutions (10^{-7} g. Hg per c.c.) become much more dil. when stored in glass vessels, owing to adsorption or combination of part of the Hg with the glass. If the precautions given are observed, 10^{-8} g. Hg may be determined to within about 25%. H. F. G.

Microchemical identification of mercury salts and some heavy metals. I. M. Korenman (Pharm. Zentr., 1933, **74**, 54—56).—Hg salts form characteristic crystals on treatment with $K_2Cr_2O_7$ and C_5H_5N vapour (sensitivity 0·00000075 g. Hg). Cu, Cd, Co, Ni, Zn, Mn, and Cr salts under the same conditions give amorphous ppts., but on rubbing with a glass rod after exposure to the C_5H_5N vapour crystals can be obtained. E. H. S.

Detection and separation of the metals of the second analytical group. C. Candea and L. I. Sauciuc (Bul. Soc. Chim. Romania, 1932, **14**, 69—71).—The mixed sulphides are extracted with warm HCl (*d* 1·2), and Hg is confirmed by dissolution in HCl–HNO_3 and addition of $SnCl_2$. From the solution, after neutralisation and addition of AcOH, $PbCrO_4$ and $(BiO)_2Cr_2O_7$ are pptd., and separated by extraction with NaOH. To the filtrate, NaOAc and $BaCl_2$ are added, the $BaCrO_4$ ppt. is removed, and aq. NH_3 is added to detect Cu; Cd is detected by means of KCN and H_2S. The method obviates evaporation with H_2SO_4. H. F. G.

Determination of aluminium oxide in aluminium alloys. W. Ehrenberg.—See B., 1933, 152.

Determination of manganese by the Procter Smith method. I. A. Pinkus and (Mlle.) L. Ramakers. **II.** A. Pinkus and C. Aronsfrau (Bull. Soc. chim. Belg., 1932, **41**, 529—548, 549—564).—I. The proportion of $Mn^{\cdot\cdot}$ oxidised in a given time to MnO_4' by $(NH_4)_2S_2O_8$ in presence of $AgNO_3$ and HNO_3 as catalyst increases with rise of temp. and initial concn. of S_2O_8'' and $AgNO_3$, but decreases with the initial concn. of $Mn^{\cdot\cdot}$ and of free acid. With sufficient excess of S_2O_8'' and at fairly low temp. the % of $Mn^{\cdot\cdot}$ oxidised increases linearly with time. These facts, combined with the induction period observed, suggest that the consecutive reactions are $2Ag^{\cdot} + S_2O_8'' + 2H_2O \rightleftharpoons Ag_2O_2 + 2SO_4'' + 4H^{\cdot}$ and $2Mn + 5Ag_2O_2 + 4H \longrightarrow 2MnO_4' + 10Ag + 2H_2O$, and that the relatively slow first stage controls the velocity of the reaction. The determination of $Mn^{\cdot\cdot}$ by this method is discussed.

II. The quant. procedure recommended is to oxidise in the cold in aq. H_2SO_4 with $AgNO_3$ as catalyst and then to stop subsequent re-oxidation by pptg. the Ag as AgCl, the MnO_4' being determined with standard Na arsenite. Accurate results are obtained by taking the mol. ratio $As_2O_3 : MnO_4'$ as 0·916, a factor which is independent of $Mn^{\cdot\cdot}$ concn. in the range $1·5\times10^{-4}$ to $6·6\times10^{-4}$ g.-atom per litre and of H_2SO_4 concn. up to 2·5*N*. Excessive Fe content produces no error if a little syrupy H_3PO_4 is added before titration. Ni

$\geqslant 2{\cdot}7\times10^{-2}$, Co $\geqslant 1{\cdot}2\times10^{-3}$, and Cr $\geqslant 1{\cdot}85$ g.-atom per litre have no effect. J. W. S.

Use of iron from iron carbonyl as a standard substance for volumetric analysis. W. Wesly (Z. anal. Chem., 1933, **91**, 341—344).—Fe from $Fe(CO)_5$ is purer than piano wire for use in standardising $KMnO_4$ and gives just as good results as electrolytic Fe. A. R. P.

Chemical analysis of modern alloy steels. W. W. Stevenson.—See B., 1933, 108.

Detection and separation of the metals of the third analytical group. C. Candea and L. I. Sauciuc (Bul. Soc. Chim. Romania, 1932, **14**, 72—75).—The mixed sulphides are extracted with warm HCl (1 : 2). The residue is dissolved in HCl–HNO_3, and Ni is detected by means of dimethylglyoxime in the diluted solution; Co is detected by addition of NH_4CNS and a mixture of amyl alcohol and Et_2O (if $Fe^{\cdot\cdot\cdot}$ is present, Na_2SO_3 is added). From the filtrate, Fe, Cr, and Mn hydroxides are pptd. and separated in the usual manner, whilst Al and Zn are detected in the filtrate, after concn. by means of aq. NH_3 and H_2S, respectively. Evaporation of strongly acid solutions is almost entirely obviated by this procedure. H. F. G.

Phosphate–ferri-phosphate analysis of the cations of the first, second, and third analytical groups in presence of the anion PO_4'''. A. P. Kreschkov (J. Gen. Chem. Russ., 1932, **2**, 593—596).—The phosphates of Fe, Al, Cr, Mn, Ba, Sr, Ca, and Mg are pptd. by $(NH_4)_3PO_4$ in presence of excess of aq. NH_3. The filtrate contains Ni, Co, Zn, Na, and K, which are detected by the usual methods. The residue is dissolved in HCl, Fe, Al, and Cr are pptd. as basic acetates by Na_2CO_3 and NaOAc, and separated as usual, whilst the filtrate is analysed for alkaline-earth metals and Mg. R. T.

Gravimetric determination of nickel at various p_H values with dimethylglyoxime. T. Nagai (Compl. Abs. Jap. Chem. Lit., 1932, **6**, 409).—The optimal p_H is 7·5—8·1. Ch. Abs.

Determination of molybdenum and lead by Fajans' method. I. C. Rajchinschten and N. Korobov (J. Gen. Chem. Russ., 1932, **2**, 661—665).—Excess of standard aq. $Pb(OAc)_2$ is added to the solution of $(NH_4)_2MoO_4$ under examination (total vol. $\geqslant$ 40 c.c.), and 0·5 c.c. of 1% alizarin-red is added to the boiling solution, which is then titrated with standard $(NH_4)_2MoO_4$, the titration being completed when the colour of the ppt. of $PbMoO_4$ changes from violet to red. Pb is determined by direct titration with standard $(NH_4)_2MoO_4$. In the absence of other salts, the mean error is $\geqslant$ 0·1%, but the presence of Sb, Cd, Cu, Fe, Zn, Ca, Ba, and Al reduces the accuracy of the method, as does also the presence of $>$ 0·4*N*-AcOH, *N*-NH_4OAc, or 2*N*-NH_4NO_3. R. T.

Analysis of radioactive minerals. A. Karl (Compt. rend., 1932, **195**, 1071—1072).—$COCl_2$ at 500—550° decomposes most minerals, volatilising as chlorides Al, Fe, Nb, Ta, Ti, and U, and converting into non-volatile chlorides most other elements except Si and Zr, which remain as oxides. Separation is quant. for artificial mixtures of U_3O_8 and ThO_2, Ce_2O_3, or $BaCO_3$, crude rare earths and TiO_2 or Nb_2O_5 with Ta_2O_5, and $BaCO_3$ and Nb_2O_5 with Ta_2O_5. To determine Ra the powdered mineral is moistened with aq. $BaCl_2$, dried, and $COCl_2$ passed over at 550°; the Ra remains as $RaCl_2$ and is determined as usual (cf. A., 1932, 355). C. A. S.

Titration of bivalent tin with potassium chlorate. R. M. Kulovarskaya (J. Appl. Chem., Russia, 1932, **5**, 668—670).—The reaction $3SnCl_2+KClO_3+6HCl=3SnCl_4+KCl+3H_2O$ is carried out, using $FeCl_3$ as indicator, at 100°; Sb^{III}, As^{III}, or O_2 does not interfere. Excess of Fe affects the sharpness of the end-point. Potentiometric titration is permissible. Ch. Abs.

Conditions for determining antimony by the permanganate method: potentiometric titration. W. Pugh (J.C.S., 1933, 1—4).—Sb may be determined accurately by titration with $KMnO_4$ in presence of H_2SO_4 and HCl, provided the ratio $[H_2SO_4]/[HCl]$ lies within certain limits. The colour change coincides with the potentiometric end-point. If Pb is present, any $PbSO_4$ pptd. must be dissolved in hot HCl and added to the solution, since the $PbSO_4$ contains occluded $Sb_2(SO_4)_3$. The solution must then be titrated at 40—60°, adding Me-orange as indicator and titrating until the colour of the latter is destroyed. D. R. D.

Reduction of antimonic acid in hydrochloric acid solution with mercury. L. W. McCay (Ind. Eng. Chem. [Anal.], 1933, **5**, 1—3).—H_3SbO_4 in HCl solution is reduced quantitatively to H_3SbO_3 by shaking with Hg for 1 hr. in an atm. of CO_2. H_3AsO_4, H_2SnO_3, $Pb^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, or $Bi^{\cdot\cdot\cdot}$ in HCl is not reduced under these conditions. $Cu^{\cdot\cdot}$ is reduced to $Cu^{\cdot}$, but is re-oxidised selectively when air is subsequently passed through the solution. Sb may be determined by this method in presence of the substances mentioned, although in presence of $Cu^{\cdot\cdot}$ the results are somewhat low. E. S. H.

Use of tri(hydroxyethyl)amine for detecting traces of gold and silver and as a characteristic reagent for manganese, nickel, and cobalt. E. Jaffe (Annali Chim. Appl., 1932, **22**, 737—743).—With salts of some metals, tri(hydroxyethyl)amine forms characteristic coloured sol. complex compounds. With Au and Ag salts, even in small amounts, metallic mirrors are formed and, with Au, also a red or blue colloidal Au solution. T. H. P.

Automatic temperature regulation with a resistance thermometer, mirror galvanometer, and optical relay. H. Moser (Z. tech. Physik, 1932, **13**, 383—385; Chem. Zentr., 1932, ii, 2337).

Automatic registration of small changes of temperature over a wide scale. H. Rieche (Z. tech. Physik, 1932, **13**, 374—377; Chem. Zentr., 1932, ii, 2337).

Micro-pyrometry; objective micro-pyrometer. G. Lewin, W. W. Loebe, and C. Samson (Z. tech. Physik, 1932, **13**, 415—420; Chem. Zentr., 1932, ii, 2337).

Design for precision platinum resistance thermometers. J. A. Hall (J. Sci. Instr., 1933, **10**,

4—10).—A Pt thermometer, in which the resistance element is wound on a frame of fused quartz in a hermetically sealed envelope, is suitable for measurements up to 1100°, with an accuracy of ±0·0005° at 100° and ±0·001° at the b.p. of S. O. J. W.

Dependence of inertia of thermometers on the viscosity of the liquid used. W. GRUNDMANN (Physikal. Z., 1933, **34**, 75—77).—Temp. indicated by thermometers filled with creosote and C_5H_{12}, respectively, were compared. A. J. M.

New cryoscopic method. A. LALANDE (Compt. rend., 1932, **195**, 1267—1269).—The method affords great accuracy, and is exemplified by application to a mixture of EtOH and Et_2O, the crystallising point of which is deduced as −117·51°. C. A. S.

Isothermal calorimeter for slow reactions. E. D. COON and F. DANIELS (J. Physical Chem., 1933, **37**, 1—11).—The apparatus described is applicable to reactions in which < 1 g.-cal. is evolved per hr. Evolution of heat is compensated by evaporating CCl_4, absorbing the vapour in SiO_2 gel, and weighing; absorption is compensated by controlled electrical heating. The heat of hydrolysis of MeOAc is 1052 g.-cal. per mol.; the heat of fermentation of yeast at 25° is 130·1 g.-cal. per g. of glucose consumed. E. S. H.

Exact determination of specific heats at high temperatures. III. Systematic study of sources of experimental error occurring in the use of a metallic calorimeter and in the measurement of specific heats of previously-worked metals. F. M. JAEGER, E. ROSENBOHM, and J. A. BOTTEMA (Rec. trav. chim., 1933, **52**, 61—84; cf. A., 1932, 220).—The laws of cooling of calorimeters consisting of a metal block surrounded by a Dewar vessel have been studied in detail. Newton's law is found not to be valid in this case, owing to the properties of the Dewar vessel, which, however, may be retained with advantage if the space between it and the metal block is filled with a conductor such as powdered graphite, and if it is in direct external contact with the H_2O of the controlling thermostat. In measuring the sp. heats of polycryst. metals, the latter must be previously stabilised by suitable thermal treatment in order to secure reproducible results. F. L. U.

Slow-combustion gas pipette. C. H. BAYLEY (Canad. J. Res., 1932, **7**, 680—681).—The combustible gas is admitted through a Pt jet and impinges directly on to an electrically-heated Pt spiral, thereby ensuring complete combustion and eliminating danger of explosion or of cracking of the apparatus. J. W. S.

Soil microscope for field and laboratory use. W. KUBIENA (Soil Res., 1932, **3**, 91—102).—Microscope and attachments for the examination of soil minerals are described and their use in soil profile studies is indicated. A. G. P.

Measurement of the after-glow of gas discharges. L. ROHDE and K. SCHNETZLER (Z. tech. Physik, 1932, **13**, 358—363; Chem. Zentr., 1932, ii, 2296).

Colorimeter for determination of phosphate. H. RICHTER.—See B., 1933, 104.

Colorimetry. C. FRICK (Chem. Fabr., 1932, 481—484).—Results obtained by fourteen observers with red, yellow, green, and blue solutions, using a standard type of colorimeter and daylight, an "opal" lamp, a special lamp, and a projection apparatus, are compared. The smallest discrepancies were obtained with the green solution and with the projection method, which permits the simultaneous use of both eyes and thus greatly reduces fatigue. H. F. G.

Duboscq colorimeter for analysis and definition of colours in different regions of the spectrum. P. WOOG and R. SIGWALT (Compt. rend., 1932, **195**, 1251—1254).—A suitable thickness of the liquid under examination is placed in one cell, and in the other a grey liquid (suspension of graphite in 0·4% aq. Na silicate with a little $CHCl_3$ or thymol). A series of coloured screens is then successively interposed before the eyepiece, and the thickness of grey liquid varied in each case until transmission through the two cells is, when possible, equal. Methods of standardising the grey liquid and of use are detailed. C. A. S.

Measurement of *X*-ray intensities as functions of voltage up to 180 kv. D. L. WEBSTER, W. W. HANSEN, and F. B. DUVENECK (Rev. Sci. Instr., 1932, [ii], **3**, 729—749).—The tube is made of steel and Pyrex glass. A very high pumping speed is used to prevent deposition of C and W on the target. Alternative connexions make possible the detection of C and a rough measurement of its retardation of cathode rays, measurement of the possible error due to positive ions, and the wearing out of sources of minute field currents. C. W. G.

Mechanical aid to the analysis of complex spectra. G. R. HARRISON (Rev. Sci. Instr., 1932, [ii], **3**, 753—759).—The wave-no. interval between each line in a spectrum and every other line within a desired range is automatically recorded by means of a tape in which holes corresponding with the lines are punched. C. W. G.

Apparatus for spectroscopic studies in the intermediate infra-red region, 20—40 μ. J. STRONG (Rev. Sci. Instr., 1932, [ii], **3**, 810—821).—A spectrometer and absorption cell having numerous advantages are described. C. W. G.

Device for the calibration of the variable-deviation spectroscope. C. F. GRAHAM (Ind. Eng. Chem. [Anal.], 1933, **5**, 54). E. S. H.

Apparatus for rapid spectrophotometry of liquids in the ultra-violet region. F. TWYMAN (Proc. Physical Soc., 1933, **45**, 1—19).—A notched wedge cell is used, and a single exposure of 20 sec. gives a set of spectra sufficient for the plotting of an absorption curve. C. W. G.

Two rulers for use in analysing rotating-crystal photographs. M. L. HUGGINS (Rev. Sci. Instr., 1933, [ii], **4**, 10—13).—Directions are given for the marking of rulers for constructing rotation diagrams and for the direct reading of interplanar distances. C. W. G.

Preparation of collodion filters for *X*-rays. H. KERSTEN and J. MAAS (Rev. Sci. Instr., 1933, [ii], **4**, 14).—Polished metal plates are repeatedly dipped

into a mixture of 50 g. MnO_2, 80 c.c. of collodion (originally containing camphor, 22% EtOH, 66% Et_2O), and 20 c.c. of 95% EtOH. C. W. G.

Photometric and spectrophotometric studies. IX. Simple recording spectrophotometer and its use in the infra-red. K. Liese and K. Schaum (Z. wiss. Phot., 1933, **31**, 217—242).—A new and quick-working apparatus is described in detail; the optical system as tested is of glass, spectra between 0·55 and 2·5 μ being recorded. Accuracy, ease of working technique, and cheapness are claimed. J. L.

Automatic titrating devices. K. Hickman and C. R. Sanford (Ind. Eng. Chem. [Anal.], 1933, **5**, 65—68).—An optical device controls the addition of the titrating liquid in vol. sufficient to reach neutrality. This vol. is registered automatically on a chart, the titrated solution is discharged to waste, and the cycle repeats. The procedure is designed primarily for determining the total acidity of alum baths, wash water, etc. in the paper industry. E. S. H.

The "Pauly" method of determining the refractive indices of liquids. F. C. Phillips and W. A. Wooster (Z. Krist., 1933, **84**, 318—320).—The method is untrustworthy. C. A. S.

Diffusion of light as a means of studying corrosion of metals. F. Canac (Compt. rend., 1933, **196**, 51—53).—The light diffused under fixed conditions at the surface of metal subjected to corrosion for varying times is measured photometrically and the result plotted against time. Two types of curve result: (*a*) uniformly concave to the time axis; consistent with a steady increase in the no. of points of attack, and characteristic of a non-oxidisable steel in 16·7 vol.-% aq. H_2SO_4; and (*b*) at first convex to the time axis, but with a point of inflexion after some time and then similar to (*a*), consistent with steady enlargement of a fixed no. of points of attack, and characteristic of light alloys, *e.g.*, duralumin in aq. NaOH+H_2O_2. C. A. S.

Pressure chamber enabling reactions at any temperature and under pressures up to 15,000 kg. per sq. cm. to be observed visually or photographed. J. Basset (Compt. rend., 1932, **195**, 1242—1245; cf. A., 1931, 59).—The pressure chamber as previously described has been modified. C. A. S.

Apparatus for the continuous recording of p_H. A. E. J. Vickers, J. A. Sugden, and R. A. Bell (Chem. and Ind., 1932, 923).—Additional details are given of the apparatus previously described (A., 1932, 828) and a method of matching the valves is outlined. H. E. B.

Micro-conductance cell. H. L. White (J. Biol. Chem., 1933, **99**, 445—449).—A micro-conductance cell, capacity 0·2 cu. mm., having an accuracy of 0·3—0·5%, and with many advantages over that of Bavliss and Walker (A., 1930, 1205), is described. H. G. R.

Apparatus for routine use of glass electrode. E. C. Gilbert and A. Cobb (Ind. Eng. Chem. [Anal.], 1933, **5**, 69—70). E. S. H.

Gaseous photo-electric cells. G. A. Boutry (J. Phys. Radium, 1932, [vii], **3**, 520—536).—The properties of the cell were studied as a function of the applied voltage and the incident light. N. M. B.

Heating by high-frequency induced currents. G. Ribaud (J. Phys. Radium, 1932, [vii], **3**, 537—554).—Theoretical. N. M. B.

High-tension electron tube. Y. Cauchois (J. Phys. Radium, 1932, [vii], **3**, 512—519).—A 40—125-kv. Lenard–Coolidge type tube is described. N. M. B.

Automatic apparatus for the determination of small quantities of sulphur dioxide in air. P. C. Capron (Bull. Soc. chim. Belg., 1932, **41**, 588—596).—The SO_2 is determined from the change in conductivity of a standard HIO_3 solution due to the reaction $3SO_2+HIO_3+3H_2O=3H_2SO_4+HI$. The vol. of air is measured by allowing the drops of HIO_3 solution to fall at a definite rate into the conductivity cell through a spiral tube, so that they entrap each time a known vol. of air. The method has been tested for the concn. range 0·5—65 p.p.m. of SO_2. O. J. W.

Trap bottle with automatic alarm. T. H. Vaughn (Proc. Indiana Acad. Sci., 1932, **41**, 257—258).—An alarm is given when H_2O from the outlet is drawn back into the apparatus. Ch. Abs.

Improved Soxhlet apparatus. A. Karssen (Chem. Weekblad, 1932, **29**, 671).—The siphon fits by means of a ground joint into the vessel in which the material to be extracted is placed, and can easily be replaced or removed for cleaning. H. F. G.

Continuous extractor. A. J. Quick (Ind. Eng. Chem. [Anal.], 1933, **5**, 76). E. S. H.

Combustion apparatus. R. N. Evans (Ind. Eng. Chem. [Anal.], 1933, **5**, 61).—When using glass joints, expansion on heating is compensated by inserting a circular, flexible piece of glass tubing in the train. The sample is introduced from a side arm of the combustion tube without interrupting the flow of gas. E. S. H.

Determination of the m.p. of fats and allied substances. M. A. Abbassi (Biochem. J., 1932, **26**, 1857—1858).—A thin film of the substance is interposed in the path of an electric current. When the substance melts the circuit is immediately completed and a bell is rung. S. S. Z.

Micro-m.p. determination with the Thiele tube. E. W. Blank (Ind. Eng. Chem. [Anal.], 1933, **5**, 74—75).—Use of capillary tubes is eliminated; the sample is held between two platelets cut from microscope cover glasses. E. S. H.

Sealing capillary tubes in the Rast modification of the Barger method of mol. wt. determination. J. R. Spies (J. Amer. Chem. Soc., 1933, **55**, 250).—In an improved method the comparatively large air space is avoided. J. G. A. G.

Use of small orifices for the measurement of small quantities of flowing gas and for determining density of gases. H. Kistner (Z. anal. Chem., 1933, **91**, 321—332).—An apparatus for determining the rate of flow of gases by measuring the drop in

pressure on passing through a small orifice is described; the results are accurate to ± 0·5% within the range 3 c.c. to 250 litres per min. The gases pass through a double filter and a drying tube before entering the measuring apparatus and the whole is immersed in a H_2O-bath to keep the temp. const. and to detect leaks in the gas circuit. Methods of standardising the orifices with various gases are described and numerous examples of the use of the apparatus are given. A. R. P.

Water-jet pumps working with mercury as high-vacuum pumps. G. Mönch and H. Sturm (Physikal. Z., 1933, **34**, 134—136).—The use of the filter-pump with Hg gives high vac. A. J. M.

Velocity of evacuation of diffusion pumps working with organic substances. H. Klumb and H. O. Glimm (Physikal. Z., 1933, **34**, 64—65).—Bu^{α}_2 phthalate, vac.-pump PhOH, and two paraffins of m.p. 42° and 68°, respectively, were used as pump fillings, and the results compared with those obtained by using Hg. The first substance appeared to be as good as Hg, but the PhOH evolved a gas. It is possible to use certain org. liquids in diffusion pumps, and to obtain vac. of the degree required in technical practice. A. J. M.

Automatic Töpler pump. A. T. Williamson (Rev. Sci. Instr., 1932, [ii], **3**, 782—789).—The supply of compressed air is controlled by an electrically operated needle valve. C. W. G.

Convenient laboratory source of hydrogen. G. W. Sargent and W. P. Davey (Physical Rev., 1931, [ii], **37**, 111).—Liquid NH_3 is cracked by passage through a hot Ni tube, traces of uncracked gas being removed by P_2O_5. L. S. T.

Volumeters for solid bodies. G. M. Dreosti (Science, 1932, **76**, 598—599).—A simple apparatus utilising the siphon principle is described. L. S. T.

Specific gravity of powdered substances, and its determination with a new type of volumeter. V. G. Gurevitsch and V. P. Vendt (J. Gen. Chem. Russ., 1932, **2**, 555—568).—The d of various powders has been determined by means of a gas-volumeter of the type described by Henglein (A., 1925, ii, 375), in which kerosene is substituted for Hg. R. T.

Viscosity measurements of liquids by the oscillating-disc method. C. E. Fawsitt (Nature, 1933, **131**, 97; cf. A., 1932, 1081).—The disc method has the advantage over the capillary method of being insensitive to the presence of dust, but the calculation of abs. or relative viscosity is less satisfactory. L. S. T.

The "Rotette," an apparatus for handling small quantities of liquids with rapidity and precision. E. L. Harrington (Science, 1933, **77**, 21—22). L. S. T.

Ultra-filtration at high pressures. W. Eissner (Biochem. Z., 1932, **255**, 420—428).—Using a high-pressure ultra-filtration apparatus, it was found that the filter (ultrafine) itself had considerable influence on the quant. composition of the ultra-filtrate. The ratio of Cl to Na is usually the same for a particular filter throughout the filtration, but is different using the same serum for different filters. There is no relationship between filter permeability for H_2O and for colloidal fluids. Preliminary charging of the filter with electrolytes considerably decreases its resistance, but the filter still shows the same modifying effect on the course of ultra-filtration. P. W. C.

Alternating-current precipitators for sanitary air analysis. I. Inexpensive precipitator unit. P. Drinker. **II. Acid formation in electric precipitators.** W. G. Hazard and T. Ishikawa (J. Ind. Hyg., 1932, **14**, 364—370).—I. Two laboratory-size precipitators, having tubes 1 cm. and 3 cm. diameter, respectively, are described; the larger operates at 15,000 volts. To reduce destruction of rubber in subsequent parts of the apparatus by gases formed in the tube during the discharge the gases are passed from the precipitator through a 10—15 cm. layer of activated C.

II. The rate of production of acid in 0·92 and 3·1 cm. diameter tubes at a.c. voltages between 5450 and 13,800, and 11,400 and 21,800, respectively, has been determined for zero flow of air, and, in the case of the smaller tube, for air velocities up to 2250 cm. per min., at a voltage of 9080. Acid production becomes negligible at velocities > 1050 cm. per sec. Errors (which may be as great as 10%) caused by the synthesised acid in determinations of the pptd. dust may be obviated by suitable choice of air velocity, tube diameter, and precipitator voltage without loss of pptn. efficiency. H. F. G.

Internal friction of molten metals and alloys. V. Flow-viscosimeter with constant pressure for substances with high surface tension. F. Sauerwald (Z. anorg. Chem., 1932, **209**, 277—280; cf. A., 1932, 117).—An experimental device for ensuring the steady flow of liquids of high surface tension is described. E. S. H.

Psychrometer without artificial aeration. H. Wald (Z. Ges. Kalte-Ind., 1932, **39**, 111—115; Chem. Zentr., 1932, ii, 743). L. S. T.

Improved electromagnetically-operated gas-density balance. E. Lehrer and E. Kuss (Z. physikal. Chem., 1933, **163**, 73—81).—The balance is similar to that of Stock and Ritter (A., 1926, 669), but is less sensitive to external magnetic fields and more nearly const. in zero. R. C.

Quantitative removal of ferric chloride from aqueous solution. A. M. Ward (Pharm. J., 1932, **129**, 536).—Et_2O is distilled and the condensed vapour is carried to the bottom of a vessel containing the solution to be extracted, above which is a layer of saturated aq. HCl–Et_2O. As the upper layer increases in vol. it overflows back to the boiler. Extraction proceeds automatically, and requires 2—3 hr. for 50 c.c. of solution. H. F. G.

Mercury-sealed gas valve. S. F. Essig (Rev. Sci. Instr., 1932, [ii], **3**, 762—763).—Two tubes are sealed under Hg by two plates of porous material (unglazed light fired porcelain, fired soapstone, or C). On pressing them together the Hg is squeezed out from between the plates, and gas diffuses through. C. W. G.

Variable-orifice flow meter. G. W. MARKS (Rev. Sci. Instr., 1932, [ii], **3**, 764—765).—An Iris diaphragm is mounted in the main tube. C. W. G.

Preparing crystals for rotation photographs, H. KERSTEN and W. LANGE (Rev. Sci. Instr., 1932, [ii], **3**, 790—791).—When the crystal is mounted in wax, it may be ground to a diameter < 1 mm. by means of an emery disc mounted on a flexible-shaft dental drill. C. W. G.

Rubber beaker rings for accelerating evaporation on steam bath. J. A. SCHERRER (Ind. Eng. Chem. [Anal.], 1933, **5**, 22).—A stout rubber ring gripping the beaker enables it to be immersed to any desired depth in the steam-bath. A suitable composition of rubber to withstand the action of steam is given. E. S. H.

Adjustable stopcock remover. R. W. WESTERMAN (Ind. Eng. Chem. [Anal.], 1933, **5**, 68). E. S. H.

Revised charts for the calculation of gas radiations. S. UCHIDA (J. Soc. Chem. Ind. Japan, 1933, **36**, 24—27B).—Hottel's data (B., 1927, 735) have been brought up to date. D. R. D.

New division of the weights [in a box of analytical weights]. F. SARTORIUS (Z. anal. Chem., 1933, **91**, 344—346).—The use of wts. in the ratio 1 : 2 : 3 : 5 : 10 instead of the usual 1 : 1 : 1 : 2 : 5 : 10 or 1 : 2 : 2 : 5 : 10 is recommended, as on the average fewer wts. are required for any given weighing. A. R. P.

Applicability of the resonance method to the measurement of dielectric constants of aqueous solutions. M. JEŻEWSKI (Physikal. Z., 1933, **34**, 88—94).—Good results can be obtained only if certain conditions, which are enumerated, are observed. A. J. M.

Investigation of radioactive minerals with the Geiger-Müller counter. W. VOGT (Physikal. Z., 1933, **34**, 79—82).—A method is described for measuring the radioactivity of minerals using the Geiger-Müller counter, which gives results as accurate as those obtained by the emanation method, and is simpler. A. J. M.

Calculation of surface tension from experiment. I. Sessile drops. A. W. PORTER (Phil. Mag., 1933, [vii], **15**, 163—170).—A crit. discussion of the formulæ of Worthington, Ferguson, and Rayleigh. H. J. E.

Measurement of surface tension. T. C. SUTTON (Proc. Physical Soc., 1933, **45**, 88—90).—Two short lengths of capillary tube of different diameter are fused together. A few mg. of liquid are introduced and the tube is placed in a vertical position. The tendency of the liquid to pass into the narrower tube is balanced by the wt. of the column. Surface tension and d may both be calc. C. W. G.

Surface tension balance. R. J. DE GRAY (Ind. Eng. Chem. [Anal.], 1933, **5**, 70—73).—The apparatus is subject to an error of $< 0{\cdot}5\%$. E. S. H.

Flame shield. C. C. VERNON (Ind. Eng. Chem. [Anal.], 1933, **5**, 6).—A tinplate can is used. E. S. H.

Helium liquefaction plant at the Clarendon Laboratory, Oxford. F. A. LINDEMANN and T. C. KEELEY (Nature, 1933, **131**, 191—192). L. S. T.

Ancient Chinese treatise on alchemy, entitled Ts'an T'ung Ch'i, written by Wei Po-yang about 142 A.D. L. C. WU [with T. L. DAVIS] (Isis, 1932, **18**, 210—289). CH. ABS.

Errors of the Doctors according to Friar Roger Bacon of the Minor Order. M. C. WELBORN (Isis, 1932, **18**, 26—62). CH. ABS.

Geochemistry.

Relative distribution and abundance of elements in the lower chromosphere. S. A. MITCHELL and E. T. R. WILLIAMS (Astrophysics J., 1933, **17**, 1—43). L. S. T.

Geochemical "clue" elements. V. M. GOLDSCHMIDT (Naturwiss., 1932, **20**, 947—948).—The use of elements of the Pt group in determining the part played by cosmic dust in the composition of sedimentary rocks is discussed. The distribution of B in various rocks is also considered. The elements can be classified as "thalassophile" or as "thalassoxene" with reference to their distribution between land and sea. To the first class belong Cl, Br, B, S (as SO_4), I, and Na. To the second class belong those elements which have been thrown down by the hydrolysis of their salts in the hydrosphere, *e.g.*, Al, Fe, Th. The thalassophile elements can be further classified according as their quantity in sea-water has increased in geological time (*e.g.*, Na), decreased (*e.g.*, B), or remained const. owing to equilibrium processes (*e.g.*, Ca). A. J. M.

Origin of nitric nitrogen in the atmosphere. G. G. RAO (Bull. Acad. Sci. Agra and Oudh, 1931—1932, **1**, 82—87).—Nitric N derived from thunderstorms can form only a small fraction of that present in the atm. It is suggested that most arises from the photochemical oxidation of NH_3 by short ultraviolet solar rays. This view is in agreement with the altitudinal, seasonal, and latitudinal variations of the nitric N content of the atm. J. W. S.

Measurements with gas-density balance. Fluctuations in density of the air, and its oxygen content. A. STOCK, H. RAMSER, and G. EYBER (Z. physikal. Chem., 1933, **163**, 82—90).—Fluctuations in d of almost $0{\cdot}1\%$ have been observed. The variations in O_2 content scarcely exceed the limits of analytical error and bear no relation to the variations in d. R. C.

Water of the Baltic and Danzig. H. VON WARTENBERG, H. WERTH, and A. ZODROW (Chem. Erde, 1932, **7**, 616—619).—H_2O of some of the deep springs from the chalk at Danzig shows an abnormally high

K content. Analyses are compared with those of sea-water from the Baltic. L. J. S.

Solution content of surface waters. K. KREJCI-GRAF (Chem. Erde, 1932, **7**, 609—615).—Diagrams show the relation between the solution content and climate and also between concn. and composition in H_2O of various types. L. J. S.

Chemical constituents of biological importance in the English Channel, November 1930 to January 1932. I. Phosphate, silicate, nitrate, nitrite, ammonia. II. Hydrogen-ion concentration, excess base, carbon dioxide, and oxygen. L. H. N. COOPER (J. Marine Biol. Assoc., 1933, [ii], **18**, 677—728, 729—753).—I. Seasonal variations of chemical constituents are correlated with plankton development.

II. The p_H changes are as in previous years. The partial pressure of CO_2 is lower than that in the atm. C. W. G.

Calcium equilibrium in sea-waters. I. Theoretical. H. GEE. **II. Sealed bottles shaken at constant temperature.** H. GEE, D. M. GREENBERG, and E. G. MOBERG. **III. Empirical variation of gas phase.** H. GEE and E. G. MOBERG. **IV. Apparatus for eliminating bacterial activity in chemical studies.** H. GEE. **V. Precipitation by removal of carbon dioxide under aseptic conditions. VI. Precipitate obtained by removal of carbon dioxide from sea-water.** R. REVELLE (Bull. Scripps Inst. Oceanogr. Univ. Calif., 1932, **3**, 145—157).—I. Tropical shoal sea-water should be approx. in equilibrium with solid $CaCO_3$.

II. The surface H_2O (La Jolla, Cal.) may be slightly supersaturated with Ca at 27°. Pptn. may be accelerated by removing CO_2 from the gas in equilibrium with the H_2O.

III. $CaCO_3$ can be pptd. from raw sea-water by reducing the total CO_2 content at 28—30°. Addition of NH_3 reduces the solubility for Ca.

IV. The apparatus employs a Berkefeld filter.

V, VI. On reducing the CO_2 content of the H_2O, $CaCO_3$ is pptd. very slowly as aragonite. CH. ABS.

p_H [of sea-water] and the tides. A. LABBE (Compt. rend., 1932, **195**, 1297—1299).—Determination of p_H of sea-water in the bay of Croisic made under conditions eliminating any photosynthetic effect shows that it varies with the tide, being a max. at high, a min. at low, water. C. A. S.

Radioactivity of springs on the Ballon d'Alsace. R. DELABY, R. CHARONNAT, and M. JANOT (Compt. rend., 1932, **195**, 1294—1297; cf. A., 1932, 139).—The Rn content is very high (62·8—93·1 *mμc* per litre) in five springs from the unfaulted granite on the summit and north thereof. Less (20·1—46·4) occurs in five others from granite lower down, and only 0·7—6·9 in four still lower from faulted granite containing quartz veins. C. A. S.

Ores in the Auerbach marble [Hesse]. R. KÜHNE (Chem. Erde, 1932, **7**, 503—539).—Sulphide and arsenide minerals are described and their metamorphic origin is discussed. L. J. S.

Weathering of granite at Schenkenberg, Odenwald. E. BLANCK (Chem. Erde, 1932, **7**, 553—565).—Analyses are given of the fresh and weathered granite and of the overlying soil. L. J. S.

Accessory minerals in the study of granite batholiths. J. F. WRIGHT (Trans. Roy. Soc. Canada, 1932, [iii], **26**, IV, 251—265).—A review is given of the work that has been done on the correlation of the granite masses in England and Scotland from a detailed examination of the heavy minerals separated from the crushed rocks. It is suggested that work on similar lines would be helpful in mapping the much larger granite masses intrusive into the pre-Cambrian shield of Canada. L. J. S.

Granites of Mauthausen, Upper Austria. E. F. MAROSCHECK (Tsch. Min. Petr. Mitt., 1933, **43**, 375—405).—Petrographical description with chemical analyses are given. L. J. S.

Kaolin. R. SCHWARZ and G. TRAGESER (Chem. Erde, 1932, **7**, 566—585).—The artificial kaolin of Noll (A., 1932, 716) is compared with natural kaolin with respect to dehydration and dilatometric curves (A., 1931, 445). L. J. S.

Endogene basic inclusions in tonalite from Adamello [Tyrol]. C. GOTTFRIED (Chem. Erde, 1932, **7**, 586—593).—Analyses of the normal tonalite and of the material of the finer-grained and darker-coloured basic streaks are given. The latter are products of the tonalite magma and not due to the inclusion of foreign material. L. J. S.

Thuringite and chamosite. H. JUNG (Chem. Erde, 1932, **7**, 594—608).—*X*-Ray photographs of dehydrated thuringite (A., 1930, 733) and chamosite (A., 1931, 1030) show certain differences, and it is concluded that there are distinct species in the chlorite group. L. J. S.

Origin and composition of astrakhanite. Labile crystallisation fields of sodium chloride and epsomite. V. I. NIKOLAEV, E. V. GRITZEVICH, E. G. STYAZHKINA, and E. I. RUDENKO (J. Appl. Chem., Russia, 1932, **5**, 744—752).—The system $MgSO_4$–$MgCl_2$–Na_2SO_4–NaCl at 25° has been studied. CH. ABS.

Mineral deposits of St. Pierre and Miquelon. E. A. DE LA RÜE (Compt. rend., 1933, **196**, 55—57).—A mixture of magnetite and ilmenite in compact form occurs at Calvary in N.-W. Miquelon (*a*), and as sand on the isthmus connecting it with Langlade (*b*), and concretionary hæmatite on Grand Columbier (*c*). The chief constituents are: (*a*) Fe_2O_3 43·1, FeO 16·20 (Fe 42·76), TiO_2 9·75, Mn_3O_4 0·62; (*b*) Fe_2O_3 75·6, FeO 3·76 (Fe 55·85), TiO_2 1·90; (*c*) Fe_2O_3 84·14, FeO 5·33 (Fe 63·05%). Numerous indications of Cu occur, the most important being in a sandstone on Langlade, which contains up to 27·3% Cu containing 240 g. Ag per metric ton. A manganiferous epidote, near to piedmontite, occurs as rose crystals in thin veins in the rhyolites of St. Pierre and several of the smaller islands. C. A. S.

Shales and brick clays of Georgia. R. W. SMITH (J. Amer. Ceram. Soc., 1933, **16**, 36—44).—The geology, general ceramic properties, and uses of the materials are described in detail. J. A. S.

Mineralogy of typical North Carolina clays and shales. W. L. FABIANIC and N. H. STOLTE (J. Amer. Ceram. Soc., 1933, **16**, 6—11).—The most common constituents of these low-grade clays are clay substance, Fe_2O_3, F_3O_4, muscovite through sericite to hydromica, and epidote, with smaller amounts of biotite, titanite, tourmaline, $ZrSiO_3$, and TiO_2. Occasionally diatoms and kaolinite are found. J. A. S.

Manner of occurrence of glauconite in calcareous media. L. CAYEUX (Compt. rend., 1932, **195**, 1050—1052).—Examination of the cretaceous gluconitic limestones of Conflans-Ste.-Honorine (Seine-et-Oise) points to the genesis of the glauconite being due to both epigene action (the glauconite replacing $CaCO_3$) and to direct pptn., but with considerable probability that $CaCO_3$ has always intervened, and that all is due to epigene action. C. A. S.

Weathering of basalt in South Hanovia. E. BLANCK [with W. DORFELDT and F. LAVES] (Chem. Erde, 1932, **7**, 540—552).—Analyses are given of fresh and altered basalt and of the overlying soil near Gottingen. L. J. S.

Composition of cancrinite from Dodo, Korea. S. KÔZU, K. SETO, and S. TSURUMI (Proc. Imp. Acad. Tokyo, 1932, **8**, 432—435).—Cancrinite from sodalite-nepheline-syenite gave SiO_2 35·22, Al_2O_3 29·79, Fe_2O_3 trace, MgO 0·05, CaO 8·17, Na_2O 18·16, K_2O 0·17, H_2O 2·71, CO_2 5·88, P_2O_5 trace, SO_3 0·08, Cl 0·03=100·26, corresponding with $2Na_2Al_2Si_2O_8,CaCO_3,H_2O$. The unit cell, a 12·72, c 5·18 Å., would contain 1½ such mols., and more probably the unit cell contains 1 mol. of $3Na_2Al_2Si_2O_8,2(CaCO_3,H_2O)$. L. J. S.

Inversion temperatures of the baryte group and anhydrite. M. MASUDA (Proc. Imp. Acad. Tokyo, 1932, **8**, 436—439).—Heating and cooling curves give the following vals.: natural baryte 1178°, artificial $BaSO_4$ 1172°, $SrSO_4$ 1166°, $PbSO_4$ 878°, $CaSO_4$ 1232°, dehydrated gypsum 1231°. L. J. S.

Native tellurium in Japan. M. WATANABE (Proc. Imp. Acad. Tokyo, 1932, **8**, 440—441).—Native Te, as slender needles up to 8 mm. long, occurs with quartz, baryte, and tetrahedrite in auriferous veins in the Te-iné mine, Hokkaido. Analysis of the ore shows Te 10·06, Se 1·73%. L. J. S.

Formula of apatite. Synthetic sodium fluoride-apatite. L. H. BORGSTROM (Finska Kem. Medd., 1932, **41**, 116—121).—The prep. of mixed crystals of the types $3Ca_3(PO_4)_2,CaF_2+3Ca_3(PO_4)_2,NaF$, and $3Ca_3(PO_4)_2,NaF+3Ca_3(PO_4)_2,NaCl$, containing up to 60% and 68%, respectively, of $3Ca_3(PO_4)_2,NaF$, and in the latter case a little $Ca_3(PO_4)_2,CaF_2$ also, is described. The val. n 1·6325 for pure NaF apatite is calc. from those of the products richest in NaF. H. A. P.

Nomenclature of plagioclases. V. ROSICKY (Z. Krist., 1933, **84**, 323—327).—Various classifications of the plagioclases according to % of albite and anorthite are compared and a new classification is proposed. C. A. S.

Phosphate [rock] containing spicules of *Calcispongi* from the Ordovician of Wales. L. CAYEUX (Compt. rend., 1932, **195**, 1188—1190).—An Ordovician phosphate rock from Montgomeryshire consists of Ca phosphate, grey from presence of C and a little pyrites, containing numerous silicified spicules of *Calcispongi* which form about 20% of the whole. The rock contains 25·48% P_2O_5 and 21·40% SiO_2. The silicification of the spicules preceded the introduction of PO_4 into the enclosing sediment. C. A. S.

Origin of tektites. L. J. SPENCER (Nature, 1933, **131**, 117—118).—Tektites are concluded to be non-meteoric in origin. They have resulted from the fusion of terrestrial rocks, especially in sandy deserts, by the heat developed by the fall of large meteoric masses. L. S. T.

Native wire silver: formation and possible significance. C. B. E. DOUGLAS (Bull. Inst. Min. Met., 1933, No. 341, 5 pp.).—When Ag_2S is fused into a button at 850° in the absence of air, small beads of Ag are usually found in the surface together with a few wires similar to those occurring native. If the button is kept for several days at 126—135° in the air, it becomes covered with a mossy film of wire Ag resembling mildew on the sides of the button away from the light. Hence it is suggested that native wire Ag is probably not formed by deposition from solution, but by growth from Ag_2S. A. R. P.

Ternary system Na_2SiO_3–$Na_2Si_2O_5$–$NaAlSiO_4$. C. E. TILLEY (Tsch. Min. Petr. Mitt., 1933, **43**, 406—421).—The binary system Na_2SiO_3–$Na_2Si_2O_5$ has been investigated by Kracek (A., 1930, 1121) and by Bowen, Schairer, and Willems (A., 1931, 170). The system Na_2SiO_3–$NaAlSiO_4$ shows a eutectic of nepheline with 53·25% Na_2SiO_3 at 906°. At 1248° nepheline inverts to carnegieite (m.p. 1526°), but in presence of Na_2SiO_3 this inversion point is lowered to 1163° owing to solid solution. In the system $Na_2Si_2O_5$–$NaAlSiO_4$, with a eutectic at 71% $Na_2Si_2O_5$ and 768°, solid solution has no effect on the nepheline–carnegieite inversion. The ternary system shows four fields, Na_2SiO_3, $Na_2Si_2O_5$, nepheline, and carnegieite, with a ternary eutectic at Na_2SiO_3 8·5%, $Na_2Si_2O_5$ 63·5%, nepheline 28·0% and 760°. Carnegieite usually crystallises as rounded grains (high-temp., cubic), but shows intricate twinning (low-temp., anorthic?). The bearing of these results on occurrence of nepheline and carnegieite in igneous rocks is discussed. L. J. S.

Gaps in the series anthophyllite–gedrite, cummingtonite–grunerite, and tremolite–actinolite. N. SUNDIUS (Tsch. Min. Petr. Mitt., 1933, **43**, 422—440; cf. A., 1931, 594).—The composition of these amphiboles and the gaps in the series are discussed further. New analyses and optical data are given. L. J. S.

Spodumene and beryl in pegmatites near Graz. F. ANGEL (Tsch. Min. Petr. Mitt., 1933, **43**, 441—446).—Beryl has been found in small amount in pegmatite veins traversing gneiss at several places around St. Radegund in Styria. One nest of spodumene was found; this has n_α 1·663, 1·668, n_γ 1·679, d 3·216, and contains SiO_2 63·21, Al_2O_3 26·92, Fe_2O_3 1·58, MnO, MgO, CaO traces, Na_2O 1·16, K_2O 0·52, Li_2O 5·83, H_2O+ 0·77=99·99. This shows an excess

of 4% SiO_2 over the formula (Li,K,Na,Al)SiO_3, due to inclusions of quartz. Muscovite associated with the spodumene contains some Li. L. J. S.

Minerals in the ore deposits of Kliening, Carinthia. O. FRIEDRICH (Tsch. Min. Petr. Mitt., 1933, **43**, 447—452).—Microscopical examination of polished sections of ores from the Au–As veins has shown the presence of several Bi minerals. L. J. S.

Bauxites containing diaspore. J. DE LAPPARENT (Compt. rend., 1933, **196**, 187—188).—Distribution indicates that the diaspore is the final product of diagenesis, and that its presence denotes formation of such bauxites under conditions of greater pressure and higher temp. than those producing bœhmite-containing bauxites (cf. A., 1928, 865). C. A. S.

Vanadinite from Herival (Vosges). L. LONGCHAMBON and H. LONGCHAMBON (Compt. rend., 1932, **195**, 1397—1398).—Cryst. vanadinite, d 6·2, contained Pb 65, V_2O_5 14, Cl 2·1, SiO_2 8, Ca 1·5, P_2O_5 1·6, F 0·5, Al_2O_3 3, As_2O_5 2·7, Fe_2O_2 0·2%, indicating an isomorphous mixture of vanadinite, pyromorphite, mimetesite, and apatite. C. A. S.

Chemical characteristics of Northwestern peat and muck soils of U.S.A. W. L. POWERS (Proc. 2nd Internat. Cong. Soil Sci., 1932, **6**, 246—256).—Analytical data and results of fertiliser trials with a no. of crops are recorded. A. G. P.

Acid–alkali coefficient of peat. I. A. SMORODINCEV and A. N. ADOVA (Proc. 2nd Internat. Cong. Soil Sci., 1932, **6**, 284—291).—Peats may be characterised by the "acid–alkali coeff.," *i.e.*, the ratio (AcOH liberated by treatment with 0·1*N*-NaOAc) : (acid adsorbed from 0·1*N*-AcOH). A. G. P.

Aachen chalk coals. Application of their study to the theory of the formation of bituminous coals. W. FUCHS (Gas- u. Wasserfach, 1932, **75**, 1017—1020).—These coals are caking coals intermediate in character between brown and bituminous coals. A typical sample contained H_2O 17·9, volatile matter 37·2%; its S content was high (2·38%). The geological history of the accompanying strata shows that these coals cannot have been subjected to pressures > those due to 500 m. of sand, or to temp. > 30—40°. A more complete chemical examination (cf. B., 1930, 800) indicates that a part only of the coal can have been formed by the decomp. of the original plant material and that the remainder must have been produced by the activity of micro-organisms. A. B. M.

Yorkshire, Nottinghamshire, and Derbyshire coalfield. South Yorkshire area. Silkstone Seam. ANON.—See B., 1933, 131.

Formation of red earth in and on the Zechstein limestone of central Germany. E. BLANCK, E. VON OLDERSHAUSEN, and G. MAURMANN (Chem. Erde, 1932, **7**, 620—640).—Chemical and mechanical analyses are given of the fresh and weathered dolomitic limestone, of the red earth occurring in crevices and pockets, and of the overlying soil. L. J. S.

Mineral constituents of American loess soils. S. KAWASE and Y. KIHARA (Bull. Agric. Chem. Soc. Japan, 1932, **8**, 3—4; Proc. Internat. Soc. Soil. Sci., 1932, **7**, 233).—Mechanical analyses are recorded. The soils contained felspar, hornblende, zircon, and magnetite with quartz. A. G. P.

Form of magnesium in Tokyo loam. T. YOKOI (J. Imp. Agric. Exp. Sta. Nishigahara, 1932, **2**, 49—58; Proc. Internat. Soc. Soil Sci., 1932, **7**, 233—234).—The soil contained approx. 2% of olivine. The nature of the Mg compounds present is indicated by extraction with acid of varying concns. A. G. P.

Morphology of laterites. C. F. MARBOT (Proc. 2nd Internat. Cong. Soil Sci., 1932, **5**, 72—80).—The high proportion of Fe_2O_3 and Al_2O_3 in laterites represents a residual accumulation brought about by the removal of SiO_2 and alkalis. It is not brought about by the actual transportation of the oxides, nor is it dependent on the presence of shallow ground H_2O. The existence of the grey and mottled horizons is not a necessary characteristic of a normal laterite. A. G. P.

Climate, clay composition, and soil type. E. M. CROWTHER (Proc. 2nd Internat. Cong. Soil Sci., 1932, **5**, 15—23).—Inter-relationships between temp., rainfall, the SiO_2 : sequioxide ratio of the clay fraction, and soil type are discussed. A. G. P.

Chemical aspects of some Illinois soils as related to their genesis and morphology. R. H. BRAY and E. E. DE TURK (Proc. 2nd Internat. Cong. Soil Sci., 1932, **5**, 118—131).—Profile development in these soils involves the decomp. of primary minerals to produce base-adsorbing secondary minerals of the beidellite–nontronite type of bentonite. Bases are retained for a period and the soil remains neutral. Gradual leaching of bases followed by the production of acid conditions leads to dispersion and downward movement of the adsorbing complexes. Poorly-drained and well-drained formations differ only in the extent to which these changes have occurred, and horizons may be differentiated by graduation in base-exchange capacity. A. G. P.

Deluvial processes in soils. J. ZOLCINSKI (Proc. 2nd Internat. Cong. Soil Sci., 1932, **6**, 203—207).—The effects of tillage operations and of natural pptn. on the removal of humus and mineral nutrients from soils are recorded. A. G. P.

Important profiles of organic soils in the Florida Everglades. R. V. ALLISON and A. P. DACHNOWSKI-STOKES (Proc. 2nd Internat. Cong. Soil Sci., 1932, **6**, 222—245).—Profiles of the low-moor soils described show the occurrence of a plastic sedimentary layer of high mineral content, but containing less CaO and N than the peaty layers. Records of analytical data are given. A. G. P.

Aggregate analysis and aggregate composition of the soil. G. I. PAVLOV (Proc. 2nd Internat. Cong. Soil Sci., 1932, **1**, 179—193).—Methods of analysis are described and their application in the examination of changes in soil structure following irrigation is recorded. A. G. P.

Significance of the composition of the clay fraction in profile studies. G. W. Robinson (Proc. 2nd Internat. Cong. Soil Sci., 1932, **1**, 194—195).—In soil profile examination the composition of the clay fractions obtained by dispersion in aq. NH_3 and without pretreatment with acid yields valuable information as to the process of eluviation. In cultivated soils derived from cryst. rocks or consolidated sedimentary rocks the SiO_2 : $(Al_2O_3+Fe_2O_3)$ ratio is approx. 1·9 and does not vary greatly in the different horizons. Soils derived from unconsolidated sedimentary rocks or alluvium show higher ratios. A. G. P.

Geology and soils of an area in the state of Perak, F.M.S. H. E. F. Savage and R. G. H. Wilshaw (Dept. Agric., Straits Settlements and Fed. Malay States, Sci. Ser., 1932, No. 10, 15 pp.)—Analytical data of five profiles are recorded. In this area decomp. of org. matter under aerobic conditions is extremely rapid and humus accumulation is rarely more than transitory. A. G. P.

Genesis and development of two profiles of a drift soil in the north-east of Scotland. A. B. Stewart (J. Agric. Sci., 1933, **23**, 73—96).—Examination of a virgin profile indicates these soils to be of a podsolised type in which the leaching process is somewhat restricted. The effect of cultivation has been to increase the proportion of weathered material and to retard leaching. Org. matter occurs chiefly in the A_1 horizon and leaching of K and Ca is small. "Regradation" to a less podsolised form brought about by cultivation has produced a soil resembling, in some respects, a brown earth. A. G. P.

Organic Chemistry.

Reaction between methane and carbon tetrachloride. R. Daur (Ges. Abhandl. Kenntn. Kohle, 1932, **10**, 155—159; Chem. Zentr., 1932, ii, 2032).—Formation of C_2Cl_6, C_2Cl_4, $CHCl_3$, C, and HCl, but not condensation to form hydrocarbons or chlorohydrocarbons, took place. Ch. Abs.

Action of water vapour on hexane and benzene. C. Matignon and M. Seon (Compt. rend., 1933, **196**, 77—79).—Hexane and H_2O vapour at 1050° in presence of ZrO_2 give varying amounts of H_2, CH_4, C_2H_2, CO, and CO_2, owing to the difficulty of obtaining a homogeneous mixture; CH_4 and C_2H_4 are intermediate products which disappear with increased contact time. C_6H_6 behaves similarly. H. B.

Production of heptane and ββδ-trimethylpentane. A. D. Petrov, D. N. Andreev, and B. A. Chapluigin (J. Appl. Chem., Russia, 1932, **5**, 573—580).—The reaction: heptaldehyde $C_7H_{15}\cdot OH \rightarrow C_7H_{16}$ gives a low yield. Complete purification of C_7H_{16} from Grozni gasoline does not appear possible. ββδ-Trimethylpentane can be obtained by hydrogenation, at 20 atm., of di*iso*butane prepared by polymerising the *iso*butane fraction of cracking gases, from $CMe_3\cdot OH$, or from *iso*-$C_4H_9\cdot OH$. Ch. Abs.

Preparation of γ-ethyloctadecane. S. Landa and V. Sliva (Coll. Czech. Chem. Comm., 1932, **4**, 538—542).—γ-Ethyloctadecan-γ-ol (modified prep. from Et palmitate) (urethane, m.p. 55°) gives, best with $ZnCl_2$ at 115—125°, *γ-ethyl-Δ$^{\beta}$-octadecene* (I), b.p. 199—202°/10 mm., hydrogenated (Ni) at 145°/120 atm. to *γ-ethyloctadecane*, m.p. −3°, b.p. 202°/12 mm., 341°/760 mm. (I) is oxidised by cold, aq. $KMnO_4$ to Et pentadecyl ketone, AcOH, $EtCO_2H$, palmitic and pentadecoic acids; $COEt_2$ was not formed. R. S. C.

Effect of rise of temperature and increase of pressure on unsaturated hydrocarbons. G. Hugel and Kohn (Ann. Office Nat. Combust. liq., 1932, **7**, 15—54; Chem. Zentr., 1932, ii, 2032—2033).—Hexadecene at 300° or 400°/5—1000 atm. for 0·5—20 hr. is partly polymerised, the chief products being dimeric substances with 32 C, *e.g.*, $(C_{16}H_{32})_2$, m.p. 53·8—54·8°, I val. 47—54, and one or more of its isomerides. At 400° and high pressures trimeric products are also formed. Ch. Abs.

Determination of double linkings in the carotene molecule. L. Zechmeister, L. von Cholnoky, and V. Vrabely (Ber., 1933, **66**, [*B*], 123—124).—Contrary to Smith (A., 1932, 619), the absorption of 22 H per mol. of β- or α+β-carotene in AcOH (Pt or Pd) is confirmed. In menthane or decahydronaphthalene hydrogenation frequently ceases after absorption of about 20 H, but may sometimes be completed in AcOH. Possibly reversible cyclisations occur during the reaction. H. W.

Number of structurally isomeric hydrocarbons of the acetylene series. D. D. Coffman and C. M. Blair [with H. R. Henze] (J. Amer. Chem. Soc., 1933, **55**, 252—253).—Theoretical. Recursion formulæ are given for calculating the no. of structural isomerides; their use necessitates the knowledge of the total no. of alkyl groups of $N-2$ and all smaller C contents.

Law of periodicity. VII. Activity of compounds with similar and dissimilar substituents. P. Petrenko-Kritschenko [with M. Gorocholinskaja and A. Trozenko] (Ber., 1933, **66**, [*B*], 194—197; cf. A., 1930, 1017).—Comparison of the halogenomethanes which occupy the lowest points in the curves (CH_2X_2, CH_2XY with strong and weak, CHX_3, CHX_2Y with weak alkalis) shows that the greatest activity is possessed by substances with dissimilar substituents. In the max. of the curves the relationships are reversed. The consts. of the action of various reagents on CH_2Cl_2 and certain bromo- and iodo-methanes show an uninterrupted decline, probably owing to the simultaneous removal of all halogen atoms. The presence of two similar substituents in $CO(NH_2)_2$ renders the substance less active than NH_2Ac or $HCO\cdot NH_2$. H. W.

Colorimetric determination of chloroform. W. G. Moffitt (Analyst, 1933, **58**, 2—4).—Conditions are given for the colorimetric determination of $CHCl_3$ by means of β-$C_{10}H_7\cdot OH$ in conc. KOH. T. McL.

Optimum temperature of decomposition of chloropicrin vapours in registering their passage through heated tubes. K. CHMUTOV and I. SHUKOV (J. Appl. Chem., Russia, 1932, **5**, 425—427).—At $> 500°$ O_3 may be formed. CH. ABS.

Reaction between [ethyl] alcohol and nitric acid in presence of metallic nitrates. A. DANSI (Gazzetta, 1932, **62**, 953—958).—When $Cu(NO_3)_2$ solution containing an excess of HNO_3 is added to EtOH at 50° and the solution is evaporated on the water-bath after completion of the reaction, almost pure CuC_2O_4 is pptd. On partial neutralisation of the filtrate with $CaCO_3$, Cu glyoxylate separates, whilst on addition of KOH a dark green ppt. containing 39—47% of Cu is formed. Similar results are obtained with $Ni(NO_3)_2$, except that the glyoxylate does not appear to be formed. Addition of oximinoacetic acid to an acid solution of $Cu(NO_3)_2$ yields a ppt. of pure CuC_2O_4, about 20% of the Cu remaining in solution, but with $HgNO_3$ solution, quant. pptn. of white plates of $Hg_2(C_2H_2O_3N)_2$ occurs; the analogous Ag derivative deflagrates violently when heated. Neither the Hg nor the Ag compound is converted into the corresponding fulminate when treated with HNO_3. H. F. G.

Oxidation of ethyl alcohol to acetaldehyde. M. Y. KAGAN and A. L. SHNEERSON (J. Appl. Chem. Russia, 1932, **5**, 389—399).—The yield of MeCHO obtained by catalytic oxidation with air is 88—96% (Cu), 94—97% (Ag). CH. ABS.

Catalytic dehydrogenation of ethyl alcohol. M. Y. KAGAN and O. M. PODUROVSKAYA.—See this vol., 235.

Catalytic oxidation of propyl alcohol. I. G. LAKOMKIN and others.—See this vol., 235.

Aliphatic *tert.*-alcohols and chlorides containing *n*-butyl groups. F. C. WHITMORE and H. M. WOODBURN (J. Amer. Chem. Soc., 1933, **55**, 361—365).—The following were prepared in 30—80% yield: $CMe_2Bu{\cdot}OH$, b.p. 139·4—140·4°/735 mm., 53—53·5°/15 mm. (*chloride*, b.p. 35—35·5°/15·5 mm.), from $COMe_2$ and MgBuBr (I); CMeEtBu·OH, b.p. 160°/732 mm., 65·2—65·8°/15 mm. (*chloride*, b.p. 55°/15 mm.), from COMeEt and (I); CMePrBu·OH, b.p. 178—179°/732 mm., 78·5—79·5°/15 mm. (*chloride*, b.p. 70·8—71·4°/14·5 mm.), from COMePr and (I); $CEt_2Bu{\cdot}OH$, b.p. 180—180·5°/733 mm., 76·5—77·5°/15 mm. (*chloride*, b.p. 46°/3 mm.), from $BuCO_2Et$ and MgEtCl; $CMeBu_2{\cdot}OH$, b.p. 91·4—92·4°/15 mm. (*chloride*, b.p. 60·5°/3·5 mm.), from EtOAc and (I); CEtPrBu·OH, b.p. 88·8—89·6°/15 mm. (*chloride*, b.p. 53—54°/2 mm.), from COEtPr and (I); *dipropylbutylcarbinol*, b.p. 101·4—102·4°/15 mm. (*chloride*, b.p. 66·5—67·5°/2·5 mm.), from $BuCO_2Me$ and MgPrBr; *ethyldibutylcarbinol*, b.p. 102·6—103·6°/15·5 mm. (*chloride*, b.p. 69·5—70°/2·75 mm.), from $EtCO_2Me$ and (I); *propyldibutylcarbinol*, b.p. 113·6—114·2°/15 mm. (*chloride*, b.p. 78·8—79·2°/3 mm.), from $PrCO_2Me$ and (I); $CBu_3{\cdot}OH$, b.p. 125°/15 mm., 99·8—100°/4 mm. (*chloride*, b.p. 91·5—92·5°/2·5 mm.), from Et_2CO_3 and (I). Other physical data are given. In one prep. of CMeEtBu·OH partial dehydration occurred; olefines, b.p. 105—108° and 119—121°/734 mm., were isolated. Dehydration of crude $CMeBu_2{\cdot}OH$ gives an olefine, b.p. 162—164°/739 mm., whilst distillation of CBu_3Cl at 20 mm. affords ε-butyl-Δ^δ-nonene, b.p. 212·5—213°/735 mm., 60°/1·2 mm. H. B.

Aliphatic *tert.*-alcohols and chlorides containing the *n*-amyl group and the related olefines and their ozonolysis. F. C. WHITMORE and F. E. WILLIAMS (J. Amer. Chem. Soc., 1933, **55**, 406—411).—The following were prepared: dimethylamylcarbinol, b.p. 162—164°/235 mm., 66·5—68·5°/15 mm. (*chloride*, decomp. when heated even below 1 mm.), from MgMeCl and Et hexoate (I); methylethylamylcarbinol, b.p. 80—81°/15 mm. (*chloride*, b.p. 72·4—74°/15 mm.), from MgEtBr and Me amyl ketone (II), which is dehydrated at 100° in presence of a little I to *γ-methyl-*Δ^β*-octene*, b.p. 143—145°/734 mm.; *methylpropylamylcarbinol*, b.p. 92—93°/15 mm. (*chloride*, b.p. 43—45°/1 mm.), from MgPrBr and (II), dehydrated to a mixture of δ-methyl-Δ^ν- and -Δ^δ-nonenes; *methylbutylamylcarbinol*, b.p. 106—107°/15 mm. (*chloride*, b.p. 52—54°/0·75 mm.), from MgBuBr and (II), dehydrated to *ε-methyl-*Δ^δ*-decene*, b.p. 75—76°/15 mm.; *methyldiamylcarbinol*, b.p. 80—83°/2 mm. (*chloride*, b.p. 63—65°/0·75 mm.), from EtOAc and Mg amyl bromide (III), dehydrated to *ζ-methyl-*Δ^ϵ*-undecene*, b.p. 90—92°/15 mm.; diethylamylcarbinol, b.p. 89·5—91·5°/15 mm. (*chloride*, b.p. 42—43°/0·5 mm.), from MgEtBr and (I), dehydrated to *γ-ethyl-*Δ^β*-octene*, b.p. 57—59°/15 mm.; *dipropylamylcarbinol*, b.p. 75—76°/1·4 mm. (*chloride*, b.p. 60—62°/0·65 mm.), from MgPrBr and (I), dehydrated to *δ-propyl-*Δ^ν*-nonene*, b.p. 84—87°/15 mm.; *dibutylamylcarbinol*, b.p. 90—92°/1·2 mm. (*chloride*, decomp. when heated), from MgBuBr and (I), dehydrated to a *hydrocarbon*, $C_{14}H_{28}$, b.p. 113—115°/15 mm.; *ethyldiamylcarbinol*, b.p. 87—89°/2 mm. (*chloride*, b.p. 74—76°/0·65 mm.), from (III) and $EtCO_2Et$, dehydrated to *ζ-ethyl-*Δ^ϵ*-undecene*, b.p. 102—105°/15 mm.; *propyldiamylcarbinol*, b.p. 81—82°/0·4 mm. (*chloride*, decomp. when heated), from $PrCO_2Et$ and (III), dehydrated to a *hydrocarbon*, $C_{14}H_{28}$, b.p. 111—114°/15 mm.; *butyldiamylcarbinol*, b.p. 99—102°/1 mm. (*chloride*, decomp. when heated), from $BuCO_2Et$ and (III), dehydrated to a *hydrocarbon*, $C_{15}H_{30}$, b.p. 126—129°/15 mm.; triamylcarbinol, b.p. 115—117°/1·5 mm. (*chloride*, decomp. when heated), from Et_2CO_3 and (III). The structures assigned to the above hydrocarbons are determined by ozonolysis. Dehydration of $CMeR(C_5H_{11}){\cdot}OH$ (R=Et, Pr, Bu) involves R rather than Me or amyl. H. B.

Pigment from tripropinylcarbinol. C. PREVOST (Compt. rend., 1932, **195**, 1082—1084).—The reddening of boiling aq. solutions of tripropinylcarbinol is catalysed by H^+ and is autocatalytic. The *pigment* (?) $CHAc{:}C(CH{:}CMe{\cdot}OH)_2$, m.p. 200°, is isolated from dil. AcOH. A. C.

Synthesis of vinylpropenyl glycol. WIEMANN (Compt. rend., 1933, **196**, 118—120).—Reduction of an equimol. mixture of acraldehyde and crotonaldehyde by Griner's method (A., 1893, i, 237) gives a *mixture* (I), b.p. 114—117°/15 mm., of two isomeric

vinylpropenyl glycols [$\gamma\delta$-dihydroxy-$\Delta^{\alpha\zeta}$-heptadienes] in addition to divinyl and dipropenyl glycols. Reduction (Pd) of (I) gives a *liquid*, b.p. 109°/15 mm., and solid, m.p. 103—104° (lit. 98—99°), $\gamma\delta$-dihydroxyheptane. Similar reduction of dipropenyl glycol affords liquid and solid dipropyl glycols. H. B.

Acetylene series. V. Isomerisation of acetylenic γ-glycols under the influence of formic acid. V. N. KRESTINSKI and L. I. BASCHENOVA-KOSLOVSKAJA (Ber., 1933, 66, [*B*], 97—100; cf. A., 1930, 574).—$\beta\varepsilon$-Dimethyl-Δ^{γ}-hexinene-$\beta\varepsilon$-diol is converted by boiling, conc. HCO_2H into resin, *$\beta\varepsilon$-dimethylhexane-$\gamma\delta$-dione*, b.p. 146°/760 mm., 48°/12 mm. (*monoxime*, m.p. 125—126°; *dioxime*, m.p. 158—160°), reduced by Na and Et_2O–H_2O to *iso*butyroin, b.p. 150°, and *$\beta\varepsilon$-dimethyl-Δ^{β}-hexen-ε-ol-δ-one* (I), b.p. 186°/760 mm., 78°/12 mm., which contains 1 OH (Zerevitinov) and is hydrogenated (spongy Pt–Et_2O) to *$\beta\varepsilon$-dimethylhexan-β-ol-γ-one*, b.p. 68—70°/12 mm. (*semicarbazone*, m.p. 144—145°, and its *by-product*, $C_{10}H_{19}O_3N_5$, m.p. 180—182°). (I) is oxidised by $KMnO_4$ to $COMe_2$, α-hydroxy*iso*butyric acid, m.p. 77—79°, and α-keto-β-hydroxy-β-methylbutyric acid (*Zn* salt, $+2H_2O$ and anhyd., *Cd* salt, $+2H_2O$ and anhyd.). The spectrochemical behaviour of (I) indicates the presence of CO; it does not appear to react with $NH_2{\cdot}OH$, $NHPh{\cdot}NH_2$, p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$, or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, and is therefore regarded as an equilibrium mixture containing β-hydroxy-$\beta\varepsilon$-dimethyl-Δ^{γ}-hexene $\gamma\delta$-oxide. H. W.

Oxonium salts. Use in preparation of hydrogen sulphates of terpene and other alcohols. O. ASCHAN and A. SCHWALBE (Finska Kem. Medd., 1932, **41**, 98—115).—*Diethyloxonium sulphate*, Et_2O,H_2SO_4, formed exothermically from cold, dry Et_2O and H_2SO_4, is particularly suited for the prep. of aliphatic and *cyclo*aliphatic alcohols from unsaturated hydrocarbons, the H sulphates of the alcohols being formed intermediately and isolated quantitatively as Ba salts. The H sulphates are also formed from the alcohols, giving a convenient method of prep. of the H sulphates of polyhydric alcohols, *e.g.*, glycol and glycerol (but not glucose). Good results are also obtained with borneol and santenol, but camphene gives much camphene hydrate. *Diisoamyloxonium sulphate* is similarly prepared, but less stable, and consequently gives less *iso*borneol with camphene. Resinification or sulphonation took place with Ph_2O, $(CH_2Ph)_2O$, and similar compounds, and no oxonium salt was isolated. H. A. P.

Preparation of glyceryl mono- and di-stearates. I. VEIKHERTZ (Khim. Farm. Prom., 1932, 284—286).—The monostearate (20 pts.) is prepared by heating at 200—240° for 40 hr. stearic acid (20 pts.) and anhyd. glycerol (20 pts.), pouring into cold H_2O, washing, and recrystallising from EtOH. For the distearate, glycerol (9·2) is dissolved in conc. H_2SO_4 (36·8), and stearic acid (56·8) in conc. H_2SO_4 (85·2 pts.); heating is continued for 3 hr. at 70°. CH. ABS.

Preparation of trialkyl phosphates and their use as alkylating agents. C. R. NOLLER and G. R. DUTTON (J. Amer. Chem. Soc., 1933, **55**, 424—425).—Et, b.p. 104—107°/16 mm., Pr$^{\alpha}$, b.p. 128—134°/15 mm., Bu$^{\alpha}$, b.p. 160—162°/15 mm., *sec.*-Bu, b.p. 119—129°/8—12 mm., and *n*-amyl, b.p. 158—163°/6 mm., phosphates are most conveniently prepared (in 44—74% yield) from the appropriate alcohol and $POCl_3$ in C_5H_5N. PhOH (1 mol.) can be alkylated by these phosphates (1 equiv.); the yield of ethers is 15—39%. H. B.

Action of chlorine and sulphuric acid on methane. R. DAUR (Ges. Abhandl. Kenntn. Kohle, 1932, **10**, 151—152; Chem. Zentr., 1932, ii, 2032).—$MeHSO_4$ is obtained in better yield than by the use of MeCl and H_2SO_4. CH. ABS.

Formation, stability, and detection of methyl hydrogen sulphate. R. DAUR (Ges. Abhandl. Kenntn. Kohle, 1932, **10**, 152—155; Chem. Zentr., 1932, ii, 2032).—Good yields are obtained only in absence of H_2O. $MeHSO_4$ is not readily hydrolysed, and is more resistant to oxidation than MeOH. Small amounts can be determined by hydrolysis and oxidation of the MeOH to CH_2O, which is determined colorimetrically with magenta. CH. ABS.

Mechanism of the reaction between phosphorus pentachloride and neutral alkyl sulphites. P. CARRÉ and D. LIBERMANN (Compt. rend., 1932, **195**, 1080—1082).—When $SO(OEt)_2$ is treated with PCl_5 (2 mols.) the reactions $SO(OEt)_2+PCl_5 \longrightarrow POCl_3+EtCl+O{\cdot}SOEtCl$ (I), (I) $+PCl_5 \longrightarrow POCl_3+EtCl+SOCl_2$ occur. With equimol. proportions (I) is formed at low temp., and decomposes on warming: (I) $\longrightarrow EtCl+SO_2$, $SO_2+PCl_5 \longrightarrow POCl_3+SOCl_2$. Pr_2SO_3 and Bu_2SO_3 afford *Pr*$^{\alpha}$, b.p. 62°/50 mm., and *Bu*$^{\alpha}$ *chlorosulphites*, b.p. 88°/45 mm. A. C.

Higher alkyl sulphonates. V. C. SEKERA and C. S. MARVEL (J. Amer. Chem. Soc., 1933, **55**, 345—349).—The following are prepared from the requisite alcohol, sulphonyl chloride, and C_5H_5N at 0°: *Bu*$^{\alpha}$ *methanesulphonate* (I), b.p. 105—106°/6 mm.; *Bu*$^{\alpha}$ (II), b.p. 169°/4 mm., *lauryl* (III), m.p. 30°, *myristyl*, m.p. 35°, *cetyl* (IV), m.p. 49°, and *stearyl*, m.p. 56°, *p-toluenesulphonates*; *decyl*, m.p. 43—44°, *lauryl*, m.p. 49°, *myristyl*, m.p. 51·5°, *cetyl*, m.p. 60°, and *stearyl*, m.p. 64—65°, *p-bromobenzenesulphonates*. (II) and (III) with C_5H_5N at 130—140° give *n-butyl-*, m.p. 114°, and *lauryl-*, m.p. 135—136°, *-pyridinium p-toluenesulphonates*, respectively, whilst NH_2Bu^{α} and (III) in PhMe afford *n-butyl-laurylamine*, b.p. 138—140°/6 mm., and *n-butyldilaurylamine*, b.p. 224—226°/6 mm. *n-Butylcetylamine*, b.p. 193—197°/6 mm., m.p. 31—32°, and *n-butyldicetylamine*, b.p. 295—297°/6 mm., m.p. 44—46°, are prepared similarly using (IV). Cetyl cyanide and Bu$^{\alpha}$CN are obtained from aq. KCN and (IV) and (II), respectively. (I) or (II) and PhONa, NaOAc, and NH_2Ph give almost identical yields of PhOBu$^{\alpha}$, Bu$^{\alpha}$OAc, and NHPhBu$^{\alpha}$, respectively. H. B.

Organic compounds of selenium. IV. W. E. BRADT and J. F. GREEN. **V.** W. E. BRADT and J. H. CROWELL (Proc. Indiana Acad. Sci., 1932, **41**, 215—225, 227—233).—Bibliographies. CH. ABS.

Extension of Otto Schmidt's double linking rule. R. ODA and S. NOMAMOTO (J. Soc. Chem. Ind.

Japan, 1932, 35, 543—546B; cf. A., 1932, 716).—The structures of most org. and inorg. acids and the existence of active H atoms in $CH_2Ac{\cdot}CO_2H$, $CH_2(CO_2H)_2$, etc. are in agreement with the double linking theory. The modes of decomp. of mixed ethers and of *tert.*-alcohols are explainable on the theory, as are the relative vals. of the dissociation consts. of mono- and di-basic acids. J. W. S.

Catalytic hydrogenation of olefinic compounds. E. H. FARMER and R. A. E. GALLEY (Nature, 1933, **131**, 60).—When an "aged" Pt catalyst is used, the hydrogenation of sorbic acid follows a course different from that previously observed (A., 1932, 365). The condition of the catalyst thus affects the relative extents to which αβγδ-tetrahydrogenation and αβ-, αδ-, and γδ-dihydrogenation occur simultaneously, and the substitutional or constitutive influence in the butadiene chains appears to be superimposed on a sp. catalytic effect which by itself can activate both unsaturated centres of the conjugated system simultaneously. Lebedev's conclusions (A., 1928, 613, 1111) with regard to the order of reducibility have been confirmed by analysis of partly reduced products for binary mixtures of Δ^{α}-, Δ^{β}-, and hexenoic acids, Δ^{γ}-pentenoic acid, allyl alcohol, and sorbic acid. In the hydrogenation of the last-named the conjugated acid disappears completely before the three resulting isomeric ethylenic acids suffer attack. L. S. T.

Ether-like compounds. VIII. Hydrolysis of alkylformylformals [alkoxymethyl formates]. M. H. PALOMAA and T. O. HERNA (Ber., 1933, **66**, [*B*], 305—310).—The following alkoxymethyl formates are prepared from $(HCO_2)_2Pb$ and the requisite CH_2Cl alkyl ether: methoxymethyl, b.p. 103·9—104·1°/778 mm.; ethoxymethyl, b.p. 118·0—118·7°/769 mm.; n-*propoxymethyl*, b.p. 47·8—48·1°/22 mm.; *iso*propoxymethyl, b.p. 127·5—128·2°/767 mm.; n-*butoxymethyl*, b.p. 57·5°/16 mm.; iso*butoxymethyl*, b.p. 53·5°/16 mm.; β-*chloroethoxymethyl*, b.p. 65·5—66·0°/6 mm.; β-chloroethyl formate has b.p. 127—129°/68 mm. The rates of hydrolysis of these ether-esters are compared with those of the esters HCO_2R and ethers $CH_2(OR)_2$ (cf. A., 1932, 1232). H. W.

Acid iodides. I. Preparation of halogen-substituted aliphatic acid iodides: atomic refractivity of iodine. II. Cleavage of aliphatic ethers by acid iodides. E. L. GUSTUS and P. G. STEVENS (J. Amer. Chem. Soc., 1933, **55**, 374—377, 378—386).—I. The following are prepared from the acyl chlorides and HI by Staudinger and Anthes' method (A., 1913, i, 616): *acetyl iodide*, b.p. 104—106°/735 mm. (cf. *loc. cit.*); *chloroacetyl iodide*, b.p. 36·5°/4 mm.; *dichloroacetyl iodide*, b.p. 54—54·5°/15 mm.; *trichloroacetyl iodide*, b.p. 74—74·2°/30 mm. Crude $CH_nBr{\cdot}COI$ decomposes at 32°/vac. and attempted prep. of $CH_2I{\cdot}COI$ from $CH_2I{\cdot}COCl$ gives I. The at. refractivity of I (calc. from the mol. refractivity of AcI) is 15·73.

II. When Pr^{α}_2O and AcI are mixed, heat is developed (probably due to oxonium complex formation) after a short time; after 89 hr. in absence of light, a mixture of $Pr^{\alpha}I$ and $AcOPr^{\alpha}$ is produced. Me_2O, Pr^{β}_2O, Bu^{α}_2O, and di*iso*amyl ether are cleaved similarly. Fission occurs rather less readily with rise in mol. wt. of the ether, and reaction proceeds much faster with di*sec.* than with diprimary ethers. The ease of fission by the iodides is $AcI > CH_2Cl{\cdot}COI > CHCl_2{\cdot}COI$; $CCl_3{\cdot}COI$ does not cause cleavage at room temp. (and little at 100°) even in presence of ZnI_2. Et_2S and AcI give SEt_3I and AcSEt; fission occurs at a slower rate than with the ethers. $(CH_2)_2O$ and AcI react vigorously at −80° to give β-iodoethyl acetate; there is no apparent reaction between $(CH_2)_2O$ and AcCl at room temp., but after 44 days about 99% of β-chloroethyl acetate (also formed more rapidly in presence of a little I or, better, conc. HCl) is isolable. $CH_2Cl{\cdot}COI$ and $MeOBu^{\alpha}$ give (after 14 days) mainly MeI and $CH_2Cl{\cdot}CO_2Bu$; a little BuI is also formed. *Me methyliso propylcarbinyl ether*, b.p. 81·2—81·5°/737 mm., from the K derivative of $CHMePr^{\beta}{\cdot}OH$ (*chloroacetate*, b.p. 180—181°/738 mm.), and $CH_2Cl{\cdot}COI$ give approx. equal amounts of MeI and $CHMe{:}CMe_2$ [which may result by loss of HI from $CHMePr^{\beta}I$ (or the rearrangement product CMe_2EtI)]. $(CH_2Cl)_2O$ is unaffected by $CH_2Cl{\cdot}COI$ after 25 days at room temp. and 6 days at 100°. Aromatic ethers react vigorously with AcI at room temp. H. B.

Stereoisomerides of α-bromo-*n*-butyric acid. R. AHLBERG (Svensk Kem. Tidskr., 1932, **44**, 301—305).—Repeated heating of α-bromo-*n*-butyric acid to 100° in a pyknometer and determination of the rotation between each period of heating appears to support the view that the acid consists of two stereoisomeric racemic forms. H. F. H.

α-Bromo-*n*-butyric acid. II. Resolution of the racemic acid. R. AHLBERG (J. pr. Chem., 1932, [ii], **135**, 325—344; cf. preceding abstract).—Resolution is effected through the *strychnine* salt, yielding *l*-α-bromo-*n*-butyric acid, $[\alpha]_D^{19}$ −32·8°. Partial resolution is effected through the (+)α-2-*hydroxy*-1-*naphthylbenzylamine* salt. *Brucine*, *cinchonidine*, (−)-α-2-*naphthylethylamine*, and (−)-*diphenylhydroxyethylamine* salts are described. A. A. L.

Steric hindrance. VII. Esterification and hydrolysis from the viewpoint of the electronic theory of union. J. VON BRAUN and F. FISCHER (Ber., 1933, **66**, [*B*], 101—104).—The theory is developed that the difficulty in the esterification of acids $CR_3{\cdot}CO_2H$ (R=alkyl) and of the alkaline hydrolysis of their esters is due to electron displacement as well as to steric hindrance, and should therefore be observed with acids, $CH(CHR_2)_2{\cdot}CO_2H$ and $CH(CR_3)_2{\cdot}CO_2H$, in which steric hindrance is not to be expected. Thus, *diisopropylacetic acid* [β-*methyl*-α-iso*propylbutyric acid*], b.p. 108—110°/12 mm., obtained in almost 90% yield from cyanodi*iso*propylacetic acid and conc. HCl, at 160—170°, is scarcely esterified by EtOH–HCl, and its *Et* ester, b.p. 65°/12 mm., obtained from the *Ag* salt and EtI in C_6H_6, is hydrolysed with great difficulty. Et di*cyclo*pentenylmalonate, from *cyclo*pentenyl chloride and $CHNa(CO_2Et)_2$, is reduced (Ni+H_2) to *Et dicyclopentylmalonate* (I), b.p. 141—144°/0·4 mm., partly hydrolysed by very prolonged treatment with KOH in EtOH–H_2O to *Et H dicyclopentylmalonate*, whence

Et dicyclopentylacetate (II), b.p. 140—142°/15 mm., which is very slowly hydrolysed by KOH. (I) is transformed by conc. HCl at 150—160° into *dicyclopentylacetic acid*, b.p. 175—180°/12 mm., m.p. 59—60°, very difficultly esterified, but transformed into (II) through the *Ag* salt. H. W.

Effect of varying conditions in catalytic hydrogenation of fatty oils on nature of reaction product. II. H. I. Waterman and C. van Vlodrop (Rec. trav. chim., 1933, **52**, 9—17).—" Homogeneous hardening " (cf. A., 1932, 1018) of Me and Et linoleates is favoured by rise of temp. and use of Ni instead of Pt catalyst. Formation of oleic from linoleic and stearic acids at 180° in presence of Pt–active C, or of Me oleate from the Me esters in presence of Ni–kieselguhr, is negligible. E. W. W.

Acetoacetic ester condensation. IV. Reaction product of aliphatic esters and sodium ethoxide. J. M. Snell and S. M. McElvain (J. Amer. Chem. Soc., 1933, **55**, 416—421).—Attempts to prepare keten diethylacetal by the method of Scheibler *et al.* (A., 1927, 1167) were unsuccessful. The so-called " primary reaction products " of Scheibler *et al.* (*loc. cit.*) from EtOAc and $Pr^{\beta}CO_2Et$ and NaOEt are mixtures of NaOEt with $CHNaAc{\cdot}CO_2Et$ and $Pr^{\alpha}CO_2Na$, respectively, and are considered not to exist. p-*Phenylphenacyl isobutyrate* has m.p. 88·5°. H. B.

Lævulic acid. IV. Vapour pressures of its *n*-alkyl esters (C_7—C_{10}). M. A. Cowley and H. A. Schuette (J. Amer. Chem. Soc., 1933, **55**, 387—391).—n-*Heptyl*, n-*octyl*, n-*nonyl*, and n-*decyl lævulates*, prepared by direct esterification (HCl), have b.p. (calc.) (at 760 mm.) 283·5°, 291·1°, 298°, and 306·5°, respectively; they decompose at the b.p./near atm. pressure. Temp.–v.p. relationships and other physical data are recorded. H. B.

Carotene dye, sensitive to light, from safran. R. Kuhn and A. Winterstein (Ber., 1933, **66**, [*B*], 209—214; cf. A., 1931, 1067).—The action of dil. NaOH on a freshly-prepared extract of safran in MeOH affords crocetin Me_2 ester (I), $C_{22}H_{28}O_4$, m.p. 222°, or an *isomeride* (II), m.p. 141°. (II) is transformed into (I) by prolonged heating at its m.p., by I in warm light petroleum, by reduction to the dihydro-compound, m.p. 93—94°, which is treated with air in presence of NaOH and C_5H_5N, or by exposure in particular to blue or violet light in light petroleum, $CHCl_3$, C_5H_5N, or CS_2. The absorption spectrum, in harmony with chemical evidence, indicates that (II) and (I) are *cis*- and *trans*-isomerides. It is proposed to abandon the use of α- and β- in the bixin and crocetin group in favour of the designations such as bixin I or stable bixin of higher m.p. H. W.

Synthesis of tartaric acid. A. C. C. Newman and H. L. Riley (J.C.S., 1933, 45—46; cf. A., 1895, i, 21).—$[\cdot CH(OH){\cdot}SO_3H]_2$ is shaken with KCN (theoretical wt.) in H_2O, the solution saturated with dry HCl, and boiled for 12 hr. Treatment with $Ca(OH)_2$ affords Ca tartrate, which yields *r*-tartaric acid. J. L. D.

Colorimetric determination of tartaric acid. A. K. Anderson, A. H. Rouse, and T. V. Letonoff (Ind. Eng. Chem. [Anal.], 1933, **5**, 19—20).—The use of Fenton's method is recommended. The p_H of the solutions should be about 6·2. The colorations of *l*- and meso-tartaric acid are equiv. to that of the *d*-acid, whereas that of the *r*-acid is approx. half as intense. T. McL.

Cadmium tartrates. Pariselle and Barbier (Compt. rend., 1933, **196**, 114—116).—Solutions of equimol. amounts of Na tartrate and $CdSO_4$ give the gelatinous salt (I), $Cd<^{O{\cdot}CH}_{O{\cdot}CO}{>}CH(OH){\cdot}CO_2H$, which is acid to litmus, slightly sol. in H_2O, and passes into the less sol., neutral, cryst. salt (II), $Cd<^{CH(OH){\cdot}CO_2}_{CH(OH){\cdot}CO}{>}Cd$, is partly converted into (I) when heated at 120°. (II) (1 mol.) and H_2SO_4 (1 mol.) give the same equilibrium mixture as is obtained from equimol. amounts of tartaric acid (III) and $CdSO_4$. (I) is completely sol. in H_2SO_4 (1 mol.); the solution subsequently deposits (II) (until the above equilibrium is reached). Addition of NaOH to a solution of equimol. amounts of (III) and $CdSO_4$ gives a permanent ppt. after 3 mols. of NaOH per 2 mols. of (III). This ppt. dissolves in NaOH (2 mols.) to a stable solution of the Na salt of (I); an excess of NaOH affords a gelatinous basic salt containing 4 $Cd(OH)_2$ per 1 mol. of neutral tartrate. The rotatory powers of the solutions obtained by adding varying amounts of NaOH to a mixture of (III) (4 mols.) and $CdSO_4$ (1 mol.) show two max. and one min. with 9, 12, and 10 mols., respectively, of NaOH; the first max. indicates the formation of the Na salt of (I). With aq. NH_3 (in place of NaOH), the max. rotation corresponds with the formation of $Cd<^{O{\cdot}CH{\cdot}CO_2NH_4}_{O{\cdot}CH{\cdot}CO_2NH_4}$, which is stable only in presence of an excess of NH_4 tartrate. H. B.

***d*-Galacturonic acid. I. Methyl 1-methyl-*d*-galacturonate and 1-methyl-*d*-galacturonic acid.** F. Ehrlich and R. Guttmann (Ber., 1933, **66**, [*B*], 220—227).—α-*d*-Galacturonic acid (I) is transformed by MeOH–HCl at 100° into *Me* α-1-*methyl*-d-*galacturonate* (II), *monohydrate*, m.p. (indef.) 139—142° (decomp.) after softening at 138°, $[\alpha]_D^{20}$ +125·0° in H_2O, *anhyd.*, $[\alpha]_D^{20}$ +131·9° in H_2O, in 33% yield. Treatment of (I) with MeOH–HCl and Me_2SO_3 gives a 55% yield of (II) with a smaller proportion of *Me* β-1-*methyl*-d-*galacturonate*, m.p. 193—194° after softening at 189°, $[\alpha]_D$ −45·6° in H_2O, separable from one another by crystallisation from $COMe_2$. (II) and (III) are readily hydrolysed by cold aq. $Ba(OH)_2$ to α-1-*methyl*-d-*galacturonic acid* (IV), *dihydrate*, m.p. 109—113° after softening at 108°, $[\alpha]_D^{20}$ +129·9° in H_2O, also *monohydrate* (possibly an open form), and β-1-*methyl*-d-*galacturonic acid* (V), *monohydrate*, m.p. 134° (decomp.) after softening at 126°, $[\alpha]_D^{21}$ −39·2° in H_2O, *anhyd.*, $[\alpha]^{20}$ −40·5° in H_2O. Dil. acid hydrolyses (IV) and (V) to (I), which is readily obtained cryst. from (IV). The non-cryst. product obtained by the action of MeOH–HCl–Me_2SO_3 on (I)(above) is a reducing syrup, transformed by $Ba(OH)_2$ into a non-cryst. acid and thence by HCl into a reducing solution which yields cryst. (I); probably, Me γ-1-methylgalacturonate is present. The customary enzymes for α- and β-glucosides and those such

as maltase, emulsin, and pectolase of varying origin which are active towards the complex galacturonic acids are indifferent towards (II), (III), (IV), and (V). (II) is hydrolysed by pectase from lucerne. H. W.

Unsaturated derivative of glycuronic acid. J. PRYDE and R. T. WILLIAMS (Nature, 1933, **131**, 57).—Methylation of glycurone with Ag_2O and MeI yields trimethylglycurone, m.p. 131—132°, $[\alpha]_{5461}$ +197·5°, and *trimethylglycuralone*, $C_9H_{12}O_6$, m.p. 88°, $[\alpha]_{5461}$ +110·8° (cf. A., 1931, 1036). The suggested structure resembles in certain respects the enolic formula ascribed to adrenal hexuronic acid. L. S. T.

Reactivity of thiol group. II. N. HELLSTROM (Z. physikal. Chem., 1932, **163**, 33—52; cf. A., 1932, 26).—Practically the sole products, in addition to HBr, of the reaction of $SH\cdot CH_2\cdot CO_2H$ with $CH_2Br\cdot CO_2H$ and with $CH_2Br\cdot CO\cdot NH_2$ in aq. solution, are thiodiacetic acid (I) and the corresponding amic acid (II), respectively. With $CH_2Br\cdot CO_2H$ reaction is slower in strongly acid solutions than in solutions initially partly or wholly neutralised. In the reaction of $CH_2I\cdot CO_2H$ with $SH\cdot CH_2\cdot CO_2H$, (*a*) the formation of (I) is accompanied by (*b*) the formation of dithiodiacetic acid. In neutral solution (*a*) predominates, but in acid solution (*b*) may be responsible for 90% of the product, the probable mechanism being $SH\cdot CH_2\cdot CO_2H + CH_2I\cdot CO_2H = SI\cdot CH_2\cdot CO_2H + AcOH$ (slow), followed by $SI\cdot CH_2\cdot CO_2H + SH\cdot CH_2\cdot CO_2H = [\cdot S\cdot CH_2\cdot CO_2H]_2 + HI$ (rapid). With increase in $[H^+]$, the net velocity of (*b*) rises towards a limit, whilst the velocity of (*a*) falls apparently, due solely to the effect of H^+ on the dissociation of the acids. Metallic ions have some catalytic effect, but only in neutral solution. In the reaction of $CH_2I\cdot CO\cdot NH_2$ the rate of the reaction corresponding with (*b*) is so small compared with the rate of formation of (II) that the net rate of reaction is smaller in acid than in neutral solutions. R. C.

Manufacture of formaldehyde by catalytic oxidation and dehydrogenation of methyl alcohol. G. NATTA and M. STRADA.—See B., 1933, 100.

Autoxidation of aldehydes in presence of hydrated manganese dioxide. J. VON BRAUN and W. KELLER (Ber., 1933, **66**, [*B*], 215—219).—The unsatisfactory results frequently obtained in the oxidation of aldehydes to acids by H_2O_2 and alkali are attributed to the slow sequence of the changes involved in the formation of the primary additive product $OH\cdot CHR\cdot O_2H$ or $OH\cdot CHR\cdot O\cdot O\cdot CHR\cdot OH$, its conversion by loss of H_2O or dissociation into $R\cdot CH<\begin{matrix}O\\O\end{matrix}$ and finally into acid, whereby opportunity is afforded for the excess of H_2O_2 to attack an incompletely stable radical R. Oxidation of aldehydes with mol. O_2 is too slow for prep. purposes and is not greatly accelerated by Fe^{II}. Finely-divided MnO_2 or, preferably, $KMnO_4$ is a suitable accelerator which retains its activity over long periods. Without obvious loss of acceleration, the amount of MnO_2 may be decreased from 1/1000 to 1/4000 mol. of MnO_2 per mol. of aldehyde; with 1/12,000 mol. reaction is appreciably slower, whilst 1/40,000 mol. appears without action. The change is probably due to the production of an unstable additive compound from the catalyst and the C:O group, whereby the substance is made more sensitive to O_2. In support of this view, aged specimens of aldehydes which readily undergo autocondensation (hept- and *n*-dec-aldehyde) are indifferent towards MnO_2; this behaviour is ascribed to the unsaturated aldehydes which have been formed, since CHPh:CH·CHO and citronellal are indifferent. Further, the addition of various olefines to a reacting aldehyde–MnO_2 mixture immediately retards or inhibits the reaction, the C:C group being more favoured by MnO_2 than the C:O group. The following oxidations are recorded: heptaldehyde to heptoic acid; *n*-decaldehyde to *n*-decoic acid; acids, $C_8H_{14}O_2$, b.p. 120—145°/13 mm., from the products of ozonisation of the olefine, C_9H_{16}, from Rumanian petroleum; *iso*valeraldehyde to *iso*valeric acid; *iso*butaldehyde to *iso*butyric acid (process unaffected by age of aldehyde and rato only temporarily depressed by addition of olefines); PhCHO to BzOH (accelerated more by MnO_2 than by Fe^{II}; addition of Fe^{II} restricts acceleration due to MnO_2): *sebacdialdehyde*, b.p. 136—138°/11 mm., m.p. 16—18° (*disemicarbazone*, m.p. 186°), obtained with the *acid* $CHO\cdot[CH_2]_8\cdot CO_2H$ (*semicarbazone*, m.p. 155°) from the products of ozonolysis of $\Delta^{\omega\omega}$-dodecadiene, to sebacic acid. The purity of the acids obtained by autoxidation is generally much greater than that of those prepared by means of H_2O_2. H. W.

Oxidation of glyoxal hydrogen sulphite by molecular oxygen to glyoxylic acid. Oxidation of glyoxal by bromine to glyoxylic and oxalic acids. C. NEUBERG and M. KOBEL (Biochem. Z., 1932, **256**, 475—484).—Oxidation of glyoxal H sulphite by O_2 in presence of PO_4''' results in the formation of glyoxylic acid (80% yield) and no $H_2C_2O_4$, whereas with aq. Br both those acids are formed. P. W. C.

Liquid keten and keten polymerides. C. D. HURD, A. D. SWEET, and C. L. THOMAS (J. Amer. Chem. Soc., 1933, **55**, 335—337).—Polymerisation of liquid keten occurs even at −80°, but is retarded by traces of quinol. Reaction does not take place (in 12 hr.) with Na, Na–K (1 : 2) alloy, $NaNH_2$ (in PhMe), or isoprene; vigorous reaction occurs with MgPhBr or $MgBu^{\alpha}Br$ in Et_2O at −78°, and $Bu^{\gamma}OH$ and *tert.*-amyl alcohol are acetylated more readily than with gaseous keten. By-products in the prep. of keten from $COMe_2$ are the dimeride (I) and dehydroacetic acid (II); details for their isolation are given. The production of (II) from (I) and C_5H_5N and of $CH_2Br\cdot CO\cdot CH_2\cdot COBr$ from (I) and Br (Chick and Wilsmore, J.C.S., 1908, **93**, 946; 1910, **97**, 1987) can be readily explained on the assumption that (I) is CHAc:CO. H. B.

Preparation of keten diethylacetal. H. SCHEIBLER (J. Amer. Chem. Soc., 1933, **55**, 425—426).—Further details (cf. A., 1927, 1167) are given in view of Snell and McElvain's failure (this vol., 258). H. B.

Preparation of keten [diethyl]acetal. J. M. SNELL and S. M. MCELVAIN (J. Amer. Chem. Soc., 1933, **55**, 427—428).—Further attempts using Scheibler's revised procedure (preceding abstract) were again unsuccessful. H. B.

Synthesis of methoxymethyl alkyl ketones. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1933, **20**, 53—62).—OMe·CH_2Cl and dry CuCN give methoxyacetonitrile, b.p. 119°, which by the Grignard reaction affords the following *methoxymethyl alkyl ketones*: *Et*, b.p. about 130° (*semicarbazone*, m.p. 84—85°; 2:4-*dinitrophenylhydrazone*, m.p. 198—198·5°); Pr$^{\alpha}$, b.p. about 117°/175 mm. (*semicarbazone*, m.p. 97—98°; 2:4-*dinitrophenylhydrazone*, m.p. 128·5—129°); *Bu*$^{\alpha}$, b.p. 131—132°/173 mm. (*semicarbazone*, m.p. 93°; 2:4-*dinitrophenylhydrazone*, m.p. 93°); iso*amyl*, b.p. 117°/87 mm. (*semicarbazone*, m.p. 105—106°; 2:4-*dinitrophenylhydrazone*, m.p. 109·5°). The odour of these ketones is unpleasant in conc., but pleasant in dil., solutions; it is not characteristic of saké. R. S. C.

Chloromethyl β-chloroethyl ketone (αδ-dichlorobutan-β-one). R. H. CARROLL and G. B. L. SMITH (J. Amer. Chem. Soc., 1933, **55**, 370—373).—Treatment of the product from $CH_2Cl·CH_2·COCl$ and Et_2O–CH_2N_2 with dry HCl gives *chloromethyl β-chloroethyl ketone* (I), b.p. 65°/3 mm., also obtained in small yield from $CH_2Cl·COCl$ and the additive compound from C_2H_4 and $AlCl_3$ in light petroleum. (I) and $CS(NH_2)_2$ afford 2-amino-4-β-chloroethylthiazole, m.p. 60° (*hydrochloride*, begins to melt at 144°, re-solidifies, and then has m.p. 166°). H. B.

Anlaysis of individual carbohydrates. V. J. HARDING, T. F. NICHOLSON, G. A. GRANT, G. HERN, and C. E. DOWNS (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 33—43).—The following strains of bacteria and yeast were used for the sp. removal of the given sugars: *Proteus vulgaris* (I), glucose (II) and galactose (III); *Monilia krusei* (IV), fructose (V) and mannose (VI) [after removal of (II) by (I)]; *Saccharomyces marxianus* (VII), sucrose (VIII) and (III) [after removal of (II), (V), and (VI) by (IV)]; *Monilia tropicalis*, maltose (IX) [after removal of (II), (III), (V), and (VI) by (VII)]. Combination of these degradations with appropriate acid hydrolyses enables a mixture of (II), (III), (V), (VIII), (IX), and lactose to be determined. F. O. H.

Transformations of sugars in ammoniacal medium at room temperature. I. Products of oxidation of sugars by oxygen and ammoniacal cupric oxide. J. PARROD (Bull. Soc. chim., 1932, [iv], **51**, 1424—1435; cf. A., 1930, 480; 1931, 852; 1932, 45, 369).—A fuller description of results previously published. In addition to $H_2C_2O_4$ and glyoxaline [*H oxalate*, m.p. 252° (decomp.)], which are given by all the sugars and also by *l*-xylose and *l*-arabinose, the following are obtained by air-oxidation in NH_3–CuO over periods of 15—60 days at room temp.: from fructose, 4-*hydroxymethylglyoxaline* (I), m.p. 93·5° [*picrate*, m.p. 206° (decomp.)], and 4-*d*-arabinotetrahydroxy-*n*-butylglyoxaline (II) [*picrate*, m.p. 123°; hydrochloride, m.p. 179° (lit. 162°)]; from glucose and *d*-mannose, (II), in good yield from the former; from *d*-galactose, 4-*d*-lyxotetrahydroxy-*n*-butylglyoxaline and its 2-*hydroxymethyl* derivative, m.p. 201°; from rhamnose, 2-methylglyoxaline, and from dihydroxyacetone, (I). In absence of air the same products are formed in smaller yield. The structure of (II) is confirmed by synthesis from glucosone, NH_3, and CH_2O. H. A. P.

Products of oxidation of fructose by ammoniacal copper carbonate and atmospheric oxygen in dilute solution at p_H 7·7 and room temperature. J. PARROD and Y. GARREAU (Compt. rend., 1932, **195**, 1110—1111).—See preceding abstract. A. C.

Wood. V. Arabogalactan in Western American larches. L. E. WISE and H. C. UNKAUF (Cellulosechem., 1933, **14**, 20—24).—Arabogalactan is probably a chemical individual, since identical products are obtained by extraction with hot or cold H_2O, and fractional pptn. with EtOH from H_2O solution gives identical fractions. A. G.

Polarographic studies with the dropping mercury cathode. XXX. Electro-reduction and determination of fructose and sorbose. A. HEYROVSKÝ and I. SMOLER (Coll. Czech. Chem. Comm., 1932, **4**, 521—530; cf. A., 1932, 1237).—Fructose (I) and sorbose, but not aldoses, are electro-reducible, and (I) can be determined by this method. Na, K, and Ba salts obscure the measurement, but Ca or Sr salts in neutral or alkaline solutions assist it. 5-Ketorhamnolactone and 6-ketorhamnohexolactone are also electro-reducible. The temp. coeff. of the reduction of (I) is abnormally high, reduction being apparently incomplete at high temp. At 40° two electrons appear to be consumed by each mol. of ketone. R. S. C.

Synthesis of sucrose. A. PICTET (Helv. Chim. Acta, 1933, **16**, 144—148).—Of 21 sugars and anhydrosugars examined, only sucrose (I) forms a complex ($C_{12}H_{22}O_{11}$,$CuSO_4$,$4H_2O$) with $CuSO_4$; (I) is recovered from the complex by warming with 70% EtOH, whereby (I) only is dissolved. A small amount of a complex has been obtained from one of five condensation products prepared by Georg (following abstract) (after hydrolysis by Zemplén's method); the sugar recovered had m.p. 184° and did not depress the m.p. of (I). H. B.

[Attempted] synthesis of the sucrose of Pictet and Vogel. A. GEORG (Helv. Chim. Acta, 1933, **16**, 130—144; cf. Irvine and Stiller, A., 1932, 500).—Attempts to synthesise sucrose octa-acetate from glucose and γ-fructose tetra-acetates (method of prep. given) by the original and slight modifications of the method of Pictet and Vogel (A., 1928, 510, 741; 1929, 913) were unsuccessful; the cryst. products isolated were the *iso*sucrose octa-acetate of Irvine *et al.* (A., 1929, 683; 1930, 197) [which is identical with the sucrose *D* octa-acetate of Pictet and Vogel (A., 1928, 1223)], traces of α- and β-glucose penta-acetates, and a mixture (?) of a *trihexose hendeca-acetate*, m.p. 60—80° (sinters at 55°), $[\alpha]_D^{21}$ +10·1° to +36·7° in C_6H_6. H. B.

Cellotriose and its importance for the structure of cellulose. L. ZECHMEISTER, H. MARK, and G. TÓTH (Ber., 1933, **66**, [*B*], 269—275; cf. A., 1929, 544; 1931, 716).—In reply to Klages (A., 1931, 927) and Dziengel and others (A., 1932, 1116), fractionation of cellotriose (I) by concn. of the solution in MeOH at room temp., or from C_5H_5N–Et_2O by gradual

increase of the amount of Et_2O or acetylation of (I) followed by repeated crystallisation and ultimate hydrolysis of the acetate with NaOMe, fails to afford evidence of the presence of heterogeneous components in (I). H. W.

[**Cellotriose.**] K. Dziengel, C. Trogus, and K. Hess (Ber., 1933, **66**, [*B*], 276; cf. preceding abstract).—The failure of Zechmeister and others to separate cellotriose into heterogeneous components is attributed to the use of too small amounts of material. H. W.

Nitrogenous glucosides. II. Synthesis of glucosidoureides. K. N. Haring and T. R. Johnston.—See this vol., 284.

Ring structure of ribose in the yeast-nucleic acids. H. Bredereck (Ber., 1933, **66**, [*B*], 198; cf. this vol., 149).—*Triphenylmethyl-adenosine*, m.p. 259—260°, $[\alpha]_D^{20}$ −8·8° in $CHCl_3$, *-cytidine*, m.p. 234—235°, $[\alpha]^{20}$ ±0 in C_5H_5N, and *-inosine*, m.p. 253—254°, are not hydrolysed by KOH–EtOH, and hence contain the CPh_3 residue attached to the C_5 atom of ribose. The four nucleosides of the yeast-nucleic acids have the furanose structure, as have the ribose residues. H. W.

Electrolytic preparation of aldonic acids. H. Kiliani (Ber., 1933, **66**, [*B*], 117—120).—The method of Isbell and Frush (A., 1931, 1038) is adapted to the identification of the sugars of glucosides which are hydrolysed with HBr; after removal of the aglucone the acid solution is neutralised with $CaCO_3$, conc. if necessary, and electrolytically oxidised in presence of $CaCO_3$. The sugars are identified as the Ca salts of the corresponding aldonic acids. Digitonin is thus shown to yield *d*-glucose, *d*-galactose, and xylose. HCl cannot replace HBr for the hydrolysis. The conversion of *d*-mannose into *d*-mannonic acid and of lactose into *d*-galactonic acid is described in detail. H. W.

Carbohydrate–fatty acid linkings in maize α-amylose. T. C. Taylor and R. T. Sherman (J. Amer. Chem. Soc., 1933, **55**, 258—264).—Preferential hydrolysis of the fatty acid groups associated with the α-amylose of maize starch occurs with EtOH–HCl, EtOH–NH_3, or lipase-free amylase; the oleyl and linoleyl groups are removed more readily than the palmityl group. H. B.

Action of aqueous alkali on starches, amyloses, and modified starches. T. C. Taylor and G. M. Salzmann (J. Amer. Chem. Soc., 1933, **55**, 264—275).—Partly-degraded starches and amyloses contain varying amounts of material (probably the original polysaccharide; two methods of determination given) which is stable to hot aq. KOH and a fraction (the altered portion) which is completely destroyed. The I consumption of the product after treatment with alkali is always much greater than that of the initial material, indicating that the reducing substance in *e.g.*, an amylose, is not glucose. Original starch (or amyloses) is almost completely resistant to hot aq. alkali. Large amounts of alkali-unstable material are produced from starch or amylose by the action of aq. acid, heat, or grinding. Dextrins produced by long heating of starch contain much more alkali-stable material than those prepared by hydrolytic methods. H. B.

Acetolysis of starch. R. Sutra (Compt. rend., 1932, **195**, 1079—1080).—Treatment of maize starch (10 g.) with cold Ac_2O (40 c.c.) and H_2SO_4 (5 c.c.) and finally at 70—95° affords α-, m.p. 120—122°, $[\alpha]_{578}$ +120·5° in $CHCl_3$, and a small proportion of β-, m.p. 165°, $[\alpha]_{578}$ +65·5° in $CHCl_3$, -maltose octa-acetate. A. C.

Preparation of soluble starch by enzyme action. A. V. Stepanov and A. Kuzin (Khim. Farm. Prom., 1932, 321—325).—3% Starch paste is heated at 60° with the enzyme (0·4% of starch); after 15 min. the temp. is rapidly raised to the b.p. and maintained for 3 min. The mixture is filtered with suction through sand; the filtrate is treated with EtOH and filtered, the solid being washed with abs. EtOH and dried in vac. Ch. Abs.

Molecular structure of polysaccharides. W. N. Haworth and E. L. Hirst (Trans. Faraday Soc., 1933, **29**, 14—17).—Determinations of the percentages of tetramethylhexoses in the products of hydrolysis of methylated polysaccharides show cellulose to consist of a chain of 100—200 β-glucopyranose units, amylose and amylopectin of 24—30 α-glucopyranose units, glycogen of 12 α-glucopyranose units, and inulin of about 30 fructofuranose units. Determinations of chain-lengths of cellodextrins by this method agree with those by the I val. method. A. G.

Chain-length of native cellulose and of acetylxylan from deciduous trees. E. Schmidt (Oesterr. Chem.-Ztg., 1933, **36**, 12).—The CO_2H content of cellulose and the OMe content of deacetylated xylan from deciduous trees indicate that the mols. contain 96 and 16 units, respectively. A. G.

Mol. wt. of cellulose acetate and nitrate. E. H. Buchner and P. J. P. Samwel (Trans. Faraday Soc., 1933, **29**, 32—40).—The osmotic pressures of cellulose acetate solutions were measured by determining the counter-hydrostatic pressure required to prevent diffusion through the membrane. The mol. wt. is not greatly affected by temp. (0—60°), concn. (1—5%), or nature of the solvent ($COMe_2$, COPhMe, $CH_2Ph{\cdot}OH$, and COPhMe+$CH_2Ph{\cdot}OH$). Preps. differing considerably in the viscosity of 1% solutions differ only slightly in mol. wt., so that $M/\eta_{sp.}$ falls markedly with increasing viscosity. In $COMe_2$ at 0° and 20° the osmotic pressure increases more rapidly than the concn. The absence of solvatation in COPhMe is shown by the f.-p. depression produced by the dissolution of $C_{10}H_8$. A. G.

Molecular aggregation of cellulose nitrate. F. D. Miles (Trans. Faraday Soc., 1933, **29**, 110—121).—The phenomena of nitration, the *X*-ray diagrams of films and fibres, and the phenomena of dissolution indicate that nitration is a homogeneous process and does not produce a heterogeneous mixture of cellulose and its trinitrate. A. G.

Behaviour of benzoyl peroxide towards amino-compounds. I. De Paolini and G. Ribet.—See this vol., 292.

Action of organo-mercury derivatives on solutions of hexamethylenetetramine. A. PERRET and A. M. KRAWCZYNSKI (Compt. rend., 1932, **195**, 1077—1078).—The following mol. *compounds* are obtained by evaporating mixed $CHCl_3$ solutions of the org. Hg derivative with excess of $(CH_2)_6N_4$ and extracting the product with PhMe: $3HgMeI,(CH_2)_6N_4$, m.p. 119°; $2HgMeBr,(CH_2)_6N_4$, m.p. 112°; $HgMeCN,5(CH_2)_6N_4$, m.p. 127°; $HgMeCl,(CH_2)_6N_4$, m.p. 141°; $HgMeSCN,(CH_2)_6N_4$, m.p. 106° (from *methylmercurithiocyanate*, m.p. 125·5°, prepared from HgMe·OH and KSCN in dil. H_2SO_4). *Methylmercury fluoride*, subliming >200°, prepared by neutralising HgMe·OH with HF, does not react with $(CH_2)_6N_4$. No additive compounds are obtained from Hg Et, Ph, and allyl derivatives. A. C.

Influence of poles and polar linkings on the course pursued by elimination reactions. X. Formation and decomposition of dibenzyldiallylammonium hydroxide. L. HEY and C. K. INGOLD. **XI. Decomposition of quaternary ammonium hydroxides containing the *tert.*-butylcarbinyl group. XII. Decomposition of quaternary ammonium alkoxides.** C. K. INGOLD and C. S. PATEL. **XIII. Decompositions of some quaternary ammonium salts containing the methyl, benzyl, and benzhydryl groups.** E. D. HUGHES and C. K. INGOLD. **XIV. Action of *tert.*-amines on triphenylmethyl halides.** E. D. HUGHES (J.C.S., 1933, 66—67, 67—68, 68—69, 69—75, 75—77). —X. The action of allyl iodide (I) or bromide (II) on $NH(CH_2Ph)_2$ in absence of solvent, in Et_2O or $MeNO_2$ (III) at 0° to b.p. gives essentially $NH(CH_2Ph)_2$ hydrohalide. Similarly, (I) and (II) with $NH_2{\cdot}CH_2Ph$ afford $NH_2{\cdot}CH_2Ph$ hydrohalide (corresponding picrate, m.p. 199—200°). Benzylallylamine and CH_2PhBr yield benzylallylamine hydrobromide and non-cryst. material. Diallylamine and CH_2PhBr in Et_2O afford diallylamine hydrobromide, whereas in (III) the *tert.*-salt is pptd. by Et_2O as a gum from which benzyldiallylamine (IV), b.p. 121—124°/20 mm. (*picrate*, m.p. 114°), is derived. (IV) and CH_2PhBr in (III) give *dibenzyldiallylammonium bromide* (corresponding *picrate*, m.p. 143°). Thermal degradation of dibenzyldiallylammonium hydroxide involves the loss of two allyl groups (which appear partly as acraldehyde) and production of $NH(CH_2Ph)_2$.

XI. *tert.*-Butylcarbinylamine (*picrate*, m.p. 205°; Ac derivative, m.p. 75°) is transformed by heating its hydrochloride with paraformaldehyde at 140° into *tert.-butylcarbinyldimethylamine* (I), b.p. 96—97° (*hydrochloride*, m.p. 182°; *hydrobromide*, m.p. 170°; *hydriodide*, m.p. 135°; *picrate*, m.p. 193°). (I) and MeI at room temp. give *tert.-butylcarbinyltrimethylammonium iodide*, m.p. 240° (decomp.). *Benzyl*-tert.-*butylcarbinyldimethylammonium bromide* has m.p. 200° (decomp.). Thermal degradation of *tert.*-butylcarbinyltrimethylammonium hydroxide yields only MeOH and $NMe_2{\cdot}CH_2{\cdot}CMe_3$; the amine and $CH_2Ph{\cdot}OH$ are derived from benzyl-*tert.*-butylcarbinyldimethylammonium hydroxide. The mode of elimination of the groups concerned in the form of alcohol is $CH_2Ph > HCH_2 > CMe_3{\cdot}CH_2$.

XII. In the thermal fission of trimethylethyl- and trimethyl*iso*butyl-ammonium methoxide and ethoxide the proportion of reaction leading to an ether and a *tert.*-amine is the same to within a few units % as that in which an alcohol is formed when the anion is OH′. $NMe_3(CH_2Ph){\cdot}OEt$ yields 65% of $CH_2Ph{\cdot}OEt$, large amounts of NMe_3, and (?) $NMe_2{\cdot}CH_2Ph$ in small quantity.

XIII. Thermal decomp. of $CH_2Ph{\cdot}NMe_3{\cdot}OH$ (cf. Collie and Schryver, J.C.S., 1890, **57**, 767) gives 65% of $CH_2Ph{\cdot}OH + NMe_3$ and 35% of $MeOH + CH_2Ph{\cdot}NMe_2$; PhCHO and $(CH_2Ph)_2O$ are produced in small amount. $CHPh_2{\cdot}NMe_3{\cdot}OH$ in hot H_2O undergoes three reactions, and the manner in which the proportions of the products change with dilution and on addition of extraneous alkali shows that the change leading to $CHPh_2{\cdot}OH$ is of lower order (probably first) than the others (probably second); one of these other reactions leads to MeOH and a *tert.*-amine, the other to a migration product (cf. Stevens and others, A., 1929, 180). Similarly, $CHPh_2{\cdot}NMe_2(CH_2Ph){\cdot}OH$ undergoes four reactions, three leading to the three possible alcohols and the fourth to a rearrangement product; the change leading to $CHPh_2{\cdot}OH$ is of lower order (probably first) than the others. The following new compounds are incidentally described: *benzhydryltrimethylammonium bromide*, m.p. 145° (decomp.) according to the rate of heating, from $CHPh_2Br$ and NMe_3 in MeCN, the corresponding *tribromide*, m.p. 138°, *picrate*, m.p. 152° (decomp.), and iodide, m.p. 170—175° (decomp.); *benzhydryldimethylamine picrate*, m.p. 196°; *dimethyl-αα-diphenylethylamine picrate*, m.p. 151° (from products of thermal decomp. of $CHPh_2{\cdot}NMe_3{\cdot}OH$); *trimethyl-αα-diphenylethylammonium iodide*, m.p. 205° (decomp.); *benzhydryldimethylethylammonium iodide*, from $CHPh_2{\cdot}NMe_2$ and EtI in MeCN, and the corresponding *picrate*, m.p. 141°; *dimeric αα-diphenylethylene*, m.p. 203°, from thermal decomp. of $CPh_2Me{\cdot}NMe_3{\cdot}OH$; *benzylbenzhydryldimethylammonium bromide* ($+H_2O$), m.p. about 125° (decomp.), from $CH_2Ph{\cdot}NMe_2$ and $CHPh_2Br$ in MeCN, and the corresponding *picrate*, m.p. 149° (decomp.); *dimethyl-ααβ-triphenylethylamine*, m.p. 128°, its *hydrochloride*, m.p. 280° when rapidly heated, and *picrate*, m.p. 218° (decomp.); *trimethyl-ααβ-triphenylethylammonium iodide*, m.p. 238°, and *picrate*, m.p. 214°; (?) *β-bromo-ααβ-triphenylethylene*, m.p. 115°; *dibenzylbenzhydrylamine*, m.p. 129°, from $CHPh_2Br$ and $NH(CH_2Ph)_2$ at 100°, its *hydrochloride*, m.p. 180—182°, and *picrate*, m.p. 145° (decomp.); *dibenzylmethylammonium bromide*, m.p. 157°, from $CHPh_2Br$ and $NMe(CH_2Ph)_2$ in MeCN, and the corresponding *picrate*, m.p. 107°; *benzylhydryldimethylammonium bromide* ($+1H_2O$), m.p. 206°, from $CHPh_2Br$ and $CHPh_2{\cdot}NMe_2$ in MeCN.

XIV. Interaction of NMe_3 and CPh_3Cl in MeCN–$CHCl_3$ at room temp. affords the *compound* $2CPh_3{\cdot}OH,NMe_3,HCl$, m.p. 190—195° (decomp.), from which H_2O extracts the salt (I) and leaves the carbinol (II), and C_6H_6 removes (II) leaving (I); it is also obtained by crystallising solutions containing (I) and (II). Replacement of CPh_3Cl by CPh_3Br or of NMe_3 by NEt_3 does not lead to similar compounds. The view that NPh_3Me salts are unstable is

supported by the observation that $NMe_2{\cdot}CPh_3$ and MeI in MeCN yield NMe_4I, I, and $CPh_3{\cdot}OH$, whereas in EtOH, NMe_4I and $CPh_3{\cdot}OEt$ are produced. The "pyridinium" bromide of Tschitschibabin and of Hantzsch has the composition $CPh_3{\cdot}OH,C_5H_5N,HBr$, whilst Norris and Calver's compound (A., 1903, i, 333) is $CPh_3{\cdot}OH,C_5H_5N,HCl$. H. W.

Nitroamines. H. Cerf (Compt. rend., 1932, **195**, 1084—1086).—$MeNO_2$ condenses with CH_2O (2 mols.) and $NHEt_2$ (2 mols.), yielding *β-nitro-αγ-tetraethyldiaminopropane*, b.p. 110°/4 mm. [*chloroplatinate*, m.p. 231° (decomp.)], reduced by Al–Hg to *αγ-tetraethyldiaminopropyl-β-amine* (I), b.p. 110°/10 mm. (*trihydrochloride*), which gives two *chloroplatinates*, $B,3HCl,PtCl_4$, m.p. 190° (decomp.), and $[B,3HCl,PtCl_4]_2,PtCl_4$, m.p. 220°, but one *chloroaurate*, $B,3HCl,AuCl_3$, m.p. 177° (decomp.). (I) is transformed into *hexaethyltriaminopropane*, b.p. 110°/10 mm., and is converted by HNO_2 into $NEt_2{\cdot}NO$ and *β-nitrosoamino-αγ-tetraethyldiaminopropane*, m.p. 43°, b.p. 147/5 mm. (*chloroaurate*, m.p. 165°), reduced to (I) by Zn and HCl in EtOH. A. C.

Action of magnesium alkyl halides on hydroxylamine and on its acyl derivatives. F. S. De Paolini and I. De Paolini (Gazzetta, 1932, **62**, 1058—1065).—In Et_2O, MgEtBr and NH_2OH form the *compound* $MgBr{\cdot}NH{\cdot}OMgBr$ (whence $NHBz{\cdot}OBz$). The Zerevitinov method shows two active H atoms in NH_2OH, in $NHBz{\cdot}OH$, and in $PhSO_2{\cdot}NH{\cdot}OH$. The Mg derivative of the last decomposes to $PhSO_2NH_2$, and with BzCl gives $PhSO_2{\cdot}NHBz$. Similarly, *p*-$C_6H_4Me{\cdot}SO_2NH{\cdot}OH$ yields *p*-$C_6H_4Me{\cdot}SO_2NH_2$. Presumably the SO_2 group first loses O, regained by migration. E. W. W.

Synthesis of glyoxaline derivatives from α-amino-acids. I. Synthesis of deaminohistidine and the constitution of ergothioneine. S. Akabori.—See this vol., 285.

Catalytic deamination of amino-acids. B. Kisch (Fermentforsch., 1932, **13**, 433—442).—A review of "omega" catalysis of oxidative deamination of NH_2-acids. A. C.

Oxidative degradation of α-amino-acids by sugars. S. Akabori (Ber., 1933, **66**, [*B*], 143—150).—*d*-Glutamic acid and glucose (I) in glycerol at 125—130° evolve CO_2 and yield 5-hydroxymethylfurfuraldehyde (II), identified as 5′-hydroxymethylfurfurylidene-1 : 3-dimethylbarbituric acid; furfuraldehyde (III) and its 5-Me derivative are obtained similarly from *l*-arabinose (IV) and rhamnose (V), respectively. δ-Ketohexaldehyde could not be detected. *l*-Leucine (VI) and (I), fructose, lactose, (IV), or (V) afford *iso*valeraldehyde (VII) and small amounts of (III) or its derivatives. (I) and *dl*-alanine (VIII), *l*-phenylalanine (IX), and *dl*-valine (X) afford, respectively, MeCHO, $CH_2Ph{\cdot}CHO$, and *iso*butaldehyde. The amount of CO_2 evolved never exceeds that which corresponds with the amount of NH_2-acid used even when the quantity of sugar is increased. Reaction therefore occurs,

$$NH_2{\cdot}CHR{\cdot}CO_2H+0{\cdot}5O_2 \longrightarrow R{\cdot}CHO+CO_2+NH_3.$$

Very little NH_3 is liberated, the bulk being used in the production of melanoids. (VI) and (II) or (III) give CO_2, a brown pigment, and (VII), whereas from (III) and (VIII), (X), (IX), and α-amino*iso*butyric acid there are formed MeCHO, *iso*butaldehyde, $CH_2Ph{\cdot}CHO$, and $COMe_2$, respectively. In general, the furfuraldehydes react at a lower temp. than the sugars with NH_2-acids. Since vanillin, piperonal, etc. do not exert an oxidising action, the effect is characteristic of the furfuraldehydes and not a general property of the CHO group. (I) with α-amino*iso*butyric acid or α-methylamino-*n*-heptoic acid gives respectively $COMe_2$ and hexaldehyde. $COMeEt$ is derived from *dl*-α-amino-α-methylbutyric acid and galactose. An intermediate stage in the oxidative degradation of α-NH_2-acids cannot be established, reaction appearing to proceed directly to CO_2, NH_3, and aldehyde or ketone. H. W.

Reactions between sugars and amino-acids. III. Separation of racemates of optically active amino-acids by glucoside formation and synthesis of a tripeptideglucoside. K. Maurer and B. Schiedt (Z. physiol. Chem., 1932, **213**, 110—118; cf. A., 1932, 605).—Various NH_2-acid glucosides were prepared by the interaction of the NH_2-acid and the acetobromo-sugar: *hepta-acetyl-leucylglycylglycine ester cellobioside*, m.p. 100°, $[\alpha]_D^{20}$ +16·20°, cryst., yielding a *compound* (? *l*- or *d*-ester), m.p. 193°; *tetra-acetyl-C-phenylglycine ester glucoside*, l-, m.p. 134°, $[\alpha]_D^{20}$ −52·21°, d-, m.p. 121°, $[\alpha]_D^{20}$ +152·9°; *hepta-acetyl-C-phenylglycine ester cellobioside*, l-, m.p. 186°, $[\alpha]^{20}$ −24·34°, d-, m.p. 144°, $[\alpha]_D^{21}$ +43·48°; *hepta-acetyl-β-phenylalanine ester cellobioside*, l-, m.p. 184°, $[\alpha]_D^{1}$ −19·50°, d-, m.p. 176°, $[\alpha]_D^{21}$ +0·08°. All rotations are in $CHCl_3$. Sarcosinamide glucoside is attacked by yeast only after hydrolysis with emulsin. J. H. B.

New method of aminating organic compounds. A. Cocco (Compt. rend., 1932, **195**, 1086—1088).—Et iminodicarboxylate (I) and acetamidocarboxylate (II) are converted into their K derivatives by EtOH–KOH. In org. solvents these do not react with CH_2PhCl or yield urethane, but alkylation occurs in absence of solvent or in urethane solution. (II) yields, with CH_2PhCl and BuCl, *acetylbenzylurethane*, b.p. 157—158°/12 mm., and butylurethane (hydrolysis of Ac group), which are hydrolysed by HBr to $CH_2Ph{\cdot}NH_2$ and NH_2Bu, respectively. (I) reacts with BuCl, yielding *Et butyliminodicarboxylate*, b.p. 150°/7 mm., which affords NH_2Bu on hydrolysis with HBr. A. C.

β-Amino-*n*-valeric acid. H. D. Dakin (J. Biol. Chem., 1933, **99**, 531—535).—Δ^{α}-Pentenoic acid (A., 1903, i, 139) when heated in aq. NH_3 solution (saturated at 5°) at 125—135° gives, after esterification of the product, the *Et* ester, b.p. 82—84°/12 mm., of *β-amino-*n*-valeric acid* (I), decomp. 160—165°, clear melt at 180° (*Cu* salt; *phosphotungstate*; *reineckate*, darkens at 156°, m.p. 171—175°), which is obtained by hydrolysis with boiling H_2O. When warmed with aq. KCNO (I) affords *β-carbamido-*n*-valeric acid*, m.p. 147—148°, converted into *4-ethylhydrouracil*, m.p. 191—192°, by boiling with 15% HCl. With PhNCO and dil. NaOH (I) gives *1-phenyl-4-ethylhydrouracil*, m.p. 192°. J. W. B.

Aminolysis of aspartic acid. K. WUNDERLY (Helv. Chim. Acta, 1933, **16**, 80—87; cf. A., 1924, ii, 841).—Aminolysis of *dl*-aspartic acid (I) occurs more readily and more completely at 80° than at 39° when a saturated aq. solution is treated with C; the products formed are MeCHO, NH_4HCO_3, and NH_4 pyruvate, lactate, and malate. The following reactions probably occur: (*a*) (I)+H_2O⟶lactic acid+NH_3+CO_2; (*b*) (I)+H_2O⟶malic acid+NH_3; (*c*) (I)−H_2+H_2O⟶oxaloacetic acid (II)+NH_3; (*d*) (II)⟶$AcCO_2H$+CO_2. H. B.

Aminolysis of aspartic acid. E. BAUR (Helv. Chim. Acta, 1933, **16**, 88—90).—The heat effects of the reactions $CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (I) ⟶ $OH{\cdot}CHMe{\cdot}CO_2'+NH_4^{\cdot}+CO_2$ and (I)+H_2O ⟶ $CO_2H{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2'+NH_4^{\cdot}$ occurring in the aminolysis of (I) (preceding abstract) are −6·1 and −2·4 kg.-cal., respectively. H. B.

Use of pure phosphotungstic acids in the precipitation of bases. I. Method of checking the purity of 1 : 24-phosphotungstic acid. II. The influence of [H$^{\cdot}$] and some other factors on the precipitation of bases. H. BARNES and R. A. PETERS (Biochem. J., 1932, **26**, 2203—2219).—I. By heating the acid first at 540° to const. wt. and then at 1000°, theoretical figures can be obtained for H_2O and WO_3.

II. Creatinine and histidine hydrochloride have been studied in detail. Other bases have also been investigated. The dissociation curves of the acids have been determined by titration. S. S. Z.

Racemisation. XII. Action of alkali on polypeptides composed of *l*-alanine. P. A. LEVENE and P. S. YANG (J. Biol. Chem., 1933, **99**, 405—416).—By usual methods the following are prepared from *l*-alanine: l-*alanyl*- (I), $[\alpha]_D^{26}$ +36·5°, *di*- (II), $[\alpha]_D^{26}$ +77·5°, *tri*- (III), $[\alpha]_D^{21}$ +115°, and *tetra*- (IV), $[\alpha]_D$ +132·5°, -l-*alanyl*-l-*alanine* (all rotations in 2*N*-HCl). The following intermediates were isolated but not analysed: *l*-bromopropionyl-, $[\alpha]^{25}$ +14·79° in H_2O, *l*-bromopropionyl-*l*-alanyl-, -di-*l*-alanyl-, and -tri-*l*-alanyl-, -*l*-alanine. Study of the racemisation of the polypeptides (I)—(IV) with various proportions (2 : 1 and 10 : 1) of 0·2*N*- and 1·0*N*-NaOH at 25° for 2, 8, or 16 days in conjunction with previous results indicates that under standard conditions the degree of racemisation of polypeptides higher than tripeptides depends mainly on the nature, and not on the no., of the constituent NH_2-acids, those components which confer stability towards hydrolytic reagents also decreasing the tendency towards racemisation. The similar course of racemisation followed by the proteins is consistent with a polypeptide, but not with a ketopiperazine, structure. J. W. B.

Behaviour of polypeptides composed solely of *l*(+)-α-aminobutyric acid towards *N*-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN and E. HAASE (Fermentforsch., 1932, **13**, 303—309).—Amination of the condensation product of *l*(+)-α-aminobutyric acid hydrochloride (I), $[\alpha]_D^{20}$ +13·95°, with *l*-α-bromobutyryl chloride gives d-α-*aminobutyryl*-l-α-*aminobutyric acid*, $[\alpha]_D^{20}$ −51·7° in H_2O. (I) condenses with *d*-α-bromobutyryl chloride (II), giving d-α-*bromobutyryl*-l-α-*aminobutyric acid*, m.p. 110°, converted by NH_3 into l-α-*aminobutyryl*-l-α-*aminobutyric acid*, m.p. 258° (decomp.), $[\alpha]^{20}$ −7·03° in 20% HCl, used also for the peptides below. Successive condensations of the latter with (II), alternated by amination, give d-α-*bromobutyryl*-l-α-*aminobutyryl*-, m.p. 179°, *di*-l-α-*aminobutyryl*-, m.p. 243°, $[\alpha]^{20}$ −46·04°, d-α-*bromobutyryldi*-l-α-*aminobutyryl*-, m.p. 217°, *tri*-l-α-*aminobutyryl*- (+H_2O), m.p. 271°, $[\alpha]^{20}$ −82·3°, d-α-*bromobutyryltri*-l-α-*aminobutyryl*-, *tetra*-l-α-*aminobutyryl*- (+H_2O), decomp. 300°, d-α-*bromobutyryltetra*-l-α-*aminobutyryl*-, and *penta*-l-α-*aminobutyryl*-l-α-*aminobutyric acid* (+H_2O), decomp. 300°. The polypeptides are attacked very slowly by *N*-NaOH, but considerable hydrolysis is generally effected in a few hr. by erepsin and trypsin-kinase; the latter is, however, slow in hydrolysing the dipeptide. A. C.

Behaviour towards erepsin and trypsin of polypeptides containing α-amino*iso*butyric acid. E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1932, **13**, 310—329).—With the exception of glycyl-α-amino*iso*butyric acid, all polypeptides containing the α-amino*iso*butyric acid unit are slowly hydrolysed by erepsin, and none by trypsin. The following new compounds are described, considerable difficulty being experienced in purifying the polypeptides, which readily pass into anhydrides. dl-α-*Bromopropionyl*-, m.p. 194—195° (dec.), dl-α-*alanyl*-, m.p. 260°, dl-α-*bromo*-n-*butyryl*-, m.p. 156—157°, dl-α-*amino*-n-*butyryl*-, m.p. ∢ 265°, dl-α-*bromo*-n-*valeryl*-, m.p. 130—131°, dl-*norvalyl*- (as anhydride), dl-α-*bromo*isovaleryl, m.p. 174—175°, dl-*valyl*- (as anhydride mixed with dimethylacrylic acid), dl-α-*bromo*-n-*hexoyl*-, m.p. 109—110° (*anhydride*), chloroacetylglycyl-, m.p. 153—155°, and *diglycyl*-α-*amino*isobutyric acids; α-*bromo*isobutyryl-*glycine*, m.p. 118°, -l-*alanine*, m.p. 134—135°, -dl-*norvaline*, m.p. 103°, -dl-*valine*, m.p. 104—105°, -dl-*norleucine*, m.p. 71—72°, -dl-*leucine*, m.p. 88—91°; α-*amino*isobutyryl-*glycine*, m.p. 265°, -l-*alanine*, -dl-*norvaline* (*anhydride*), -dl-*valine*, -dl-*norleucine*, -dl-*leucine*+methylacrylylleucine, m.p. 267°, -*glycylglycine*, m.p. 206—210° (sublimes); dl-α-*bromo*isovaleryl-, m.p. 243—245°, and dl-*valyl*-*triglycylglycine* +$\frac{3}{2}H_2O$, dl-α-*bromo*isovaleryl-, m.p. 234—236°, and dl-*valyl*-*tetraglycylglycine*, dl-α-*bromo*isovaleryl-, m.p. 184—185°, and dl-*valyl*-*diglycyl*-dl-*valine*. A. C.

Physical properties of polypeptides composed of *l*(+)-norleucine and their behaviour towards erepsin and trypsin. E. ABDERHALDEN and K. PLOTNER (Fermentforsch., 1932, **13**, 443—450).—*d*-α-Bromo-*n*-hexoyl chloride (I) and *l*-norleucine afford d-α-*bromo*-n-*hexoyl*-l-*norleucine*, m.p. 86°, $[\alpha]_D^{21}$ +20·38° in EtOH, aminated to l-*norleucyl*-l-*norleucine* (+0·5H_2O) (II), m.p. 264°, $[\alpha]_D^{20}$ +16·92° in AcOH, +6·0° in 20% HCl. Repeated condensation of the polypeptide with (I) alternated by amination gives rise to d-α-*bromo*-n-*hexoyl*-l-*norleucyl*-l-, m.p. 155°, $[\alpha]^{20}$ −7·14° in EtOH; *dl*-l-*norleucyl*-l- (+0·5H_2O) (III), decomp. 305°, $[\alpha]_D^{20}$ −1·39° in AcOH; d-α-*bromo*-n-*hexoyl*-*di*-l-*norleucyl*-l-; *tri*-l-*norleucyl*-l- (+2H_2O) (IV), decomp. 360°, $[\alpha]_D^{20}$ −18·09° in AcOH; d-α-*bromo*-n-*hexoyltri*-l-*norleucyl*-l-; and *tetra*-l-*nor*-

leucyl-l-*norleucine* (+2H_2O) (V), decomp. 360°, $[\alpha]_D^{20}$ −26·96° in AcOH. Colloidal properties appear in the tripeptide. Erepsin hydrolyses (II) and (III) at p_H 7·8 and 37°, whilst (IV) and (V) are stable. Trypsin hydrolyses (II) and (III) at p_H 8·4, and (IV) and (V) less readily, which may be due to their sparing solubility. A. C.

Behaviour of polypeptides containing sarcosine and methyl-leucine units towards *N*-alkali, erepsin, trypsin-kinase, and yeast extract. E. ABDERHALDEN, E. SCHWAB, and J. G. VALDECASAS (Fermentforsch., 1932, **13**, 396—407).—By heating $CH_2Cl{\cdot}CO_2Et$ with NH_2Me in a sealed tube *sarcosine-methylamide hydrochloride*, m.p. 222°, is formed in addition to sarcosine. The following new polypeptides and intermediates are described. *Sarcosyl*-l-*tyrosine* (I) (+H_2O), m.p. 232°, $[\alpha]_D^{20}$ +31·7° in *N*-HCl; *chloro-acetyl*- (IX), m.p. 93°; *glycyl*- (II), m.p. 185° (decomp.); dl-α-*bromo*iso*hexoylglycyl*- (X), dl-*leucylglycyl*-dl-*methyl*-*leucine* (III), m.p. 195°; *sarcosyl*-dl-*leucine* (IV), m.p. 139°; dl-α-*bromo*iso*hexoyl*-, m.p. 76°; dl-*leucyl*- (V), m.p. 181°; dl-*methyl*-*leucyl*-*sarcosyl*-dl-*leucine* (VI), m.p. 195—197° (decomp.); *sarcosyl*- (VII), m.p. 231°; *chloroacetyl*-dl-*leucylglycyl*-, m.p. 192°; *sarcosyl*-dl-*leucylglycyl*-*leucylglycine* (VIII), m.p. 237°; dl-α-*bromo*iso*hexoylsarcosine*, m.p. 52·8°, converted by NH_3 into α-*hydroxy*iso*hexoylsarcosine-amide*, m.p. 144—145°. These are all slowly hydrolysed by *N*-NaOH at 37°. Erepsin hydrolyses sarcosyl-*dl*-alanine, (III), and (VIII), but not sarcosylglycine, glycylsarcosine, (I), (II), (IV), (V), (VI), and (VII). Trypsin-kinase hydrolyses (I), (III), (VI), (VII), (VIII), (IX), (X), but not (IV), (V), and sarcosyl-*dl*-alanine. Yeast extract hydrolyses sarcosyl-*dl*-analine, (II), (IV), (VII), and *dl*-methyl-leucylglycine. A. C.

Enzyme systems contained in erepsin- and trypsin-complex. E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1932, **13**, 330—362).—Leucylglycine is an inadequate test substrate for erepsin. Several di- and tri-peptides have been prepared as optically pure as possible from optically active NH_2-acids, and their behaviour towards erepsin and trypsin has been examined. The following are new, $[\alpha]_D$ referring to EtOH and 0·2*N*-HCl solutions of the intermediate Br-compounds and the polypeptides, respectively, unless otherwise stated: *glycyl*-d-*norvaline*, $[\alpha]_D^{20}$ +26·3°, in *N*-HCl, +25·8° in H_2O; d(+)-α-*bromo*-n-*hexoyl*-, m.p. 77—80°, $[\alpha]_D^{17}$ +50·1°; l-*norleucyl*-, $[\alpha]_D^{18}$ +82·5° in H_2O; l(−)-α-*bromo*-n-*hexoyl*-, m.p. 84—86°, $[\alpha]_D^{20}$ −46·5°; d-*norleucylglycine*, $[\alpha]_D^{18}$ −77·0° in H_2O; l(−)-α-*bromo*-n-*hexoyl*-l(+)-; d-*norleucyl*-l-, $[\alpha]_D$ −64·6° in H_2O; d(+)-α-*bromo*-n-*hexoyl*-l(+)-, $[\alpha]_D^{18}$ +19·3°; l-*norleucyl*-l-*alanine*, $[\alpha]_D^{16}$ +20·6° in H_2O; d(+)-α-*bromo*-n-*hexoylglycyl*-l-, m.p. 142—144°, $[\alpha]_D^{20}$ +2·5°; l-*norleucylglycyl*-l- (A), m.p. 229° (decomp.), $[\alpha]_D^{20}$ −17·8°; l(−)-α-*bromo*-n-*hexoylglycyl*-l-, m.p. 134—136°, $[\alpha]_D$ −45·7°; d-*norleucylglycyl*-l- (D), m.p. 252° (decomp.), $[\alpha]_D^{20}$ −57·9°; d(+)-α-*bromo*-n-*hexoylglycyl*-d-, m.p. 135—136°, $[\alpha]_D^{20}$ +50·6°; l-*norleucylglycyl*-d-*leucine* (J), m.p. 252° (decomp.), $[\alpha]_D^{20}$ +54·8°; d(+)-α-*bromo*iso*hexoylglycyl*-l-, m.p. 114—120°, $[\alpha]_D^{20}$ +39·7°; l-*leucylglycyl*-l- (B), m.p. 252° (decomp.), $[\alpha]_D$ +14·8°; l(−)-α-*bromo*iso*hexoyl-glycyl*-l-, m.p. 157—158° (decomp.), $[\alpha]_D$ −40·3°; d-*leucylglycyl*-l- (E), m.p. 254° (decomp.), $[\alpha]_D^{20}$ −46·8°; d(+)-α-*bromo*iso*hexoylglycyl*-d-, m.p. 158° (decomp.), $[\alpha]^{20}$ +40·9°; l-*leucylglycyl*-d-*norleucine* (K), m.p. 252—253° (decomp.), $[\alpha]_D$ +48·1°; l(−)-α-*bromo*iso-*hexoylglycyl*-l-, m.p. 155—156° (decomp.), $[\alpha]_D^{20}$ +28·1°; d-*leucylglycyl*-l- (F), m.p. 250° (decomp.), $[\alpha]_D^{20}$ +40·9°; d(+)-α-*bromo*iso*hexoylglycyl*-d-, m.p. 153—154° (decomp.), $[\alpha]_D^{20}$ +27·2°; l-*leucylglycyl*-d- (L), m.p. 250—251° (decomp.), $[\alpha]_D^{20}$ +41·2°; d(+)-α-*bromo*-n-*hexoyl-glycyl*-l-, m.p. 147—148° (decomp.), $[\alpha]_D^{20}$ +45·2°; l-*norleucylglycyl*-l- (C), m.p. 227° (decomp.), $[\alpha]_D^{20}$ +24·2°; l(−)-α-*bromo*-n-*hexoylglycyl*-l-, m.p. 132—136°, $[\alpha]^{20}$ −19·2°; d-*norleucylglycyl*-l- (G), m.p. 247° (decomp.), $[\alpha]_D^{20}$ −41·1°; d(+)-α-*bromo*-n-*hexoyl-glycyl*-d-, m.p. 138°, $[\alpha]_D^{20}$ +22·3°; l-*norleucylglycyl*-d-iso*leucine* (M), m.p. 247—248°, $[\alpha]_D^{20}$ +42·0°; l(−)-α-*bromo*-n-*hexoylglycyl*-l-, m.p. 107—109°, $[\alpha]_D^{20}$ −45·2°; d-*norleucylglycyl*-l- (H), m.p. 250—252° (decomp.), $[\alpha]_D$ +55·0°; d(+)-α-*bromo*-n-*hexoyl-glycyl*-d-, m.p. 106—108°, $[\alpha]_D^{20}$ +44·7°; l-*norleucyl-glycyl*-d-*norvaline* (N), m.p. 251—252° (decomp.), $[\alpha]_D^{20}$ +52·8°.

The tripeptides containing, apart from glycine, only *l*-constituents [*l*-leucylglycyl-*l*-leucine, (A), (B), and (C)] are hydrolysed by erepsin and trypsin. Those of the (*d*)-glycyl-(*l*-) type [*d*-leucylglycyl-*l*-leucine, (D), (E), (F), (G), (H)] are attacked by trypsin-kinase but not by erepsin. The (*l*)-glycyl-(*d*-) compounds are hydrolysed by erepsin [(J), (K), (L), (M), (N)] (glycerol extracts of intestine are more active than erepsin preps.), but not by trypsin, with the exception of (N), which is attacked. This may be due to the presence of a trace of (*l*)-glycyl-(*d*)-tripeptide, which is attacked by trypsin, liberating NH_2-acid capable of stimulating ereptic action (cf. A., 1931, 766). *d*-Leucylglycyl-*d*-leucine is stable to both enzymes. Several dipeptides are found to be stable to trypsin, and hydrolysed by erepsin unless a *d*-constituent is present. Glycyl-*d*-leucine, however, is hydrolysed by some erepsin preps. Dipeptides containing *alloiso*leucine are not attacked by one prep. of erepsin. Another prep. is found to split those with *l*- but not those with *d*-*alloiso*leucine. A. C.

Comparison of the qualitative fission of polypeptides and various derivatives, and of the speed of degradation by *N*-alkali at 37°. E. ABDERHALDEN and A. L. NEUMANN (Fermentforsch., 1932, **13**, 382—395).—Hydrolysis by *N*-NaOH of *dl*-leucylglycylglycine, *dl*-leucyl-*dl*-leucylglycine, and *dl*-dileucylglycylglycine occurs in stages starting at the terminal NH_2-acid. Introduction of Bz, $C_{10}H_7{\cdot}SO_2$, and SO_2Ph groups, respectively, stabilises some and labilises other polypeptides to NaOH. The following new polypeptides are described: *benzoylhexa*-, *benzoylhepta*-, *benzenesulphonyltri*-, m.p. 150°; *benzenesulphonylhepta-glycylglycine*. A. C.

Sulphur in proteins. V. Effect of alkalis on cystine, with special reference to the action of sodium hydroxide. C. J. B. THOR and R. A. GORTNER (J. Biol. Chem., 1933, **99**, 383—403).—Alkalis remove N from *l*-cystine (I) at the same rate as S, and practically all the remaining N is as α-NH_2-N. Increasing concn. of NaOH causes decreasing destruc-

tion of (I), and the fall in optical activity of (I) is more rapid than the decomp. The stability of (I) towards NaOH is due to a reaction between a decomp. product and undecomposed (I), leading to stabilisation of the latter. The small extent of deamination of (I) is due to actual stability. H. G. R.

Application of phospho-18-tungstic acid (Folin's reagent) to the colorimetric determination of cysteine, cystine, and related substances. I. Reduction of phospho-18-tungstic acid by various substances. II. Determination of thiol compounds and disulphides already existing in solution. J. W. H. Lugg (Biochem. J., 1932, **26**, 2144—2159, 2160—2165).—I. The reduction by different substances under varying conditions has been investigated. The reaction between cystine and sulphites in cold aq. solution is probably $R{\cdot}S{\cdot}S{\cdot}R + H_2SO_3 \rightleftharpoons R{\cdot}SH + RHS_2O_3$.

II. An aliquot portion of the unknown solution is added to a mixture of citrate buffer, reagent, and NaOAc and the colour produced is matched against a standard of the same mixture containing a known amount of cystine and buffered sulphite. S. S. Z.

Iodometric titrations of cysteine and allied substances. C. C. Lucas and E. J. King (Biochem. J., 1932, **26**, 2076—2089).—Temp. and [H·] exert a marked effect on the amount of I which combines with cysteine (I) in solution. Esterification of the CO_2H group lowers the temp. and almost eliminates the [H·] effect. Acetylation of the NH_2-group increases the max. amount of I absorbed and alters its position on the p_H curves. Concn. of (I) and of I affects the extent of oxidation. In presence of 0·5% KI (I) can be determined by indirect iodometric titration at 0° and *N*-acidity. Glutathione reduces theoretical amounts of I only below p_H 5 and 25°. Temp. does not affect this reaction as much as in the case of (I). Liver does not contain (I). The reaction of ergothioneine is only slightly affected by temp., [H·] below neutrality, and by dilution. Simple mercaptans may be determined by direct titration at room temp. In the case of thiol acids, I is absorbed only at or near 10°. The influence of [H·] is not apparent on the acid side of neutrality. S. S. Z.

o-Quinone test for cysteine. O. Baudisch and E. Dyer (J. Biol. Chem., 1933, **99**, 485—492).—The colour reaction (A., 1932, 530) given by cysteine with excess of a $CHCl_3$ solution of *o*-benzoquinone (improved prep. described) has been examined with many related S and N compounds which are classified into groups (*a*) giving no colour, (*b*) giving a red colour only in the aq. layer, and (*c*) giving a red colour in the $CHCl_3$ layer. In (*c*), use of dil. HCl differentiates cysteine from all compounds investigated except benzidine and NH_2Ph (cf. this vol., 151), the colour reaction (orange-pink changing to orange) being differentiated by comparative tests. The test is not affected by use of other org. solvents in place of $CHCl_3$, and from the $CHCl_3$ layer was isolated a brown *substance* containing N and S, pyrocatechol being separated from the aq. layer. J. W. B.

Preparation and storage of nitrosomethylcarbamide. F. Arndt and H. Scholz (Angew. Chem., 1933, **46**, 47—48).—Me_2SO_4 (300 g.) is added slowly to 400 c.c. of well-cooled and well-stirred aq. NH_3 (*d* 0·88) and the mixture is heated for 2 hr. on the water-bath, boiled vigorously for 10—15 min., treated with 250 c.c. of H_2O and 150 g. of KCNO, boiled for 20 min., filtered, and, after addition of 120 g. $NaNO_2$ in 200 c.c. of H_2O, cooled and poured into a mixture of 120 c.c. of H_2SO_4 (*d* 1·84) and 500 g. of ice. The compound is collected, washed with H_2O at 0°, dried in vac., and stored in a refrigerator. The corresponding Et compound can be prepared in a similar way from Et_2SO_4. A. R. P.

Mercuration of compounds containing a reactive (CH_2) group by means of mercuric chloride. II. K. G. Naik and R. P. Patel (J. Indian Chem. Soc., 1932, **9**, 533—537).—Addition of aq. $NaHCO_3$ to a hot EtOH solution of $HgCl_2$ and various monoaryl-substituted malonamides (I) gives compounds of the type $Hg{:}C(CO{\cdot}NH_2){\cdot}CO{\cdot}NHAr$, and thus are obtained the *amide*, m.p. 286°, *anilide*, m.p. 275—278°, o-, m.p. 278—279°, and m-, m.p. 255°, *-toluidide*, α-, m.p. 269°, and β-, m.p. 270°, *-naphthylamide*, and 1 : 3 : 4-*xylidide*, m.p. 270°, of mercurimalonamic acid. From the appropriate compounds containing a reactive CH_2 group are similarly obtained: *Et mercurimalonate*, decomp. 300°, *Et mercuriacetoacetate*, decomp. > 270°, and *mercuriacetoacet-anilide*, m.p. 205°, -o-, m.p. 230°, and -p-, m.p. 243—247°, *-toluidide* (all m.p. with decomp.). These compounds give (I) with hot 0·25*N*-HCl, give HgS with H_2S, Hg with $NHPh{\cdot}NH_2$, and react with aq. KI to give (I) with liberation of 2 equiv. of KOH. J. W. B.

Alkylated complex cyanides. I. Isomerism of the alkylated ferrocyanides. II. Hexaethylated ferrocyanides. E. G. J. Hartley and (in part) H. M. Powell (J.C.S., 1933, 101—104, 105).—I. Only the α-isomeride of the compounds obtained by Hölzl (A., 1927, 864) by heating $[Fe(CNMe)_6]Cl_2$ is identical with the author's, the other exhibiting different properties. An explanation of the isomerism is given and *compounds* $[Fe(CNMe)_6]I_2,2HgI_2$ (I) and $[Fe(CNMe)_4(CNEt)_2]I_2,2HgI_2$ (II) are prepared from $Fe(CNMe)_4(CN)_2$ by heating with HgI_2 and excess of alkyl halide. The two forms of (I) are identical, but those of (II) show definite solubility and crystallographic differences, these facts supporting the explanation given.

II. $Ag_4Fe(CN)_6$ at room temp. with excess of EtI affords an ethylated compound, which with $AgNO_3$ yields a very sol. nitrate, converted by H_2SO_4 in dry EtOH into the *compound* $[Fe(CNEt)_6](HSO_4)_2$ (cf. J.C.S., 1912, **101**, 705; A., 1888, 571). J. L. D.

Formation of organo-metalloidal compounds by micro-organisms. I. Trimethylarsine and dimethylethylarsine. F. Challenger, (Miss) C. Higginbottom, and L. Ellis (J.C.S., 1933, 95—101).—Sterile bread crumbs containing cultures of four strains of *Penicillium brevicaule* on treatment with aq. solutions of As_2O_3, Na methylarsinate, or Na cacodylate afford $AsMe_3$ [*di*-, m.p. 264—265° (decomp.) (I), and *mono-mercurichloride*, m.p. 224—226°, identical with the mercurichlorides obtained from authentic $AsMe_3$ (A., 1931, 77)], which with HNO_3 affords *hydroxytrimethylarsonium nitrate*, m.p. 128—

129° (also obtained from synthetic $AsMe_3$), converted into hydroxytrimethylarsonium picrate by Na picrate in H_2O. (I) affords with H_2O_2 *hydroxytrimethylarsonium chloride mercurichloride*, m.p. 135—136°. Cultures of *P. brevicaule* with Na ethylarsinate in H_2O afford $AsMe_2Et$ (II) [*dimercurichloride*, m.p. 240—241° (decomp.), also prepared from $AsMe_2Et$ (A., 1932, 1119)]. The "mould gas" (II) affords with HNO_3 and then Na picrate in H_2O, *hydroxydimethylethylarsonium picrate*, m.p. 162—163°, and with CH_2PhCl and Na picrate, *benzyldimethylethylarsonium picrate*, m.p. 113—114°. The following are described: *benzyltriethylarsonium chloride*, m.p. 167—168°, and *picrate*, m.p. 83—84·5°; *hydroxytriethylarsonium picrate*, m.p. 121—122°. J. L. D.

Beryllium. V. Organic compounds of beryllium. H. S. Booth and (Miss) D. G. Pierce (J. Physical Chem., 1933, **37**, 59—78; cf. A., 1932, 1223).—The prep. and properties of the following *compounds* are described: $[C_6H_4Me\cdot SO_3]_2Be,xH_2O$, m.p. 133·8° [anhyd., m.p. 318·5° (decomp.)]; Be *p*-xylenesulphonate, $+5H_2O$, m.p. 143·2—144·2°; Be 2-chlorotoluene-5-sulphonate, decomp. 384·7—399·7°; $(PhSO_3)_2Be,xH_2O$, m.p. 72·9—74·9° (anhyd., 94·4°); Be 2-nitrotoluene-4-sulphonate, $+xH_2O$, m.p. 140·6—141·6° [anhyd., 273·6° (decomp.)]; Be *m*-nitrobenzenesulphonate, $+xH_2O$, m.p. 146·8° (anhyd., 203·7—204·7°); Be benzoylacetonate, m.p. 210·2—211·2°; Be dibenzoylmethane, m.p. 214—215°; Be Et acetoacetate, m.p. 60·6—61·1°. The solubilities are compared. E. S. H.

Applications of thallium compounds in organic chemistry. IX. Changes observed on replacing dialkylthallium by trimethylplatinum in chelate rings. R. C. Menzies and E. R. Wiltshire (J.C.S., 1933, 21—22).—Interaction of $CH_2(COEt)_2$, $CH_2Ac\cdot CO_2Et$, or $COMe\cdot CH_2Bz$ in boiling C_6H_6 with $PtMe_3I$ in slight excess and TlOEt affords $PtMe_3$ derivatives (cf. A., 1928, 509) which resemble the corresponding Tl compounds (cf. this vol., 56), although their association in freezing C_6H_6 is about 2. This is probably due to co-ordination of a Pt atom of 1 mol. with an O atom of another, thereby raising the effective at. no. to 86 and the co-ordination no. of Pt to 6. *Et* (*trimethylplatini*)*acetoacetate*, m.p. 200° (decomp.), *trimethylplatinum dipropionylmethane*, decomp. 190°, and *benzoylacetone*, decomp. 187°, are described. J. L. D.

Organic compounds of gold. C. S. Gibson (Nature, 1933, **131**, 130).—$HAuBr_4$ and Mg pentamethylene bromide in Et_2O yield a colourless, sparingly-sol. spiro*bis*(*pentamethylene*) *gold bromide* (I) in which the Au atom is 4-covalent with an octet of electrons. *Ethylenediamino*spiro*bis*(*pentamethylene*) *gold bromide* (II) is more sol. in H_2O than (I), and the Au atom is 6-covalent. (II) should be optically resolvable. L. S. T.

Metallic cerium in organic synthesis. J. B. Lal and S. Dutt (J. Indian Chem. Soc., 1932, **9**, 565—571).—Numerous examples (yields recorded) of the successful use of Ce powder in place of other metals in the Friedel–Crafts, Lincke, Reformatski, and Ullmann reactions, and as a reducing agent either in dry distillations in H_2 or in neutral NH_4Cl solution at room temp. are given. J. W. B.

Carbon rings. XXI. Röntgen measurements with high-membered cyclic compounds. A. Müller (Helv. Chim. Acta, 1933, **16**, 155—161).—Data are given for the *cyclo*paraffins containing 12, 15—18, 22, 24, 26, and 28—30 C atoms, and for *cyclo*tetracosane-1 : 13- and *cyclo*octacosane-1 : 15-diones. The mols. contain double chains of the same structure as the *n*-paraffins. H. B.

Catalytic desulphurisation of benzene containing thiophen by destructive hydrogenation. B. Moldavski and N. Prokopchuk (J. Appl. Chem., Russia, 1932, **5**, 619—627).—C_6H_6 is not hydrogenated at 450° in presence of MoS_3, whilst thiophen is hydrogenated ($C_4H_4S \longrightarrow C_4H_8S \longrightarrow BuSH$); at 350°, 90% of the C_4H_4S is decomposed. MoS_3 is converted into stable MoS_2. Ch. Abs.

[Preparation of] phenol from chlorobenzene. M. I. Ushakov and N. D. Zelinski (J. Appl. Chem., Russia, 1932, **5**, 364—369).—Cu_2O and CuO are better catalysts than Cu. In presence of Cu_2O and a melt containing 60 g. Cu per 2·5 g. Cu_2O the reaction proceeds at 260—280°, whilst at 320° a 95—98% yield is obtained after 25 min. Addition of 30% Ph_2 to PhCl reduces the NaOH required from 3 mols. to 2·25 mols. Ch. Abs.

Decomposition of phenyl iodide dichloride. VI. Action of sodium ethylmercaptide. E. V. Zappi and P. Egea (Anal. Asoc. Quím. Argentina, 1932, **20**, 87—95).—The action of NaSEt on $PhICl_2$ yields Et_2S_2 and PhI in almost quant. yield, with traces of PhIO. Compounds in which one or both Cl atoms are replaced by S or groups containing S are not formed. H. F. G.

Mode of studying nitration. J. A. Hetherington and I. Masson (J.C.S., 1933, 105—114).—The extent of nitration of $PhNO_2$ by a ternary H_2SO_4–HNO_3–H_2O mixture depends on the acid concns., complete nitration being achieved only if the concn. of H_2O exceeds that required to form H_2SO_4,H_2O. Nitration is inhibited by excess of $PhNO_2$, but not appreciably by $C_6H_4(NO_2)_2$, unless the concn. of H_2SO_4 is low. Reaction proceeds in the inorg. layer, the org. layer decreasing the reaction velocity. Distribution experiments indicate that $PhNO_2$ competes with H_2O for the H_2SO_4, this being an intermediate stage in the nitration which, it is suggested, occurs through the irreversible action of HNO_3 on $(NO_2Ph\cdot H)^+$. J. L. D.

Nitration of xylene with dilute acid in presence of mercury. N. A. Kholevo and I. I. Eitingon (J. Appl. Chem., Russia, 1932, **5**, 612—618).—Nitration of *m*-xylene with 50·2% HNO_3 in presence of Hg affords mainly 4-nitro-*m*-xylene and 3 : 4-$C_6H_3Me(NO_2)\cdot CO_2H$. Ch. Abs.

Beryllium salts of *para*-derivatives of benzenesulphonic acid and their hydrolysis. V. Cupr and J. Širučeк (Pub. Fac. Sci. Univ. Masaryk, 1932, No. 157, 1—28, and J. pr. Chem., 1933, [ii], **136**, 159—175).—The *salts* $Be(XC_6H_4\cdot SO_3)_2,6H_2O$ (X=Et, Cl, Br, and OH) have been prepared. The p_H of solutions $< 0{\cdot}1M$ is $-0{\cdot}85 \log [Be^{\cdot\cdot}] + 1{\cdot}85$. The $[H^{\cdot}]/[Be^{\cdot\cdot}]$–

[Be$^{\cdot\cdot}$] curve has a min. corresponding with 0·1—0·25*M* solutions. R. T.

Monothioethylene glycol. IV. Aryl β-hydroxy- and β-chloroethyl sulphides. G. BADDELEY and G. M. BENNETT (J.C.S., 1933, 46—48; cf. A., 1927, 870).—Interaction of thiols in aq. KOH at 60—100° with $CH_2Cl{\cdot}CH_2{\cdot}OH$ affords aryl β-hydroxyethyl sulphides, converted by $SOCl_2$ in C_5H_5N and CCl_4 (or by fusion with PCl_5) into the chloroethyl sulphides, oxidation of which with H_2O_2 in AcOH affords sulphoxides, and with aq. $KMnO_4$ and $MgSO_4$, sulphones. Hydroxyethyl sulphones are prepared by heating the K salts of the requisite sulphinic acids for 2—8 hr. at 100—120° with $CH_2Cl{\cdot}CH_2{\cdot}OH$. The following are described: *mesityl* β-*hydroxy*-, m.p. 25°, and β-*chloro-ethyl sulphide*, m.p. 44° (*sulphoxide*, m.p. 76°; *sulphone*, m.p. 60·5°); p-*chlorophenyl* β-*hydroxy*- (an oil) and β-*chloro-ethyl sulphide*, m.p. 34° (*sulphone*, m.p. 96°); p-*bromophenyl* β-*hydroxy*- (an oil), and β-*chloro-ethyl sulphide*, m.p. 39° (*sulphone*, m.p. 109°); p-*iodophenyl* β-*chloro*-, m.p. 54°, p-*anisyl* β-*hydroxy*-, m.p. 41°, and β-*chloro-ethyl sulphide*, b.p. 110°/1 mm. 2 : 4-*Dichlorothiophenol*, m.p. 20° (*Bz* derivative, m.p. 97°), obtained from dichloroaniline, affords with $K_3Fe(CN)_6$ 2 : 4 : 2′ : 4′-*tetrachlorodiphenyl disulphide*, m.p. 82·5°, and with $CH_2Cl{\cdot}CH_2{\cdot}OH$, an oily hydroxyethyl sulphide and thence 2 : 4-*dichlorophenyl* β-*chloroethyl sulphide*, b.p. 218°/15 mm. (*sulphoxide*, m.p. 96·5°). Similarly, 2 : 5-dichlorothiophenol affords 2 : 5-*dichlorophenyl* β-*hydroxy*-, m.p. 32°, and β-*chloro-ethyl sulphide*, b.p. 176°/15 mm. (*sulphoxide*, m.p. 68°); 2 : 4 : 6-*trichlorothiophenol* (from trichloroaniline), m.p. 60° (*Bz* derivative, m.p. 170°), on oxidation affords 2 : 4 : 6 : 2′ : 4′ : 6′-*hexachlorodiphenyl disulphide*, m.p. 165°, and, in the usual manner, 2 : 4 : 6-*trichlorophenyl* -*hydroxy*-, m.p. 41°, and β-*chloro-ethyl sulphide*, m.p. 71°. Thio-α-naphthol affords an oily β-hydroxyethyl sulphide (*sulphone*, m.p. 122°) converted into α-*naphthyl* β-*chloroethyl sulphide* (*sulphone*, m.p. 74°). β-*Naphthyl* β-*hydroxyethyl sulphide* (from thio-β-naphthol) has m.p. 64° (*sulphone*, m.p. 108°), gentle reaction with PCl_5 affording β-*naphthyl* β-*chloroethyl sulphide*, m.p. 53° (*sulphone*, m.p. 100°), whereas more vigorous conditions lead to ?-*chloro*-β-*naphthyl* β-*chloroethyl sulphide*, m.p. 52°. p-*Nitrophenyl* β-*chloroethyl sulphone*, m.p. 128°, and *phenyl* γ-*chloropropyl sulphone*, m.p. 26°, are obtained by oxidation of the corresponding sulphides. J. L. D.

Action of lithium on tolane. III. E. BERGMANN and W. SCHREIBER (Annalen, 1933, **500**, 118—122; cf. A., 1931, 948).—The hydrocarbon $C_{26}H_{22}$, m.p. 183°, formed from Li and tolane (or αα-dichloro-ββ-diphenylethylene) (A., 1928, 1034) is 2 : 3-*diphenyl*-1-*benzylidenehydrindene*, since it is reduced (P, HI–AcOH) to 2 : 3-diphenyl-1-benzylhydrindene, m.p. 115°. 2 : 3-Diphenylhydrindone and $CH_2Ph{\cdot}MgCl$ give 1-*hydroxy*-2 : 3-*diphenyl*-1-*benzylhydrindene*, m.p. 155°, dehydrated by AcCl to 1 : 2-diphenyl-3-benzylindene, which is not reduced by P and HI, but with Na and amyl alcohol affords an isomeric 2 : 3-*diphenyl*-1-*benzylhydrindene*, m.p. 143—144°. 1-Lithio-2 : 3-diphenylindene and PhCHO give 2 : 3-diphenyl-1-benzylideneindene. H. B.

Double linking. VI. Allyl grouping in arylated olefines. E. BERGMANN, D. WINTER, and W. SCHREIBER (Annalen, 1933, **500**, 122—136; cf. A., 1931, 948).—Ph αβ-diphenylethyl ketone (I) and $CH_2Ph{\cdot}MgCl$ give β-*hydroxy*-αβγδ-*tetraphenylbutane* (II), m.p. 149°, dehydrated by AcCl to two αβγδ-*tetraphenyl*-Δ^{α}-*butenes*, m.p. 149—150° (III) (main product) and 95—96° (IV), both of which are oxidised (CrO_3–AcOH) to (I). (IV) and Na in Et_2O give (after decomp. with EtOH) αβγδ-*tetraphenyl*-Δ^{β}-*butene* (V), m.p. 80°, whilst (III) similarly affords (V) and (mainly) 2 : 3-*diphenyl*-1-*benzylhydrindene* (VI), m.p. 184° (cf. preceding abstract). (VI) is also prepared (with m.p. 190°) from (II) and AcOH–conc. H_2SO_4, from (III) and $SnCl_4$ in C_6H_6–HCl, and by reduction of (III) with P and HI. Reduction of (III) with Na and amyl alcohol gives (VI) and αβγδ-*tetraphenylbutane*, m.p. 96°; the formation of the same compounds from (V) and Na shows that (V) can react as (III) [thereby producing (VI)]. (V) is partly converted into (VI) by distillation in high vac. Ph α-phenylstyryl ketone and $CH_2Ph{\cdot}MgCl$ give *Ph* αβγ-*triphenylpropyl ketone*, m.p. 178—179°, converted by AcCl into an *isomeride*, m.p. 197—198°.

αβγδ-Tetraphenyl-$\Delta^{\alpha\gamma}$-butadiene (VII), best prepared by dehydration of βγ-dihydroxy-αβγδ-tetraphenylbutane (VIII) with Ac_2O–AcCl [the use of AcCl (cf. Orékhov, A., 1914, i, 265) leads to the production of a 1 : 1 *compound*, m.p. 199—200°, of (VII) and (VIII)], is converted by Na (and subsequent hydrolysis) into (mainly) (V) and (VI). Decomp. of the intermediate Na derivative with Hg affords isomeric 2 : 3-*diphenyl*-1-*benzylidenehydrindenes*, m.p. 146° and 183° (cf. *loc. cit.*); the former of these is reduced (Na, amyl alcohol) to (VI) and αβγδ-tetraphenylbutane, both of which are also formed (together with αβ-diphenylethyl alcohol) by similar reduction of (VII). (VII) and $SnCl_4$ in C_6H_6 give 2 : 3-diphenyl-1-benzylindene, whilst oxidation (CrO_3–AcOH) of (V) affords 1-*acetyl*-2 : 3(or 1)-*diphenyl*-1(or 3)-*benzylindene*, m.p. 156°. Ozonolysis of the dibromide, m.p. 165°, of (VII) in EtOAc and subsequent decomp. with H_2O gives (VIII), thus not showing the constitution of the dibromide (cf. Orékhov, *loc. cit.*).

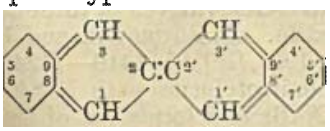
Didesyl reacts (unexpectedly) with only 1 mol. of $CHNaPh_2$ to give a *compound*, $C_{11}H_{34}O_2$, m.p. 198°, which is either Ph γ-hydroxy-αβγδδ-pentaphenylbutyl ketone or 2-hydroxy-2 : 3 : 4 : 5-tetraphenyl-5-benzhydryltetrahydrofuran. *iso*Didesyl reacts difficultly with 2 mols. of $CHNaPh_2$ to form a *compound*, $C_{54}H_{46}O_2$, m.p. 213° (in one case isomerisation to didesyl occurred), converted by AcCl into tetraphenylethane and a *substance*, $C_{30}H_{26}O$, m.p. 235—236°. H. B.

Synthesis of cadalene. E. DE B. BARNETT and J. W. COOK (J.C.S., 1933, 22—24).—Bromination of 1 : 6-$C_{10}H_6Me_2$ in CS_2 affords 4-*bromo*-1 : 6-*dimethylnaphthalene*, b.p. 171—172°/15 mm. (*picrate*, m.p. 114°), the Mg compound of which in dry Et_2O at 0° with CO_2 affords 1 : 6-*dimethyl*-4-*naphthoic acid*, m.p. 188—189° [*Et* ester (I), b.p. 166°/3—5 mm.]. MgMeI in dry Et_2O below 0° and (I) afford a carbinol (II) (gum) which on dehydration with picric acid in EtOH affords 1 : 6-*dimethyl*-4-iso*propenylnaphthalene* (*dehydrocadalene*) (III), b.p. 154°/14 mm. (*picrate*, m.p.

118—119°). Reduction of (III) in boiling EtOH with Na and dehydrogenation of the product with Se at 300—320° affords 1 : 6 : 4-$C_{10}H_5Me_2Pr^{\beta}$ (picrate identical with cadalene picrate) (cf. A., 1922, i, 562). Reduction of (II) with HI in boiling AcOH affords mainly the *dimeride* of dehydrocadalene, m.p. 218° [also obtained from (III) in boiling AcOH containing HCl], but also some cadalene. Et 4-methyl-1-naphthoate with MgMeI as above affords *dimethyl-(4-methyl-α-naphthyl)carbinol*, m.p. 90°, which with HCl–EtOH at 100° affords an olefine (*picrate*, m.p. 88°, also obtained by heating the carbinol with picric acid) which on reduction with Na in boiling EtOH and dehydrogenation with Se affords 1 : 4-$C_{10}H_6MePr^{\beta}$ (*apo*-cadalene) (cf. A., 1922, i, 1001). J. L. D.

Aromatic hydrocarbons. XIX. Regularities in the structure of the absorption spectra of aromatic hydrocarbons. E. Clar (Ber., 1933, 66, [*B*], 202—208).—Examination of the absorption spectrum of phenanthrene in the light of the author's "distance rule" discloses the existence of two series of bands, thus confirming the conclusion that the hydrocarbon exists in the 9 : 10-diyl condition and that one of the side nuclei is activated so that it can react as a $C_{10}H_8$ derivative. $C_{10}H_8$ and 2 : 6-$C_{10}H_6Me_2$ have an *o*- and a *p*-diyl condition. C_6H_6 can act optically in at least two conditions. The "distance rule" appears to afford definite evidence of the constitution of hydrocarbons, to which and to their immediate derivatives it can be applied with certainty. With hydrocarbons carrying strongly polar substituents the discrepancies are greater. It appears to apply generally to all bands which are caused by radical C atoms. H. W.

Nomenclature of the rubrenes referred to a prototype "rubene." C. Dufraisse (Bull. Soc. chim., 1932, [iv], **51**, 1486—1490).—The name "rubene," and the numeration indicated in formula are proposed for the parent hydrocarbon of the rubrene series (cf. this vol., 5). H. A. P.



Reduction of aromatic nitro-compounds to amines. G. Kirkhgof (Bull. Nauch.-Issledov. Khim.-Farm. Inst., 1930, 7).—Reduction by Fe (cf. G.P. 269,542) is carried out in presence of a slight excess of 4—6*N*-HCl, and NaCl is added after filtration of the hot solution to ppt. the amine hydrochloride completely. Ch. Abs.

Identity of the chloroacetyl-*l*-alanine-splitting component of erepsin solutions with that which hydrolyses chloroacet-*o*-nitroanilide and related compounds. E. Abderhalden, E. von Ehrenwall, E. Schwab, and O. Zumstein.—See this vol., 315.

***m*-Nitroaniline.** G. Kirkhgof and I. T. Eskin (Bull. Nauch.-Issledov. Khim.-Farm. Inst., 1930, 24).—*m*-$C_6H_4(NO_2)_2$ (1 mol.) in H_2O (800 c.c.) at 85° is treated simultaneously from dropping funnels with hot conc. aq. Na_2SO_3 (1·5 mol.) and hot conc. aq. NH_4Cl (1·5 mol.). Of the NH_4Cl 67% may be replaced by HCl; the NH_4Cl is then added first. The temp. is spontaneously maintained at 95°. The yield of pure product is 90%. Ch. Abs.

Condensation of chloral with tolyl- and nitrophenyl-carbamides. F. D. Chattaway, M. T. Kerr, and C. G. Lawrence (J.C.S., 1933, 30—32).—By condensation of chloral with the appropriate carbamide at 0° the following *N*-substituted N′-βββ-*trichloro-α-hydroxyethylcarbamides* (A), $CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NHR$, are prepared: o-, m.p. 146° (decomp.) [Ac_2 derivative, m.p. 114° (decomp.)], and p-*tolyl*-, m.p. 181° (decomp.) [Ac_2 derivative, m.p. 120° (decomp.)]; p-, m.p. 196° (decomp.) [Ac_2 derivative, m.p. 128° (decomp.)], and m-*nitrophenyl*-, m.p. 173° (decomp.) [Ac_2 derivative, m.p. 126° (decomp.)]. The Ac_2 derivatives, when kept or heated in aq. NaOH, are hydrolysed to $CHCl_3$, HCO_2Na, and the parent carbamide. The above compounds in NaOH at 0° give with Ac_2O the following bis-*N*′-substituted *bis-(βββ-trichloro-α-carbamidoethyl) ethers* (B), $[NHR{\cdot}CO{\cdot}NH{\cdot}CH(CCl_3){\cdot}]_2O$: *di*-o-, m.p. 198° (decomp.) [Ac_2 derivative, m.p. 166° (decomp.), and -p-*tolyl*-, m.p. 203° (decomp.) [Ac_2 derivative, m.p. 167° (decomp.)]; *di*-p-, m.p. 203° (decomp.) [Ac_2 derivative, m.p. 151° (decomp.)], and -m-*nitrophenyl*-, m.p. 217° (decomp.) [Ac_2 derivative, m.p. 170° (decomp.)]. The ethers (B) with the appropriate Na alkoxide, or, better, the carbamides (A) in KOH–EtOH (or –MeOH) with Ac_2O afford N-o-*tolyl*-N′-βββ-*trichloro-α-ethoxy*-, m.p. 136° (decomp.), and -α-*methoxy*-, m.p. 157° (decomp.), N-p-*tolyl*-N′-βββ-*trichloro-α-ethoxy*-, m.p. 136° (decomp.), and -α-*methoxy*-, m.p. 149° (decomp.), N-p-*nitrophenyl*-N′-βββ-*trichloroethyl-α-methoxy*-, m.p. 192° (decomp.), and -α-*ethoxy*-, m.p. 161° (decomp.), and N-m-*nitrophenyl*-N′-βββ-*trichloroethyl-α-methoxy*-, m.p. 170° (decomp.), and -α-*ethoxycarbamide*, m.p. 146° (decomp.). R. S. C.

Solubility relationships amongst optically isomeric salts. III. Mandelates and α-bromocamphor-π-sulphonates of α-phenylethylamine and α-*p*-tolylethylamine. A. W. Ingersoll, S. H. Babcock, and F. B. Burns (J. Amer. Chem. Soc., 1933, **55**, 411—416).—*dl*-Mandelic acid [*dl*-α-phenylethylamine, m.p. 138° (all m.p. are corr.), and *dl*-α-*p*-tolylethylamine, m.p. 136°, salts], is resolved by *d*- and *l*-α-phenylethylamines (cf. Smith, A., 1912, i, 113), and *dl*-α-*p*-tolylethylamine can be resolved by *d*-α-bromocamphor-π-sulphonic acid. The following stable salts are prepared: *d*-, *l*-, and *dl*-, m.p. 176°, -α-phenylethylamine and *d*-α-*p*-tolylethylamine, m.p. 140°, *d*-mandelates; *d*-α-phenylethylamine, m.p. 177°, and *d*-, m.p. 146°, and *l*-, m.p. 140°, -α-*p*-tolylethylamine *l*-mandelates; *d*- ($+H_2O$), m.p. (anhyd.) 170°, and *dl*- ($+H_2O$), m.p. (anhyd.) 155°, -α-phenylethylamine and *dl*-α-*p*-tolylethylamine, m.p. 161°, *dl*-α-bromocamphor-π-sulphonates; *d*-, m.p. 183—186°, and *l*-, m.p. 205°, -α-phenylethylamine and *d*-α-*p*-tolylethylamine ($+H_2O$), m.p. (anhyd.) 165°, *d*-α-bromocamphor-π-sulphonates. Solubility data for the above salts are given. The salts are classified according to the scheme previously proposed (A., 1932, 263). H. B.

Constitution of azo-indicators. II. Higher homologues of helianthin and methyl-red. K. H. Slotta and W. Franke (Ber., 1933, 66, [*B*], 104—

108).—Ph·N_2·SO_3H couples almost quantitatively with $NPhPr^{\alpha}_2$ and $NPhBu^{\alpha}_2$ (I) to *propyl-*, m.p. 225°, decomp. 238°, and *butyl-*, decomp. 198°, *-helianthin*. Reaction is not observed with *di*-n-*amylaniline*, b.p. 280—284° (from NH_2Ph, amyl bromide, and KOH at 105°), whereas n-*hexylhelianthin*, decomp. 259°, is obtained in 20% yield. Diazotised anthranilic acid with (I) and dihexylaniline affords respectively *butyl-red*, m.p. 117°, and *hexyl-red*. Loss of alkyl groups during coupling is not observed. The indicator properties of the compounds are tabulated. H. W.

Constitution of azo-indicators. III. Alkylation of naphthol-orange. K. H. Slotta, W. Franke, and G. Haberland (Ber., 1933, 66, [*B*], 108—112).—Dimethyl-α-naphthol-orange (cf. A., 1931, 345) is shown to be Me 4-methoxynaphthaleneazobenzene-*p*-sulphonate by reduction with $ZnCl_2$ and HCl to 4-methoxy-α-naphthylamine and aniline-*p*-sulphonic acid. Methyl- and hexyl-α-naphthol-orange (*Ca* salts) are prepared as described (*loc. cit.*), but for no apparent reason the experiments frequently yield solely unchanged initial material. The Me group is very sensitive to acids, a sample of methyl-α-naphthol-orange monohydrate passing at 135° into α-naphthol-orange (II). The assumption (*loc. cit.*) that the labile monoalkyl derivatives of (II) contain Me attached to N (*loc. cit.*) is invalidated by the failure to prepare (I) from naphthaquinone and $SO_2H·C_6H_4·NMe·NH_2$. If the $C_{10}H_8$ is replaced by the C_6H_6 ring the alkoxy-groups have normal stability towards acid hydrolysis. 4-4′-Hydroxy-3′-methoxybenzeneazopyridine is hydrolysed by dil. HCl. β-Naphthol-orange and CH_2N_2 afford exclusively *Me* β-*naphthol*-1-*azobenzenesulphonate*. H. W.

Stability of diazonium chlorides. Influence of various substituents, temperature, and concentration. C. C. Snow.—See this vol., 130.

Velocity of decomposition of diazo-compounds in aqueous solution. IX. E. Yamamoto.—See this vol., 233.

Aryl *p*-bromobenzenesulphonates as derivatives for identification of phenols. V. C. Sekera (J. Amer. Chem. Soc., 1933, 55, 421—422).—Aryl *p*-bromobenzenesulphonates are obtained from phenols, *p*-$C_6H_4Br·SO_2Cl$, and C_5H_5N (4 equivs.) at or below 15°; the following are described: *Ph*, m.p. 115·5°; α-, m.p. 104°, and β-, m.p. 151—152°, *-naphthyl*; o-, m.p. 78—79°, m-, m.p. 69—70°, and p-, m.p. 100°, *-tolyl*; o-, m.p. 97—98°, m-, m.p. 108—109°, and p-, m.p. 112°, *-nitrophenyl*; o-*bromophenyl*, m.p. 125°; 4-iso*propyl*-m-*tolyl*, m.p. 103·5°; o-*methoxyphenyl*, m.p. 103—104°, and 2 : 4 : 6-*tribromophenyl*, m.p. 139—140°, p-*bromobenzenesulphonates*. H. B.

Rearrangement of phenyl and tolyl alkenyl ethers and syntheses of *iso*propenylphenols and their reduction products. J. B. Niederl and E. A. Storch (J. Amer. Chem. Soc., 1933, 55, 284—294).—Ph *iso*propenyl ether is rearranged by AcOH–conc. H_2SO_4 to *o-iso*propenylphenol (Br_6 derivative, m.p. 84°) (synthesised from PhOH, allyl alcohol, and conc. H_2SO_4 and subsequent distillation of the polymeride formed), which is reduced (H_2, PtO_2, EtOH) to *o*-$C_6H_4Pr^{\beta}·OH$ (further identified by conversion into *o*-$C_6H_4Pr^{\beta}·O·CH_2·CO_2H$). *p*-Tolyl *iso*propenyl ether is similarly rearranged to 3-*iso*propenyl-*p*-cresol, also prepared (as above) from *p*-cresol and allyl alcohol. Rearrangement of *m*-tolyl *iso*propenyl ether (or condensation of *m*-cresol and allyl alcohol) gives 4-*iso*propenyl-*m*-cresol (2 : 5 : 6-Br_3-derivative *dibromide*, m.p. 103—104°), reduced to thymol and thence to a menthol. *o*-Tolyl *iso*propenyl ether is rearranged to 5-*iso*propenyl-*o*-cresol (Br_5-derivative, m.p. 202°), reduced to 5-*iso*propyl-*o*-cresol [Br_4-derivative, m.p. 236—237°, which is identical with the 3 : 4 : 6-tribromo-5-*iso*propyl-*o*-cresol of Niederl and Natelson (A., 1931, 838) and (probably) of Jesurum (A., 1886, 696)]. 2-*Methyl*-4-iso*propenyl-* and *-iso*propyl-*phenoxyacetic acids* have m.p. 110—111° and 140—141°, respectively. In the above and analogous rearrangements (cf. A., 1931, 346, 1288) *o*-migration of the side-chain is favoured except where one or both *o*-positions are occupied (when *p*-migration predominates). A mechanism based on the theories of van Alphen (A., 1927, 660), Lapworth (J.C.S., 1898, 73, 445), and Latimer (A., 1930, 9) is given; the Claisen mechanism (cf. A., 1926, 1241) is inapplicable. H. B.

Methylation of *p*-aminophenol. O. Y. Magidson and G. I. Menshikov (Khim. Farm. Prom., 1932, 117—122).—Preferably, CHPh:N·C_6H_4·OH is methylated with Me_2SO_4; alternatively, CH_2:N·C_6H_4·OH is hydrated in presence of activated Al. Ch. Abs.

Acetylation of phenetidine. E. A. Tzofin (Khim. Farm. Prom., 1932, 215—216).—Phenetidine (1 pt.) is heated for 6 hr. with glacial AcOH (1 pt.); dry C_6H_6 (2 pts.) is added, the temp. is raised to the b.p. and then lowered to −5°, when 95% of phenacetin crystallises. Ch. Abs.

Reactions of bromonitro-derivatives of toluene with sodium thiophenoxide. E. Bourgeois and J. Henrion (Bull. Soc. chim., 1932, [iv], 51, 1416—1424).—Interaction of the bromonitrotoluenes with NaSPh results in elimination of NaBr and formation of the corresponding diaryl sulphide when Br and NO_2 are in the *o*- or *p*-position to each other, the reaction occurring more readily with the *o*-substituted derivatives. When these groups are situated in the *m*-position to each other no elimination of NaBr occurs, but Ph_2S_2 and coloured reduction (?) products, of unknown constitution, of the bromonitrotoluene are formed. 4-Bromo-2-nitrotoluene undergoes the latter reaction much less readily than its 6 : 4-isomeride. 5-Bromo-2 : 4-dinitrotoluene is exceedingly reactive. The following are described: 3-*nitro*-6-*phenylthioltoluene*, m.p. 81—82°, b.p. 260°/62 mm. (*sulphone*, m.p. 104°); 2-*nitro-*, m.p. 72°, 4-*nitro-*, m.p. 59·5°, and 2 : 4-*dinitro*-5-*phenylthioltoluene*, m.p. 114·5°. H. A. P.

Structure of *x*-chlororesorcinol. B. F. Clark (J. Amer. Chem. Soc., 1933, 55, 319—320).—The chlororesorcinol, m.p. 88·5—89° (corr.), of Reinhard (A., 1878, 726) is the 4-derivative as shown by its prep. from 4-chloro-*m*-phenylenediamine. H. B.

Constitution of cholesterol and of the bile acids. A. Windaus (Z. physiol. Chem., 1932, 213, 147—186).—A crit. review. J. H. B.

Formation and inversion of cholesteryl ether. T. WAGNER-JAUREGG and L. WERNER (Z. physiol. Chem., 1932, **213**, 119—124).—Cholesteryl bromide (I) with 2 mols. of NaI at 100—125° in $COMe_2$ yields cholestadiene. Cholesteryl chloride (II) or (I) heated in MeOH (or EtOH) at 125° gives the normal Me ether (III) (or *Et ether*, m.p. 89°). With 6 mols. of KOAc or LiOAc in MeOH, (II) gives the Me ether isomeride (IV). Hydrogenation of (III) (Pt sponge) affords the *dihydro*-derivative, m.p. 82·5—83°, hydrolysed by 66% HBr at 130°, but not by conc. HCl at 100°. (IV) may be similarly hydrogenated, giving the *dihydro*-derivative, m.p. 78—78·5°, not hydrolysed by conc. HCl at 100°. J. H. B.

Halochrome substances in the sterol series. G. EHRENSVÄRD (Svensk Kem. Tidskr., 1932, **44**, 306—310).—The red coloration produced by the action of conc. H_2SO_4 on cholesterol is due to the formation of a halochrome additive product of the composition $C_{27}H_{45}\cdot OH,2H_2SO_4$ (I). The red substance formed by the action of $SbCl_3$ on a cholesterol solution is an additive product, $C_{27}H_{45}\cdot OH,2SbCl_3$ (II), analogous to the compounds formed by $SbCl_3$ with C_6H_6, PhMe, Ph_2, camphor, and isoprene. Measurements are given of the absorption bands shown by the $CHCl_3$ solutions of (I) and (II). H. F. H.

Liebermann–Burchard colour reaction with cholesterol. A. BLOCH (Biochem. Z., 1933, **257**, 171—179; cf. A., 1931, 755).—Two independent processes occur during the reaction as usually carried out. The first, a physical or reversible chemical change, results in production of a transient red colour. The second, which involves esterification of the cholesterol, results in slow production of a green colour which attains its max. after 15 min., two thirds of the cholesterol having then been esterified. Then the green colour weakens with formation of a dark brown resinous end-product. The reaction is equally satisfactory with cholesteryl esters. W. McC.

Liebermann–Burchard colour reaction for cholesterol. I. A. MIRSKY and M. BRUGER (J. Lab. Clin. Med., 1932, **18**, 304—306).—The conditions for obtaining reproducible results are studied. By allowing the colour reaction to take place in a refrigerator (5°) duplicate results check within 2%. NUTR. ABS.

Hexahydro-derivatives of irradiation products of ergosterol. G. AHRENS, E. FERNHOLZ, and W. STOLL (Annalen, 1933, **500**, 109—118).—Reduction (H_2, Pt-black, AcOH) of dihydrolumisteryl acetate and subsequent hydrolysis (EtOH–KOH) give *hexahydrolumisterol* (I), m.p. 127°, $[\alpha]^{18}$ +9·5° {*acetate*, m.p. 69°, $[\alpha]_D^8$ +5° in $COMe_2$ (all other rotations are in $CHCl_3$)}, converted by NaOEt at 200° into *epihexahydrolumisterol*, m.p. 86—95°, $[\alpha]_D^{18}$ +10·3° (*acetate*, m.p. 65°, $[\alpha]_D^{19}$ +20°), also prepared by reduction of *epi*dihydrolumisterol (A., 1932, 381), which, unlike (I), is pptd. by digitonin. *Hexahydrovitamin-*D_2, m.p. 96—97°, $[\alpha]_D^{18}$ −7·4° to −8·8°, now obtained (cf. *ibid.*, 311) cryst. by hydrolysis (MeOH–KOH) of its 3 : 5-*dinitrobenzoate*, m.p. 131°, $[\alpha]_D^{13}$ +6·4°, is not rearranged by NaOEt at 200°. Similar reduction of suprasterol I (as acetate, m.p. 72°) (A., 1930, 1577) and subsequent 3 : 5-dinitrobenzoylation in C_5H_5N gives two 3 : 5-*dinitrobenzoates*, m.p. 187—188°, $[\alpha]_D^{19}$ +30·8°, and m.p. 154°, $[\alpha]_D^8$ +32·4°, separable through their differing solubilities in $COMe_2$ or Et_2O; these are hydrolysed (MeOH–KOH) to *suprastanol* IA, m.p. 116°, $[\alpha]_D^{18}$ +11·2° to +12°, and *suprastanol* IB, m.p. 146—147°, $[\alpha]_D^{19}$ +18·4°, respectively. Reduction (H_2, Pt-black, Et_2O–AcOH) of suprastervl II allophanate affords the *allophanate*, decomp. > 234°, $[\alpha]_D^{20}$ −41·8°, of *tetrahydrosuprasterol* II, m.p. 99—102°, $[\alpha]_I^{19}$ −50·4° (3 : 5-*dinitrobenzoate*, m.p. 110—112°, $[\alpha]_D^{18}$ −23·7°). Reduction in EtOAc affords two *allophanates*, m.p. 230—232°, $[\alpha]_D^{18}$ +22°, and m.p. 222—225°, $[\alpha]_D^{20}$ +6·9°; hydrolysis of the crude allophanate and subsequent 3 : 5-dinitrobenzoylation gives the 3 : 5-*dinitrobenzoate*, m.p. 180—181°, $[\alpha]_D$ −11·1°, of *suprastanol* II, m.p. 130—131°, $[\alpha]_D$ −18·4°. The above hexahydro-derivatives do not consume O when titrated with BzO_2H and none of them is identical with ergostanol, *epi*ergostanol, or *u*-ergostanol. H. B.

Surface potentials of unimolecular films of ergosterol. Photochemical formation of vitamin-*D*. R. J. FOSBINDER.—See this vol., 325.

Action of ozone on stigmasterol. A. GUITERAS (Z. physiol. Chem., 1933, **214**, 89—90).—With O_3, stigmasterol (I) gives β-*methyl-α-ethylbutaldehyde* (II) (*semicarbazone*, m.p. 127—128°, $[\alpha]_D^{20}$ +9·13° in EtOH). Oxidation of (II) with $KMnO_4$ in the cold gives the corresponding optically active acid [amide, m.p. 136°; anilide, m.p. 120—122°; *p*-toluidide, m.p. 138—140° (cf. lit.)], racemised at 165° with 10% KOH and affording $COMe_2$ on oxidation with CrO_3. Thus (I) contains the γ-methyl-β-ethylbutylidene group in the side-chain. J. H. B.

Molecular rearrangement of α-glycols. VI. Relative electronegativities of *p*-anisyl and naphthyl radicals. VII. Relative electronegativities of β-naphthyl and diphenylyl radicals. M. MIGITA (Bull. Chem. Soc. Japan, 1932, **7**, 377—382, 382—388; cf. this vol., 68).—VI. p-*Anisyl* β-*naphthyl ketone* (I), m.p. 93° (from PhOMe, β-naphthoyl chloride, and $AlCl_3$, yield 54%), with Zn in AcOH at room temp. gives s-*di*-p-*anisyldi*-β-*naphthylethylene glycol*, m.p. 110°, converted by hot AcOH into β-*naphthyl di*-p-*anisyl*-β-*naphthylmethyl ketone*, m.p. 185° (decomp.), also obtained (*a*) in the above reduction at higher temp., and (*b*) from the glycol with AcCl and AcOH in C_6H_6, and hydrolysed to β-naphthoic acid and *di*-p-*anisyl*-2-*naphthylmethane*, m.p. 89—90° (decomp.), no *p*-anisic acid being detected. (I) in EtOH is unaffected by sunlight.

VII. Similar reduction of β-*naphthyl diphenylyl ketone* (II), m.p. 136° (yield 40%), at room temp. gives β-*naphthyldiphenylylcarbinol*, m.p. 118°. (II) with Mg and MgI_2 in Et_2O–C_6H_6 gives s-*di*-β-*naphthylbis-diphenylylethylene glycol*, m.p. 163° (decomp. 156°; when remelted sinters 90°, m.p. 123°) (yield 65%), which rearranges as above to a mixture (approx. 50%) yielding β-naphthoic and *p*-phenylbenzoic acids on hydrolysis, the former being formed more rapidly. A. A. L.

Autoxidation of ethylene oxides. E. P. KOHLER and E. M. NYGAARD (J. Amer. Chem. Soc., 1933, **55**, 310—314).—βγ-Oxido-αγγ-triphenylpropyl alcohol (I) (A., 1931, 354) does not undergo autoxidation when

exposed to air which has been passed through dil. aq. NH_3 or NaOH. Autoxidation occurs with air containing a little HCl; the products formed are the peroxide (II), $\overset{CPh_2}{O}\!>\!CH\cdot O\cdot O\cdot CHPh\cdot OH$ (*loc. cit.*), HCO_2H, BzOH, $COPh_2$, and αα-diphenylethylene glycol α-monobenzoate. (I) undergoes rapid fission in solutions containing a trace of acid into PhCHO and αα-diphenylethylene oxide (III) (which then rearranges to $CHPh_2\cdot CHO$); the reverse change PhCHO+(III) ⟶ (I) could not be accomplished. A solution of (III) in PhCHO undergoes no change in N_2, but in air the above autoxidation products are produced. It is suggested that the formation of (II) from (I) involves the following changes: (*a*) fission of (I) into PhCHO and (III), (*b*) autoxidation of PhCHO [probably to a "moloxide" (IV) and not BzO_2H], (*c*) synthesis of (II) from (III) and (IV). Exposure of a solution of (III) in *o*-$C_6H_4Cl\cdot CHO$ to air gives the *peroxide*, $\overset{CPh_2}{O}\!>\!CH\cdot O\cdot O\cdot CH(OH)\cdot C_6H_4Cl$, m.p. 140—141° (decomp.); (III) and MeCHO similarly give *αα-diphenylethylene glycol α-monoacetate*, m.p. 91°. H. B.

Chlorination of sodium benzoate. J. C. Smith (Nature, 1933, **131**, 28).—The chlorination of BzOH yields 48% of *o*-, 32% of *m*-, and 20% of *p*-$C_6H_4Cl\cdot CO_2H$ (cf. A., 1904, i, 159). L. S. T.

Mechanism of reaction between hydroxamic acids and bromine. I. De Paolini (Gazzetta, 1932, **62**, 1053—1058; cf. A., 1927, 135).—The reaction $R\cdot CO\cdot NH\cdot OH + Br \longrightarrow R\cdot CO_2H + N_2O + HBr$ is immediate, and therefore not due to disturbance of hydrolytic equilibrium by Br. Probably $R\cdot CO\cdot NBr\cdot OH$ is formed, and gives rise to $NHBr\cdot OH$ and to RCO_2H in a labile form; in EtOH, RCO_2Et results, also the diacylhydroxylamine, obtainable in Et_2O. Thus $NHBz\cdot OH$ yields BzOEt and $NHBr\cdot OBr$, whilst $CH_2Ph\cdot CO\cdot NH\cdot OH$ yields $CH_2Ph\cdot CO_2Et$ and O-(*phenylacetyl*)*phenylacethydroxamic acid*, m.p. 159° (decomp.). E. W. W.

Oxidation of tyrosine, tyramine, and phenylalanine with hydrogen peroxide. H. S. Raper (Biochem. J., 1932, **26**, 2000—2004).—In presence of $FeSO_4$ phenylalanine yields tyrosine, *l*-tyrosine yields *l*-3 : 4-dihydroxyphenylalanine, and tyramine yields 3 : 4-dihydroxyphenylethylamine. S. S. Z.

Cholatrienic acid. T. Shimizu, T. Oda, and H. Makino (Z. physiol. Chem., 1932, **213**, 136—146).—Distillation of cholic acid in vac. gives α-cholatrienic acid I, m.p. 163—164, $[\alpha]^{20}$ −22·6° (all rotations in $CHCl_3$), as obtained by Wieland and by Borsche, *α-cholatrienic acid* II, m.p. 169—170°, $[\alpha]^{20}$ −12·6° (*Me* ester, m.p. 103—104°), and mixed crystals, m.p. 141—142°, from which acid II was obtained by esterification and hydrolysis. Hydrogenation of II (PtO_2) gives a cholenic acid identical with Wieland's β-cholenic and Borsche's *apo*cholanic acid. With Pd-black the Me ester of II gives (as ester) *γ-cholenic acid*, m.p. 137—138°, $[\alpha]_D^{14}$ +43·1° (*Me* ester, m.p. 95°). Acid I after repeated recrystallisation from aq. EtOH was separated into *α-cholatrienic acid* III, m.p. 176—178°, $[\alpha]_D^{20}$ −8·07°, and *γ-cholatrienic acid* IV, m.p. 157—158°, $[\alpha]^{20}$ −24·5°. Hydrogenation of III or IV gives cholanic acid. Acid I gives a 10% yield of Br_4-derivative, m.p. 205—206° (*Me* ester, m.p. 198°). Debromination and hydrolysis of the ester afford *α-cholatrienic acid* V, m.p. 160—161°, $[\alpha]_D^{20}$ −75·36°. Hydrogenation of V (Pd-black) gives cholanic acid. J. H. B.

Percinnamic acid. K. Bodendorf (Ber., 1933, **66**, [*B*], 165—166).—Dicinnamoyl peroxide in $CHCl_3$ at 0° is transformed by EtOH–NaOEt into *Na percinnamate*, whence *percinnamic acid* (I), m.p. 67—68°, separated from $CHPh{:}CH\cdot CO_2H$ by $NaHCO_3$. (I) is at least as stable as BzO_2H. H. W.

1 : 3-Dimethylbarbituric acid as reagent for aldehydes. S. Akabori.—See this vol., 284.

Reduction of semicarbazones, thiosemicarbazones, diketotriazines, and ketothiontriazines of α-ketonic acids. (Mlle.) L. Popovici (Ann. Chim., 1932, [x], **18**, 183—240).—Reduction of semicarbazones of α-keto-acids $R\cdot C(:N\cdot NH\cdot CO\cdot NH_2)\cdot CO_2H$ (I) with 3% Na–Hg gives the corresponding α-semicarbazido-acids $R\cdot CH(NH\cdot NH\cdot CO\cdot NH_2)\cdot CO_2H$ (II), and thus are obtained *α-semicarbazido-β-phenylpropionic*, m.p. 164°; *-phenylacetic*, m.p. 208°; *-γ-phenyl-*n*-butyric*, m.p. 172°; *-propionic*, m.p. 181° [different from the acid, m.p. 166—168°, assigned this constitution by Thiele and Bailey (A., 1899, i, 164)], and *-β-naphthylacetic*, m.p. 226°, *acid*. *β-Naphthylglyoxylic acid*, m.p. 171° {*semicarbazone*, m.p. 230° (decomp.), converted by dil. NaOH into 6-*β-naphthyl*-3 : 5-*diketo*-2 : 3 : 4 : 5-*tetrahydro*-1 : 2 : 4-*triazine*, m.p. 289° [*mono-*, m.p. 217°, and *di-*, m.p. 179° (? 279° elsewhere in paper), *-benzyl* derivatives]; *thiosemicarbazone*, m.p. 226° (decomp.), similarly converted into 6-*β-naphthyl*-5-*keto*-3-*thion*-2 : 3 : 4 : 5-*tetrahydro*-1 : 2 : 4-*triazine*, m.p. 274°; *Na*, *K*, *Ca*, *Ba*, *Mg*, *Pb*, *Ag*, and *Cu* salts}, is best prepared by oxidation of β-$C_{10}H_7Ac$ with $KMnO_4$ in alkaline solution, Rousset's specimen (A., 1898, i, 591) being a mixture of α- and β-compounds. Derivatives of type (II) are reducing agents, being oxidised by Nessler's solution back to (I), and may be determined by addition of 0·1*N*-I to the Hg ppt. and titration of excess of I by $Na_2S_2O_3$. Oxidation of (II) by I in Na_2CO_3 gives the semicarbazone of the next lower aldehyde $R\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$. Na–Hg reduction of the diketotriazines $R\cdot C\!<\!\overset{N=NH}{CO\cdot NH}\!>\!CO$ obtained from (I) (Bougault, A., 1916, i, 609) also gives (II), initial ring fission to the semicarbazones taking place, whilst *α-(methylsemicarbazido)-β-phenylpropionic acid*, m.p. 119°, is similarly obtained from the appropriate Me derivative, which also behaves like the unsubstituted diketotriazine towards Nessler's solution or I–Na_2CO_3. Analogous reduction of the thiosemicarbazones or ketothiontriazines with Na–Hg affords *α-thiosemicarbazido-β-phenylpropionic*, m.p. 198°; *-phenylacetic*, m.p. 168°; *-γ-phenyl-*n*-butyric*, m.p. 176°; *-propionic*, m.p. 145°; and *-β-naphthylacetic*, m.p. 216°, *acid*. Since the thiocarbazones themselves are further oxidised by Nessler's solution, this reaction follows the initial oxidation of the thiosemicarbazido-acid, which hence requires 4 instead of 2 atoms of I per mol. Oxidation of the thiosemicarbazido-acids with I–Na_2CO_3 and

reduction of the ketothiontriazines with Na–Hg follow the same courses as do the O compounds.

J. W. B.

Velocity and mechanism of racemisation. II. Mandelic acid. A. N. CAMPBELL and A. J. R. CAMPBELL.—See this vol., 130.

Isomeric (−)menthyl α-naphthylglycollates. A. McKENZIE and (MISS) E. R. L. GOW (J.C.S., 1933, 32—37).—The resolution of *r*-α-naphthylglycollic acid (I), m.p. 98·5—99·5°, is improved and the pure (−)*acid*, m.p. 124—125°, isolated. (−)Menthyl *dl*-α-naphthylglycollate, m.p. 38·5—39·5°, $[\alpha]_{5893}^{21}$ −51·6° (all rotations in $COMe_2$), was resolved by crystallisation from ligroin, and partly by fractional distillation in vac.; the esters of the (+) and (−)acids, m.p. 71—72° and 62—63°, $[\alpha]^{20}{}_{3}$ +21·4° and −125·0°, respectively, are, however, better obtained by esterification of the active acids. $SOCl_2$ acts on these esters in Et_2O with very little displacement racemisation, the resulting (−)menthyl (−), (+), and *dl*-α-naphthylchloroacetates, oils, having $[\alpha]_{5893}^{21}$ −97·2°, −19·9°, and −62·3°, respectively. PCl_5, however, causes nearly complete racemisation of the (−)ester of the (−)acid, and slight racemisation of the ester of the (+)acid, the products from the (−)esters of the (−), (+), and *dl*-acids having $[\alpha]_{5893}^{20\cdot6}$ −65·9°, −66·9°, and −64·8°, respectively. *dl*-(I) and $SOCl_2$ give dl-α-*naphthylchloroacetic acid*, dimorphous, m.p. 111—112° and 131·5—132·5°, whence the (−)*menthyl* ester, b.p. 228—230°/4 mm., $[\alpha]_{5893}^{20\cdot6}$ −63·0°, is obtained. When *dl*-(I) is fractionally esterified with (+) or (−)menthol, the unesterified acid is lævo- or dextrorotatory, respectively, whilst hydrolysis of the esters formed with KOH–EtOH gives partly and nearly racemised acids, respectively. When a trace of KOH is added to (−)menthyl (−) and (+)-α-naphthylglycollate in EtOH, the rotation changes slowly to lower and higher vals., respectively; "Umesterung" takes place, accompanied possibly by asymmetric catalytic racemisation. In many of the above reactions (I) differs from mandelic acid (A., 1925, i, 823; 1931, 483). It is probable that PCl_5, but not $SOCl_2$, causes Walden inversion. R. S. C.

Synthesis of santenic acid. T. ENKVIST (Finska Kem. Medd., 1932, **41**, 74—84).—Et_2 5-methyl*cyclo*penta-2 : 3-dione-1 : 4-dicarboxylate (A., 1899, i, 676) is converted by MeI and NaOMe into a Me_2 and 4-Me derivatives; the latter is hydrolysed and reduced by Na–Hg to 2 : 3-dihydroxy-5-methyl*cyclo*pentane-1 : 4-dicarboxylic acid, further reduction of which with HI gives iso*santenenic acid*, $\begin{matrix}CH=\!=\!=C(CO_2H)\\ CH_2\cdot C(CMe\cdot CO_2H)\end{matrix}>CHMe$, m.p. 198—199°. Still further reduction with Pd–H_2 gives cis-allo*santenic acid* (I), m.p. 150—151° (possibly accompanied by isomerides) (*anhydride*, m.p. 93·5°), which is also obtained by oxidation of α-santenol, and occurs in Aschan's *iso*santenic acid, which is a mixture of this with santenic acid (II). Both (I) and (II) give, when heated with HCl and AcOH in a sealed tube, the corresponding trans-*acids*, m.p. 129—130° and 166—167°, respectively. The isomerism of the santenic acids is therefore geometrical, and structural formulæ are assigned on the basis of the more ready anhydride formation of (I). H. A. P.

Santenone derivatives. Preliminary note. T. ENKVIST (Finska Kem. Medd., 1932, **41**, 85—88).—Reduction of Aschan's santenenic acid with Pd–H_2 gives *cis-allo*santenic acid (cf. preceding abstract) and the former must therefore have the structure $\begin{matrix}CH_2—C(CO_2H)\\ CH_2\cdot CMe(CO_2H)\end{matrix}>CMe.$ It follows that, as santenenic acid is prepared by bromination of santenic acid and removal of HBr from the product, santenic and *cis-allo*santenic acid are geometrical isomerides, and that the accepted structure of santenic acid is confirmed. *Bromo-*, m.p. 203·5—204·5°, and *dehydro-*, m.p. 142·5—143·5°, *-homosantenenic acids* are prepared by methods similar to those used in the camphor series (cf. J.C.S., 1900, **77**, 1053). α-Santenol is converted by Na and NaOEt in warm paraffin into an *isomeride*, m.p. 104—106°. H. A. P.

Diphenyl-α-naphthylmethane series. A. BISTRZYCKI and G. KRAUSE (Helv. Chim. Acta, 1933, **16**, 100—115).—Benzilic acid (I) and 1-$C_{10}H_7$·Me in AcOH with H_2SO_4 (*d* 1·84) at 35—40° give *diphenyl*-4-*methyl*-α-*naphthylacetic acid*, m.p. 250—251° (darkening and decomp.) [*Na* salt (+5H_2O); *Me* ester, m.p. 185—186°], converted by 25% KOH at 170—180° into *diphenyl*-4-*methyl*-α-*naphthylmethane* (II), m.p. 149° (slight previous sintering), and by abs. H_2SO_4–AcOH at 35—40° into *diphenyl*-4-*methyl*-α-*naphthylcarbinol* (III), m.p. 124—125° (slight previous sintering), which is also prepared from Mg 4-methyl-α-naphthyl bromide and $COPh_2$. (III) heated with HCO_2H and HCO_2Na affords *di*(*diphenyl*-4-*methyl*-α-*naphthylmethyl*) *ether*, two modifications, m.p. 135° and 159°, whilst reduction with HI, $SnCl_2$, and conc. HCl in AcOH yields (II). 1 : 6-$C_{10}H_6Me_2$ and (I) similarly give *diphenyl*-4 : 7-*dimethyl*-α-*naphthylacetic acid*, m.p. 271—272° (sinters at 265°) [*Na* salt (+4H_2O); *Me* ester, m.p. 161—162°], decarboxylated (as above) to *diphenyl*-4 : 7-*dimethyl*-α-*naphthylmethane*, m.p. 134—135°. $C_{10}H_8$ and (I) afford *diphenyl*-α-*naphthylacetic acid*, two modifications, decomp. 246° and 258—259°, (+AcOH), decomp. 217°, (+$COMe_2$), m.p. 263—264°, decarboxylated at 250—260° (or as above) to diphenyl-α-naphthylmethane, two modifications, m.p. 134° and 149°. 2 : 7-$C_{10}H_6(OH)_2$ and (I) give *diphenyl*-2 : 7-*dihydroxy*-α-*naphthylaceto*-2-*lactone*, m.p. 265° (*Ac* derivative, m.p. 180°; 7-O-*Bz* derivative, m.p. 200—201°; 7-*Me ether*, m.p. 161—162°), which with EtI and EtOH–KOH affords *diphenyl*-2 : 7-*diethoxy*-α-*naphthylmethane*, m.p. 107—108°, also obtained from 2 : 7-$C_{10}H_6(OEt)_2$ and $CHPh_2$·OH in AcOH–conc. H_2SO_4. H. B.

Phthalyl fluoride. A. T. DANN, W. DAVIES, A. N. HAMBLY, R. E. PAUL, and G. S. C. SEMMENS (J.C.S., 1933, 15—21).—*Phthalyl fluoride* (I), best prepared from phthalyl chloride (II) and NaF in a Pt flask at 250—300°, is obtainable only in one form, m.p. 42—43°, b.p. 224—236°/760 mm., 135°/54 mm., lachrymatory, which is shown to be acyclic, $C_6H_4(COF)_2$, by chemical reactions and by parachor measurements. (I) with hot C_6H_6 and $AlCl_3$ gives diphenylphthalide [change to cyclic (II) being assumed to be the primary action], but with NH_2Ph in cold

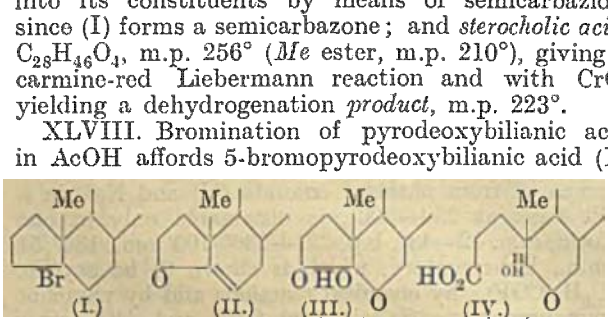
C_6H_6 gives phthalyldianilide, m.p. 253—255° [the m.p. 231°, recorded in the lit., is due to small amounts of anhydride present in the (II) used]. BzF, b.p. 155—156° (best prepared from BzCl and ZnF_2 in a Cu vessel at 150—195°), and (I) react very slowly with boiling anhyd. HCO_2H, whereas both forms of (II) give CO and HCl at a low temp. (I) or either form of (II) in C_6H_6 gives with aq. NH_3 at room temp. *o*-$CN{\cdot}C_6H_4{\cdot}CO_2H$. Quant. study shows (i) that (I) is at first more reactive with MeOH than either form of (II), but later about equally reactive, (ii) acyclic (II) reacts 200 times as fast as does (I) with $Pr^{\beta}OH$, but in the former case reaction appears to cease after 85% of the (II) has reacted, and (iii) BzCl reacts 500 times as fast as BzF with $Pr^{\beta}OH$. The last result shows that fluorides react more slowly than do chlorides, thus establishing the relationship of (I) to acyclic (II). The curve for the reaction of (I) with MeOH shows a break after 50% has reacted. The following vals. for the parachor are recorded, the figures in parentheses being the calc. vals. using 25·0 for the parachor of F: (I) 315·4 and 315·6 (acyclic 320·3, cyclic 305·6); *o*-$C_6H_4Me{\cdot}SO_2F$ 333·4 and 333·6 (339·7); *p*-$C_6H_4Me{\cdot}SO_2F$ 338·5. The negative discrepancy for *o*-compounds is perhaps due to strain. Colour reactions for the differentiation of cylic and acyclic dihalides are not characteristic. R. S. C.

Bile acids. XXXVII. M. Schenck (Z. physiol. Chem., 1933, **214**, 42—46; cf. A., 1932, 1132).—The difficult inversion of the ketoxime ring B of the Wieland modification of the Rosenheim–King formula is discussed. J. H. B.

Conversion of cholic acid into anthropodeoxycholic acid. S. Kawai (Z. physiol. Chem., 1933, **214**, 71—74).—Incomplete hydrogenation (2 mols. of H_2) of dehydrocholic acid reduces the 3- and 7-keto-groups affording 3 : 7-dihydroxy-12-cholanic acid. The semicarbazone of the latter heated at 180° with Na in EtOH gives anthropodeoxycholic acid. J. H. B.

Bile acids. XLVII. Two new acids from ox-bile. H. Wieland and S. Kishi. **XLVIII. Bromination of pyrodeoxybilianic acid.** H. Wieland and T. Posternak (Z. physiol. Chem., 1933, **214**, 47—58, 59—62; cf. this vol., 158).—XLVII. From ox-bile in addition to the known acids there were isolated: *Weyland's acid*, m.p. 165°, a compound of 1 mol. of anthropodeoxycholic acid and 1 mol. of 3-hydroxy-6-ketocholanic acid (I), which was separated into its constituents by means of semicarbazide, since (I) forms a semicarbazone; and *sterocholic acid*, $C_{28}H_{46}O_4$, m.p. 256° (*Me* ester, m.p. 210°), giving a carmine-red Liebermann reaction and with CrO_3 yielding a dehydrogenation *product*, m.p. 223°.

XLVIII. Bromination of pyrodeoxybilianic acid in AcOH affords 5-bromopyrodeoxybilianic acid (I),



m.p. 174—176° (decomp.), which in aq. NaOH gives the 5-*hydroxy-acid*, m.p. 272°. Boiling with C_5H_5N converts (I) into the unsaturated *diketo-acid* (II), $C_{23}H_{32}O_4$, m.p. 214—216°, oxidised by $KMnO_4$ in AcOH to *hydroxyketopyrodeoxybilianic acid* (III), m.p. 225—228°. With KOH in MeOH, (III) gives a *hydroxydiketocarboxylic acid*, $C_{23}H_{34}O_7$ (IV), m.p. 218—219°. J. H. B.

[Manufacture of] substituted naphthalene derivatives [aminocyanonaphthols]. Imperial Chem. Industries, Ltd., W. Bradley, and R. Robinson.—See B., 1933, 101.

Manufacture of arylamino-2-hydroxynaphthoic acids. I. G. Farbenind. A.-G.—See B., 1933, 140.

Manufacture of a 1-hydroxyanthracenecarboxylic acid. I. G. Farbenind. A.-G.—See B., 1933, 141.

Oxidation of toluene to benzaldehyde and benzoic acid. Z. E. Zinkov (J. Appl. Chem., Russia, 1932, **5**, 604—611).—Yields are increased by removing the products from the $K_2Cr_2O_7$–H_2SO_4 mixture as soon as they are formed. Ch. Abs.

Interaction of keten with aromatic aldehydes and its bearing on the Perkin reaction. C. D. Hurd and C. L. Thomas (J. Amer. Chem. Soc., 1933, **55**, 275—283).—Keten and PhCHO in presence of a little anhyd. KOAc give *cinnamic acetic anhydride* (I) (prepared also from cinnamic acid and keten in Et_2O) and some β-hydroxy-β-phenylpropionic acid lactone (proved by the formation of styrene when the reaction mixture is distilled); the primary product of the reaction is considered to be OH·CHPh·CH:C:O, which is then converted into OAc·CHPh·CH:C:O, and this subsequently undergoes anionotropic conversion into CHPh:CH·CO·OAc. Furfuraldehyde similarly affords β-2-*furylacrylic acetic anhydride* (also prepared from β-2-furylacrylic acid and keten) and some β-lactone (which when heated gives β-2-furylethylene), whilst *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ furnishes *m*-nitrocinnamic acetic anhydride (which when heated affords m-*nitrocinnamic anhydride*, m.p. 206°) and (probably) some β-lactone. The similarity of the above and the Perkin reaction [Kalnin's mechanism (A., 1929, 63) of which is criticised] is noted. H. B.

Polarographic studies with the dropping mercury cathode. III. Reduction of benzaldehyde. G. Semerano and G. De Ponte.—See this vol., 131.

Symmetrical triad prototropic systems. IX. Influence of polynuclear aryl groups on the mobility and equilibrium in the αγ-diarylmethyleneazomethine system. C. W. Shoppee (J.C.S., 1933, 37—45; cf. A., 1932, 384).—In the methyleneazomethine system, (*A*) CHAr:N·CH_2Ph (*B*) CH_2Ar·N:CHPh, the following order of mobility is obtained, when the group named is Ar: α- > β-$C_{10}H_7$- > p- > *m*-C_6H_4Ph > 9-phenanthryl, whilst the % of form (*A*) at equilibrium are 9-phenanthryl 18·5, α-$C_{10}H_7$ 27·0, *m*-C_6H_4Ph 56·0, β-$C_{10}H_7$ 59·0, *p*-C_6H_4Ph 61·0. These sequences are those expected from the $\pm T$ effects, except for 9-phenanthryl in the first and *m*-C_6H_4Ph in the second series; possible causes of these discrepancies are discussed, including the disturbances due to inductive effects (which cannot be foretold). 9-Bromophen-

anthrene, m.p. 63°, b.p. 225°/15 mm., yields the Grignard reagent in Et_2O–PhOMe, whence phenanthrene-9-carboxylic acid (I), m.p. 290—291° (*chloride*, m.p. 102°; *Me* and *Et* esters, m.p. 115° and 61°, respectively), is obtained, the *anilide*, m.p. 218°, of which with PCl_5 in $C_2H_2Cl_4$ gives the iminochloride (not isolated), converted by $SnCl_2$–HCl and subsequent hydrolysis into *phenanthrene-9-aldehyde*, m.p. 101° [*semicarbazone*, m.p. 222—222·5°; *p-nitrophenylhydrazone*, m.p. 265°; *acetal* (or *semiacetal*), an oil; oxidised by alkaline $KMnO_4$ to (I)]. This yields 9-*phenanthrylidenebenzylamine*, m.p. 72—72·5°, whilst the *oxime*, m.p. 155° [*hydrochloride*, m.p. 126—127°; dehydrated by Ac_2O to 9-cyanophenanthrene, m.p. 109° (lit. 103°), and hydrolysed by H_2SO_4–AcOH to (I)], with 3% Na–Hg and AcOH gives 9-*phenanthrylmethylamine*, m.p. 107° [*picrate*, m.p. 241° (decomp.); *benzoate*, m.p. 167°; *Ac* derivative, m.p. 182·5°], which leads to *benzylidenephenanthrylmethylamine*, m.p. 103·5°. β-Naphthanilide gives by way of the iminochloride β-naphthaldehyde, m.p. 59° (*p-nitrophenylhydrazone*, m.p. 230°), whence β-*naphthylidenebenzylamine*, m.p. 83·5°, is obtained. ω-Bromo-2-methylnaphthalene (prepared by bromination at 200°) with $C_6H_4(CO)_2NK$ at 180° gives *phthalo-β-naphthylmethylamide*, m.p. 150—151°, hydrolysed by N_2H_4 to β-naphthylmethylamine [*picrate*, m.p. 230—231° (decomp.); *benzoate*, m.p. 163°; *benzylidene* derivative, m.p. 88·5°]. α-Naphthaldehyde (similarly prepared), m.p. 156°/15 mm., gives α-*naphthylidenebenzylamine*, b.p. 208°/0·4 mm. *Phthalo-α-naphthylmethylimide*, m.p. 175—176°, yields α-naphthylmethylamine, b.p. 174—175°/19 mm. [*picrate*, m.p. 227° (decomp.); *benzoate*, m.p. 142·5—143°; *benzylidene* derivative, m.p. 55·5°]. 4-Aminodiphenyl gives (Sandmeyer) a 45% yield of 4-cyanodiphenyl, m.p. 86°, b.p. 190—193°/20 mm. (contrast lit.), which led to diphenyl-4-carboxylic acid (*chloride*, m.p. 107—108°, b.p. 185—186°/12 mm.; *anilide*, m.p. 220°), diphenyl-4-aldehyde, m.p. 60° [*semicarbazone*, m.p. 243° (decomp.); *p-nitrophenylhydrazone*, m.p. 216·5°], and 4-*phenylbenzylidenebenzylamine*, double m.p. 52° and 60°. Diphenyl-4-aldoxime with hot Ac_2O gives the nitrile, and with Na–Hg and AcOH 4-*phenylbenzylamine*, m.p. 53—54°, b.p. 195°/20 mm. [*picrate*, m.p. 218° (decomp.); *benzoate*, m.p. 151°; *Ac* derivative, m.p. 182°; *benzylidene* derivative, m.p. 76°]. 4-Aminodiphenyl and H_2SO_4 at 170° give the 4′-*sulphonic acid*, m.p. 270° (eventual decomp.), the orientation of which is proved by conversion into the *diazonium complex*, decomp. 161°, converted by Zn dust and dry Et_2O into the diphenyl-4-sulphonate, converted by $K_4Fe(CN)_6$ in CO_2 into 4-cyanodiphenyl and its polymeride [both hydrolysed to (I)]. 3-Cyanodiphenyl, m.p. 48° (modified prep.), gives by Stephen's method *diphenyl-3-aldehyde*, b.p. 187—188°/21 mm. [*$NaHSO_3$* compound; *semicarbazone*, m.p. 193°; 2 : 4-*dinitrophenylhydrazone*, m.p. 229°; *p-nitrophenylhydrazone*, m.p. 188°; *oxime*, an oil (*hydrochloride*, m.p. 118—119°) oxidised by alkaline $KMnO_4$ to the corresponding acid], also obtained by Sonn and Muller's method from *diphenyl-3-carboxyanilide*, m.p. 184°. 3-*Phenylbenzylidenebenzylamine* has b.p. 224°/1 mm. 3-Methyldiphenyl (modified prep.), b.p. 159—160°/27 mm., with Br at 195° gives ω-bromo-3-methyldiphenyl, m.p. 57—58°, b.p. 205—210°/24 mm., which affords *phthalo-m-diphenylmethylimide*, m.p. 138°, and thence 3-phenylbenzylamine, m.p. 29°, b.p. 182°/18 mm. [*hydrochloride*; *picrate*, m.p. 220° (decomp.); *Ac* derivative, m.p. 115—116°; *benzylidene* derivative, b.p. 220°/1 mm.]. Stephen's and Sonn and Muller's methods fail for the prep. of diphenyl-4-aldehyde. Attempts to prepare diphenyl-3-sulphonic acid failed. R. S. C.

Condensation of *o*-nitrobenzaldehyde with aniline. I. Tanasescu and A. Silberg (Bull. Soc. chim., 1932, [iv], **51**, 1357—1365).—Condensation of o-$NO_2{\cdot}C_6H_4{\cdot}CHO$ with NH_2Ph,H_2SO_4 under the influence of $ZnCl_2$ (cf. A., 1883, 981) gives 2-*nitro*-4′ : 4″-*diaminotriphenylmethane* (I), m.p. 163° [*Ac_2*, m.p. 220°, *Bz_2*, m.p. 141°, and (*CHPh*:)$_2$, m.p. 173°, derivatives], p-*aminophenylanthranil*, $C_6H_4<\begin{matrix}C(C_6H_4{\cdot}NH_2)\\N\end{matrix}>O$ (II), m.p. 113° (*Ac*, m.p. 202°, *Bz*, m.p. 224°, and CHPh:, m.p. 148—149°, derivatives; *hydrochloride*, m.p. 228°), and its o-*nitrobenzylidene* derivative (III), m.p. 155°; these are separated by virtue of the supreme basicity of (I) and the poor solubility of (III) in org. solvents. Reduction of (I) with Zn and NH_4Cl gives 2 : 4′ : 4″-triaminotriphenylmethane, m.p. 167—168° (*loc. cit.*) (*Ac* derivative, m.p. 152°), which gives a red to violet coloration with H_2O_2 in acid solution. (II) is similarly reduced to 2 : 4′-diaminobenzophenone, and thus identified. With BzCl and Ac_2O (III) gives the Bz and Ac derivatives of (II); it is readily hydrolysed to (II) by dil. HCl, and with $NH_2{\cdot}NHPh$ and a trace of HCl in AcOH gives *o*-nitrobenzaldehydephenylhydrazone. H. A. P.

Photochemical reactions in the *o*-nitrobenzylideneacetal series. VI. Constitution of products of photochemical isomerisation of *o*-nitrobenzylideneacetal. I. Tanasescu and E. Macovski (Bull. Soc. chim., 1932, [iv], **51**, 1371—1377; cf. A., 1930, 1039).—*Ag* o-*nitrosobenzoate* condenses with β-bromoethyl benzoate at 60—80° to give *benzoyl*-o-*nitrosobenzoylethylene glycol*, m.p. 112—113°, identical with the Bz derivative of the insolation product from *o*-nitrobenzylidene glycol. The open-chain structure (I) is therefore the most probable for this substance, and similar formulæ probably hold for the products from the other acetals examined, but the possibility of their existence in tautomeric equilibrium :

(I.) $HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}NO \rightleftharpoons$ $\begin{matrix}CH_2{\cdot}O\\CH_2{\cdot}O\end{matrix}>C(OH){\cdot}C_6H_4{\cdot}NO$ is not excluded. *o*-$NO{\cdot}C_6H_4{\cdot}CO_2H$ is conveniently prepared by insolation of o-$NO_2{\cdot}C_6H_4{\cdot}CHO$ in H_2O. H. A. P.

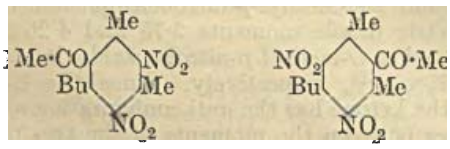
Configurations of the aldoximes, from measurements of electric dipole moment. T. W. J. Taylor and L. E. Sutton (J.C.S., 1933, 63—65).—α- and β-*O*-Methyl-*p*-nitrobenzophenoneoximes have electric dipole moments 3·75 and $4{\cdot}26\times10^{-18}$, and α- and β-*O*-methyl-*p*-nitrobenzaldoximes $3{\cdot}39_5$ and $3{\cdot}88_5\times10^{-18}$, respectively. Since the β-derivative of the ketone has the *anti*-configuration and the differences between the moments of the two pairs is almost equal, the β-derivative of the aldoxime, and thus also the β-aldoxime, is the *anti*-form in agreement

with Meisenheimer's views. *O*-Methylation probably does not affect the configuration; but since, if it does so, it must affect aldoxime and ketoxime equally, the above conclusions remain valid. R. S. C.

Lignin and cellulose. XXI. Lignin. K. FREUDENBERG and F. SOHNS (Ber., 1933, **66**, [*B*], 262—269).—Treatment of lignin (I) suspended in H_2O with O_3–O_2 affords AcOH and $H_2C_2O_4$; intermediate products could not be isolated. Moist combination of (I) with CrO_3 yields 6% of AcOH, whereas none is obtained from "polymerised" coniferyl alcohol. HI at 150° does not form fragments of lower mol. wt. from (I). Reactions between carbinols and C_6H_6 derivatives are divided into two classes, in which (*a*) the reactants are initially separate (*e.g.*, $CH_2Cl{\cdot}CH_2{\cdot}OH$ and (I)) and reaction ceases after their union, and (*b*) the components are present in the same mol. (*e.g.*, *o*-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$) and the product possesses the same functions and reacts further until a highly-polymerised state is reached. The lignin acetals and other lignin preps. obtained with glycols, phenols, and other org. solvents are of very heterogeneous composition. Ligninsulphonic acid (II) is prepared from (I) and $Ca(HSO_3)_2$ at 100° and then at 120—125° and purified through the quinoline salt. S is entirely present as $\cdot SO_3H$ and, apart from the entry of about 10% of HSO_3H, (I) appears unchanged. Reactions of (I) with *p*-$C_6H_4Cl{\cdot}SO_2Cl$, *p*-$C_6H_3Me{\cdot}SO_2Cl$, and *m*-nitro-*p*-toluenesulphonyl chloride are described. (II) contains 1 SO_3H to 4 OMe originally present in (I), and this amount can be increased by further treatment with $Ca(HSO_3)_2$. The no. of double linkings established in (I) is inadequate to account for the production of (II), and nuclear reaction must be assumed to occur. The CH_2O_2 group is not due to an impurity in (I), since it is present in (II) and almost in unchanged amount in the residue left after the half-decomp. of (I) by O_3. Treatment of (I) with *N*-NaOH at 100° removes the CH_2O_2 group in favour of OH. (I) and CH_2N_2 give a product containing at most 19% OMe (not 21% as recorded previously). The ability of (I) to adsorb solvent is very marked. [α] of (I), if existent, is $< 5°$. H. W.

Reaction between oximinoacetophenone and magnesium phenyl bromide in ether solution. D. V. CHANG and C. L. TSENG (Trans. Sci. Soc. China, 1932, **7**, 225—232).—2 Mols. of the compound and 1 mol. of MgPhBr are involved, both the keto- and oximino-groups being attacked. The resulting organometallic compound with H_2O yields β-hydroximino-αα-diphenylethyl alcohol. CH. ABS.

Structure of musk ketone. A. E. TSCHITSCHIBABIN (Bull. Soc. chim., 1932, [iv], **51**, 1436—1462).—The unsymmetrical formula (I) of Baur (cf. A., 1898, i, 523) for musk ketone is rejected and replaced

(I) 

(II)

by the symmetrical formula (II) on the following grounds: (1) the nitro-derivatives possessing a plane of symmetry are generally solid and have an odour of musk, whereas those of unsymmetrical structure are usually liquid, and do not have the musk odour; (2) in the dinitration of (III) (below) two mono-NO_2-derivatives should be formed, but actually only one is known; (3) during nitration the ·COMe group is partly replaced by NO_2, according to the conditions, 2-NO_2- or 2 : 4-$(NO_2)_2$-derivatives of 1 : 3-dimethyl-5-butylbenzene, but no 4-NO_2- or 4 : 6-$(NO_2)_2$-derivatives, being formed. The structure (II) assigned is definitely proved by conversion of Baur's "Me ketone" (III) from AcCl and *s*-butylxylene by NH_2OH,HCl and MeOH at 160° into 2-*acetamido*-1 : 3-*dimethyl*-5-*butylbenzene*, m.p. 160° (Baur gives m.p. 81°) (cf. A., 1892, 314), which fixes its structure as 2 : 6-*dimethyl*-4-*butylacetophenone* (III). The NHAc-compound is synthesised for comparison from 2-nitro-1 : 3-dimethyl-5-butylbenzene.

Nitration of (II) in cold Ac_2O gives the 3-NO_2-derivative (IV), m.p. 56°, in 70—80% yield, and some 2-nitro-1 : 3-dimethyl-5-butylbenzene, m.p. 85°. The COMe group in (IV) is not removed by cold conc. H_2SO_4 or by boiling syrupy H_3PO_4; its presence is proved by further nitration to (II) and oxidation by 20% HNO_3 to Baur's bis-(3-nitro-2 : 6-dimethyl-4-butylbenzoyl)furoxan. Oxidation of (III) with alkaline $KMnO_4$ under Baur's conditions gave a product from which no definite compound could be isolated to correspond with Baur's dimethylbutylphenylglyoxylic acid. Further oxidation of a portion with H_2O_2 did not improve the product. The bulk was therefore fully oxidised by MnO_4 and dil. H_2SO_4 at the b.p. and gave 2 : 6-*dimethyl*-4-*butylbenzoic acid* (V), m.p. 168° (+$0{\cdot}5C_6H_6$; lost rapidly at 100°) [*amide* (VI), m.p. 136°], and 3-*methyl*-5-*butylphthalic acid*, m.p. 180° (decomp.), the *anhydride* of which, m.p. 128—129°, is formed without loss of CO_2 (cf. Baur, *loc. cit.*) above the m.p. The attempted conversion of (VI) into the amine by Hoffmann's method (KOBr) gave instead 2-bromo-1 : 3-dimethyl-5-butylbenzene, m.p. 45°. Sulphonation of (III) occurs by displacement of the ·COMe group, and fusion of the sulphonic acid of this or of *s*-butylxylene with alkali gives 2 : 6-*dimethyl*-4-*butylphenol*, m.p. 84°. Diazotisation of 4 : 6-dinitro-2-amino-1 : 3-dimethyl-5-butylbenzene and decomp. of the diazo-compound gives 3 : 5-*dinitro*-2 : 6-*dimethyl*-4-*butylphenol*, m.p. 192° [*Me ether* (Me_2SO_4), m.p. 137°]; reduction of the diazonium salt with EtOH gives in addition 4 : 6-*dinitro*-1 : 3-*dimethyl*-5-*butylbenzene*, m.p. 84°. The orientation of other compounds described by Baur (*loc. cit.*) needs adjustment. H. A. P.

Photochemical reduction of ketones to hydrols. W. E. BACHMANN (J. Amer. Chem. Soc., 1933, **55**, 391—395).—Exposure of a solution of $COPh_2$ in $Pr^{\beta}OH$ containing a little $Pr^{\beta}ONa$ to sunlight gives (after 4 days) a nearly quant. yield of $CHPh_2{\cdot}OH$. The following reactions occur: (i) $2COPh_2+Pr^{\beta}OH \longrightarrow (\cdot CPh_2{\cdot}OH)_2+COMe_2$ (cf. Cohen, A., 1919, i, 210); (ii) $(\cdot CPh_2{\cdot}OH)_2 \xrightarrow{Pr^{\beta}ONa} (\cdot CPh_2{\cdot}ONa)_2 \rightleftharpoons 2CPh_2{\cdot}ONa$ (cf. following abstract); (iii) $2CPh_2{\cdot}ONa+2Pr^{\beta}OH \longrightarrow 2Pr^{\beta}ONa+2CPh_2{\cdot}OH$; (iv) $2CPh_2{\cdot}OH \longrightarrow COPh_2+CHPh_2{\cdot}OH$. The rates of reduction of $COPh_2$ to benzpinacol (in $Pr^{\beta}OH$ alone) and to $CHPh_2{\cdot}OH$ (as above) are nearly the same owing to

the rapid decomp. of the pinacol by $Pr^{\beta}ONa$. The following are similarly reduced to the corresponding hydrols: 4-methyl-, 4:4′-dimethyl-, 4-methoxy-, 4-chloro-4′-methyl-, 4-phenyl- (I), and 4-chloro-benzophenones. 4:4′-Tetramethyldiaminobenzophenone and α-$C_{10}H_7Bz$ are not reduced, whilst fluorenone undergoes a reaction which is not photochemical. Contrary to Cohen (*loc. cit.*), (I) is reduced in $Pr^{\beta}OH$ to 4:4′-diphenylbenzpinacol. H. B.

Action of sodium alkoxide and of sodium amalgam on aromatic pinacols. W. E. Bachmann (J. Amer. Chem. Soc., 1933, **55**, 355—361).—Benzpinacol, 4:4′-diphenyl-, 4:4′:4″:4‴-tetraphenyl- and -tetramethyl-benzpinacols, and fluorenopinacol are converted by a little NaOEt (NaOMe, $NaOPr^{\beta}$, KOEt, LiOMe, $CHPh_2$·ONa) in Et_2O–C_6H_6 (after hydrolysis with dil. acid) into a mixture (1:1) of $COAr_2$ and $CHAr_2$·OH. A deep blue colour (due to ketyl formation) is developed in the reaction mixture; this disappears after a short time (even in absence of air). The reaction mechanism is considered to be: (i) $(\cdot CAr_2\cdot OH)_2 \xrightarrow{NaOEt} (\cdot CAr_2\cdot ONa)_2 \rightleftharpoons 2\dot{C}Ar_2\cdot ONa$; (ii) $2CAr_2\cdot ONa + (\cdot CAr_2\cdot OH)_2 \longrightarrow 2CAr_2\cdot OH + (\cdot CAr_2\cdot ONa)_2$; (iii) $2CAr_2\cdot OH \longrightarrow COAr_2 + CHAr_2\cdot OH$. In some cases the following reaction may occur (partly or exclusively): $OH\cdot CAr_2\cdot CAr_2\cdot ONa \longrightarrow CAr_2\cdot OH + CAr_2\cdot ONa \longrightarrow CHAr_2\cdot ONa + COAr_2$. This is supported by the production of $CHPh_2$·OH and dianisyl ketone from αα-diphenyl-ββ-dianisylethylene glycol. The above change is also effected by a small amount of the ketyl from $COPh_2$. Benzpinacol (and the above *s*-pinacols) is reduced by 1·5% Na–Hg in Et_2O–C_6H_6 to $CHPh_2$·OH (and the corresponding hydrols) in nearly quant. yield; interruption of the reaction gives pinacol, $COPh_2$, and $CHPh_2$·OH. A 1:1 mixture of $COPh_2$ and $CHPh_2$·OH similarly affords $CHPh_2$·OH. In all these reductions ketyl formation occurs; the ketyl may be partly reduced by H_2 (from $CHPh_2$·OH and Na–Hg), but it is shown that such reaction is slow. Benzpinacol and 40% Na–Hg in Et_2O–C_6H_6 give nearly pure $CHPh_2$·OH without liberating H_2. A mechanism of the reduction (similar to the above) is suggested. H. B.

Constitution and reactivity. IV. The alleged polysulphonation of anthraquinone. K. Lauer (J. pr. Chem., 1932, [ii], **135**, 361—368).—The polyhydroxyanthraquinones shown in parentheses were isolated from the mixtures of hydroxydisulphonic acids obtained in attempts to sulphonate further the following anthraquinonedisulphonic acids: 2:6- (1:2:4:6-, 1:3:5:7-, 1:2:4:5:6:8-); 2:7- (1:2:4:7-, 1:2:4:5:7:8-); 1:6- (1:3:8-, 1:2:4:5:8-, 1:2:4:5:7:8-); and 1:7- (1:2:4:5:6:8-). No higher sulphonation products are formed. Addition of Hg or its salts improves the yield in some cases, but does not alter the course of the reaction. A. A. L.

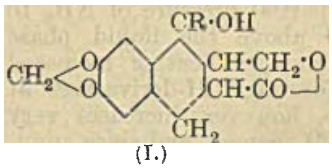
Amination by ammonolysis. I. Properties and reactions of aqueous ammonia system. II. Effect of metal catalysts in ammonolysis. P. H. Groggins and A. J. Stirton (Ind. Eng. Chem., 1933, **25**, 42—46, 46—49).—I. By use of suitable indicators (usually thymol-blue) the p_H of a 28% aq. NH_3 solution heated in sealed Pyrex glass tubes is shown to decrease from 11·8 at 25° to 8·2 at 175°. In presence of NH_4Cl (0·027 g. per c.c.) the p_H decrease is from 10·7 at 25° to 8·2 at 120°, and extrapolation of this curve indicates that at 200° the p_H would approximate to neutrality (5·6). In amination of aromatic halogen compounds evidence in the lit. shows that NH_3 and not NH_4OH is the active reagent, the function of the H_2O being probably that of providing more effective contact between the reactants. Since the reaction occurs in the liquid phase, the free space in autoclaves should be a min. For a definite NH_3 concn the ratio of partial pressure of NH_3 to partial pressure of H_2O above the liquid phase decreases with rise of temp., indicating increased activity of the H_2O in forming OH-derivatives at higher temp. This ratio, however, increases very rapidly with increasing NH_3 concn., and since amination is approx. proportional to the latter, the use of conc. NH_3 solutions at the lowest temp. necessary to activate the halogen compound results in more rapid and more complete conversion, greater purity of product, and inhibition of hydroxylation.

II (cf. B., 1931, 964). In amination of halogenoanthraquinones using Cu catalysts no advantages accrue from keeping the Cu in a reduced state, since its function is merely to provide a regulated quantity of dissolved Cu, the effective catalyst most probably being a ternary complex of the aryl compound, NH_3, and Cu, the aq. mother-liquor containing organically combined Cu. In the ammonolysis of 2-chloroanthraquinone with 28% aq. NH_3 at temp. between 180° and 200°, reduced purity of product results when Cu or Cu oxides are employed, yields of 95—98% (average purity 91·25%) being obtained without catalysts. Improved results are obtained by using an oxidant with the Cu. Thus with a $CuNO_3,6H_2O$–$KClO_3$ catalyst a 96·6% yield of a product 97·0% pure is obtained at 200°, the control without catalyst giving a 95·1% yield of 95·9% purity. Similar improvement results from the combined use of NH_4NO_3 and Cu_2O. Ammonolysis of 4′-chloro-2-phenylanthraquinone (and, in general, where the halogen is directly attached to a Ph nucleus) is not practicable unless a Cu compound is used, but with addition of NH_4NO_3–$KClO_3$ a 96% yield of the 4′-NH_2-compound (97·5% purity) is obtained. Slightly lower yields (98% purity) result when $PhNO_2$ is used as the oxidant. J. W. B.

Manufacture of anthraquinone derivatives. A. G. Bloxam. From Soc. Chem. Ind. in Basle.—See B., 1933, 141.

Podophyllotoxin. A. Robertson and R. B. Waters (J.C.S., 1933, 83—86).—Dehydration of picropodophyllin with Ac_2O results in α-*apo*picropodophyllin, m.p. 244—245°, $[\alpha]_{5461}^{21}$ −17·5° in $CHCl_3$, converted by Ac_2O and C_5H_5N into the β-compound, m.p. 216°, $[\alpha]_{5461}^{13}$ +117·6° in $CHCl_3$, which shows a different reaction with H_2SO_4 (cf. Spath *et al.*, A., 1932, 1137). Both α- and β-lactones and NaOH give *apo*picropodophyllic acid, m.p. 174° (decomp.), $[\alpha]_{5461}^{21}$ −279·4° in $CHCl_3$, which forms only the α-compound when heated at 185°. Podophyllomeronic acid may be obtained from α- or β-*apo*- and HI, as well as from picropodophyllin. Reduction by Zn–Hg of the

mixture of acids derived from the condensation of veratrole and methylsuccinic anhydride with $AlCl_3$ gives rise to acids which on ring closure with H_2SO_4 form a mixture of 1- and 4-*keto*-6 : 7-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 102—110°. The mixed ketones are reduced by Zn–Hg to 6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which is dehydrogenated by Se to the corresponding naphthalene compound, m.p. 100°. The Me$_2$ ether is hydrolysed to 6 : 7-dihydroxy-, m.p. 165°, converted by CH_2I_2 into 6 : 7-methylenedioxy-2-methylnaphthalene (podophyllomerol), identical with the product of decarboxylating podophyllomeronic acid. It is suggested that α- and β-*apo*picropodophyllin are geometrical isomerides and that (I) represents the formula of picropodophyllin. F. R. S.



(I.)

Constitution of podophyllotoxin and picropodophyllin. E. Späth, F. Wessely, and E. Nadler (Ber., 1933, **66**, [*B*]. 125—130).—Further insight into the constitution of podophyllotoxin and picropodophyllin (I) (cf. A., 1932, 1137) is derived by the oxidation of (I) by $KMnO_4$ in alkaline solution to 4 : 5-*methylenedioxy*-2-3′ : 4′ : 5-*trimethoxybenzoylbenzoic acid* (II), m.p. 214—216° (*Me* ester, m.p. 128—129°), reduced by Zn dust and KOH in MeOH–EtOH to the *lactone*, $CH_2O_2.C_6H_2<\begin{matrix}CO\\CH[C_6H_2(OMe)_3]\end{matrix}>O$, m.p. 218° [obtained also by direct oxidation of (I)], and decarboxylated by Cu-bronze in boiling quinoline to 3 : 4 : 5-*trimethoxy*-3′ : 4′-*methylenedioxybenzophenone* (III), m.p. 125—127°. (III) is prepared synthetically from pyrocatechol methylene ether, $C_6H_6(OMe)_3$·COCl, and $AlCl_3$ in CS_2. (II) appears identical with the acid obtained by Borsche and Niemann (A., 1932, 1258) by mild oxidation of podophyllic acid with $KMnO_4$. H. W.

Purification and constitution of theelol. D. W. MacCorquodale, S. A. Thayer, and E. A. Doisy (J. Biol. Chem., 1933, **99**, 327—334).—Various improved methods for the prep. of cryst. theelol (I) (A., 1931, 879) based on the insolubility of its alkali metal salts in solutions of the alkali hydroxides are described. (I) is unaltered physiologically and chemically by prolonged treatment with NaOH at 100°, and NH_2·NH·CO·NH_2 and NH_2OH fail to indicate the presence of any ketonic substance. The results and conclusions of Marrian and Haslewood (A., 1932, 1253) are confirmed, but the m.p. (all corr.) for the phenoldicarboxylic acid, $C_{18}H_{22}O_5+H_2O$ and anhyd., m.p. 210—211° (*Me ether*, m.p. 200—201°), its Me ether anhydride, m.p. 179° (sinters 171°), and of hexahydrotheelol, m.p. 268°, are higher than those recorded by these authors. J. W. B.

Polyterpenes and polyterpenoids. LXXIX. Constitution of cholesterol and bile acids. L. Ruzicka and G. Thomann (Helv. Chim. Acta, 1933, **16**, 216—227).—The evidence (lit.) for the C_{13}·Me group in cholesterol is held to be inconclusive. Chrysene is not obtained when cholatrienic acid is dehydrogenated by Diels and Karstens' method (A., 1930, 470); the products isolated are the hydrocarbon $C_{18}H_{16}$ ($C_{17}H_{14}$?) (I), m.p. 124—125°, of Diels *et al.* (A., 1928, 169), and *hydrocarbons*, $C_{18}H_{12}$ (C_1-$H_{..}$?), m.p. 239—240°, $C_{22}H_{18(16)}$ ($C_{21}H_{16}$?), m.p. 274—275°, and $C_{22}H_{16}$ ($C_{12}H_{14}$?), m.p. 315—324° (sinters at 305°, decomp. at 310°). (I) forms a 1 : 1-*compound*, m.p. 147—148°, with $C_6H_3(NO_2)_3$ and could not be dehydrogenated further by S, Se, or Pd–C, thus rendering it unlikely that (I) is tetrahydrochrysene (cf. Rosenheim and King, A., 1932, 736). (I) may contain a five-membered ring attached to the phenanthrene nucleus, and the above Me group may be attached to C_{15} of cholesterol. The chrysene of Diels and Karstens (*loc. cit.*) may be a mixture. H. B.

Preparation of marubiin. L. J. Mercier and F. Mercier (Compt. rend., 1932, **195**, 1102—1104).—An improvement on the method of Gordin (A., 1908, i, 344). The cold $COMe_2$ extract of horehound is evaporated, extracted with Et_2O, and the insol. residue boiled, refluxed with EtOH–KOH, pptd. with H_2O, and recryst. from EtOH; m.p. 157·5—157·8° (lit. 154·5—155°). A. C.

Elemic acid from Manila elemi resin. VI. Oxidation product of α-elemolic acid. M. Mladenović (Monatsh., 1932, **61**, 365—368).—The acid (A., 1932, 397) (termed *elemonic acid*) formed with α-elemonic acid by oxidation (CrO_3–AcOH) of α-elemolic acid is $C_{30}H_{46}O_3$, m.p. 220°, $[\alpha]_D^{19}$ +32·43° in $CHCl_3$, is unsaturated, contains a CO group, and is probably identical with the δ-elemic acid of Ruzicka (A., 1932, 749). H. B.

The strophanthins of *Strophanthus eminii*. W. A. Jacobs and N. M. Bigelow (J. Biol. Chem., 1933, **99**, 521—529).—The glucosidic mixture obtained from the seeds of *S. eminii* (extraction described) consists of easily hydrolysable (I) and stable (II) glucosides. Hydrolysis of (I) with 0·15% HCl at 75° gives an aglucone mixture from which strophanthidin was isolated and its presence confirmed by isolation of the methylal of dianhydrostrophanthidin after treatment of the aglucone mixture with 5% HCl in MeOH at 100°. The presence also of periplogenin (the aglucone of *Periploca græca*) was proved by the formation of a separable mixture of *dihydrostrophanthidol*, m.p. 172—175°, resolidifying and remelting at 195°, $[\alpha]_D^{25}$ +35·0° in 95% EtOH, and dihydroperiplogenin (A., 1928, 1359; *Bz* derivative, m.p. 214—216°) when the aglucone mixture is reduced (H_2, PtO_2, EtOH). (II) are separated into a $CHCl_3$-sol. *monoside* (III), $C_{30}H_{46}O_9$, m.p. 174—180° (previous sintering), $[\alpha]_D^{25}$ +22° in 95% EtOH, of an aglucone, $C_{23}H_{36}O_5$ (IV) and a Me ether deoxysugar, $C_7H_{14}O_5$ (either identical or isomeric with digitalose), and a *bioside* (V), $C_{36}H_{56}O_{14}$, m.p. 195—200° (previous sintering), $[\alpha]_D^{25}$ +8° in 95% EtOH, derived from (IV) with an additional hexose (? glucose). With 5% HCl in MeOH at 100° either (III) or (V) affords the same *trianhydroglucone*, $C_{23}H_{28}O_2$, m.p. 154—156°, $[\alpha]_D^{25}$ −84·6° in C_5H_5N, isomeric with trianhydroperiplogenin. J. W. B.

A new carotene. R. Kuhn and H. Brockmann (Naturwiss., 1933, **21**, 44).—*γ-Carotene*, m.p. 178°, optically inactive, distinguished by the longer wave-

lengths of its absorption bands, is present to the extent of 0·1% in ordinary carotene and is found in apricots. It resembles a pigment isolated from *Convallaria* (A., 1932, 785). Doses of 5×10^{-6} g. per day cure vitamin-*A*-deficient rats. R. K. C.

Molecular compounds of cineole. F. D. DODGE (J. Amer. Pharm. Assoc., 1933, **22**, 20—21).—Cineole forms additive *compounds* with *o*-$C_6H_4Cl\cdot OH$ (1 mol.), m.p. 57—59°, *o*-$C_6H_4Br\cdot OH$ (1 mol.), m.p. 75·5—76°, *o*-$C_6H_4I\cdot OH$ (1 mol.), m.p. 89—90·5°, and *p*-$OH\cdot C_6H_4\cdot CO_2H$ (about 0·5 mol.), m.p. 63—65°. R. S. C.

Unsaturated peroxides. [Mechanism of] oxidation processes. K. BODENDORF (Arch. Pharm., 1933, **271**, 1—35).—Ascaridole (I) in EtOH absorbs 1 mol. of H_2 in presence of PtO_2 very rapidly and a second mol. more slowly to give pure 1 : 4-terpin. Partial hydrogenation (1 mol.) (Pd–C) gives *p*-Δ^2-menthene-1 : 4-diol. The constitution of (I) is thus proved. (I) in EtOH, when shaken with N_2 and PtO_2, is partly isomerised. Substances containing two conjugated ethylenic linkings are oxidised by O_2 without a catalyst much more rapidly than are substances containing only one ethylenic linking. The products are shown to be multimol. peroxides of type (A), formed by intermol. 1 : 4-addition; they do not show the full normal reactivity of peroxides. The reaction is autocatalytic, but the catalytically active substance ("inductor") formed during the reaction is unstable. Thus, a small amount of freshly-oxidised α-terpinene (II) very greatly increases the rate of oxidation of a second batch, but the isolated peroxide or oxidised (II) which has been kept is inactive. Similarly, interruption of the oxidation leads to decreased velocity when oxidation is resumed, the decrease being greater the longer is the interruption. The inductor formed from α-phellandrene (III) catalyses the oxidation of (III), but not that of (II). However, the inductor formed from (II) catalyses the oxidation of both (II) and (III). The latter is an example of a true induced oxidation, which probably plays an important part in biological reactions. The inductor is assumed to be a moloxide. The energetics of the oxidation are discussed. (II) in EtOH with dry O_2 gives an undistillable *peroxide*, $(C_{10}H_{16}O_2)_x$, mol. wt. about 430, which, when shaken with H_2 and PtO_2 or Pd–C in EtOH, is partly isomerised, and, when partly hydrogenated, gives mainly an unsaturated glycol, which is probably impure *p*-Δ^2-menthene-1 : 4-diol, since it is oxidised by alkaline $KMnO_4$ to αα-dihydroxy-α-methyl-α′-*iso*propyladipic acid. (III) gives a similar *peroxide*, which, when partly reduced and then oxidised, gives a ketonic *acid*, $C_{10}H_{18}O_5$, b.p. 60°/0·2 mm., probably *αδ-dihydroxy-ε-keto-β-isopropylheptoic acid*. Reduction (PtO_2) of the peroxide gives in 3% yield an unsaturated glycol, $C_{10}H_{20}O_2$, m.p. 176·5—178°, probably p-Δ^1-*menthene*-3 : 6-*diol*, and a complex mixture. The peroxides resemble (I) closely in absorption spectra and vermicidal action. *cyclo*Hexadiene is more slowly oxidised to a *peroxide*, $(C_6H_8O_2)_x$, mol. wt. 470, slowly reduced to a mixture of *cis*- and *trans*-quinitol. βγ-Dimethylbutadiene (at 30—40°) and isoprene give similar *peroxides*, which, when hydrogenated, give CH_2O and mixtures of decomp. products. R. S. C.

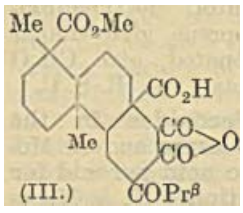
Organic peroxides. I. Peroxides in the camphoric acid series. N. A. MILAS and A. MCALEVY. **II. Use of camphoric acid peracid for the determination of unsaturation.** N. A. MILAS and I. S. CLIFF (J. Amer. Chem. Soc., 1933, **55**, 349—352, 352—355).—I. *d*-Camphoric anhydride (in Et_2O) and Na_2O_2 in cold H_2O give the *peracid* (I), CO_2H(*tert.*)-$C_8H_{14}\cdot CO\cdot O_2H$(*sec.*), m.p. 49—50° (sealed tube), or *dicamphoryl peroxide*, m.p. 142° (explosive decomp.), according to the conditions used. (I) hydrolyses in dil. aq. solution to camphoric acid and H_2O_2 and decomposes slowly at room temp. and explosively at 80—100° to camphoric acid and O_2. Me (*sec.* or *tert.*) H camphorate and PCl_3 afford the *ester chloride*, $CO_2Me\cdot C_8H_{14}\cdot COCl$ (*sec.*), which with aq. Na_2O_2 gives the *peroxide* (II), $[CO_2Me(tert.)\text{-}C_8H_{14}\cdot CO\cdot O\cdot]_2$, m.p. 102°; with the Ba salt of MeO·OH (Ricche and Hitz, A., 1929, 1268), the *perester*, $CO_2Me(tert.)\text{-}C_8H_{14}\cdot CO\cdot O_2Me$, results. (II) and NaOMe in Et_2O give the impure *peracid ester*, $CO_2Me(tert.)\text{-}C_8H_{14}\cdot CO\cdot O_2H$.

II. (I) (in $CHCl_3$) is more stable than BzO_2H (in $CHCl_3$) at 25°; there is little difference in their stabilities at 0°. The no. of mols. of (I) consumed by the following are given in parentheses: anethole (0·983), *iso*safrole (0·979), *iso*eugenol (0·981), citronellol (0·983), cholesterol (0·98) (oxide isolated), ergosterol (3), limonene (1·957), *d*-pinene (1·01) (oxide isolated), nonene (0·947), βδ-dimethyl-Δ^β-pentene (0·972), $\Delta^{\beta\delta}$-hexadiene (0·923), oleic acid (0·997), linoleic acid (2), cinnamic acid (0), cinnamaldehyde (0·57), abietic acid (0·84), crotonic acid (0·15), mesityl oxide (0·49); the reaction is carried out in $CHCl_3$ for 30 min. (except with the last seven substances). H. B.

Preparation and optical resolution of ammonium *dl*-α-bromocamphor-π-sulphonate. A. W. INGERSOLL and S. H. BABCOCK (J. Amer. Chem. Soc., 1933, **55**, 341—345).—Details are given for the resolution of NH_4 dl-α-*bromocamphor-π-sulphonate*, m.p. 250—254° (decomp.), prepared from *dl*-α-bromocamphor (satisfactory method of prep. given) by Kipping and Pope's method (J.C.S., 1895, **67**, 356), with *l*-α-*p*-tolylethylamine. l-α-p-*Tolylethylamine* d- and l-α-*bromocamphor-π-sulphonates* (both $+H_2O$) have m.p. (anhyd.) 232° (corr.) and 165° (corr.), and $[\alpha]_D^{25}$ +59·4° and −62·7° in H_2O, respectively. H. B.

Polyterpenes and polyterpenoids. LXXVIII. Position of the carboxyl group and double linkings in abietic acid. L. RUZICKA, H. WALDMANN, P. J. MEIER, and H. HOSLI (Helv. Chim. Acta, 1933, **16**, 169—181).—Abietinol (I) is oxidised ($K_2Cr_2O_7$, dil. H_2SO_4) to abietinal, the *semicarbazone*, m.p. 215°, of which with NaOEt at 210—220° gives methylabietene (II), b.p. 135—138°/0·15 mm. (II) is dehydrogenated (Se at 300—330°) to retene, proving that the change $>CMe\cdot CH_2\cdot OH \longrightarrow >CMe_2$ occurs in the conversion of (I) into (II). The adduct (A., 1932, 1254) from Me abietate and maleic anhydride is oxidised (O_3) to a *keto-acid*, $C_{25}H_{34}O_8$ (probably III),

m.p. 277—278° whilst Me abietate and O_3 give [after esterification (Me_2SO_4)] of the acidic products] a *Me*$_2$ ester, $C_{17}H_{26}O_5$, b.p. 180°/0·2 mm. (amorphous oxime and semicarbazone), and material of higher b.p. (cf. A., 1925, i, 1419). Contrary to the previous statement (A., 1922 i, 547), dihydroabietic acid is not isomerised by HBr–AcOH; the *lactone*, m.p. 130—131°, of a *OH-acid*, $C_{20}H_{34}O_3$, m.p. 162—163°, results. The above results support the formula for abietic acid previously proposed (A., 1932, 1254).



(III.)

The conclusions of Vocke (A., 1932, 1036) are criticised. It is shown that the Me esters of dihydro-*cyclo*geranic acid (IV) and 2 : 2 : 4 : 6-tetramethyl-Δ^3-*cyclo*hexenecarboxylic acid, *i.e.*, esters containing >CH·CO$_2$Me, are more difficultly hydrolysed than Me abietate and dihydro-*d*-pimarate, *i.e.*, esters containing C·CO$_2$Me. (IV) and conc. H_2SO_4 at 70—90° give 0·9 mol. of CO, showing that the production of CO under such conditions is not confined to *tert.*-acids. The acid $C_{10}H_{14}O_4$, m.p. 176—177° (decomp.), formed from the bromoanhydrotricarboxylic acid of Vocke (*loc. cit.*) and cold 2*N*-NaOH may be 1 : 2-dimethyl-Δ^2-tetrahydro*iso*phthalic acid, since a pinacolin rearrangement can occur. H. B.

Conjugated systems in the furan types. H. Gilman and J. B. Dickey (Iowa State Coll. J. Sci., 1932, **6**, 381—388).—Furfurylidencacetophenone (I) and *p*-thiocresol afford 90% of 1-*benzoyl*-2-*furfuryl*-2-p-*thiotolylethane* (II), m.p. 78·5°; (I) and p-C$_6$H$_4$Me·SO$_2$Cl afford 35% of 1-*benzoyl*-2-*furfuryl*-2-p-*tolylsulphonylethane*, m.p. 141°. (I) and Mg *p*-thiotolyl iodide afford a small quantity of (II). Ch. Abs.

Absolute method for establishing orientation in the furan series. M. G. van Campen, jun., and J. R. Johnson (J. Amer. Chem. Soc., 1933, **55**, 430—431).—Addition of maleic anhydride to furan derivatives does not occur when CO$_2$Et, CN, NO$_2$, or ·C:C· is a nuclear substituent; the adducts (substituted 3 : 6-endoxo-Δ^4-tetrahydrophthalic anhydrides) from 2- (I) and 3-bromofurans (II), furfuryl Me ether, furfurylidene diacetate, and furfurylacetone have m.p. 116°, 131·5—132°, 97°, 126·5—127°, and 86—87°, respectively. Since the adducts can be converted into substituted phthalic acids (or anhydrides) (cf. Diels and Alder, A., 1931, 1426), the position of a substituent in the furan ring can be determined. The adducts from 2-methylfuran, (I), and (II) are converted by HBr–AcOH into 3-methyl-, m.p. 111—113°, 3-bromo-, m.p. 134—135°, and 4-bromo-, m.p. 108—110°, -phthalic anhydrides, respectively. H. B.

Stabilising effect of nuclear nitro-groups in furan types. 5-Nitro-2-furfuryl chloride and 5-nitro-2-furfuryl methyl ether. H. Gilman and R. R. Burtner (Iowa State Coll. J. Sci., 1932, **6**, 389—394).—5-Nitro-2-furfuryl chloride, b.p. 122—124°/6 mm., obtained from furfuryl chloride, fuming HNO$_3$, and Ac$_2$O at −25°, and 5-nitro-2-furfuryl Me ether, b.p. 114—117°/4 mm., vesicant, are described. Ch. Abs.

Furan reactions. V. Derivatives of furfuryl alcohol. C. D. Hurd and C. L. Thomas (J. Amer. Chem. Soc., 1933, **55**, 423—424).—The *monofurfuryl ether*, m.p. 223°, of 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene is prepared from the diol, furfuryl alcohol (*CPh$_3$ ether*, m.p. 137—139°), and Ac$_2$O. H. B.

Furfuraldehyde sulphoxylate. A. E. Porai-Koshitz and S. M. Itenberg (J. Appl. Chem., Russia, 1932, **5**, 761—769).—The yield by reduction (Zn dust, AcOH) of furfuraldehyde H sulphite is 80—85%; solutions retain 60% of their reducing power on storage for 11 days in closed bottles, and can be evaporated in vac. without loss of activity. Ch. Abs.

Structure of reactants and extent of acetal formation. N. Minné and H. Adkins (J. Amer. Chem. Soc., 1933, **55**, 299—309).—Equilibrium consts. for the reactions between 1 mol. of tetrahydrofurfuraldehyde (I), b.p. 144—145° (corr.)/740 mm. (convenient prep. given), MeCHO (II), and other aldehydes and numerous alcohols (5—11 mols.) in presence of a little HCl are determined or re-determined. Previous results (A., 1925, i, 785; 1927, 1172; 1928, 274; 1931, 798) are recalc. to a comparable basis. Different % conversions at equilibrium are found for *cyclo*hexanol, *sec.*-BuOH, *sec.*-octyl alcohol, and Bu$^\gamma$OH with (I) and (II) and for the methyl*cyclo*hexanols with (I), indicating that the relative affinity shown by two compounds for the formation of a given type of linking is not independent of the second component of the reaction. The effects of other factors on the extent of the reaction are discussed. The following are new: *acetaldehyde di*-n-*heptylacetal*, b.p. 153°/12 mm., and *di*(*phenylpropyl*)*acetal*, b.p. 182—185°/2 mm.; *furfuraldehyde di*-β-*ethoxyethylacetal* (I), b.p. 131—132°/2 mm.; *tetrahydrofurfuraldehyde di*-n-*butyl*-, b.p. 114°/9·5 mm., *di*-n-*amyl*-, b.p. 145°/9·5 mm., *di*-n-*hexyl*-, b.p. 167—173°/15 mm., *di*-β-*ethoxyethyl*- (II), b.p. 135°/4 mm., *di*-β-*phenylethyl*-, b.p. 195—198°/3 mm., *di*(*phenylpropyl*)-, b.p. 226°/9·5 mm., and *ditetrahydrofurfuryl*-, b.p. 163°/9·5 mm., *-acetals*; *tetrahydrofurfuryl* β-*ethoxyethyl ether*, b.p. 76°/9 mm. [formed with (II) when (I) is reduced with a Ni catalyst]. H. B.

Constitution of methyluvic acid. T. Reichstein and A. Grüssner (Helv. Chim. Acta, 1933, **16**, 6—10; cf. A., 1932, 1255).—Et α-acetyl-β-propionylpropionate and boiling 10% H_2SO_4 give (after hydrolysis with MeOH–KOH) 2-*methyl*-5-*ethyl*-3-*furoic acid*, m.p. 98·5—99° (corr.), which is identical with methyluvic acid (Dietzel, A., 1889, 593). Et acetonedicarboxylate, Et chloromethyl ketone, and NH_3 in Et$_2$O afford some Et$_2$ ester, b.p. 110—116°/0·25 mm., of 3-carboxy-4-ethyl-2-furylacetic acid, m.p. 192—193° (decomp.); the acid is decarboxylated to 2-*methyl*-4-*ethyl*-3-*furoic acid*, m.p. 105—106° (corr.). H. B.

Orientation in the furan nucleus. III. 5-Methyl-3-furoic acid. H. Gilman, R. R. Burtner, and E. W. Smith (J. Amer. Chem. Soc., 1933, **55**, 403—406).—*Me*(4) *H furan*-2 : 4-*dicarboxylate*, m.p. 132·5° (prepared by partial hydrolysis of the Me$_2$ ester with MeOH–KOH), and SOCl$_2$ in C$_6$H$_6$ give the

chloride, m.p. 83—84°, which is reduced (Rosenmund method) to *Me* 2-*aldehydofuran*-4-*carboxylate*, m.p. 93·5° (*phenylhydrazone*, m.p. 114—115°). The free acid, m.p. 158—159° (hydrazone, m.p. 145—146°), is reduced (Wolff–Kishner) to 5-*methyl*-3-*furoic acid*, m.p. 119°, decarboxylated (quinoline and Cu-bronze at 215°) to 2-methylfuran. All the methylfuroic acids are now known. H. B.

Synthesis of 2 : 3- and 3 : 4-dimethylfurans. T. REICHSTEIN and A. GRUSSNER (Helv. Chim. Acta, 1933, **16**, 28—37).—The oximino-derivative from Et 4-carbethoxy-2 : 3-dimethyl-5-furylacetate (A., 1932, 1255), EtONO, and EtOH–NaOEt is hydrolysed (aq. KOH). The product, heated with Ac_2O, gives ω-*cyano*-2 : 3-*dimethyl*-4-*furoic acid* (I), m.p. 156—157° (corr.). (I) heated with quinoline and Cu-bronze gives 5-cyano-2 : 3-dimethylfuran, b.p. 77—78°/11 mm., hydrolysed (aq. EtOH–KOH) to 2 : 3-*dimethyl*-5-*furoic acid* (II), m.p. 158·5—159° (corr.), which is decarboxylated to 2 : 3-dimethylfuran (III), b.p. 42°/115 mm. 2 : 3-*Dimethylfuran*-4 : 5-*dicarboxylic acid*, m.p. 252° (corr.; decomp.), from (I) and 50% KOH at 140—150°, is decarboxylated to 2 : 3-*dimethyl*-4-*furoic acid*, m.p. 130—131° (corr.), and thence to (III). (III), HCN, and HCl in Et_2O at −15° to 20° afford 4 : 5-dimethylfurfuraldehyde, b.p. about 87°/11 mm., oxidised by Ag_2O to (II). Reduction (H_2, Pd–$BaSO_4$, xylene) of 3-methyl-4-furoyl chloride gives 3-methylfuran-4-aldehyde, b.p. 55°/11 mm. [*semicarbazone*, m.p. 217—218° (decomp.)], the hydrazone, m.p. 44—45°, of which with NaOMe at 220° affords 3 : 4-dimethylfuran, b.p. 49°/125 mm. This is converted (as above) into 3 : 4-dimethylfurfuraldehyde, b.p. about 84°/11 mm., oxidised (Ag_2O) to 3 : 4-*dimethyl*-2-*furoic acid*, m.p. 156—158° (corr.). H. B.

Synthesis of *p*-substituted β-furyl-δ-alkyl- and β-furyl-β-aryl-propiophenones. N. MAXIM and J. ANGELESCU (Bull. Soc. chim., 1932, [iv], **51**, 1365—1370).—Addition of the Grignard reagent to furfurylideneacetophenones, as with other αβ-unsaturated ketones, occurs at the ends of the conjugated chain: ·CH:CH·CO· $\xrightarrow{X}$ ·CHR·CH_2·CO· (cf. A., 1931, 1069). The following are thus prepared in yields of 70—95% of theory; p-*tolyl* β-2-*furyl*-n-*butyl ketone*, b.p. 175°/11 mm. (*semicarbazone*, m.p. 152°); p-*tolyl* β-2-*furyl*-n-*propyl ketone*, b.p. 170°/12 mm. (*semicarbazone*, m.p. 166°); p-*tolyl* β-2-*furyl*-γ-*methyl*-n-*butyl ketone*, b.p. 188°/13 mm. (*semicarbazone*, m.p. 148°); p-*tolyl* β-2-*furyl*-δ-*methyl*-n-*amyl ketone*, b.p. 191°/12 mm.; p-*tolyl* β-2-*furyl*-β-*phenylethyl ketone*, m.p. 64°, b.p. 252°/19 mm.; p-*chlorophenyl* β-2-*furyl*-n-*butyl ketone*, b.p. 197°/10 mm. (*semicarbazone*, m.p. 118°); p-*bromophenyl* β-2-*furyl*-n-*butyl ketone*, b.p. 207°/10 mm. (*semicarbazone*, m.p. 138°). *Furfurylidene*-p-*chloro*-, m.p. 78°, and -p-*bromo*-*acetophenone*, m.p. 81°, are described. H. A. P.

Alkamine esters. Novocaine analogues. III. M. T. LEFFLER and H. C. BRILL (J. Amer. Chem. Soc., 1933, **55**, 365—370).—The following data are reported: menthylamine, b.p. 97°/56 mm.; β-menthylethylamine, b.p 70·5°/4 mm. [hydrobromide, m.p. 306° (decomp.)]; β-β′-menthylethylaminoethyl alcohol, b.p. 79°/4 mm. [hydrochloride, m.p. 274° (decomp.); *benzoate*, m.p. 155°; *tetrahydropyran*-4-*carboxylate*, m.p. 166° (*hydrochloride*, m.p. 142°, which loses HCl readily)]. The following alkamine ester *hydrochlorides* are prepared: β-4-morpholinoethyl benzoate, m.p. 205°, phenylacetate, m.p. 131°, β-phenylpropionate, m.p. 139°, cinnamate, m.p. 211°, and tetrahydropyran-4-carboxylate, m.p. 145°; β-*N*-piperidinoethyl benzoate, m.p. 176°, phenylacetate, m.p. 139°, β-phenylpropionate, m.p. 116°, cinnamate, m.p. 158°, and tetrahydropyran-4-carboxylate, m.p. 103°. The cinnamates possess the highest anæsthetic activity. H. B.

Synthesis of 4-hydroxycoumarones and *iso*tubaic (rotenic) acid. T. REICHSTEIN and R. HIRT (Helv. Chim. Acta, 1933, **16**, 121—129).—5-*iso*-Propylfurfuraldehyde (I) (A., 1932, 1255), lævulic acid, and NaOAc at 165—175° give β-5-iso*propyl*-*furfurylidenelævulic acid*, m.p. 136°, which when distilled at 250—310° (bath) in N_2 affords 4-*hydroxy*-6-*acetyl*-2-iso*propylcoumarone*, m.p. 145·5°. This with KOH at 180—190° gives a poor yield of 4-*hydroxy*-2-iso*propylcoumarone*-6-*carboxylic acid*, m.p. 200—215° (decomp.). 4-*Hydroxycoumarone*-6-*carboxylic acid*, m.p. 259° (decomp.), is obtained similarly from 4-hydroxy-6-acetylcoumarone. Furfuraldehyde (1 mol.), Na succinate (2 mols.), and Ac_2O (2 mols.) at 140° give some 4-*hydroxycoumarone*, m.p. 57·5°. 5-Methylfurfuraldehyde similarly affords 4-*hydroxy*-2-*methylcoumarone* (II), m.p. 64°, and αδ-*di*-(5-*methyl*-2-*furyl*)-$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 108° (corr.), whilst (I) yields 4-*hydroxy*-2-iso*propylcoumarone* (III), m.p. 37—39°, and αδ-*di*-(5-iso*propyl*-2-*furyl*)-$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 78° (corr.). (III) is identical with *iso*tubanol (=roteol) prepared from rotenone by Takei's method (A., 1928, 765). (II), NaOMe, and CO_2 at 180° give 4-*hydroxy*-2-*methylcoumarone*-5-*carboxylic acid*, decomp. 190—210°, whilst (III) similarly affords 4-*hydroxy*-2-iso*propylcoumarone*-5-*carboxylic acid*, m.p. about 183° (decomp.), which is identical with *iso*tubaic (rotenic) acid (Takei *et al.*, A., 1930, 609). H. B.

New method of synthesising benzopyrylium compounds. M. N. GOSWAMI and A. K. CHAKRAVARTI (J. Indian Chem. Soc., 1932, **9**, 599—600).—Phenols and their ethers heated with coumarin and $POCl_3$ on a H_2O-bath afford 2-phenylbenzopyrylium salts. Thus from resorcinol Me_2 ether is obtained 2′ : 4′-*dimethoxy*-2-*phenylbenzopyrylium ferrichloride*, m.p. 175°, identical with a specimen prepared from salicylaldehyde and dimethoxyresacetophenone by Robinson and Robertson's method (A., 1926, 1042). Resorcinol similarly yields 2′ : 4′-*dihydroxy*-2-*phenylbenzopyrylium chloride*, m.p. 185°, the alternative synthesis of which was, however, unsuccessful. J. W. B.

Synthetical experiments on the nature of betanin and related nitrogenous anthocyanins. (MRS.) A. M. ROBINSON and R. ROBINSON (J.C.S., 1933, 25—29).—3-*Nitro*-4-*methoxybenzoyl chloride*, m.p. 52°, obtained from 3-nitroanisic acid, gives with CH_2N_2 ω-*diazo*-3-*nitro*-, m.p. 139°, which loses N in AcOH to form 3-*nitro*-ω-*acetoxy*-4-*methoxyacetophenone*, m.p. 110°, reduced to the 3-*amino*-compound

(I), m.p. 119—120°, by $FeSO_4$–NH_3. 2-Hydroxy-4 : 6-dimethoxybenzaldehyde and 4-amino-ω-acetoxyacetophenone in HCl yield, after addition of $HClO_4$, *4′-amino-3-hydroxy-5 : 7-dimethylflavylium perchlorate* ($+H_2O$). (I) condenses with 2-hydroxy-4-methoxybenzaldehyde to form *3′-amino-3-hydroxy-7 : 4′-dimethoxy-* ($+2H_2O$), and with 2-hydroxy-4 : 6-dimethoxybenzaldehyde to give *3′-amino-3-hydroxy-5 : 7 : 4′-trimethoxy-flavylium perchlorate* ($+2H_2O$). *O*-Benzoylphloroglucinaldehyde and 3′-nitro-ω-acetoxy-4-methoxyacetophenone condense in dry EtOAc and HCl to *3′-nitro-3 : 7-dihydroxy-5-benzoyloxy-4′-methoxy-* ($+2H_2O$), hydrolysed to *3′-nitro-3 : 5 : 7-trihydroxy-4′-methoxy-flavylium chloride*. 4 : 6-Dihydroxy-2-benzoyloxybenzaldehyde and 4-nitro-ω-acetoxyacetophenone afford a chloride which is hydrolysed to *4′-nitro-3 : 5 : 7-trihydroxyflavylium chloride* ($+H_2O$). β-Resorcylaldehyde gives with 4-aminoacetophenone, *4-amino-7-hydroxy-*, and with 4-amino-ω-acetoxyacetophenone, *4′-amino-3 : 7-dihydroxy-flavylium chloride*. 4-Amino-ω-acetoxyacetophenone and 4 : 6-dihydroxy-2-benzoyloxybenzaldehyde afford the *hydrochloride* of the Schiff's base and *4′-amino-3 : 7-dihydroxy-5-benzoyl-* ($+2H_2O$), hydrolysed to *4′-amino-3 : 5 : 7-trihydroxy-flavylium chloride* ($+H_2O$) (II). Colour reactions of the flavylium salts are described and absorption curves of seven of them are given. (II) resembles betanin in colour of acid solution, behaviour with reagents (except HNO_2), and in stability of the coloured flavylium salt towards excess HCl. The NO_2-substituted salts illustrate the bathochromic effect of NO_2 in the series.

F. R. S.

Synthesis of 2-substituted 1-methylpyrrolines. L. C. Craig (J. Amer. Chem. Soc., 1933, **55**, 295—298; cf. Lukes, A., 1930, 1296).—Grignard reagents (2 mols.) react with 1-methylpyrrolidone (1 mol.) to give 2-substituted 1-methyl-Δ^2-pyrrolines; the following are prepared: 2-phenyl-, b.p. 105—109°/11 mm. (*picrate*, m.p. 139°; *oxalate*, m.p. 138°); 2-*n*-*butyl*-, b.p. 86—87°/30 mm. (*picrate*, m.p. 66°); 2-*n*-propyl-, b.p. 176—177°; 2-ethyl-, b.p. 148—149° (*picrate*, m.p. 114°), and 2-methyl- (I), b.p. 130—131°. Distillation of (I) probably causes reversible polymerisation to a dimeride. H. B.

Thiocyano- and thio-pyrroles and pyrrole disulphides. P. Pratesi (Atti R. Accad. Lincei, 1932, [vi], **16**, 443—448).—When treated with NH_4SCN and Br, Et 2 : 4-dimethylpyrrole-3-carboxylate yields *Et 5-thiocyano-2 : 4-dimethylpyrrole-3-carboxylate*, m.p. 169·5°. *Et 3-thiocyano-2 : 4-dimethylpyrrole-5-carboxylate*, m.p. 114°, similarly obtained gives *Et 3-thiol-2 : 4-dimethylpyrrole-5-carboxylate*, m.p. 140° (HgCl *derivative*, m.p. 243—245°; Hg *derivative*, m.p. 257—258°), on reduction with Zn and AcOH, and *bis-2 : 4-dimethyl-5-carbethoxy-3-pyrryl disulphide*, m.p. 234°, when either boiled in EtOH containing animal C or reduced with Na and EtOH. A *dithiolcyanopyrrole*, m.p. 114°, was alone obtained in an attempt to thiocyanate pyrrole completely in MeOH at −10°. The CNS derivatives are highly stable and serve for identifying pyrroles. T. H. P.

Conversion of 2 : 6-dichloro-4-cyanopyridine and 2 : 6-dibromo-4-cyanopyridine into dihalogenopyridylmethylamines. J. P. Wibaut and J. Overhoff (Rec. trav. chim., 1933, **52**, 55—60).—These compounds treated with $SnCl_2$ and HCl yield 2 : 6-*dichloro-4-pyridylmethylamine*, m.p. 70° (*Ac* derivative, m.p. 102°; corresponding *-methyl alcohol*, m.p. 131—132°), and 2 : 6-*dibromo-4-pyridylmethylamine*, m.p. 92—93° (*Ac* derivative, m.p. 116—118°; corresponding *-methyl alcohol*, m.p. 111—112°), respectively.

[With P. J. Hubers.] 2 : 6-Dihydroxypyridine-4-carboxylamide with $POCl_3$ gives only 27% of 2 : 6-dichloro-4-cyanopyridine (cf. A., 1929, 704).

E. W. W.

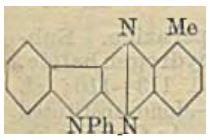
Reaction between 2-picoline and aromatic aldehydes. B. D. Shaw and E. A. Wagstaff (J.C.S., 1933, 77—79).—Formation of stilbazoles from 2-picoline and aromatic aldehydes proceeds best with Ac_2O as condensing agent and appears to take place according to $C_5H_4N{\cdot}Me+CHO{\cdot}C_6H_4R \overset{a}{\rightleftharpoons} C_5H_4N{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_4R$ (I)$\rightarrow C_5H_4N{\cdot}CH{:}CH{\cdot}C_6H_4R$, stage (*a*) being the rate-determining factor. Comparative rates of reaction for PhCHO and methyl- and nitro-benzaldehydes are given, the former being least and the latter most reactive. (I) is formed at 130—150° in presence of H_2O, and when heated at 140—200° with H_2O is in part converted into the aldehyde and 2-picoline. The following are described: 2-nitro-2-stilbazole, m.p. 101° (*nitrate*, m.p. 148°; picrate, m.p. 220°); *4′-methyl-2-stilbazole*, m.p. 87°; *4′-methyl-2-stilbazolealkine*, m.p. 96°; *3′-nitro-3-stilbazolealkine*, m.p. 98°; 3′-nitro-2-stilbazole, m.p. 129°; and 4′-nitro-2-stilbazole, m.p. 136° [sulphate, m.p. 274°; nitrate, m.p. 155° (decomp.); picrate, m.p. 272°]. F. R. S.

Nitration of β-phenylethylpyridines and related compounds. I. B. D. Shaw and E. A. Wagstaff (J.C.S., 1933, 79—83).—Nitration of 2-β-phenylethylpyridine (*nitrate*, m.p. 91°) gives 16·0% of 2-β-o-, m.p. 36° (picrate, m.p. 156°; methiodide, m.p. 184°), 64·5% of 2-β-p-, m.p. 96° [picrate, m.p. 171°; methiodide, m.p. 198°; perchlorate, m.p. 150°; nitrate, m.p. 138° (decomp.)], and 3·4% of 2-β-m-*nitrophenylethylpyridine* (I), m.p. 76°, isolated as the picrates. Reduction (P, HI) of the corresponding nitro-2-stilbazoles gives 2-β-o-, m.p. 61° (hydrobromide, m.p. 295°), 2-β-m-, m.p. 72°, and 2-β-p-*aminophenylethylpyridine*, m.p. 57° (mononitrate, m.p. 224°). Nitration of the Ac derivative of the *p*-compound yields 2-(β-*3′-nitro-4′-aminophenylethyl*)-*pyridine*, m.p. 150°, deaminated to (I). 2-Stilbazole forms a *nitrate* ($+2H_2O$), m.p. 89°, anhyd. *salt*, m.p. 123° (decomp.), methosulphate, m.p. 160°, and picrate, m.p. 212°. Nitration of 2-stilbazole gives 40·1% *o*- and 49·0% *p*- with no *m*-NO_2-derivative (thermal analysis), the *op*-ratio decreasing with increase of concn. of HNO_3 or decrease of the quantity of acid. Further nitration of 2′-(or 4′-)nitrostilbazole gives the 2′ : 4′-$(NO_2)_2$-compound, whilst the 3-NO_2-compound affords *3′ : 4′-dinitro-2-stilbazole*, m.p. 168°. *2-Phenylacetylenylpyridine nitrate*, m.p. 85° (decomp.), is nitrated in H_2SO_4 to 28·7% of 2-o-, m.p. 55° [*picrate*, m.p. 175° (decomp.)], 62·7% of 2-p-, m.p. 157° [picrate, m.p. 206° (decomp.)], and 0·6% of 2-m-*nitrophenyl-*

acetylenylpyridine, m.p. 93° (picrate, m.p. 199°) (obtained from 3'-nitro-2-stilbazole dibromide and KOH). F. R. S.

Condensations of isatin with acetone by the Knoevenagel method. F. BRAUDE [with H. G. LINDWALL] (J. Amer. Chem. Soc., 1933, **55**, 325—327).—Isatin (I), $COMe_2$, and $NHEt_2$ give 3-*hydroxy*-3-*acetonyloxindole* (II), m.p. 166—167° (decomp.) [*N-Me* derivative (III), m.p. 145°, prepared similarly from *N*-methylisatin], dehydrated by EtOH–conc. HCl to 3-*acetonylideneoxindole*, m.p. 168—171° [*N-Me* derivative, m.p. 120—122°, formed similarly from (III)]. (II) heated with aq. EtOH–KOH for 1 hr. gives (I); after 8 hr., 2-methylcinchoninic acid [the Pfitzinger synthesis (A., 1898, i, 207) of this is considered not to involve (II)] results. (I) (1 mol.), (II) (1 mol.), and EtOH–$NHEt_2$ give *di*-(3-*hydroxy*-3-*oxindolylmethyl*) *ketone*, m.p. 212—214° (decomp.) [*oxime*, m.p. 158—160°; *NN'-Me*$_2$ derivative, m.p. 178—181° (decomp.), from (III) and *N*-methylisatin], also formed from (I) (2 mols.), $COMe_2$ (1 mol.), and EtOH–$NHEt_2$. H. B.

Derivatives of *N*-substituted oxindoles and isatins. R. STOLLE [with H. HECHT and W. BECKER] (J. pr. Chem., 1932, [ii], **135**, 345—360).—1-Ethyloxindole (I) is unaffected by alkali at 180°. Condensation of (I) or 1-phenyloxindole (II) (*hydroxymethylene* derivative, m.p. 194°) with the appropriate aldehydes in alkaline EtOH gives *phenyl-*, m.p. 194° (changes colour, 185°), and p-*anisyl-di*-(1-*ethyloxindolyl*)*methane*, m.p. 170°, and *phenyl-*, m.p. 220°, p-*anisyl-*, m.p. 213°, p-*dimethylaminophenyl-*, m.p. 221° (changes colour, 185°), and o-*chloro*-p-*diethylaminophenyl-di*-(1-*phenyloxindolyl*)*methane*, m.p. 170°. Condensation of (I) or (II) with aldehydes in presence of piperidine gives 3-p-*dimethylaminobenzylidene*-1-*ethyloxindole*, m.p. 154° (? second form, m.p. 134°), and 3-*anisylidene-*, m.p. 139°, and 3-p-*dimethylaminobenzylidene*-*phenyloxindole*, m.p. 176° (? second form, m.p. 186°), reduced to p-*dimethylaminobenzylphenyloxindole*, m.p. 112°. (II) with PhN_2Cl gives 1-*phenylisatinphenylhydrazone*, m.p. 147°, also obtained by the usual methods. 1-Phenylisatin (III) (*semicarbazone*, m.p. 217°) with 2 mols. of (II) and NaOEt gives 3 : 3-di-(1-phenyloxindolyl)-1-phenyloxindole, m.p. 290° (decomp.), also obtained, besides diphenyl*iso*indigotin, by the action of nitrosodimethylaniline and NaOEt on (II) (cf. A., 1930, 1593). *Chloroacet*-β-*naphthylanilide*, m.p. 67°, would not give an oxindole. *Chloroacetdi*-β-*naphthylamide*, m.p. 122°, with $AlCl_3$ in CS_2 gives 1-β-*naphthyl*-4 : 5-*benzo-oxindole*, m.p. 203°, converted by the action of nitrosodimethylaniline in AcOH into 1-β-naphthyl-4 : 5-benzoisatin. Interaction of β-naphthylethylamine and oxalyl chloride gives 1-ethyl-4 : 5-benzoisatin, and a little *oxaldi*-(β-*naphthylethyl*)*amide*, m.p. 252°. (III) with *o*-tolylenediamine hydrochloride in AcOH gives 1-*methyl*-9-*phenylindophenazine* (annexed formula), m.p. 204°, whilst with $NPhMe_2$ and $ZnCl_2$ it gives 1-*phenyl*-3 : 3-*bis*-(p-*dimethylaminophenyl*)*oxindole*, m.p. 192°. (III) with MgPhBr gives the *anhydride*, m.p. 161°, of 1 : 2 : 3-triphenyl-2 : 3-dihydroxyindolin, and a *substance*, m.p. 238°. Distillation of (II) with Zn gives 1-phenylindole. A. A. L.



Mode of formation of quinoline derivatives from carboxyanilides and transformations of acetanilide imidochloride. A. HEYMONS and W. ROHLAND (Ber., 1933, **66**, [*B*], 130—138; cf. A., 1931, 237).—The action of PCl_5 on NHPhAc in CCl_4 gives the corresponding imide chloride, which, when heated after removal of solvent, rapidly passes into diphenylchlorovinylacetamidine (I), thus disproving the hypothesis of Backeberg (A., 1932, 623) that (I) results from the amide chloride. Ring closure does not take place when the imide chloride from $CH_2Cl{\cdot}CO{\cdot}NHPh$ is warmed, but 3-chloro-4-anilino-2-chloromethylquinoline is readily produced when the solution in $POCl_3$ is saturated with HCl, consequently from the amide chloride. The production of 4-anilino-2-methylquinoline (II) does not take place similarly. Attempts to effect ring closure of (I) by HCl in $POCl_3$ yielded much resin, NHPhAc, diphenylacetamidine, and the base $NPh{:}CMe{\cdot}NPh{\cdot}C(:CH_2){\cdot}NPhAc$ (III), consistently obtained in small amount as by-product of the prep. of (II) from PCl_5 and NHPhAc. Thermal decomp. of (I) in PhMe affords acetanilide imidochloride and the *compound* $C_{24}H_{22}N_3Cl$, m.p. about 190° (decomp.), hydrolysed to (III) and converted by conc. HCl into diphenylacetamidine (IV), NH_2Ph, and AcOH and by EtOH into (IV), NH_2Ph, and EtOAc. (III) is transformed by dry HCl in a neutral medium into the hydrochloride of (IV) and $NPhAc_2$. The following scheme is suggested:

$2NPh{:}CMe{\cdot}NPh{\cdot}C(:CH_2){\cdot}Cl \longrightarrow$
$[NPh{:}CMe{\cdot}NPh{\cdot}C(:CH_2){\cdot}NPh{\cdot}C(:CH_2){\cdot}NPh{\cdot}C(:CH_2){\cdot}Cl]$
$\longrightarrow NPh{:}CMe{\cdot}NPh{\cdot}C(:CH_2){\cdot}NPh{\cdot}C(:CH_2){\cdot}Cl +$
$CH_2{:}CCl{\cdot}NHPh \longrightarrow NPh{:}CMe{\cdot}NPh{\cdot}C(:CH_2){\cdot}NPhAc$
$\longrightarrow NPh{:}CMe{\cdot}NHPh,HCl + CH_2{:}CCl{\cdot}NPhAc \longrightarrow$
$NPhAc_2$.

The final product of the action of $POCl_3$ on (I) is β-*anilinocrotonylacetdiphenylamidine* (V), $NPh{:}CMe{\cdot}NPh{\cdot}CO{\cdot}CH{:}CMe{\cdot}NHPh$, m.p. 117° [*picrate*, m.p. 158°; *chloroplatinate*, m.p. 201—203° (decomp.)], which yields the *dihydro*-base, $C_{24}H_{25}ON_3$, m.p. 146°. (V) is hydrolysed by conc. HCl to NHPhAc, NH_2Ph, and AcOH, affords an amorphous compound and (II) when distilled, and yields an additive *product*, m.p. 256°, with $POCl_3$, hydrolysed to NHPhAc, NH_2Ph, and $NHPh{\cdot}CO{\cdot}CH_2Ac$. The exceptional position of NHPhAc among anilides is attributed to the transition from amide- to imide-chloride being so rapid that condensation to a quinoline derivative cannot occur and ring closure is possible only under extreme conditions through the chlorovinyl base. H. W.

An extension and a limitation of the thiocyanate method for the preparation of 2-thiohydantoins. B. H. NICOLET (J. Biol. Chem., 1933, **99**, 429—433).—αα-Bisacetamidopropionic acid is converted by NH_4CNS in Ac_2O–AcOH into the 1-*Ac* derivative, m.p. 230°, of 5-*acetamido*-5-*methyl*-2-*thiohydantoin*, m.p. 248° (decomp.), obtained by hydrolysis with *N*-NaOH (cf. A., 1912, i, 53). 5-*Benzamidomethyl*-2-*thiohydantoin*, m.p. 255° (decomp.), and its 1-*Bz* derivative, m.p. 211—212° (decomp.), are similarly obtained from αβ-bisbenzamidopropionic acid, but

no thiohydantoin formation occurs with the corresponding αα-acid or its azlactone (cf. A., 1913, i, 1105), this failure being ascribed to the stabilising of the azlactone ring on the ordinary Thorpe–Ingold valency deflexion hypothesis. J. W. B.

Formation and stability of polybromide derivatives of heterocyclic compounds. I. Bromination of diphenyl-ψ-thiohydantoin and its o-tolyl homologue. M. O. Farooq and R. F. Hunter (J. Indian Chem. Soc., 1932, 9, 545—552).—Treatment of 2-anilo-4-keto-3-phenyltetrahydrothiazole (diphenyl-ψ-thiohydantoin) with Br in $CHCl_3$ at 0° affords a *hydropentabromide* (I), m.p. 161—163° (decomp. after loss of Br at 140°), which loses Br when exposed to air, giving a *hydrotribromide*, m.p. 145—146° (decomp.). Both Br compounds are converted by H_2SO_3 into 2-*anilo*-4-*keto*-3-p-*bromophenyltetrahydrothiazole*, m.p. 175° [also obtained by heating NHPh·CS·NH·C_6H_4Br, $CH_2Cl·CO_2H$, and C_5H_5N in EtOH, and converted by Br and HBr in AcOH into (I)], which similarly yields an unstable *octabromide*, m.p. 161—162°, converted by H_2SO_3 into a Br_2-derivative, m.p. 121°, and by excess of aq. KI into 2-*anilo*-4-*keto*-3-(2′ : 4′-*dibromophenyl*)-*tetrahydrothiazole*, m.p. 119—120°. By similar methods ditolyl-ψ-thiohydantoin affords an unstable *hydroheptabromide*, m.p. 120—121° (decomp.) [converted by loss of Br into a *hydrotribromide*, m.p. 132° (decomp.)], of 2-o-*tolylimino*-4-*keto*-3-p(?)-*bromo*-o-*tolyltetrahydrothiazole* (II), m.p. 129°, which is obtained by reduction with H_2SO_3. o-Tolylthiocarbimide and p-bromo-o-toluidine afford 3-o-*tolyl*-(4-*bromo*-2-*methylphenyl*)*thiocarbamide*, m.p. 152°, from which, however, (II) could not be synthesised. The constitutions of these derivatives are discussed. J. W. B.

Nitrogenous glucosides. II. Synthesis of glucosidoureides. K. M. Haring and T. B. Johnson (J. Amer. Chem. Soc., 1933, 55, 395—402).—Tetra-acetyl-d-glucosethiocarbimide (modified prep. given; cf. Fischer, A., 1914, i, 662) and $CO_2Et·CH_2·NH_2$,HCl in $CHCl_3$–C_5H_5N give *Et tetra-acetyl*-d-*glucosidothiohydantoate* (I), m.p. 151—152·5°, $[\alpha]^{20}$ +6° in $CHCl_3$, deacetylated by cold EtOH–HCl to the *Et* ester (+EtOH), melts partly at 119—121° (decomp.) and liquifies completely at 154—155°, $[\alpha]_D^{20}$ −31·3° in H_2O, m.p. (EtOH-free) 152—155° (decomp. about 162°) [*hydrochloride*, m.p. 73—75° (decomp.)], of d-*glucosidothiohydantoic acid* (II), decomp. 180·5—181°, $[\alpha]_D^{20}$ −36·1° in H_2O. The *K* salt, decomp. 137—141°, of (II) and hot 6*N*-HCl give N-1-d-*glucosido*-2-*thiohydantoin*, m.p. 224—225° (decomp.) (darkens at about 216°), $[\alpha]_D$ +22·8° in H_2O, and a substance (does not contain a glucose residue), decomp. 221—231° (darkens at about 199°). (I) and aq.-EtOH–$AgNO_3$ afford *Et tetra-acetyl*-d-*glucosidohydantoate*, m.p. 149—149·5°, $[\alpha]_D^{20}$ −3° in $CHCl_3$, hydrolysed by EtOH–KOH to d-*glucosidohydantoic acid* (III), m.p. 169·5—170° (decomp.), $[\alpha]_D^{27}$ −25·8° in H_2O. The *K* salt of this and hot 6*N*-HCl give N-1-d-*glucosidohydantoin* (IV), decomp. 270—271°, $[\alpha]_D^{20}$ +5° in H_2O, and a substance, m.p. 178—194° (decomp.). (III) and (IV) readily reduce Fehling's solution; they resemble glucosido-amino-acids and -peptides rather than glucosido-pyrimidines and -purines. H. B.

Hydroxyallantoin. (Mlle.) A. Pinguet (Compt. rend., 1933, **196**, 112—114).—Condensation of parabanic acid and $CO(NH_2)_2$ by Grimaux's method (A., 1880, 105) gives (probably) $(·CO·NH·CO·NH_2)_2$ (I) and hydroxyallantoin (II), $CO<^{NH·CO}_{NH·C(OH)·NH·CO·NH_2}$, decomp. > 270° without melting (cf. Ponomarev, A., 1885, 760), separable by rapid dissolution of the mixture in dil. NaOH at 0° and neutralisation with dil. AcOH, whereby the Na salt of (II) separates. (II) is repptd. from its solution in conc. H_2SO_4 by H_2O, gives the biuret reaction, is hydrolysed (not quant.) by alkali to $H_2C_2O_4$ and $CO(NH_2)_2$, and is attacked slowly by NaOBr. (I) is repptd. as a gelatinous mass from its solution in conc. H_2SO_4, does not give the biuret reaction, is hydrolysed (quant.) by alkali, and gives N_2 (quant.) with NaOBr. H. B.

Autoxidation of dialuric acid. G. M. Richardson (Biochem. J., 1932, **26**, 1959—1977).—The rate of atm. oxidation of dialuric acid (I) has been determined with reference to p_H, temp., concn. of (I), and influence of catalysts. The reactants combine in equimol. proportions. In presence of Fe the proportion of O is halved. Alloxantin behaves as (I) + alloxan. S. S. Z.

1 : 3-Dimethylbarbituric acid as reagent for aldehydes. S. Akabori (Ber., 1933, **66**, [*B*], 139—143).—1 : 3-Dimethylbarbituric acid (I) reacts rapidly with furfuraldehydes and aromatic aldehydes in boiling H_2O or H_2O–EtOH giving cryst. compounds suited to identification of the aldehydes. The following 2-substituted 1 : 3-dimethylbarbituric acids are described: *benzylidene*-, m.p. 164—165°; *cinnamylidene*-, m.p. 196—197°; *anisylidene*-, m.p. 148·5—149°; p-*methylbenzylidene*-, m.p. 142—142·5°; *vanillylidene*-, m.p. 222·5—223°; *piperonylidene*-, m.p. 201·5—202°; m-, m.p. 233—234°, and p-, m.p. 297—298°, -*hydroxybenzylidene*-, o-, m.p. 156·5—157°, and p-, m.p. 196—196·5°, -*nitrobenzylidene*-; *furfurylidene*-, m.p. 195—196°; 5′-*methylfurfurylidene*-, m.p. 172—172·5°; 5-*hydroxymethylfurfurylidene*-, m.p. 181—182°; 5-*ethoxymethylfurfurylidene*-, m.p. 112·5—113°; *furylacrylidene*-, m.p. 223—224°; β-*indolylidene*-, m.p. 291—292°; *citrylidene*-, m.p. 101—101·5°. (I) and o-OH·C_6H_4·CHO give a *substance* $C_{13}H_{12}O_4N_2$, m.p. 177—178°, passing when cryst. repeatedly from BuOH into *salicylidenebisdimethylbarbituric anhydride*, m.p. 236—237°; o-vanillin gives similar *products*, $C_{14}H_{14}O_5N_2$, m.p. 180—181°, and $C_{20}H_{20}O_7N_4$, m.p. 237—238°. Sensitive colour reactions of furfuraldehyde, methyl- and hydroxymethyl-furfuraldehyde with barbituric acid (II), (I), NH_2Ph acetate (III), (II) and NH_2Ph, (II) and (III) are recorded. H. W.

One-sided substitution in piperazine. Substituting agents which eliminate hydrogen halide. K. R. Jacobi (Ber., 1933, **66**, [*B*], 113—116; cf. Moore and others, A., 1929, 331).—Monosubstituted piperazines are prepared with AcCl, Ac_2O, $ClCO_2Et$, BzCl, or p-C_6H_4Me·SO_2Cl if the p_H of the mixture

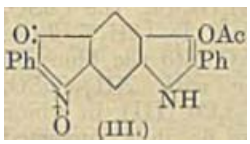
is maintained at 2·75. With smaller p_H hydrolysis of the substituting agent occurs, whereas disubstituted products are formed in solutions of higher p_H (exclusively at p_H 5). The nature of the substituent is immaterial. All the substituents are readily removed by dil. alkali. Thus are prepared: *benzoylpiperazine*, m.p. about 75° [*hydrochloride*, m.p. 274° (decomp.)]; *acetylpiperazine*, m.p. 52° (*hydrochloride*, m.p. 181°); carbethoxypiperazine, b.p. 121°/12 mm. (*hydrochloride*, m.p. 145° after softening at 138°); *p-toluenesulphonylpiperazine hydrochloride*, m.p. 175° after softening at 168°. H. W.

Glyoxaline group. V. Some benziminazole derivatives and the opening of the glyoxaline ring. B. Oddo and P. Ingraffia (Gazzetta, 1932, **62**, 1092—1100).—Benziminazole with MgEtBr forms Mg benziminazolyl bromide, which with Ac_2O yields 1-acetylbenziminazole (*picrate*, m.p. 158°; *iodate*, explodes 205°), with EtCOCl and Pr$^{\alpha}$COCl yields 1-*propionyl-* and 1-*butyryl-benziminazole*, m.p. 125° (*picrate*, m.p. 228°) and 45° (*picrate*, m.p. 145°), respectively, and, with $ClCO_2Et$, *Et benziminazole-1-carboxylate*, m.p. 107° (*picrate*, m.p. 178°; *perchlorate*, explodes 145°); with BzCl the main product is *o*-$C_6H_4(NHBz)_2$, with 1-*benzoylglyoxaline*, m.p. 215° (*picrate*, m.p. 224°; *perchlorate* and *iodate*, exploding at about 130° and 200°, respectively). E. W. W.

Synthesis of glyoxaline derivatives from α-amino-acids. I. Synthesis of deaminohistidine and the constitution of ergothioneine. S. Akabori. **II. Synthesis of glyoxaline derivatives and constitution of pilocarpine.** S. Akabori and S. Numano (Ber., 1933, **66**, [*B*], 151—158, 159—165).—I. Treatment of glycine with EtOH–HCl at 100° followed by partial removal of the solvent after addition of C_6H_6, addition of ice, and reduction with Na–Hg in acid solution affords the aldehyde, converted directly by NH_4CNS into 2-thiolglyoxaline, m.p. 225—227°. 2-Thiol-4-methylglyoxaline, m.p. 245—246°, is derived similarly from *dl*-alanine. Et glutamate hydrochloride (prepared from pyrrolidonecarboxylic acid with EtOH–HCl) when reduced and treated with NH_4CNS affords β-2-*thiolglyoxaline-4-propionic acid* (I) +H_2O, m.p. 205—206·5°, oxidised by $FeCl_3$ or H_2O_2 to deaminohistidine [β-glyoxaline-4-propionic acid], m.p. 206—208° [chloroplatinate, m.p. 208—209°; *Et* ester, b.p. 143—157°/0·05—0·07 mm., and its oxalate, m.p. 159—160°; hydrazide (II), m.p. 142—143°]. (II) is transformed by BuO·NO and EtOH–HCl into histamine. Reduction of the β-thiolglyoxaline-4-acrylic acid from ergothioneine (III) yields (I), thus showing the SH group of (III) to be in position 2.

II. The following *-glyoxalines* are prepared by reduction of the requisite NH_2-acid ester by Na–Hg and treatment of the product with KCNS or NH_4CNS: 2-*thiol*-4-iso*butyl-*, m.p. 183—184°, whence 4-iso*butyl-*, b.p. 143—144·5°/6 mm., m.p. 72—73°, from leucine; 2-*thiol*-4-*benzyl-*, m.p. 221—222°, whence 4-*benzyl-*, b.p. 145—148°/0·12—0·15 mm., m.p. 84—85°, from phenylalanine; 2-*thiol*-4-n-*amyl-*, m.p. 114—115·5°, whence 4-n-*amyl-*, b.p. 188—188·5°/16 mm., m.p. 44—46°, from α-amino-*n*-heptoic acid, m.p. 291—292° (*Et* ester, b.p. 82—85°/5 mm.); 2-*thiol*-3-*methyl*-4-n-*amyl-*, m.p. 143—144°, whence 3-*methyl*-4-n-*amyl-* (I), b.p. 152—152·5°/13 mm. (*picrate*, m.p. 130—130·5°), from α-*methylamino*-n-*heptoic acid*, m.p. 260—262° in sealed capillary (*Et* ester, b.p. 80—82°/5 mm.). (I) is closely similar to the product obtained by Jowett (J.C.S., 1904, **83**, 447), but identity is not regarded as established. H. W.

Isatogens. X. Synthesis of an isatogen and indoxyl of the benzopyrrole series. P. Ruggli and A. Zimmermann (Helv. Chim. Acta, 1933, **16**, 69—79).—The 3-O-*Ac* derivative (I), m.p. 224°, of 6-nitro-2-phenyl-5-α-chlorostyrylindoxyl (II), m.p. 207—208° (rapid heating) (A., 1932, 175), is, unlike (II), sensitive to light. Exposure of a solution of (I) in C_5H_5N to sunlight gives the *isatogen* (III), m.p. 242°, converted by Zn dust and Ac_2O–AcOH into 3 : 5-*diacetoxy*-2 : 6-*diphenylbenzodipyrrole*, m.p. 243—244°. 6-Nitro-2-phenyl-5-styrylisatogen (*loc. cit.*) is reduced by NH_2·NHPh in EtOH to 6-*nitro*-2-*phenyl*-5-*styrylindoxyl*, m.p. 207° (decomp.) (darkens above 160° and then sinters) [3-O-*Ac* derivative (IV), orange, m.p. 203°, yellow (+0·75 C_6H_6), m.p. 203°], reduced (Zn dust, AcOH) to 6-amino-2-phenyl-5-styrylindoxyl [ON-Ac_2 derivative (V), m.p. 276°; 3-O-*Ac* derivative, m.p. 266—267° (decomp.), prepared by reduction (Zn dust, AcOH) of (IV) and acetylated further to (V)]. H. B.



(III.)

Benzoyl derivatives of indigotin. H. de Diesbach and H. Lempen (Helv. Chim. Acta, 1933, **16**, 148—154; cf. Hope and Richter, this vol., 75).—Fusion of Ciba-yellow with NaOH at 300—310° gives BzOH, *o*-$C_6H_4(CO_2H)_2$, (mainly) a *compound* (I), $C_{15}H_{10}O_2N_2$, m.p. > 350°, a *base* (II), $C_{14}H_{10}N_2$, m.p. 323—325°, and bases which are sol. in acids and in alkalis. (I) and PCl_5 in $PhNO_2$ give a *dichloride*, $C_{15}H_8N_2Cl_2$, m.p. 210°; with boiling HNO_3 (*d* 1·4), a *compound*, $C_{13}H_8O_6N_4$, m.p. > 320°, results. (II) and HNO_3 (*d* 1·4) similarly give a *compound*, $C_{14}H_8O_5N_4$, m.p. > 350°, whilst oxidation (CrO_3, AcOH) affords an *acid*, $C_{12}H_8O_5N_2$, m.p. 305°. Hochst-yellow R (III), $C_{30}H_{18}O_4N_2$, prepared from indigotin, BzCl, and $ZnCl_2$ or from the "Dessoulavy compound" $C_{30}H_{17}O_3N_2Cl$ (IV) and conc. H_2SO_4, when fused with NaOH gives BzOH, *o*-$C_6H_4(CO_2H)_2$, and two bases (one of which is $C_{15}H_{10}O_3N$, m.p. 248°); Hochst-yellow U, $C_{23}H_{12}O_2N_2$, from (III) or (IV) and conc. H_2SO_4 at 100° (bath), gives analogous results. H. B.

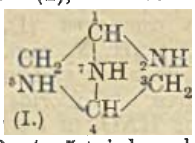
Natural and synthetic indican. A. Robertson and R. B. Waters (J.C.S., 1933, 30).—Synthetic indican (A., 1927, 960) has now been shown to be identical with a natural specimen. Acetylation of indican (both synthetic and natural) with Ac_2O and NaOAc affords a second form of the Ac_5 compound (*B*), m.p. 112°, $[\alpha]^{18}_{5461}$ −47·11° in $COMe_2$, which can be transformed into the (*A*) form, m.p. 147° (*loc. cit.*). Me 3-*O*-tetra-acetyl-β-glucosidoxyindole-2-carboxylate has $[\alpha]^{18}_{5461}$ −46·67° in $COMe_2$, and 3-β-glucosidoxyindole-2-carboxylate, −48·41° in H_2O. F. R. S.

Cyanine dyes. IV. Penta- and hepta-methinecyanine. T. Ogata (Proc. Imp. Acad. Tokyo, 1932, **8**, 421—423; cf. A., 1932, 756).—Trimethyl-

indolenium methiodide and quinaldine and lepidine ethiodides when treated with propenedianil yield 1 : 1′ : 3 : 3 : 3′ : 3′-*hexamethylpentamethineindocyanine iodide*, m.p. 205°, and 1 : 1′-*diethyl*-2 : 2′- and 1 : 1′-*diethyl*-4 : 4′-*pentamethinequinocyanine iodides*, m.p. 270° and 158°, respectively (both decomp.). Similarly, pentadienedianil in presence of suitable condensing agents yields the corresponding *heptamethine* derivatives, m.p. 185—186°, 235° (decomp.), and 165° (decomp.), respectively. Increase of the polymethine chain is accompanied by a displacement of the sensitisation max. towards the infra-red. F. O. H.

Complex salts of 1 : 2 : 4-triazole. II. I. De Paolini and C. Goria (Gazzetta, 1932, **62**, 1048—1053).—Whilst the $CuSO_4$ salt (A., 1931, 1310) of 1-phenyl-1 : 2 : 4-triazole treated with 20% HCl gives the *salt* $[(C_2H_2PhN_3)_2Cu(H_2O)_2]Cl_2$, the $CuSO_4$ salt of triazole yields a green salt (I), $C_2H_3N_3Cl_2Cu$. This is slowly converted by H_2O into the blue *salt* (II), $C_2H_2N_3Cu,2H_2O$. Triazole with NH_3–$CuSO_4$ gives a violet-blue *salt*, $(C_2H_2N_3)_2Cu$ (III), in which Cu probably has a co-valency of 6; it is converted by HCl into (II), re-converted into (III) by aq. NH_3. Formulæ are suggested for (I) and (II). E. W. W.

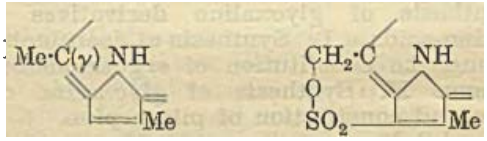
Heterocyclic compounds obtained by interaction of benzoins and hydrazine hydrochloride. I. J. Van Alphen (Rec. trav. chim., 1933, **52**, 47—54).—The compound $C_{28}H_{22}N_2$, m.p. 261°, obtained from benzaldazine (A., 1912, i, 146), is prepared, together with the latter and 2 : 3 : 5 : 6-tetraphenylpyrazine, by heating benzoin with N_2H_4,2HCl in EtOH. It is regarded as a derivative of (I), named "trimidine," viz., 1 : 3 : 4 : 6-*tetraphenyl*-Δ^2-[*dehydro*]*trimidine* (5 : 7-*Ac*$_2$ and 5 : 7-*Bz*$_2$ derivatives, m.p. 151° and 198°, respectively). It is not obtained by heating benzoin, benzil, and NH_3, which give 2 : 4 : 5-triphenylglyoxaline and tetraphenylpyrazine.


(I.)

E. W. W.

Heterocyclic compounds. II. A. C. Sircar and I. B. Pal (J. Indian Chem. Soc., 1932, **9**, 527—532).—By fusion of 2 : 3-diaminoquinoxaline (I) (improved prep. described) with the appropriate acid anhydride are obtained: o-*benzoylene*-, m.p. above 300°, o-*naphthoylene*-, *camphoroylene*-, m.p. 280°, and o-*diphenoylene*-2 : 3-*quinoxalinoglyoxaline*, all of the type $C_6H_4<\begin{matrix}N:C\cdot N:C-R\\N:C-N-CO\end{matrix}$. Condensation of (I) with the appropriate aldehyde in C_5H_5N affords 4 : 5-*quinoxalino*-2-*phenylglyoxaline*, and its 3′- and 4′-NO_2-, 2′-*OH*-, 2′ : 4′-(OH_2)-, 4′-*MeO*-, and 4′-NMe_2-derivatives, and 4 : 5-*quinoxalino*-2-*furfurylglyoxaline*, all not melting < 300° and all of type $C_6H_4<\begin{matrix}N:C\cdot NH\\N:C-N\end{matrix}>CR$. Similar condensations in the absence of a solvent yield *N*-substituted glyoxalines and thus are obtained: 4 : 5-*quinoxalino*-1-*benzyl*-, m.p. > 300°, and -1-o-*hydroxybenzyl*-, m.p. > 300°, -2-*phenyl*- and 4 : 5-*quinoxalino*-1-p-*methoxybenzyl*-2-p-*anisyl-glyoxaline*, m.p. 243—245°. J. W. B.

Chlorophyll. XXIX. Synthesis of four isomeric phylloporphyrins. H. Fischer, W. Siedel, and L. Le Thierry d'Ennequin (Annalen, 1933, **500**, 137—202).—γ-Phylloporphyrin XV (I) [*Me* ester, m.p. 230°; *Et* ester, m.p. 240° (*Cu* salt, m.p. 254°), identical with the "analytical" *Et* ester, m.p. 238° (*Cu* salt, m.p. 251°)] is obtained in 1·37—3·12% yield by fusion of the following pairs of pyrromethenes with methylsuccinic acid at 150°: (i) 3 : 5 : 3′-trimethyl-4-ethyl-4′-β-carboxyethylpyrromethene hydrobromide (II) and 5 : 4′-dibromo-4 : 3′-dimethyl-3 : 5′-diethylpyrromethene hydrobromide (III) [the *perbromide*, $C_{15}H_{19}N_2Br_4$, m.p. > 300°, of which is formed from 5-carboxy-4 : 3′-dimethyl-3 : 5′-diethylpyrromethene hydrobromide and Br in HCO_2H]; (ii) (II) and the product from the exhaustive bromination of (III); (iii) (III) and the 5′-Br-derivative of (II); (iv) (IV) and the 5′-Br-derivative of (II); (v) (II) and 5-*bromo*-4 : 3′-*dimethyl*-3 : 5′-*diethylpyrromethene hydrobromide*, m.p. 195° (free *base*, m.p. 111°) (from 5-bromo-2-formyl-4-methyl-3-ethylpyrrole, 4-methyl-2-ethylpyrrole, and 48% HBr in AcOH). Numerous other porphyrins are produced in these condensations either by self-condensation of the components or decomp. of the porphyrins produced intermediately; the following are isolated: *αγ-dimethyldeuteroætioporphyrin* II [αγ : 1 : 3 : 5 : 7-*hexamethyl*-2 : 6-*diethylporphin*] (*Cu* salt; *hæmin*), *γ-phylloætioporphyrin* V, m.p. 267°, deuteroætioporphyrin II (*hæmin*), and mono- and di-bromodeuteroætioporphyrin II. (I) (as *A*) and oleum



(*A*.) (*B*.)

(20% SO_3) give a *sultone* (as *B*) [*Me* ester, $C_{33}H_{36}O_5N_4S$, m.p. 279·5—280° (*Cu* salt, m.p. 298°)], identical with that obtained similarly from "analytical" phylloporphyrin, and converted by 15% HCl into the *hydroxy-sulphonic acid hydrochloride*, $C_{32}H_{37}O_6N_4SCl$, which loses HCl when treated with C_5H_5N or Na_2CO_3 but is not reconverted into the sultone.

2 : 4-*Dipropionyl*-3 : 5-*diethylpyrrole*, m.p. 132°, prepared from $CH_2(COEt)_2$ by Knorr's method, is reduced (Wolff–Kishner) to 3 : 5-*diethyl*-4-*propylpyrrole*, b.p. 120°/11 mm. [*azo*-dye, m.p. 232° (sinters at 215°), by coupling with diazobenzenesulphonic acid (V)], and hydrolysed by H_2SO_4 to 3 : 5-*diethylpyrrole*, b.p. 85—90°/12 mm. [*azo*-dye, decomp. 200—210°, from (V)]. Mg 2 : 3-diethylpyrryl bromide and $ClCO_2Et$ give Et 3 : 5-diethylpyrrole-2-carboxylate, b.p. 150°/10 mm., m.p. 51°. The product from MgEtBr and 4-*methyl*-3 : 5-*diethylpyrrole* (VI), b.p. 95—96°/11 mm., 205°/730 mm. [*picrate*, m.p. 110°; *azo*-dye, decomp. 247—248°, with 1 mol. of (V); *substance*, colourless, $C_{21}H_{34}O_3S$, m.p. 225°, from 2 mols. of (VI) and 1 mol. of (V)] (from Et 4-methyl-3 : 5-diethylpyrrole-2-carboxylate, NaOEt, and N_2H_4,H_2O at 160°), with HCO_2Et affords 2-*formyl*-4-*methyl*-3 : 5-*diethylpyrrole* (VII), m.p. 112° (*oxime*, m.p. 95°; *azine*, m.p. 228°), which with opsopyrrole and 48% HBr in EtOH gives 4 : 3′-*dimethyl*-3 : 5 : 4′-*triethylpyrromethene hydrobromide*, decomp. 165—170° [free *base*, m.p. 66° (*Cu* salt, $C_{32}H_{46}N_4Cu$, m.p. 139°)], brominated in AcOH to 5′-*bromo*-4 : 3′-*dimethyl*-3 : 4′-*diethyl*-5-*bromoethylpyrromethene hydrobromide* (VIII).

2 : 3-Dimethylpyrrole, β-5-carboxy-2-formyl-4-methyl-3-pyrrylpropionic acid, and 48% HBr in AcOH afford 5-*carboxy*-4 : 4′ : 5′-*trimethyl*-3-β-*carboxyethylpyrromethene hydrobromide*, decomp. 129—130° (darkens at 124°), which with Br in HCO_2H gives 5 : 3′-*dibromo*-4 : 4′ : 5′-*trimethyl*-3-β-*carboxyethylpyrromethene hydrobromide* (IX). 4 : 4′-*Dimethyl*-3 : 5 : 3′ : 5′-*tetraethylpyrromethene hydrochloride*, decomp. 191° (free *base*, m.p. 81°), is prepared from (VI), (VII), and conc. HCl. Fusion of (VIII), (IX), and methylsuccinic acid at 150° gives the following: *mono*- and *di-bromodeuteroporphyrin* V; *bromo*-δ-*phylloporphyrin* XV, m.p. 288°; *αγ-dimethylætioporphyrin* I [*αγ*-1 : 3 : 5 : 7-*hexamethyl*-2 : 4 : 6 : 8-*tetraethylporphin*], m.p. 276—280° (*Cu* salt); δ-*phylloporphyrin* XV [*Me* ester, m.p. 214° (sinters at 198°) (*Cu* salt, m.p. 189°)]; pyrroporphyrin XV and its Br-derivative; deuteroporphyrin V, and ætioporphyrin I. Similar fusion of 3′ : 5′-dibromo-4 : 5 : 4′-trimethyl-3-β-carboxyethyl- and 5-bromo-4 : 3′-dimethyl-3 : 4′-diethyl-5′-bromoethyl-pyrromethene hydrobromides gives 0·2% of β-*phylloporphyrin* XV (*Me* ester, m.p. 213°), *bromo*-β-*phylloporphyrin* XV, m.p. 296°, and other porphyrins.

2-Formyl-3-methyl-4 : 5-diethylpyrrole, opsopyrrolecarboxylic acid, and 48% HBr in EtOH give 3 : 3′-*dimethyl*-4 : 5-*diethyl*-4′-β-*carboxyethylpyrromethene hydrobromide*, m.p. 171° [5′-*Br*-derivative (X), decomp. 180°], whilst 5-carboxy-4 : 3′ : 5′-trimethyl-3-ethylpyrromethene hydrobromide and Br in HCO_2H afford 5 : 4′-*dibromo*-4 : 3′ : 5′-*trimethyl*-3-*ethylpyrromethene hydrobromide* (XI), blackens at 232°. 5′-*Bromo*-3 : 5 : 3′-*trimethyl*-4′-*ethyl*-4-β-*carboxyethylpyrromethene hydrobromide* (XII), darkens at 240°, is prepared by brominating the 5′-H compound in AcOH. 2-*Formyl*-3-*methylpyrrole*, m.p. 92° [*phenylhydrazone*, m.p. 124°; *azine*, m.p. 201° (corr.)], obtained by decarboxylation of its 4-carboxylic acid, 3-methyl-2 : 4-diethylpyrrole, and EtOH–HBr give 3 : 4′-*dimethyl*-3′ : 5′-*diethylpyrromethene hydrobromide*, m.p. 178° [4 : 5-Br_2-derivative (XIII), decomp. 230°]. Fusion of (X), (XI), and methylsuccinic acid gives 0·64% of α-*phylloporphyrin* XV [α : 1 : 3 : 5 : 8-*pentamethyl*-2 : 4-*diethyl*-7-β-*carboxyethylporphin*] {*Me* ester, m.p. 213° (corr.) (sinters at 211°) [*Cu* salt, m.p. 223° (corr.); *hæmin*, m.p. 254° (corr.)]}, converted by oleum into (probably) a rhodin; other compounds isolated from the fusion are *αγ-dimethylmesoporphyrin* V [*Me* ester, m.p. 277° (corr.)], mesoporphyrin V, and *deuteroætioporphyrin* II, m.p. 326° (corr.) [*Cu* salt, m.p 308° (corr.); Br-derivative *Cu* salt, m.p. 306° (corr.)] [also obtained by fusion of (XI) with succinic acid]. Similar fusion of (XII) and (XIII) affords α-phylloporphyrin XV (1·73%), bromo-α-phylloporphyrin, and other porphyrins. α-, β-, and δ-Phylloporphyrins resemble pyrroporphyrin in their general properties.

Et 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate and SO_2Cl_2 in Et_2O give (after hydrolysis and esterification) *Et* 4-*methyl*-3-*ethylpyrrole*-2 : 5-*dicarboxylate*, b.p. 173—175°/10 mm., m.p. 50°. When this is partly hydrolysed (aq. EtOH–NaOH), the resultant mixture of Et H esters heated at 210—230°, and then distilled in vac., *Et* 4-*methyl*-3-*ethylpyrrole*-2-*carboxylate*, m.p. 75°, separates from the distillate. Treatment of $CH_2Ac{\cdot}CO_2Et$ in AcOH with aq. $NaNO_2$ at 5—7°, addition of $EtCO{\cdot}CH_2{\cdot}CO_2Et$ to the reaction mixture, and subsequent treatment with Zn dust gives *Et* 4-*methyl*-2-*ethylpyrrole*-3 : 5-*dicarboxylate*, m.p. 116° (corr.), hydrolysed by conc. H_2SO_4 below 35° to the 5-*Et* 3-*H* ester, m.p. 263° (corr.), which when heated affords Et 4-methyl-2-ethylpyrrole-5-carboxylate, m.p. 75° (3-Ac derivative, m.p. 134°, formed by the action of Ac_2O in presence of $AlCl_3$ and CS_2).

H. B.

Structural formulæ of the chlorophylls. J. B. CONANT and E. M. DIETZ (Nature, 1933, **131**, 131).—The purest samples of the phæophorbides of the "*a*" series do not yield phæopurpurin 7 (I). Under special conditions of oxidative hydrolysis a Me compound can be isolated as the sole product with its CO_2Me group forming part of the side-chain attached to the bridge (γ-position). This accords with the position of the OMe group in Fischer's formula for chlorophyll-*a*. Mother-liquors from the purification of the phæophorbides yield a substance closely resembling phæophorbide-*a* which gives (I) on oxidative hydrolysis and this material was responsible for the (I) previously obtained (A., 1931, 1075). The oxidative hydrolysis of crude chlorophyll or of chlorophyllides shows that a precursor of (I) is present to 1—5% in many plants. Two forms of chlorophyll-*a* differing in the position of a OMe group and perhaps of chlorophyll-*b* appear to exist. The lactam formula previously mentioned (*loc. cit.*) and not the anhydride formula given satisfies the requirements which this possibility involves. L. S. T.

Chlorophyll. III. Composition of chlorophyll. A. STOLL and E. WIEDEMANN (Helv. Chim. Acta, 1933, **16**, 183—206).—Improved methods of prep. of phæophorbides *a*, $C_{35}H_{38}O_5N_4$, and *b*, $C_{35}H_{38}O_6N_4$, methylphæophorbides *a*, $C_{36}H_{40}O_5N_4$, and *b*, $C_{36}H_{40}O_6N_4$, chlorin *e*, $C_{34}H_{36}O_6N_4$, and rhodin *g*, $C_{34}H_{36}O_7N_4$, are given. Many samples of the above substances contain varying amounts of H_2O and are hygroscopic; the method of drying is described. The various structures suggested (Fischer; Conant) for chlorophylls *a* and *b* (and derivatives) are reviewed and criticised. Various reactions are discussed which support the author's structures (A., 1932, 1265). The formula $C_{35}H_{37}O_5N_4Cl$ for chloroanhydrophæophorbide *b* (this vol., 167) is confirmed by analysis. H. B.

Dioximes. XCVII. G. PONZIO. **XCVIII.** E. DURIO and A. SBURLATI (Gazzetta, 1932, **62**, 1025—1034, 1035—1040).—XCVII. Chlorophenylglyoxime and PCl_5 give 3-chloro-5-phenyl-1 : 2 : 4-oxadiazole, of which the 3-OEt-analogue (A., 1927, 470) is converted by HI into the 3-OH-compound. With $POCl_3$ phenylcarbamylhydroxamic acid is formed, with a *compound* $Ph(C_2N_2O)Cl$, m.p. 37—38°, which with NaOH yields the OH-compound (I), m.p. 201—202° [NH_4, Na (+H_2O), Ca (+$3H_2O$), and Ag salts]. The OMe- and OEt-derivatives of this, m.p. 58—59° and 47—48°, respectively, are identical with those described by Yang and Johnson (A., 1932, 757) as 3-alkoxy-5-phenyl-1 : 2 : 4-oxadiazoles. This formulation is not accepted, since (I) is easily decomposed by AcOH to $NHBz{\cdot}CO{\cdot}NH_2$ and reacts with NH_2Ph

and with *o*-toluidine to give NHPh·CO·NHBz and NHBz·CO·NH·C_6H_4Me, respectively. (I) is also obtained from hydroxyphenylglyoxime and $POCl_3$.

XCVIII. $POCl_3$ may replace PCl_5 in the prep. of 1 : 2 : 4-oxadiazoles. Thus β-phenylmethylglyoxime (broken down by PCl_5) yields 3-phenyl-5-methyl- (also obtained from the α form), and β-benzylmethylglyoxime 3-benzyl-5-methyl-1 : 2 : 4-oxadiazole. α-Benzildioxime gives the 3 : 5-Ph_2 compound, but the β-form is converted into oxanilide; in the cold the γ-form yields the oxadiazole and NHPh·CO·NHBz, in the hot the latter only. α-Anisildioxime gives the oxadiazole, β- largely ox-*p*-anisidide. E. W. W.

Action of hydroxylamine on saccharin, on some of its derivatives, and on 3-thion-1 : 2-benzdithiole. (Sna.) A. Mannessier-Mameli (Gazzetta, 1932, 26, 1067—1092).—Saccharin with NH_2OH in EtOH forms an additive product (I), which, having an acid reaction and being easily reconverted into saccharin by acid or heating, is considered to be $C_6H_4<\overset{C(OH)(NH\cdot OH)}{\underset{SO_2}{\quad}}>NH$, m.p. 157° (decomp.) (*Na* salt); this with Ac_2O gives *N*-acetylsaccharin, new m.p. 198°. With the last, NH_2OH· reacts to form saccharin and some (I), which is also obtained from NH_2OH and *N*-methylsaccharin. *Saccharinoxime*, m.p. 208—210° [*Na* salt, m.p. 280° (decomp.); *Ac*, m.p. 225°, and *Bz*, m.p. 250° (decomp.), derivatives], is prepared from thiosaccharin and NH_2OH. 3-Thion-1 : 2-benzdithiole forms 3-*oximino*-1 : 2-*benzdithiole*, m.p. 210° (decomp.) (*Bz* derivative, m.p. 147°). Colour reactions of the above with $FeCl_3$ are discussed. E. W. W.

Acid oxidation of methylene-blue. I. V. Kulikov (Khim. Farm. Prom., 1932, 218—221).—Methylene-blue (112 g.), H_2O (2·5 litres), and HCl (*d* 1·19, 50 c.c.) are slowly treated at 80° with 10% $K_2Cr_2O_7$ (800 c.c.), with violent agitation. After 0·5 hr. the mixture is treated at > 50° with saturated aq. NaCl (2·5 litres). The ppt. of dimethylthionine is centrifuged, redissolved in H_2O (2 litres) and HCl, (15 c.c.), and repptd. with NaCl; yield 87—94%. Ch. Abs.

Indophenine. II. G. Heller (Chem.-Ztg., 1933, 57, 74—75; cf. A., 1930, 369).—Polemical. The new evidence brought forward by Steinkopf and Roth (A., 1932, 752) against the quinonoid formula for indophenine is inconclusive. H. A. P.

New group of animal pigments [lyochromes]. P. Ellinger and W. Koschara.—See this vol., 298.

Constitution of carpaine. II. G. Barger, A. Girardet, and R. Robinson (Helv. Chim. Acta, 1933, 16, 90—99; cf. J.C.S., 1910, 97, 466).—Carpaine (I), $C_{14}H_{25}O_2N$ [N-*Bu*, m.p. 97—98°, N-*Ac* (II), m.p. 114°, and N-CO_2Et, m.p. 167°, derivatives], contains 1 active H atom (as NH) (Zerevitinov method at 95°) and is hydrolysed by 20% HCl (cf. *loc. cit.*) to carpamic acid (III) [*Me* ester, m.p. 70°; Et ester (*hydrochloride*, m.p. 173—174°, which shows only two active H atoms; *nitrite*; *Ac* derivative)]. (III) (as hydrochloride) and aq. CH_2O at 120—130° give (after esterification with EtOH–HCl) *Et* N-*methylcarpamate*, b.p. 225°/15 mm. (O-*acetate*, b.p. 230°/15 mm.), thus demonstrating the presence of NH (and OH) in (III). (II) is hydrolysed by cold 2% MeOH–KOH (not by aq. KOH) to *N*-acetylcarpamic acid, the *Me* ester, m.p. 64°, of which could not be dehydrated by P_2O_5 or conc. H_2SO_4; the $COMe_2$-sol. part of the oil formed during these attempted dehydrations is oxidised ($KMnO_4$) and the resulting acid esterified (CH_2N_2), whereby a *Me* ester, $C_{17}H_{31}O_5N$, m.p. 91—92°, is obtained. (I) and Cl_2 in *N*-HCl at 0° give (probably) a *chloroamine*, $C_{14}H_{24}O_2NCl$, m.p. 265° (darkens at 240°), which gradually changes (in solution) to the hydrochloride of an unsaturated base. (I) and Se at 280°/15 mm. give *carpyrine*, $C_{14}H_{21}O_2N$, b.p. 210°/5 mm. (which gives the pyrrole reaction with *p*-$NMe_2\cdot C_6H_4\cdot CHO$) [reduced (Adams) to a stereoisomeride, m.p. 118—119°, of (I)], a *substance*, $C_{13}H_{21}O_2N$ (? mixture), b.p. 270°/5 mm., and a non-homogenous solid, m.p. 163°; at 360°/atm. pressure, apo*carpyrine*, $C_{11}H_{17}N$ ($C_{10}H_{15}N$ or $C_{12}H_{19}N$), b.p. 145—150°/21 mm., which gives the pyrrole reaction, results. (I) contains, therefore, the pyrrolidine nucleus. Oxidation of (III) (as hydrochloride) with 2% $KMnO_4$ affords suberic acid, also formed with azelaic acid by oxidation of (I) or (III) (or its esters) with HNO_3. Alternative structures are suggested for (I). H. B.

Stereochemical arrangement about the carbinol carbon atom in quinine alkaloids. J. Suszko and A. Tomanek (Rec. trav. chim., 1933, 52, 18—24).—Cinchonine in C_5H_5N gives a p-*toluenesulphonyl* derivative (I), m.p. 173° (decomp.), $[\alpha]_D^{20}$ +51° in EtOH [*hydrochloride*, m.p. 166° (decomp.), $[\alpha]_D^{20}$ +45·5° in EtOH], stable towards acids and to Na_xHg_y, unstable towards KOH–EtOH. With KOBz, (I) gives the *Bz* derivative, m.p. 192°, $[\alpha]_D^{20}$ −37° in 96% EtOH, of epi*cinchonine*, (II), $C_{19}H_{22}ON_2$, m.p. 179—180°, $[\alpha]_D^{18}$ +151° in EtOH [*picrate*, m.p. 206° (decomp.); *methiodide*, m.p. 204°]. (II) differs in properties from the *epi*cinchonine of Rabe (A., 1932, 290), but must be regarded as a stereoisomeride of cinchonine about the carbinol C atom, since its *benzylochloride*, m.p. 215—217°, is convertible by 10% KOH into *N*-benzylcinchotoxin. E. W. W.

***Cinchona* alkaloids. XXVIII. Synthesis of mirror-image isomerides of hydroquinine and hydroquinidine.** P. Rabe and A. Schultze (Ber., 1933, 66, [*B*], 120—122; cf. A., 1931, 1433).—β-3-Ethyl-4-pyridylacrylic acid is hydrogenated to the corresponding propionic acids, the mixed hydrochlorides of which are transformed into the esters and treated with *l*-tartaric acid in EtOH, whereby (−)-*homocincholoipon H* l-*tartrate* (I), m.p. (indef.) 123—124° (decomp.), is obtained. (I) is transformed into (−)-*homocincholoipon Et* ester, b.p. 124°/0·2 mm., the *Bz* derivative, b.p. 197—200°/0·2—0·3 mm., of which is condensed with Et quinate to the corresponding toxin, transformed without further purification into (−)-*hydroquininone* (II), m.p. 98—99° (corr.), $[\alpha]_D^{20}$ −70·0° (final val.) in EtOH. Hydrogenation of (II) (spongy Pd and HCl–H_2O) affords a mixture of bases from which (−)-*hydroquinidine*, m.p. 171° (corr.), $[\alpha]_D$ −237·7° in EtOH, and (+)-*hydroquinine*, m.p. 171·5° (corr.), $[\alpha]_D^{\theta}$ +143·5°, are separated. r-*Hydroquinine*, from equal amounts of the *d*- and *l*-isomerides, has m.p. 175—176·5° (corr.). H. W.

Alkaloids of *Rauwolfia serpentina*, Benth. I. S. SIDDIQUI and R. H. SIDDIQUI (J. Indian Chem. Soc., 1932, **9**, 539—544).—Ajmaline, $C_{21}H_{26}O_2N_2$,0·5H_2O (I) (A., 1932, 203; probably identical with rauwolfine isolated by Van Itallie and Steenhauer, A., 1932, 664), contains no OH or OMe groups, but the presence of a NHMe group is indicated by the presence of 1 active H (Zerevitinov) and by the formation of a *NO*- +0·5H_2O, m.p. 209°, and a *Bz*, m.p. 180° (softens at 134°), derivative. With MeI (I) gives the *hydriodide*, m.p. 230—231°, of *methylajmaline*, m.p. 130—131° (softens at 127°) [*hydrochloride*, softens at 125°, loses H_2O of crystallisation at 132—134°, m.p. 272°; *picrate*, froths at 176°, m.p. 186°, and *chloroplatinate*, darkens at 203°, m.p. 215—220° (decomp.)]. (I) becomes anhyd. at 150° and at 200° yields *pyroajmaline*, m.p. 256° [*hydrochloride*, softens at 230°, m.p. 238—240° (decomp.)]. Ajmalinine and serpentine each contain 1 OMe group. J. W. B.

Alkaloids of *Holarrhena antidysenterica*. I. Three new alkaloids from the bark of Indian *Holarrhena*. Isolation and purification of conessine. S. SIDDIQUI and P. P. PILLAY (J. Indian Chem. Soc., 1932, **9**, 553—563).—The extraction and separation of the alkaloids (2·1% yield calc. on wt. of dried bark) into three main fractions: (A) those giving sulphates insol. in H_2O, (B) those giving carbonates insol. in ligroin, and (C) those sol. in moist ligroin but not giving carbonates on passage of CO_2, are described. From (C) pure conessine, m.p. 126° (corr.) [*hydrochloride*, darkens at 335°, m.p. 338—340° (decomp.); *hydriodide*, m.p. 308° (decomp.); *picrate*, m.p. 222—224° (decomp.); *oxalate*, m.p. 372° (decomp.)], is isolated in 0·4% yield. From (B), by fractional pptn. with NH_3, is isolated (0·12% yield) *conessimine*, $C_{20}H_{36}N_2$, m.p. 100°, b.p. 230°/1·8 mm., $[\alpha]_D^{25}$ −22·25° in $CHCl_3$, and +2H_2O, m.p. 91° [*carbonate*, softens at 70°, m.p. indef. up to 105°; *hydrochloride*, m.p. 342—344°, $[\alpha]_D$ −15·10° in H_2O; *hydriodide*, m.p. 318—319° (decomp.); *chloroplatinate*, m.p. 301° (decomp.); *chloroaurate*, m.p. 140°, decomp. 165°; *picrate*, m.p. 172—174°], a diacid base containing 1 active H and 2 NMe groups, one of which is *sec.*, since it yields a *NO*-derivative, m.p. 240—241° (decomp.). Fractionation of (A) affords *holarrhine*, $C_{20}H_{38}O_3N_2$, m.p. 240°, $[\alpha]_D^{25}$ −17·01° in MeOH (*chloroplatinate*, darkens at 270°, chars > 300°; *picrate*, darkens at 275°, not melting < 320°), in minute yield. From the mother-liquor is obtained *holarrhimine*, $C_{21}H_{36}ON_2$, m.p. 183° (corr.), $[\alpha]_D^{25}$ −14·19° in $CHCl_3$ [*carbonate*, begins to lose CO_2 at 80°; *hydrochloride*, m.p. 345°, $[\alpha]^{25}$ −22·81° in MeOH; *hydrobromide*, m.p. 358—360° (decomp.); *chloroplatinate*, darkens at 270°, chars > 300°; *picrate*, m.p. 198—200° (decomp.) and hydrated, m.p. 108—110°; and *sulphate*, m.p. 337°], which contains no OMe or NMe groups, but has three active H atoms (? 1 OH, 2 NH groups). The possible relationships of these alkaloids to those previously isolated (Pyman, J.C.S., 1919, **115**, 163; Ghosh and Bose, A., 1932, 406; Haworth, *ibid.*, 406) are discussed. J. W. B.

***Strychnos* alkaloids. LXX. Degradation of brucinonic acid, $C_{23}H_{24}O_8N_2$, to the base $C_{19}H_{20}O_3N_2$ and the acid $C_{16}H_{17}O_9N_3$.** H. LEUCHS and F. KRÖHNKE. **LXXI. Behaviour of strychnine towards stannous chloride and hydrochloric acid.** H. LEUCHS and H. BEYER (Ber., 1933, **66**, [*B*], 252—259, 259—262).—LXX. The acid (I), $C_{20}H_{22}O_6N_2$, from brucinonic acid, $BaCO_3$, and BaO_2 (A., 1932, 866), is most conveniently isolated as the *perchlorate*. (I) and MeI–NaOH in MeOH yield the N-*Me* compound separated as the *perchlorate* (II), $C_{20}H_{24}O_6N_2,HClO_4$. (I) is transformed by 12*N*-HCl into (*a*) the lactonic *acid*, $C_{20}H_{23}O_6N_2Cl$, darkening without melting at 220°, (*b*) the OH-*acid*, $C_{20}H_{23}O_6N_2Cl$, m.p. 220—225° (decomp.), transformed by Na_2CO_3 into (I), and (*c*) the unsaturated Cl-*acid* (III), $C_{20}H_{21}O_5N_2Cl$, m.p. 250° (decomp.) when slowly heated (*hydrochloride*, *perchlorate*), catalytically reduced to the *substance* $C_{20}H_{24}O_5N_2$, decomp. 305° (*perchlorate*). Treatment (III) with boiling $Ba(OH)_2$ or NaOH affords the resinous *base*, $C_{19}H_{20}O_3N_2$ (IV) (*perchlorate*), and a compound isolated as the *perchlorate*, $C_{20}H_{24}O_7N_2$,2$HClO_4$. Catalytic reduction of (IV) yields the compound $C_{19}H_{24}O_3N_2$ (*perchlorate*).

(I) is oxidised by 5*N*-HNO_3 to the N-*nitrosonitroquinone hydrate*, $C_{18}H_{16}O_{11}N_4$, from which NO is removed by boiling 12*N*-HCl with production of the *nitroquinone hydrate*, $C_{18}H_{17}O_9N_3$ (*hydrochloride*), analogous to cacotheline. Oxidation of the nitrosoamine with Br leads to the dicarboxylic *acid*, $C_{16}H_{17}O_9N_3$, not molten below 300°, which absorbs 3H_2 when catalytically reduced.

LXXI. Treatment of strychnine at 130° with 12*N*-HCl in presence or absence of $ZnCl_2$ yields only brown products. With $SnCl_2$–12*N*-HCl at 110—115° there are formed (*a*) *dihydroallostrychnyl chloride* isolated as the *picrate* $C_{21}H_{23}ON_2Cl,C_6H_3O_7N_3$, m.p. 262—265°, and *hydrochloride*, $C_{21}H_{23}ON_2Cl$,2HCl,3H_2O, $[\alpha]_D$ +59°/*d*, and reduced (PtO_2) to *tetrahydroallostrychnyl chloride* [*picrate*, m.p. 233—236° (decomp.)], and (*b*) a compound isolated as the *picrate* $C_{21}H_{22}O_2N_2,C_6H_3O_7N_3$. H. W.

Homologues of berberine. K. FEIST, W. AWE, and (in part) (MISS) H. ETZRODT (Arch. Pharm., 1933, **271**, 36—51).—9-Benzyldeoxyberberine (modified prep.), m.p. 136° (lit. 161—162°), with $Hg(OAc)_2$ in aq. AcOH loses the CH_2Ph group and gives berberinium salts. It is reduced electrolytically to 9-benzyldihydrodeoxyberberin, m.p. 164° [methiodide, m.p. 220—225° (decomp.) (lit. 227°); *methosulphate*, m.p. 213—215° (decomp.)], the *ψ*-compound, m.p. 146° (lit. amorphous, m.p. 126°), and amorphous mixtures, whilst I–EtOH affords 9-benzylberberinium salts. 9-*o*-*Tolyldeoxyberberine* (prepared in the usual way), m.p. 189°, is reduced (amalgamated Zn, 30% AcOH–H_2SO_4) to 9-*o*-*tolyldihydrodeoxyberberine*, m.p. 204°. The m.p. (135°) of 9-methyldeoxyberberine is confirmed. 9-Phenyldeoxyberberine (I) with $Hg(OAc)_2$ leads to 9-phenylberberinium salts (II) (*mercurichloride*) (probably identical with those obtained from oxyberberine and MgPhBr), reduced by Zn and H_2SO_4 in AcOH to 9-phenyldihydrodeoxyberberine (III). (II) with I–EtOH gives *iso*-9-phenylberberinium salts (IV), also reduced to (III). Possible constitutions of (II) and (IV) are discussed. R. S. C.

Solanidine. C. SCHOPF and R. HERRMANN (Ber., 1933, **66**, [*B*], 298—305).—Analyses of solanidine (I), m.p. 218—219°, agree better with the formula $C_{27}H_{43}ON$ than with $C_{26}H_{41}ON$ (Zemplén and Gerecs, A. 1929, 51). The presence of the NMe group could not be established, but an alcoholic OH is shown to be present by the prep. of the *formyl*, m.p. 168—169°, *Ac*, m.p. 206—208°, and *palmityl* (II), m.p. 83° [*hydrochloride* (III), m.p. 225—226°], derivatives. When the hydrochloride of (I), (II), or (III) is heated *solanidene* (II), $C_{27}H_{41}N$, m.p. 167° (*hydrochloride*, m.p. above 300°; *methiodide*, m.p. 270°), is obtained, catalytically hydrogenated to *solanidane* (V), m.p. 161—162°. (IV) and (V) are possibly identical, respectively, with the solanthrene and dihydrosolanthrene of Dieterle and Schaffnit. Oxidation of (I) with CrO_3 in AcOH or H_2SO_4 proceeds at an approx. uniform rate until 10 O have been consumed and leads to a non-cryst. NH_3-acid. The presence of a *sec.* OH in (I) is established by its transformation by Cu powder at 160—300°/11 mm. into *solanidone* (VI), m.p. 218° (*oxime*, m.p. 228°, and its *hydrochloride*; *semicarbazone*, m.p. 237°). Condensation of (VI) with PhCHO or piperonal gives amorphous products. With amyl nitrite (VII) in AcOH–HCl, (VI) gives a *compound*, $C_{29}H_{42}O_5N_3Cl$, m.p. 330—335°, whereas *dioximinosolanidone*, m.p. 242° (decomp.), is smoothly obtained by means of (VII) and NaOEt, thus establishing the presence of $CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}$ in (I). PCl_5 in $POCl_3$ transforms (I) into *trichlorosolanidone*, m.p. 188—190°, and 270° after re-solidification at 200°. The attempted Hofmann degradation of *solanidine methiodide*, m.p. 285—286°, leads to regeneration of (I). CNBr and (I) at 130° yield two cryst. products containing more Br than is required for simple addition. (I) contains at least 3 CMe groups. (I) resembles samandarine in giving a violet colour when its solution in HCl is exposed to air.

H. W.

Solanocapsine, a new alkaloid with a cardiac action. J. M. WATT, H. L. HEIMANN, and E. EPSTEIN.—See this vol., 311.

New derivatives of *p*-arsanilic acid. IV. *p*-Arsonoadipanilic acid and related compounds. G. T. MORGAN and E. WALTON (J.C.S., 1933, 91—93).—Me H adipate and $SOCl_2$ give δ-*carbomethoxyvaleryl chloride*, b.p. 141°/36 mm., which with atoxyl forms *Me* p-*arsinoadipanilate* (I) (*Na* salt) [corresponding *Et* ester from δ-carbethoxyvaleryl chloride (*Na* salt)]. (I) is hydrolysed to p-*arsinoadipanilic acid* and reduced by SO_2 in HCl to p-*dichloroarsino*-, m.p. 138°, hydrolysed to p-*oxyarsinoadipanilic acid*. Treatment of (I) with the appropriate amine affords *adipanilamide*- (*Na* salt), *adipanilomethyl*- (*Na* salt), *-dimethyl*- (*Na* salt), *-ethyl*- (*Na* salt), and -n-*propyl-amide*-p-*arsinic acid* (*Na* salt), *adipanilide*-p-*arsinic acid* (*Na* salt), and *adipanilide*-pp′-*diarsinic acid* (*Na* salt). Atoxyl and succinic anhydride form p-*arsinosuccinanilic acid*, and *succinal*-p-*arsinic acid* is obtained as described in A., 1931, 636. The Na salts show marked trypanocidal activity.

F. R. S.

Di(carbanilidomethyl) arylthioarsinites and their complex [salts with] mercuric [chloride]. M. G. SCHUSTER (J. Pharm. Chim., 1933, [viii], **17**, 28—43).—The following *di*(*carbanilidomethyl*) *arylthioarsinites*, $ArAs(S{\cdot}CH_2{\cdot}CO{\cdot}NHPh)_2$, are prepared, the m.p. in parentheses being those of the complex *salts* with $4HgCl_2$: o-, m-, and p-$NO_2{\cdot}C_6H_4{\cdot}$, m.p. 163° (212°), 149° (198°), and 115° (208—210°), respectively; p-$NH_2{\cdot}C_6H_4{\cdot}$, m.p. 156° (208°); p-$C_6H_4Cl{\cdot}$, m.p. 162° (218°). *Carbanilidomethyl diphenylthioarsinite* has m.p. 83° (203—205°). The m.p. of these compounds, together with titration by I, may be used for identification of arylarsinic acids. The prep. of thiolacetic acid is modified.

R. S. C.

Diarsyls. IV. Interaction of di-iododiphenyldiarsyl with alkali, phenylarsine, and diphenylarsine. F. F. BLICKE and L. D. POWERS (J. Amer. Chem. Soc., 1933, **55**, 315—318).—Di-iododiphenyldiarsyl (I) (in Et_2O) and aq. NaOH in N_2 give PhAsO and a *compound*, $C_{12}H_{10}As_2$, m.p. 195—197° (sealed tube in N_2), which resembles arsenobenzene (II), but [unlike (II)] absorbs O_2 and is converted into (II) by Et_2O–HCl or –HBr. Di-iododianisyldiarsyl similarly affords *p*-OMe·C_6H_4·AsO and a *compound*, m.p. 220—230° (converted by Et_2O–HCl or –HBr into 4 : 4′-dimethoxyarsenobenzene). (I) and $AsHPh_2$ in cold EtOH give $(\cdot AsPh_2)_2$ and (II); it is probable that the hexaphenyltetra-arsine of Steinkopf and Smie (Ber., 1926, **59**, [*B*], 1462) is a mixture of these. (I) and AsH_2Ph similarly afford (II) [and probably not the cyclic triphenyltriarsine of Steinkopf and Smie (*loc. cit.*)].

H. B.

Modes of reaction of phosphorus pentachloride. III. Action on derivatives of acetylene. IV. Action on ethylenes. E. BERGMANN and A. BONDI (Ber., 1933, **66**, [*B*], 278—286, 286—291; cf. A., 1931, 947).—III. CH·CPh is converted by PCl_5 in C_6H_6 followed by hydrolysis into β-*chloro*-β-*phenylvinylphosphinic acid* (I) $CPhCl{:}CH{\cdot}PO_3H_2$, m.p. 162° (*Ag* salt; *Me*$_2$ ester, b.p. 202—203°/14 mm.), converted by KOH into *phenylacetylenylphosphinic acid*, m.p. 142°, which is reduced to β-phenylethylphosphinic acid. (I) is also obtained together with BzOH from α-chlorostyrene, presumably with intermediate formation of $CPhCl_2{\cdot}CH_2{\cdot}PCl_4$. *o*-Chlorocinnamic acid, m.p. 208°, is transformed into its *Et* ester, b.p. 162°/12 mm., and thence into the *dibromide* and o-*chlorophenylpropiolic acid* (II), m.p. 131—132°. (II) when treated with $NaHCO_3$ and $CuCl_2$ and then with steam affords o-*chlorophenylacetylene*, b.p. 71°/18 mm., whence β-*chloro*-β-o-*chlorophenylvinylphosphinic acid*, m.p. 187° (Ag_2 salt), and o-*chlorophenylacetylenylphosphinic acid*, m.p. 134°. *Et* o-*methoxycinnamate*, b.p. 172°/18 mm., yields successively the *dibromide*, *o*-methoxyphenylpropiolic acid, m.p. 128°, o-*methoxyphenylacetylene*, b.p. 92°/14 mm., and β-*chloro*-β-o-*anisylvinylphosphinic acid*, m.p. 125—127° (decomp.) [*monohydrate*, m.p. 64—67°]. p-*Methoxyphenylpropiolic acid*, m.p. 141—143° (decomp.), gives *p*-methoxyphenylacetylene, b.p. 86—87°/17 mm., m.p. 28—29°, and the unstable β-*chloro*-β-p-*anisylvinylphosphinic acid*, m.p. 105°. CH·CPh is converted by the successive action of Na in Et_2O and Me_2SO_4 into *phenylmethylacetylene*, b.p. 67—68°/14 mm., transformed by PCl_5 and H_2O into (?) β-*chloro*-β-*benzylvinylphosphinic acid*, probably in cis–trans-*forms*, m.p.

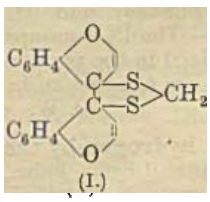
179° and 154°, respectively (*Ag* salt), hydrolysed to benzylacetylene. Δ^{α}-Heptinine and PCl_5 afford β-*chloro*-β-n-*amylvinylphosphinic acid* (*Pb* salt, *Et*$_2$ ester, m.p. 152°/17 mm.). No reaction occurs between PCl_5 and tolane, diphenyldiacetylene, *p*-nitrophenylacetylene or *phenylethylacetylene*, b.p. 87—80°/18 mm.

IV. *iso*Butylene is transformed by the successive action of PCl_5 in C_6H_6 and H_2O into the unstable β-*chloro*-β-*methylpropylphosphinic acid*, m.p. 95—97° (unstable *Ag* salt). In contrast to α-chlorostyrene, β-chloro-Δ^{α}-propene and β-bromo-γ-phenyl-Δ^{α}-propene do not add PCl_5; ω-bromostyrene is passive. α-*Phenyl*-α-*o*-*tolylethylene*, b.p. 145—146°/13 mm., from MgMeI and 2-methylbenzophenone or Mg *o*-tolyl bromide and COPhMe followed by dehydration, slowly adds PCl_5, giving, after addition of H_2O, β-*phenyl*-β-*o*-*tolylvinylphosphinic acid*, m.p. 154°, hydrogenated to β-*phenyl*-β-*o*-*tolylethylphosphinic acid*, m.p. 160—161°. β-*Phenyl*-β-2-*naphthylvinylphosphinic acid*, m.p. 220°, is derived from α-*phenyl*-α-2-*naphthylethylene*, b.p. 220°/24 mm., m.p. 52° (from β-naphthyl Me ketone and MgPhBr), whilst β-*phenyl*-β-1-*naphthylvinylphosphinic acid*, m.p. 188°, is obtained more slowly from α-phenyl-α-1-naphthylethylene, m.p. 60° (from COPhMe and Mg 1-naphthyl bromide). α-*Phenyl*-α-*o*-*anisylethylene*, b.p. 154—156°/15 mm., m.p. 37°, does not appear to react with PCl_5. 9 : 9-*Diphenyl*-10-*methylene*-9 : 10-*dihydroanthracene*, m.p. 187°, by treatment of 9 : 9-diphenylanthrone with MgMeI and subsequently with AcOH–H_2SO_4, yields the *acid* $Ph_2C<^{C_6H_4}_{C_6H_4}>C{:}CH{\cdot}PO_3H_2$, m.p. 205°. Indene is transformed by PBr_5 in PBr_3 into 1 : 2-dibromohydrindene, b.p. 140°/12 mm., whilst CH:CPh and PBr_5 in C_6H_6 afford αβ-dibromostyrene, b.p. 126—128°/12 mm. H. W.

Organo-metallic compounds. I. Action of sodium on thionaphthen and thioacetals. A. SCHONBERG, E. PETERSEN, and H. KALTSCHMITT **II. Action of organo-alkali-metallic compounds on disulphides, diselenides, carbon disulphide, and thionylamine derivatives and synthesis of dimeric diphenylthioketen.** A. SCHONBERG, A. STEPHENSON, H. KALTSCHMITT, E. PETERSEN, and H. SCHULTEN. **III. Action of lithium phenyl on trimethylene-1 : 3-disulphide and syntheses of dichromylenes.** A. SCHONBERG, H. KALTSCHMITT, and H. SCHULTEN (Ber., 1933, **66**, [*B*], 233—236, 237—244, 245—250).—I. Thionaphthen is converted by Na in Et_2O at 25—30° into 2-*sodiothionaphthen*, transformed by CO_2 into thionaphthen-2-carboxylic acid, m.p. 236° (Me ester, m.p. 71—73°). Benzildiphenylmercaptal, $CPhBz(SPh)_2$, similarly affords NaSPh and *disodiodeoxybenzoin*, identified as deoxybenzoin, m.p. 57°. Dixanthylene and NaSPh are derived from xanthonediphenylmercaptal and $CPh_2{:}CPh_2$ and its Na_2-derivative from benzophenonediphenylmercaptal. Benzaldehydebenzylmercaptal appears unaffected by Na.

II. Alkali organo-metallic compounds and disulphides react, $SR'{\cdot}SR'+R''X=R'SR''+R'SX$, frequently with great readiness in Et_2O. Thus, Ph_2S_2 and LiPh afford Ph_2S, b.p. 159°/16 mm., and LiSPh; CPh_3Na and Ph_2S_2 yield NaSPh and $PhSCPh_3$, m.p. 106°; $(p\text{-}C_6H_4Me)_2S_2$ and LiPh give *p*-C$_6$H$_4$Me·SPh, m.p. 15·5°, and $LiSC_6H_4Me$, *p*; Et_2S_2 and LiPh afford LiSEt and PhSEt. Analogously, Ph_2Se_2 with LiPh gives Ph_2Se [dibromide, m.p. 145° (decomp.)] and with Li *p*-methoxyphenyl affords Ph *p*-methoxyphenyl selenide [*dibromide*, m.p. 125° (decomp.)]. αβ-Disodiobisdiphenylene-ethane is transformed by Ph_2S_2 into αß-bisdiphenylene-ethylene, m.p. 185°; analogously, disodiotetraphenylethane and Et_2S_2 yield NaSEt and tetraphenylethylene. NPh_2K and $(\beta\text{-}C_{10}H_7)_2S_2$ yield $KSC_{10}H_7$ and (?) β-*naphthylthioldiphenylamine*, $NPh_2{\cdot}SC_{10}H_7$, m.p. 92° (decomp.), CPh_3 and Ph_2S_2 in C_6H_6 afford $PhS{\cdot}CPh_3$, thus indicating the partial decomp. of Ph_2S_2 into radicals with S$^{\text{I}}$ (confirmed by the non-adherence of Ph_2S_2 in $C_{10}H_8$ at 100° to Beer's law). CS_2 in Et_2O is converted by Li α-naphthyl into dithio-α-naphthoic acid, identified as di-α-thionaphthoyl disulphide, m.p. 169°. CS_2 and $CHPh_2Na$ give the non-cryst. *diphenyldithioacetic acid*, which passes at 130—140° into dimeric diphenylthioketen, m.p. 257—258°. Thionylaniline reacts vigorously with LiPh and Li α-naphthyl giving respectively benzenesulphin-anilide, m.p. 112°, and -α-*naphthylamide*, m.p. 126°. These compounds are distinguished from the corresponding sulphonamides by their inability to react with CH_2N_2. Benzenesulphon-anilide and -β-naphthylamide, ethanesulphonanilide, and saccharin give Me derivatives with CH_2N_2 and methiondianilide gives the Et_2 derivative with $CHMeN_2$.

III (cf. A., 1931, 1305, 1419). The conversion of 4 : 4 : 5 : 5 - tetraphenyltrimethylene - 1 : 3-disulphide into $CPh_2{:}CPh_2$ by LiPh (*loc. cit.*) is accompanied by the production of LiSPh; the suggested scheme for the reaction is $CH_2<^{S\cdot CPh_2}_{S\cdot CPh_2}+LiPh\longrightarrow$ $CH_2<^{S\text{——}CPh_2}_{S(Li)(SPh)\cdot CPh_2}$ —— $CPh_2{:}CPh_2+LiSPh+[CH_2{:}S]$. 4-Thiochromone and CH_2N_2 in Et_2O readily yield the compound (I), decomp. above 170°, converted by LiPh into LiSPh and (?) non-cryst. dichromylene (mixture of *cis*- and *trans*-forms). 4-Thioflavone and Cu powder in boiling PhMe afford 2 : 2′-diphenylchromylene $[C_6H_4<^{O\cdot CPh}_{C\text{—}CH}]_2$ m.p. 224° (A., 1931, 1305), whilst α-naphtha-4-thioflavone is transformed by the successive action of CH_2N_2 and LiPh into *di*-α-*naphthaflavylene*, $C_{38}H_{24}O_2$, m.p. 252°. Thioxanthen and CH_2N_2 yield the *compound* $C_{27}H_{18}S_4$, m.p. 168—170° (decomp.), transformed into dithioxanthylene by LiPh; dixanthylene is similarly prepared. H. W.



(I.)

Organic compounds of sulphur. XXII. Action of sodium diphenylmethyl on diphenyl sulphoxide; radical migration. A. SCHONBERG and A. STEPHENSON (Ber., 1933, **66**, [*B*], 250—252).—Ph_2SO and $CHPh_2Na$ in Et_2O yield $CHPh_3$ (as such) and PhSONa (I) oxidised by air to $PhSO_2Na$; $CHPh_2Na+Ph_2SO=[CHPh_2{\cdot}SPh{\cdot}ONa]\longrightarrow CHPh_3+PhSONa$. Ph_2S_2 and PhSH, observed by Bergmann

and Tschudnovski (A., 1932, 507), are formed by the action of H_2O on (I). H. W.

Organic compounds of mercury. V. Arylation of mercuric oxide by aromatic iodoxy-compounds. A. N. NESMEJANOV and L. G. MAKAROVA (Ber., 1933, 66, [*B*], 199—201).—Reaction follows the course $R{\cdot}IO_2+HgO\longrightarrow R{\cdot}Hg{\cdot}+IO_3'$ and occurs in presence of every type of cold alkali (when shaken), best in that of Ag_2O. It is most complete when the mixture of IO_2-compound, freshly pptd. HgO, and Ag_2O is heated in boiling H_2O. The base can be isolated as such, but is more readily obtained as the halide. Examples cited are: HgPhBr, m.p. 275°, from $PhIO_2$; Hg *p*-tolyl bromide, m.p. 235°, from p-$C_6H_4Me{\cdot}IO_2$; Hg *o*-chlorophenyl chloride, m.p. 147°, from o-$C_6H_4Cl{\cdot}IO_2$; Hg *m*-chlorophenyl chloride, m.p. 210°, from m-$C_6H_4Cl{\cdot}IO_2$; Hg *p*-chlorophenyl chloride, m.p. 240°, from p-$C_6H_4Cl{\cdot}IO_2$; Hg *o*-nitrophenyl chloride, m.p. 185°; Hg *m*-nitrophenyl chloride, m.p. 236°; Hg *p*-nitrophenyl chloride, m.p. 265°. H. W.

Structural chemistry of proteins. I. Ring closure and increase in oxygen content on methoxylation of glycinin. A. KIESEL and M. ZNAMENSKAYA (Z. physiol. Chem., 1932, 213, 89—109).—In the formation of glycinin hydrochloride (I) and of the Me ester hydrochloride (II) a part of the protein constituent undergoes change. In (I) some of the acidic groups are eliminated with removal of H_2O, probably owing to internal esterification. In (II) some amide-N is eliminated and about half the weakly basic NH_2-N disappears, again owing to removal of H_2O. The power of combining with HCl is not diminished. O enters the mol. during esterification, and lysine and tryptophan disappear, whilst arginine, tyrosine, and histidine are decreased. A small proportion of the protein becomes sol. in the HCl–MeOH mixture. J. H. B.

Mode of combination of proline in gelatin and collagen. M. BERGMANN, L. ZERVAS, and H. SCHLEICH (Collegium, 1933, 6—9).—The :NH groups of proline and oxyproline are involved in the peptide chains in gelatin and collagen and are the first to be freed during ereptic action. D. W.

Determination of carbon and hydrogen by the centigram method. K. KÜSPERT (Chem. Fabr., 1933, 6, 63—64).—Modified apparatus is described. Cu (reduced from CuO) is used in place of PbO_2 for removing oxides of N, and the stream of O_2 is replaced by air. E. S. H.

Rapid determination of chlorine in organic compounds. N. M. MILOSLAVSKI and V. F. VEPRITZKAYA (J. Appl. Chem., Russia, 1932, 5, 860—867).—Combustion of an EtOH solution in a current of air, absorption of HCl in aq. $AgNO_3$, and titration with KCNS are employed. CH. ABS.

Determination of iodine in organic compounds containing selenium. F. M. HAMER (Analyst, 1933, 58, 26—27).—The substance is heated with fuming HNO_3 and $AgNO_3$ at 300°. The resulting ppts. are boiled with H_2O, filtered hot, and washed with boiling 20% HNO_3. After drying and weighing, the AgI is dissolved in KCN to obtain the wt. of the Gooch crucible. T. McL.

Determination of chloroform in alcohol–water mixtures. D. N. POPOV (Khim. Farm. Prom., 1932, 222—224).—The EtOH concn. is adjusted to 15%, when $CHCl_3$ is thrown out of solution, and its vol. is measured. If the $CHCl_3$ content is very small a known amount of light petroleum is added. CH. ABS.

Thermometric titration of acetaldehyde in presence of organic and inorganic acids. S. I. RUIBIN (J. Appl. Chem., Russia, 1932, 5, 463—469).—Somiya's method is satisfactory. CH. ABS.

Behaviour of benzoyl peroxide towards amino-compounds. I. DE PAOLINI and G. RIBET (Gazzetta, 1932, 62, 1041—1048).—With primary amines, Bz_2O_2 yields BzO_2H and RNHBz (cf. A., 1931, 209), and with *sec.* amines, BzOH and RR'N·OBz; it may therefore be used to differentiate these. It is mixed with the amine in EtOH, and, after keeping, dilution, addition of NaOH, and boiling, Fehling's solution is added. Reduction indicates a *sec.* amine (tested with $NHEt_2$, $NHPr^{\alpha}_2$, piperidine, and tetrahydroquinoline), negative reaction a primary amine (tested with heptyl-, *iso*butyl-, *iso*undecyl-, and benzyl-amine). *iso*Undecylamine, ethylenediamine, and semicarbazide yielded their Bz, Bz_2, and Bz derivatives, respectively, whilst $N(CH_2Ph)_3$ gave a mixture of PhCHO and $NH(CH_2Ph)_2$,2BzOH, and NPr^{α}_3 gave $NHPr^{\alpha}_2$. E. W. W.

Mercuro-reductive power of certain amino-acids. C. SANNIÉ and R. TRUHAUT (Compt. rend., 1933, 196, 65—67).—Of various NH_2-acids tested the following reduce Nessler's reagent in alkaline solution: glycine, serine, histidine, tryptophan, phenyl-β-alanine, dihydroxyphenylalanine, proline, creatine, creatinine, and cystine. W. O. K.

Test for phenols and copper. C. C. FULTON.—See this vol., 245.

Reaction of benzidine with acidic derivatives of selenium and tellurium. A. G. KRETOV (J. Appl. Chem., Russia, 1932, 5, 634—636).—The compound formed by H_2SeO_4 or its salts (but not H_2SeO_3, H_2TeO_3, or H_2TeO_4) with benzidine, which is rather more sol. in H_2O than the H_2SO_4 compound, can be titrated with 0·1—0·2*N*-alkali in presence of phenolphthalein. CH. ABS.

Detection of papaverine. L. EKKERT (Pharm. Zentr., 1933, 74, 24—25).—Papaverine (0·01 g.) or the hydrochloride, dry $ZnCl_2$ (0·02 g.), and BzCl (5 drops) on careful heating give rose-red, blood-red, and finally yellow to gold colours with a green fluorescence (yellowish-green under the quartz lamp). Addition of 1—2 c.c. of EtOH gives a greenish-yellow fluorescence. The reaction is sensitive to 0·02 mg. and with atropine, scopolamine, narcotine, and cryptopine only the initial red colour is formed. E. H. S.

Biochemistry.

Comparison of metabolic respiration of eels in various stages of development. (Mlle.) A. Raffy (Compt. rend., 1933, **196**, 374—376).—Respiration (c.c. O_2 consumed per g.-hr.) of eels in various stages of development is more rapid the smaller is the body-wt., sex being without appreciable influence. J. W. B.

Oxygen affinity of hæmoglobin expressed by the constant $1/k$ and the plasma-p_H, and the factors which may affect it. G. Litarczek, H. Aubert, and I. Cosmulesco (Compt. rend. Soc. Biol., 1931, **106**, 740—742; Chem. Zentr., 1932, ii, 2326). A. A. E.

Effect of temperature on the carbon dioxide absorption curve of human blood. A. J. Eisenman (J. Biol. Chem., 1933, **99**, 359—381).—Lowering the temp. of blood with const. CO_2 tension increases CO_3'' and HCO_3', the latter being directly proportional to the hæmoglobin content. The effect of temp. on the CO_2 capacity of serum is 1·1 times that on whole blood. The effect on p_H also depends on the hæmoglobin content: anæmic blood shows a decrease, whilst normal blood shows an increase at lower temp. H. G. R.

Absorption of ultra-violet radiation by hæmoglobin and some of its derivatives. H. F. Holden and C. S. Hicks (Austral. J. Exp. Biol., 1932, **10**, 219—223).—The bands observed with their heads and extinction coeffs. are as indicated. Rabbit hæmoglobin (λ 422·8 mμ, ε 123×10^3; λ 272·0 mμ, ε 37×10^3). Opossum hæmoglobin (λ 419·5 mμ, ε 127×10^3; λ 262·7 mμ, ε $28{\cdot}2\times10^3$). Denatured ox globin-hæmochromogen (λ 423·7 mμ, ε 110×10^3; λ 332·3 mμ, ε $31{\cdot}4\times10^3$; λ 270·5 mμ, ε $27{\cdot}7\times10^3$). Cyano-hæmochromogen, λ 435·0 mμ, ε $91{\cdot}0\times10^3$; λ 338·0 mμ, ε $24{\cdot}7\times10^3$; λ 264·0 mμ, ε $24{\cdot}7\times10^3$). Reduced hæmatin (λ 393·5 mμ, ε $44{\cdot}1\times10^3$; λ 264·6 mμ, ε $14{\cdot}7\times10^3$). W. O. K.

Mol. wts. of globin of different hæmoglobins G. S. Adair, (Mme.) Adair, J. Roche, and (Mme.) Roche (Compt. rend., 1932, **195**, 1433—1435).—The apparent mol. wts. of globin, paraglobin (denatured globin), and hæmoglobin, determined osmometrically, are 37,000, 99,000, and 67,000, respectively, for the ox, and 29,000, 63,000, and 65,000 for the horse. Globin and paraglobin are in equilibrium with polymerides in solution. A. C.

Detection of blood by 2 : 7-diaminofluorene hydrochloride. J. Schmidt and M. Eitel (Ber., 1932, **65**, [*B*], 1867).—The reagent (A., 1932, 242) does not become discoloured if the pure salt is dissolved in H_2O which has been boiled and allowed to cool in CO_2 and the solution is again saturated with CO_2 and preserved in a tightly-closed vessel. H. W.

Difficulties encountered in obtaining a satisfactory Wright stain [for blood]. H. J. Conn and L. A. Margolena (Stain Tech., 1933, **8**, 35—36).—It is important to work at the correct [H·] and to use pure MeOH. H. W. D.

Solubility of plasma-proteins. I. Dependence on salt and plasma concentrations in concentrated solutions of potassium phosphate. A. M. Butler and H. Montgomery (J. Biol. Chem., 1933, **99**, 173—195).—Solubility curves of horse and human serum-proteins in varying concns. of an equimol. solution of K_2HPO_4 and KH_2PO_4 at p_H 6·5 and 25° are plotted. The fibrinogen complex has a negligible solubility in 1·2*M* solution. The human plasma curve shows no break corresponding with the separation of the pseudoglobulin complex, whilst a larger content of albumin is indicated. By assuming a linear relationship between the log. of the protein solubility and the salt concn. for each portion of the curve, the concn. of the less sol. plasma-protein fractions at the concns. selected for fractional pptn. and the concn. of the individual proteins are compared with vals. from the analysis of ppts. obtained by 1 and ½ vol.-% saturation with $(NH_4)_2SO_4$ at 25° and 14·5 and 22% Na_2SO_4 at 37°. H. D.

Effect of water ingestion on ratio of albumin to globulin in blood-serum. C. Auguste (Compt. rend. Soc. Biol., 1932, **111**, 718—719).—The ingestion of 500 c.c. of distilled H_2O produced alterations in the ratio of albumin to globulin in the blood-serum. The changes thus produced varied from subject to subject, but, on the whole, the increase in the ratio paralleled that of the hydræmia. Nutr. Abs.

Critical temperature of serum. VII. Electrical conductivity of serum in relation to temperature. P. Lecomte du Nouy (Ann. Inst. Pasteur, 1933, **50**, 127—142).—Above 55° a fixation of H_2O by the serum-proteins occurs, which gives rise to (*a*) an increase in salt concn. with an increase in *K*, and (*b*) an increase in the vol. of the non-conducting mols., with a consequent reduction in *K*. Theoretically the latter effect should predominate, as it does qualitatively, but to an extent > that indicated by existing theories. With globulin suspensions adsorption of electrolytes occurs, but this does not explain the results where the mols., although subject to swelling, still remain in solution. P. G. M.

Micro-determination of copper and its application to blood, hæmocyanin, and animal tissues. R. Guillemet (Bull. Soc. Chim. biol., 1932, **14**, 1350—1385).—The technique of a method for the determination of upwards of 0·01 mg. Cu with an error of 3% is described. From the aq. HNO_3 solution of the ash of the material to be examined, Fe is removed by C_5H_5N and Cu pptd. in the presence of Ni as $Cu(OH)_2$. An aq. H_2SO_4 solution of the latter is electrolysed and the Cu deposit determined volumetrically by the phosphomolybdic acid method. The Cu content of the blood of various animals and its distribution between the corpuscles and the plasma is determined. Determinations of the Cu in the spleen and liver of dogs are made, and, in the case of the liver, the variations in the Cu content caused by bleeding and after ingestion of Cu. A modification of the method is used to determine the Cu in the hæmocyanin of *Helix pomatia*, *Maia squinado*, and *Cancer pagurus*. In these cases the no. of atoms of Cu is shown to be equal to no. of atoms of combined O. A. L.

Determination of magnesium in blood with 8-hydroxyquinoline. C. Bomskov (J. Biol. Chem., 1932, **99**, 17—18).—A comparison of the author's method (this vol., 35) with that of Greenberg and Mackey (*ibid.*, 764). The Mg content of blood ranged from 1·7 to 2·6 mg. per 100 c.c. for normal men, from 1·3 to 2·3 mg. for normal children, and from 0·8 to 1·1 mg. for children with florid rickets. H. G. R.

Determination of magnesium in blood with 8-hydroxyquinoline. D. M. Greenberg and M. A. Mackey (J. Biol. Chem., 1932, **99**, 19).—Polemical (cf. preceding abstract). H. G. R.

Individual variation in serum-calcium in normal men and women. R. E. Boynton and E. M. Greisheimer (Proc. Soc. Exp. Biol. Med., 1931, **28**, 907—913).—Serum-Ca in the morning was: men 10·31, women 10·01 mg. (average) [per 100 c.c. ?]. In normal women vals. decreased in the menstrual or post-menstrual period. Ch. Abs.

Is there an unknown compound of the nature of calcium citrate present in the blood? D. M. Greenberg and L. D. Greenberg (J. Biol. Chem., 1932, **99**, 1—15).—There is no definite evidence of the existence of an org. citrate-like compound of Ca in blood. H. G. R.

Reciprocal relationship of calcium and inorganic phosphorus of the blood of sheep. A. H. H. Fraser (Biochem. J., 1932, **26**, 2166—2168).—In sheep under outdoor conditions, fed on a basal ration deficient in Ca, or such a ration supplemented with cod-liver oil, there is a relative constancy of the Ca×P product. S. S. Z.

Effect of anticoagulants on the determination of inorganic phosphate and protein in plasma. O. H. Gaebler (J. Biol. Chem., 1932, **99**, 99—107).—Plasma always contains less inorg. phosphate and less total N than serum, due to H_2O being drawn from the cells. With native plasma as standard, the inorg. phosphate of oxalate-plasma is low and that of serum is high. Oxalate-plasma left in contact with the cells at 10° for 5 hr. shows no change. Fluoride interferes with the Benedict–Theis and Fiske–Subbarow reactions; thus is prevented by AlCl$_3$. H. G. R.

Reactions of lead compounds with serum and serum-models. M. Jowett (Biochem. J., 1932, **26**, 2108—2122).—When CO_3'' is the only precipitant ion $PbCO_3$ is formed. In presence of PO_4''' (and Cl′) the product is $Pb_5Cl(PO_4)_3$. When Ca is also present, the product approximates to $Pb_5Cl(PO_4)_3$,Ca·$Cl(PO_4)_3$. Pb ion reacts very rapidly, but the union of Ca is less rapid than that of Pb and may be incomplete under unfavourable conditions. Solubility and extent of surface determine the rate of reaction of solid Pb compounds with PO_4'''. An approx. val. is obtained for the solubility product of $PbCO_3$ at 37·5°. The solubilities in serum of $PbCO_3$, $PbHPO_4$, $Pb_3(PO_4)_2$, and $Pb_5Cl(PO_4)_3$ are calc.; the last compound is the least sol. S. S. Z.

Micro-colorimetric determination of iodine in blood. R. G. Turner and M. Z. Weeks (J. Amer. Chem. Soc., 1933, **55**, 254—258).—The method previously described (A., 1930, 1463) is satisfactory provided I-free K_2CO_3 (or KOH), H_2SO_4 containing $< 0·00008\%$ Fe, and EtOH purified by Castille and Henri's method (A., 1924, ii, 581) are used. H. B.

Volatile chlorine of blood. S. Morris and N. Morris (Biochem. J., 1932, **26**, 2015—2020; cf. A., 1931, 248).—The presence of O_2 is essential for the loss of Cl to take place. The heating of an olive oil–NaCl mixture (I) at $> 100°$ leads to loss of Cl. There is a close similarity between blood and (I) as far as the loss of Cl is concerned, except that heat is required in the latter case, whilst drying in a desiccator is sufficient to produce a loss of the Cl complex in the former case. Org. Cl can be extracted from blood by removing H_2O with $COMe_2$ and Et_2O and subsequent extraction by an EtOH–Et_2O mixture. S. S. Z.

Method for measuring cholesterol. P. G. Schube (J. Lab. Clin. Med., 1932, **18**, 306—309).—The green colour obtained with cholesterol (I), H_2SO_4, and Ac_2O and employed in the usual colorimetric determination of (I), on keeping at 20° in the dark for 12—24 hr. fades into a yellow colour. Tables show that colorimetric determination of (I) using the yellow colour for comparison gives much greater accuracy than when the green is used. A table also compares the yellow and green vals. for the (I) contents of a no. of samples of blood. Nutr. Abs.

Effect of infra-red rays on blood-cholesterol. S. Malczynski (Compt. rend. Soc. Biol., 1932, **110**, 808—810; Chem. Zentr., 1932, ii, 1797).—Energetic irradiation has no effect, but weaker prolonged irradiation causes a transient rise. A. A. E.

Protein–lipin combinations in blood and body-fluids. I. Normal human and dog plasma and horse serum. M. E. Turner and R. B. Gibson (J. Clin. Invest., 1932, **11**, 735—746).—Fatty acids, phospholipins, and cholesterol were determined in the protein fractions. 50% of the lipins were co-pptd., particularly by the globulins. Ch. Abs.

Micro-determination of phosphatides in blood. S. Katsura, T. Hatakeyama, and K. Tajima (Biochem. Z., 1933, **257**, 22—31; cf. A., 1931, 858).—Lecithin is quantitatively pptd. when a saturated solution of $CaCl_2$ in $COMe_2$ is added to a $COMe_2$ solution of a fat mixture. The method described, which is based on this fact, makes possible the determination of 0·1 mg. of lecithin with an error of ±2—3% and the determination of the phosphatide content of 0·15—0·2 c.c. of blood with an error of ±2—5%. W. McC.

Effect of ingestion of a large amount of fat and of a balanced meal on the blood-lipins of normal man. E. B. Man and E. F. Gildea (J. Biol. Chem., 1932, **99**, 61—60).—Vals. for the distribution of serum-lipins of normal individuals are given. Ingestion of 3·5—4·0 g. of fat per kg. produces a marked rise in serum-fatty acids and a moderate increase in phospholipins. Ingestion of a balanced meal containing at least 0·6 g. of fat per kg. produces a rise in serum-fatty acids. H. G. R.

Modification of the Stoddard and Drury method for the determination of fatty acids in blood-serum. E. B. MAN and E. F. GILDEA (J. Biol. Chem., 1932, **99**, 43—60).—A titrimetric method for the determination of serum-fatty acids (exclusive of very unsaturated or H_2O-sol. fatty acids), based on that of Stoddard and Drury (A., 1930, 103), is described. H. G. R.

Optical activity of blood-filtrates. II. Effect of acidity and the relation between rotation and reduction values. H. N. NAUMANN (Biochem. Z., 1933, **257**, 32—40; cf. A., 1932, 1053).—The rotation of the blood-filtrate (I) obtained in the method of Folin and Wu increases with the degree of acidity, reaching a max. (dextro) at p_H " $-0{\cdot}7$," the reducing power meanwhile remaining unaffected. The increase (II) is due to alteration of the non-sugars, since it also occurs after removal of the sugar as well as in normal urine and does not occur in the filtrates from Zn and Cd treatment. Very probably (II) is due partly to liberation of org. *d*-acids from *l*-salts and partly to hydrolysis of *l*-polypeptides and glycuronates, whilst mutarotation also causes slight increases or decreases. In the (I) of normal persons and in that of diabetics the max. *d*-rotation of the filtrates corresponds with the reducing powers as measured by the Hagedorn and Jensen method. The results indicate that (I) contains the usual equilibrium mixture of glucose modifications and not a special modification. W. McC.

Interference of non-glucosidic substances, particularly lactic acid, on the measurement of the optical rotatory power of blood-sugar. J. THOMAS (Bull. Soc. Chim. biol., 1932, **14**, 1279—1289).—The change with change of p_H in the rotatory power of dialysed blood cannot be due to the presence of substances known to be in the blood, such as NH_2-acids and lactic acid, because the change is too great, and still persists after the extraction of the lactic acid. The change is not observed in the dialysed blood of diabetics, but reappears after the administration of insulin. These facts are considered to indicate that the phenomenon is due to a change in the equilibrium of two forms of glucose, or the presence of an unstable combination of this and an unknown substance, or to some unknown product of carbohydrate metabolism. A. L.

Distribution of sugar in blood and the permeability of red blood-corpuscles. L. MOSONYI (Biochem. Z., 1932, **256**, 308—325).—Red cells of man and dog contain less sugar than the plasma. When sugar is administered by mouth to dogs, the sugar content of the red cells relatively to that of the plasma at first decreases and then increases, the cell content becoming $>$ that of the plasma. In man with mild diabetes the sugar distribution is the same as in normal man. In the blood of depancreatised dogs, the ratio of sugar in cells to that in plasma is $<$ with normal dogs. Injection of insulin decreases the cell sugar content. The bearing of the results on the permeability of the cells is discussed. P. W. C.

Determination of monosaccharides in presence of disaccharides and its application to blood analysis. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1932, **99**, 249—255).—The solution containing monosaccharides and reducing disaccharides is heated with a modified Barfoed's reagent in which AcOH is replaced by lactic acid. The pptd. Cu_2O is determined colorimetrically by the acid molybdate method. Such a reagent is applicable to filtrates from blood deproteinised by Fe pptn. (A., 1932, 1276). F. O. H.

Determination of blood-sugar. III. Method of Ionesco-Matiu and Vitner. R. RAZAFIMAHERY (Ann. Chim. Analyt., 1933, [ii], **15**, 1—10; cf. this vol., 82).—The method, which depends on the reduction of a Hg salt to metallic Hg and determination of this with 0·01*N*-NaCl in the presence of Na nitroprusside after dissolving in a mixture of H_2SO_4 and HNO_3, is considered inferior to the Hagedorn–Jensen and Baudoin–Lewin methods. P. G. M.

Hagedorn and Jensen's method for determining blood-sugar. R. C. FORMIGUERA (Compt. rend. Soc. Biol., 1932, **110**, 730—731, 743—744; Chem. Zentr., 1932, ii, 1809).—Deproteinisation with Zn and cooling to 10° after reduction are recommended. A reagent containing 3·3 g. $K_3Fe(CN)_6$ and 10·6 g. Na_2CO_3 (anhyd.) per litre is employed; 2 c.c. are required for the filtrate corresponding with 0·05—0·1 c.c. of blood. A. A. E.

Utilisation of galactose in physiological and pathological conditions. I. Technique. H. KOSTERLITZ (Z. ges. exp. Med., 1932, **81**, 792—799; Chem. Zentr., 1932, ii, 1935).—Corley's method for determining blood-glucose and -galactose is suitable; *Saccharomyces Ludwigii* is used instead of baker's yeast, and a phosphate buffer of p_H 5·6 instead of 0·9% NaCl. A. A. E.

Micro-determination of galactose in blood. A. SCHRUMPF (Compt. rend. Soc. Biol., 1932, **109**, 105—106; Chem. Zentr., 1932, ii, 1943).—The difference between the reducing power of whole blood and that after pptn. of galactose with EtOH in the cold, corr. for the " residual reducing val." of the blood, gives the quantity of galactose present. A. A. E.

Lactic acid in the blood of resting man. A. V. BOCK, D. B. DILL, and H. T. EDWARDS (J. Clin. Invest., 1932, **11**, 775—788).—Blood-lactic acid is not directly related to p_H. It originates partly from muscle activity, and partly perhaps from carbohydrate mobilised for general metabolism. CH. ABS.

Micro-determination of organic acids in blood-serum. H. BRÜHL (Biochem. Z., 1932, **256**, 293—307).—A method using 2 c.c. of serum and depending on electrometric titration with 0·05*N*-HCl of 1 c.c. of ultrafiltrate obtained by pressure filtration (3 atm.) is described, the error being $\pm 3\%$. The normal concn. of acid lies between $N/130$ and $N/97{\cdot}5$ and the mean dissociation const. at p_K 3·6. The highest concn. of acid obtained in uræmia and on ketogenic diets was $N/34{\cdot}4$. Disappearance of org. acids from brain during tetany is detected. P. W. C.

Tyrosine fraction in the blood-serum of Japanese and its relation to the skin tint and skin diseases. Y. MATSUMOTO (Japan. J. Dermatol., 1932, 32, 191—213).—The val. (average 2·5 mg. per

100 c.c.) does not change with age, but in females is < in males; it varies with the season, the skin tint, and skin diseases. CH. ABS.

Content of uric acid, free amino-nitrogen, and hydrogen-ion concentration of blood of silk-worm pupæ. A. AKAO (J. Chosen Med. Assoc., 1931, **21**, 769—771).—The (average 6·51) moves with age towards alkalinity. The uric acid content is max. at the early pupa stage. Free NH_2-N increases with age, decreasing slightly just before the imago emerges. Uric acid plays no part in regulating the acidity of the body-fluid. CH. ABS.

Effect of human blood-serum on (*a*) toxicity of bile salts, (*b*) bile salt hæmolysis. J. W. WILLIAMS (Proc. Soc. Exp. Biol. Med., 1932, **29**, 916—917, 918—919).—With mice, intraperitoneal injection of Na taurocholate in normal saline was twice as toxic as that in fresh human blood-serum. Serum also protects red blood-cells against hæmolysis. CH. ABS.

Inhibition of blood-clotting by bile *in vitro*. H. ELBEL (Biochem. Z., 1932, **256**, 398—405).—The view is supported that bile acids remove Ca from non-protein serum constituents, cholate inhibiting clotting by degrading the lipin–Ca complex of thrombokinase. P. W. C.

Determination of antiprothrombin in blood-serum. A. FISCHER (Klin. Woch., 1932, **11**, 936—937; Chem. Zentr., 1932, ii, 2200).—Serum-globulins are regarded as albumin–heparin complexes. Serum-globulin vals. are a direct measure of the antithrombin or heparin. There is complete correspondence between the globulin content and the coagulability of plasma. Serum (0·03 c.c.) is added to *N*/180-AcOH (9 c.c.), and, after shaking, 0·1*N*-NaOAc (1 c.c.) is added, the turbidity being determined after 10 min. A. E. E.

Total carbohydrate content of heart muscle. F. LASCH (Z. ges. exp. Med., 1932, **83**, 36—46; Chem. Zentr., 1932, ii, 2842).—The total carbohydrate content of the left heart muscle normally, in compensated disease of the heart, and in wasting or infectious disease, was 0·4—1% (moist wt.), and was in these cases higher than that of the right ventricle muscle. A. A. E.

Occurrence of a substance similar to acetylcholine in skeletal muscle. I, II. F. PLATTNER and E. KRANRICH (Pflüger's Archiv. 1932, **229**. 730—737; **230**, 356—362; Chem. Zentr., 1932, ii, 1935, 2075).—I. The substance was extracted from frog's muscle with 0·01*N*-HCl in EtOH, and purifying with Et_2O the residue obtained on evaporation. The distribution of the substance in the musculature is recorded; muscle contains the more of the substance the greater is the demand on it for continuous work.

II. The distribution of the substance in the tortoise is described. A. A. E.

Muscle-creatine and creatinine coefficient. A. CHANUTIN and F. W. KINARD (J. Biol. Chem., 1933, **99**, 125—134).—The standard deviations of the creatine contents of the muscles of the dog, rat, rabbit, and guinea-pig are almost identical, indicating a const. variation in creatine concn. Statistical analysis of the data obtained shows no relationship between the muscle-creatine and creatinine elimination. H. D.

Relationship between water and glycogen content of the liver. A. G. HOLMQUIST (Skand. Arch. Physiol., 1932, **65**, 9—17).—No relation was found between the glycogen and H_2O contents of the liver (rabbit, mouse, hedgehog, rat, pigeon). NUTR. ABS.

Occurrence of invertase in the hen's gizzard. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1932, **256**, 406—410).—Further attempts have been made to discover the source of the invertase of the different layers of the hen's gizzard (cf. A., 1932, 1274). P. W. C.

Glycogen in cartilage. H. B. FELL and R. ROBISON (Nature, 1933, **131**, 62).—A discussion (cf. this vol., 176). L. S. T.

Hydroxyapatite, the chief constituent of inorganic bone- and tooth-material. R. KLEMENT and G. TROMEL (Z. physiol. Chem., 1932, **213**, 263—272; cf. A., 1929, 1328).—*X*-Ray examination of bone residue confirms the view that the residue consists principally of hydroxyapatite (I), $Ca_{10}(PO_4)_6(OH)_2$. On shaking (I) with phosphate buffer solution the ratio $Ca : PO_4$ increases from 1 : 0·60 to 1 : 0·62, but the structure revealed by the *X*-ray diagram is unchanged. When $CaHPO_4,2H_2O$ is treated with Tyrode solution, (I) results. J. H. B.

Composition of bone. XIII. Direct gravimetric determination of calcium, magnesium, and phosphate. M. L. WASHBURN and M. J. SHEAR (J. Biol. Chem., 1932, **99**, 21—41).—A method is described whereby Ca, Mg, and PO_4 may be determined in the same mixture with an accuracy of ±0·3%. In analysis of bone solutions the presence of dissolved org. matter and of other ions must be taken into consideration. H. G. R.

Detection of barium in human bones. S. KUNOWSKI (Deut. Z. ges. gerichtl. Med., 1932, **19**, 265—278; Chem. Zentr., 1932, ii, 2324—2325).—Human bones normally contain no Ba; a positive spectrographic reaction indicates Ba poisoning, but a negative one does not exclude it. A. A. E.

Barium in animal bones. F. TIMM (Deut. Z. ges. gerichtl. Med., 1932, **19**, 279; Chem. Zentr., 1932, ii, 2324).—The Ba content of the bones of wild and domesticated animals is < 0·001%. A. A. E.

Fluorine content of fossil bones. T. VON SZELÉNYI (Zentr. Min. Geol., 1932, **B**, 405—414; Chem. Zentr., 1932, ii, 2308—2309).—Analysis of fossilised human bones shows that the F content gives no indication of the geological age. A. A. E.

Chemistry of skin. A. LOEWY and G. CRONHEIM (Biochem. Z., 1932, **256**, 411—431).—The H_2O, fat, total and residual N contents, and the mineral content (K, Cl, Ca, Mg, Na) of the skin of normal rats and guinea-pigs and of animals kept at varying diminished pressures, kept in the dark, irradiated, and treated with vigantol are investigated. Large variations of H_2O and fat content were obtained

and smaller variations of the remaining constituents, but variations typical of the particular set of conditions could not be detected, due probably to the very slow establishment of any such differences.
P. W. C.

Oxidase of the crystalline style. C. BERKELEY (Nature, 1933, **131**, 94).—The reaction of the crystalline styles towards guaiacum is marked in the case of *Ostrea virginica*, *lurida*, and *gigas*. *Schizotheurus Nuttalli*, *Cardium corbis*, and *Bankia setacea* also contain the oxidase system in their styles.
L. S. T.

Oysters and anæmia. E. J. COULSON, H. LEVINE, and R. E. REMINGTON (Amer. J. Pub. Health, 1932, **22**, 1141—1146).—The oyster is a good source of Fe and Cu. CH. ABS.

Iron and copper in liver and liver extracts. A. E. MEYER and C. EGGERT (J. Biol. Chem., 1932, **99**, 265—270).—The livers of horses, dogs, and pigs are uniformly rich in Fe, whilst those of oxen contain considerably less Fe but a greater amount of Cu. Aq. extraction removes only a part of the metals, and this is found in the ppt. on pptn. with 67% EtOH. Subsequent ppts. with higher concns. of EtOH contain less Cu and very little Fe.
F. O. H.

Copper content of liver and spleen in the dog; effect of bleeding and of ingestion of copper. R. GUILLEMET (Compt. rend. Soc. Biol., 1932, **111**, 731—733).—Negligible amounts of Cu were found in the spleen, but variable amounts (markedly increased on a diet rich in Cu) were found in the liver of dogs. Bleeding caused a fall in the Cu content of the liver if the animal had previously been on a diet low in Cu, but no significant change when the previous diet was high in Cu. NUTR. ABS.

Calcium and phosphorus in the brain in different conditions. E. C. EAVES (Brit. J. Exp. Path., 1931, **12**, 112—122).—In normal human brain only a trace of Ca is extractable by H_2O, and 33% of the total by AcOH; much more P is extractable by H_2O, probably as glyceryl ester. In pathological conditions an increase in Ca is relatively uncommon; decrease in P is more common. CH. ABS.

Bielschovsky staining technique. Factors influencing its specificity for nerve fibres. R. H. BEECH and H. A. DAVENPORT (Stain Tech., 1933, **8**, 11—30).—Avoidance of over-staining assisted differentiation between connective-tissue and nerve-fibres. Staining of fine fibres was favoured by the addition of AcOH to the CH_2O used for fixation, or by the addition of C_5H_5N to the $AgNO_3$-bath.
H. W. D.

Phosphatides of human brain. IV. Separation of α- and β-cephalins. V. Isolation of simple cephalins. U. NISHIMOTO and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, **8**, 424—427, 428—431).—IV. A crude cephalin prep. (A., 1932, 958) was purified by treatment with $CdCl_2$, Et_2O, etc. and then pptd. by basic Pb acetate. Fractionation of the ppt. by Et_2O–EtOH and C_6H_6–EtOH mixtures yielded the α- (I) and β-series (II) of cephalins consisting of derivatives of the α- and β-glycerophosphates of $NH_2{\cdot}C_2H_4{\cdot}OH$, respectively.

V. Bromination and subsequent treatment of (I) and (II) with org. solvents indicated the following compounds to have been originally present: α-cephalins in (I): distearyl-, m.p. 174—176°, oleostearyl-, and oleodocosatetraenyl- (?) (Br-derivative, m.p. 222—226°); β-cephalins in (II): stearyldocosatetraenyl- (?) (Br-derivative, m.p. 247—249°) and oleostearyl-. F. O. H.

Solubility of tissue-lipins in glycerol. L. BOUISSET and C. SOULA (Compt. rend. Soc. Biol., 1932, **110**, 673—674; Chem. Zentr., 1932, ii, 2191).—Cold EtOH extracts more lipin than does glycerol.
A. A. E.

Determination of lipin in tissue. C. ARTOUR (Bull. Soc. Chim. biol., 1932, **14**, 1386—1421).—A crit. survey of various methods of lipin determination is given, that of Lemeland (A., 1923, ii, 347) combined with a volumetric determination of the fatty acids in the total extract as made by Kumagawa and Suto (A., 1908, ii, 331) being considered most advantageous. The technique of a method based on the above and suitable for quantities of 10—20 mg. of fatty acid is described. To determine (*A*) the total lipin-P, (*B*) phosphoaminolipin-P, carnithine-P (*A*—*B*), non-phosphoaminolipin-P, and the total fatty acid, the following method is used. The blood or tissue is extracted with EtOH, finally with EtOH and $CHCl_3$, and the solvents are evaporated under reduced pressure. Part of a $CHCl_3$ solution of the residue is used for determining total P, the remainder being pptd. thrice with $COMe_2$ containing 2% EtOH saturated with $MgCl_2$. The fatty acid is then determined in the $COMe_2$ solution after saponification and extraction with light petroleum, and in the ppt. after saponification and extraction with Et_2O. This method can be used satisfactorily on 1 g. of material with an error $< 5\%$. A. L.

Fatty acids of liver-lecithin. R. H. SNIDER and W. R. BLOOR (J. Biol. Chem., 1933, **99**, 555—573).—Analyses of three samples of ox liver-lecithin indicate that the proportion of unsaturated to saturated fatty acids as determined by a modification of the Pb soap method of Twitchell (A., 1921, ii, 662) is 55—40. From the mean mol. wt. (276) of solid acid fractions, the saturated acids consist of 71% stearic to 29% palmitic. The distribution of the unsaturated acids, determined by separation of the Br-derivatives, is linoleic 45%, arachidonic 31%, and oleic acid 21%, no acids with three double linkings being present. Acids above C_{20} were found in small quantity in one sample of lecithin. A. L.

Analysis and composition of fatty material produced by the decomposition of herring in sea-water. R. C. WELLS and E. T. ERICKSON (J. Amer. Chem. Soc., 1933, **55**, 338—341).—The fatty material (I) (time of action of sea-water not known) contains C 63·63, H 10·06, N 0·43, S 0·93, Ca 5·0, Mg 0·82, K 0·03, Na 0·26, Al_2O_3 0·12, PO_4 0·19, NaCl 2·72, SiO_2 0·2, and undetermined (mainly O) (by difference) 15·61%, a trace of Fe_2O_3, no SO_4 or CO_3, and loses 5·9% at 105°/1 hr. (I) consists largely of Ca and Mg salts of fatty acids, since treatment with HCl gives a mixture of unsaturated [8·2% of (I)] and saturated fatty acids (palmitic, myristic, and lower acids)

(64·5%), and unsaponifiable matter (cholesterol) (0·6%).

The origin of petroleum in sedimentary deposits is discussed briefly, partly with reference to the observation that palmitic acid, Ca palmitate, and (I) all yield a petroleum-like product when heated at 350°/7 days in sealed tubes. H. B.

B.P. 1932 method for determining inorganic iodine in desiccated thyroid gland. H. G. Rees and A. H. Salway (Quart. J. Pharm., 1932, **5**, 627—628).—The method (Harington and Randall, A., 1930, 504) is said to be invalidated by the fact that >50% of the thyroglobulin in thyroid gland desiccated below 40° remains undenatured and extractable with cold H_2O. The org. I represented by this fraction falsely appears as inorg. I. W. S.

Water-soluble iodine content of desiccated thyroid gland. C. R. Harington and S. S. Randall (Quart. J. Pharm., 1932, **5**, 629—632).—The results of Rees and Salway (cf. preceding abstract) are corroborated. An alternative method of denaturation by treatment with EtOH followed by desiccation at 55—60° is recommended. W. S.

3 : 4-Dihydroxyphenylacetic acid as precursor of the pigment in the wing covers of the meal-worm insect, *Tenebrio molitor*, L. H. Schmalfuss, A. Heider, and K. Winkelmann (Biochem. Z., 1933, **257**, 188—193; cf. A., 1930, 1217).—The wing covers (I) of the meal-worm insect contain 3 : 4-dihydroxyphenylacetic acid, which can be isolated by a method described. In (I) the acid acts as precursor of the pigment which develops after death. W. McC.

Tegumentary porphyrin of *Lumbricus terrestris*. C. Dhéré (Compt. rend., 1932, **195**, 1436—1438).—The presence of free protoporphyrin in the skin of the earth-worm is shown by spectrum analysis of the fluorescence in ultra-violet light of the skin and extracts of it with org. solvents and 2*N*-HCl. Fluorescence is prevented *in vivo* by combination with Fe or Cu, and/or storage of the porphyrin in colloidal solution. A. C.

New group of animal pigments [lyochromes]. I. P. Ellinger and W. Koschara (Ber., 1933, **66**, [*B*], 315—317).—Pigments, sol. in H_2O, insol. in indifferent media, which fluoresce with a yellowish-green light and contain much N and O, are present in the liver and kidney of man and dog. The isolation of *lyochrome* A (C 33·5, H 4·0, N 21·6%) and *lyochrome* B (C 35·7, H 3·3, N 32·0%) from whey is described. H. W.

New class of natural pigments. R. Kuhn, P. Gyorgy, and T. Wagner-Jauregg (Ber., 1933, **66**, [*B*], 317—320).—Vitamin-B_2 (I) is adsorbed from acid solution by fuller's earth. Elution of the adsorbates is effected by dil. C_5H_5N or NH_3 preferably in presence of EtOH, and pptn. of impurities is accomplished by addition of EtOH or $COMe_2$ to the solutions from which C_5H_5N has been removed. In such solution (I) has a bright yellow colour with intensely green fluorescence. In all cases the intensity increases with increasing biological activity. There is an intimate relationship between the distribution of (I) and yellow pigments sol. in H_2O with green fluorescence in plant and animal. It remains undecided whether (I) is a pigment. Possibly a large class of pigments exists of which only one or few are related to (I). The new pigments contain N, are amphoteric, sol. in H_2O, insol. in Et_2O and light petroleum. When treated with 2*N*-Na_2CO_3 the fluorescence disappears, but the colour remains, but can be discharged by $Na_2S_2O_4$; addition of 2*N*-H_2SO_4 and Br–H_2O causes reappearance of the colour, whilst the green fluorescence is restored by addition of NaOAc. The pigments are not decomposed by boiling Br–H_2O, showing that conjugated >C:N linkings are causative of colour. They are optically closely allied to xanthopterin (cf. Wieland and Schopf, A., 1925, i, 1465). For the pigments the term "flavin" is proposed, that from ovalbumin being named ovoflavin. H. W.

Carotene in the endocrine glands of the ox. R. Netter (Bull. Soc. Chim. biol., 1932, **14**, 1554—1559).—Carotene has been obtained from suprarenal cortex, ovaries, and testes. It appears to be present in the pituitary, but not in thymus or thyroid. H. G. R.

Electro-chemistry of liver and bile. R. Keller (Biochem. Z., 1933, **257**, 78—85).—Neutral electrolytes (salts) are electrolytically decomposed to a much greater extent in the liver than in other organs. The electro-chemical theory provides explanations for some of the processes which occur in the liver. W. McC.

Biochemistry of spermatozoa and ova. R. Keller (Biochem. Z., 1933, **257**, 86—88; cf. preceding abstract).—Unfertilised ova (I) and spermatozoa (II) are composed of electropositive and electronegative constituents. In (I) the surfaces and germinal spots are electropositive. The heads of (II) are strongly electronegative. W. Mc.C.

Glutathione in hens' eggs during incubation. S. Castagna and M. Talenti (Arch. Farm. sperim., 1933, **55**, 28—34).—Initially hens' eggs contain no gluthathione, but as development proceeds during incubation increasing amounts, up to 0·036%, are found. R. K. C.

Immunological behaviour of the second protein [livetin] of hen's egg-yolk. T. H. Jukes and H. D. Kay (J. Exp. Med., 1932, **56**, 469—482).—Livetin from egg-yolk and the hen's serum-globulin are closely related, but not identical. Serum-euglobulin and -pseudoglobulin can also be distinguished by the complement-fixation test. Ch. Abs.

Action of hot glycerol on egg-white. N. Ivanovsky (Biochem. Z., 1933, **257**, 57—61).—Glycerol (I), in proportion to its amount, increases the acidity of aq. solutions of protein (ovalbumin) and does not prevent the production of alkali albuminates when the protein is heated in an alkaline medium. The pptn. of the protein by $(NH_4)_2SO_4$ is progressively reduced by increasing the concn. of (I). W. McC.

Detection of urea in the normal and pathologically modified optic lens. Schmerl (Klin. Woch., 1932, **11**, 952—953; Chem. Zentr., 1932, ii, 2330).—In rabbits the capsule contains more urea

than the fibres; in cataract less is present than normally. A. A. E.

Significance of oxidation-reduction conditions for vital staining, especially the nuclear staining of living cells. W. ALEXANDROV (Protoplasma, 1932, **17**, 161—217).—The partition of dyes in cells is examined in relation to intracellular changes in r_H and p_H. A. G. P.

Supravital staining of intercellular cement substance. D. A. IRWIN (Stain Tech., 1933, **8**, 36).—Thin pieces of tissue are immersed in 0·1% indigotintetrasulphonate in normal saline for 10 min. They are rinsed and put into 0·2% methylene-blue in normal saline for 1 min. They can be fixed in 10% NH_4 molybdate (12 hr.), dehydrated in EtOH, and cleared in xylene. The intercellular cement substance stains purplish-red and the nuclei and cytoplasm a faint blue. H. W. D.

Fixation of tissues vitally stained with trypan-blue. D. C. HETHERINGTON and E. H. TOMPKINS (Stain Tech., 1933, **8**, 31—34).—The fixative recommended is: $CHCl_3$ 2 pts., EtOH 2 pts., AcOH 1 pt., $HgCl_2$ to saturation. After fixing for 1—2 hr. the tissue is transferred to 95% EtOH for 12 hr., EtOH for 12—24 hr., EtOH+xylene for 30 min., xylene, and then embedded in paraffin. H. W. D.

Rapid technique for permanent mounting of minute fresh-water organisms. P. GRAY (J. Roy. Micros. Soc., 1932, **52**, 370—373).

Urea content of saliva. R. VLADESCO and M. POPESCO (Compt. rend. Soc. Biol., 1931, **107**, 862—864; Chem. Zentr., 1932, ii, 1798).—Urea has been detected in the normal saliva of the parotid and the submaxillary glands. A. A. E.

Potential of the mucous membrane of the stomach. I. E. MISLOWITZER and S. SILVER. **II. Potential of the gastric mucosa and absorption.** E. MISLOWITZER, S. SILVER, and M. ROTHSCHILD (Biochem. Z., 1932, **256**, 432—443, 444—449).—I. The potential of the gastric mucosa is influenced slightly by acid, alkali, and various drugs on the blood side and strongly on the reverse side by Li, CN, and I.

II. Sugar placed in the stomach is not absorbed but recovered quantitatively after 4 hr. both with normal animals and animals rendered strongly hypoglycæmic with insulin. When KI solution is placed in the stomach, absorption of I occurs, and if in addition $Li^{\cdot}$ and CNS' (which decrease the potential) are present a greater amount of I is absorbed. P. W. C.

Carbon dioxide content of the gastric mucosa. L. IRVING and M. J. WILSON (J. Cell. Comp. Physiol., 1932, **2**, 141—148).—Changes in the CO_2 content of gastric mucosa during secretion are insufficient to indicate alteration of the acid-base equilibrium of the tissue as a whole. No appreciable excess of strong acid occurs in the mucosa during secretion or as a result of penetration after secretion. A. G. P.

Post-mortal formation of acid in the gastric mucosa. L. IRVING (J. Cell. Comp. Physiol., 1932, **2**, 149—156).—The CO_2 content of gastric mucosa decreases after excision. Post-mortal production of acid is not due to a persistence of the vital secretion of HCl, but probably results from the breakdown of the intrinsic metabolic processes of the tissue. A. G. P.

Determination of pepsin in stomach contents with the Zeiss-Pulfrich photometer. S. PETERSEN (Mikrochem., 1932, **12**, 215—222).—The use of a Pulfrich photometer in place of a nephelometer enables the method of Rona and Kleinmann, as modified by Stern (A., 1931, 1090), to be used as a clinical method. F. L. U.

Effect of pyloric obstruction on gastric secretion. D. R. WEBSTER and J. C. ARMOUR (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 109—120).—In dogs with experimental pyloric obstruction the gastric secretion is dependent on the quality and quantity of food introduced into the intestine, no hypersecretion occurring if a proper balance of food is maintained. F. O. H.

Determination of bile acids. M. A. ETCHEVERRY (Arch. Argent. enfern. ap. digest., 1932, **7**, No. 3).—Bile or duodenal juice (2 c.c.) is treated with 25% aq. $Pb(OAc)_2$ (0·5 c.c.), diluted to 10 c.c. with 95% EtOH, and filtered. The filtrate (1 c.c.) is mixed with 1 c.c. of 2% vanillin in EtOH, diluted to 10 c.c. with 50% H_2SO_4, and heated at 100° for 8 min. After centrifuging, the solution is compared colorimetrically with standards prepared from cholic acid (0·0125—0·2%) similarly treated. CH. ABS.

Determination of urobilin. M. ROYER (Semana méd., 1932, II, 1348—1351).—Urine: 1 c.c. is mixed with 2 drops of 3% tincture of I, solid $Zn(OAc)_2$, and EtOH to 20 c.c., and filtered; bile pigment must be removed previously with $(NH_4)_2CO_3$ and $CaCl_2$. Bile: 4 c.c. are treated with 4 c.c. of 20% aq. $FeCl_3$, 8 c.c. of 20% aq. NH_3 are added, and the mixture is shaken and filtered. 8 c.c. of the filtrate are acidified with HCl; $Zn(OAc)_2$ and EtOH to 16 c.c. are added, and the mixture is filtered. Blood: 2—3 c.c. are treated with 2 vols. of EtOH and $Zn(OAc)_2$, and the mixture is centrifuged after 2 hr. The factor for correcting the error caused by contraction of the liquids is 0·96. Fæces: 1—2 g. are treated with 1% HCl–EtOH and centrifuged after several hr. at 38—40°. The sediment is again extracted with EtOH. The total EtOH extract is measured, and filtered after addition of $Zn(OAc)_2$. Tissues: 4—5 g. are ground with sand, extracted several times with EtOH for 24 hr. at 37°, and centrifuged. The fluorescence of a solution of 0·05 mg. of trypaflavine in 1 litre of H_2O is compared with that of the bilirubin and Zn salt; 1 c.c.=0·0000128 mg. of bilirubin. For dilution of the test solution, a solution of $Zn(OAc)_2$ (25 g.), NaOAc (70 g.), HCl (*d* 1·19, 4 c.c.), and EtOH (60%, to 1000 c.c.) is employed. CH. ABS.

Relative immutability of hydrogen-ion concentration of the bile. Buffering effect in bactericidal experiments. R. OTTENBURG and J. KAHN (Proc. Soc. Exp. Biol. Med., 1932, **29**, 573—576).—Alkali given by the mouth or vein and HCl by the mouth did not appreciably affect the bile-p_H. The bile secretion is relatively independent of those conditions of H_2O and electrolytes in the blood which

influence the secretion of urine. The bactericidal effect of alkali solutions is destroyed by addition of bile. CH. ABS.

Catalase of milk. A. ZEILINGER (Milchw. Forsch., 1932, **14**, 342—377).—A gas-volumetric method and an iodometric method are described for determining catalase in milk. The influence of shaking of the reaction vessel on O_2 production is studied. The rate of gas production decreases with time according to a hyperbolic equation. The optimum temp. for catalase action is 20—21°. E. B. H.

Cholesterol content of the milk of various animal species. H. NAKANISHI (Nagoya J. Med. Sci., 1931, **5**, 190—191).—Vals. (mg. per 100 c.c.) are: sow 145, rabbit 109, cat 63, bitch 55, ewe 22·5, woman 16·4, goat 14, cow 12·67, mare 11·5. CH. ABS.

Differentiation of caseinogen and casein by the biological serum-precipitation method. E. NICOLAS (Lait, 1932, **12**, 593—603; Chem. Zentr., 1932, ii, 1984).—Sp. rabbit antisera can be obtained. A. A. E.

Manganese content of milk. M. SATO and K. MURATA (J. Dairy Sci., 1932, **15**, 461—467).—The average Mn content of normal milks was in the order sheep > horse > cow. Vals. for the colostrum of cows (especially the first sample after parturition) were much > normal. Sheep milk increases in Mn content towards the end of the lactation period. A. G. P.

Phosphorus compounds of milk. Differentiation, demonstration, and behaviour during lactation. W. HOCHHEIMER (Z. Kinderheilk., 1932, **54**, 49—64).—Curves showing the variation in total P, acid-sol. P, and the portion of that fraction precipitable by strychnine-molybdic acid are given for goat's and human milk during the first part of lactation. The curves in each case run fairly parallel and indicate a relationship between the fractions during the observation period. In cow's milk the acid-sol. org. P is about 8·0 mg. per 100 g. of milk, of which 3·3 mg. are present as hexosemonophosphoric acid and 4·5 mg. as pyrophosphate-P, the remainder being present as adenosinephosphoric acid. Ultraviolet irradiation had no effect on the hexosemonophosphoric acid content of cow's milk. The presence of creatinephosphoric acid in cow's and goat's milk was demonstrated. NUTR. ABS.

Dietary factors affecting lactation in the albino rat. L. J. PEET (Iowa State Coll. J. Sci., 1932, **6**, 463—465). CH. ABS.

Effect of iodoacetic acid on the lactic fermentation of milk. K. HINSBERG and G. HOLLAND (Klin. Woch., 1932, **11**, 1338; Chem. Zentr., 1932, ii, 2198).—Addition of 2—5 mg. of $CH_2I{\cdot}CO_2H$ per 100 c.c. of unboiled milk restrains lactic fermentation and spontaneous coagulation. A. A. E.

Presence of methylglyoxal in urine. A. PI-SUNER and M. FARRAN (Biochem. Z., 1932, **256**, 241—251).—The 2 : 4-dinitrophenylhydrazones obtained from urine contain the bishydrazone of methylglyoxal. P. W. C.

Incidence of albumin and sugar in the urine of normal women. G. W. THEOBALD (Lancet, 1932, **223**, 1380—1383).—Data for the clinical amounts of albumin found in women of different occupations are recorded. The incidence of albuminuria is apparently not related to the age at which menstruation commences. L. S. T.

Comparison of colour tests for fructose, pentoses, and glycuronates in urine. F. D. WHITE and A. C. GREEN (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 145—157).—Selivanov's test is most sensitive when dil. HCl and 30 sec. boiling are used. Clarification of urine by 50% HCl and C at 100° renders such a modification effective with 0·3% of fructose. Bial's reagent or naphtharesorcinol is unsuitable for the detection of pentoses (I) or glycuronates (II), owing to the presence of some unknown interfering substance. By a method using the red colour given on heating (I) with NH_2Ph and AcOH, (I) may be detected down to 0·03%, whilst (II) do not interfere. F. O. H.

Modification of Grimbert and Morel's method for determining free organic acid in urine. M. LAFARGUE (Compt. rend. Soc. Biol., 1931, **107**, 1286—1288; Chem. Zentr., 1932, ii, 1809—1810).

Citric acid content of urine and its variations in abnormal conditions. O. ØSTBERG (Acta med. Scand., 1932, Suppl. 50, 172—176).—The normal excretion of citric acid (I) lies between 0·2 and 1 g. per day. This amount is diminished by a shift of the body's reaction to the acid side and increased by a shift to the alkaline side. The (I) excreted under the latter conditions is sufficient to play an important part in neutralising the excess of alkali, and may help to retain Ca salts in solution. The source of the (I) is unknown. Large quantities of citrates by mouth do not increase the amount excreted. NUTR. ABS.

Amount of calcium excreted in the urine of healthy Koreans. H. Y. OH and C. H. KIM (J. Chosen Med. Assoc., 1932, **22**, 538—541).—Daily urinary Ca was 0·291 g. (male), 0·173 g. (female). CH. ABS.

Influence of urinary reaction on excretion of lime and magnesia. N. K. AYYAR (Indian J. Vet. Sci., 1932, **2**, 301—305).—*Ragi* straw when fed to bullocks resulted in an alkaline urine, whereas on a ration of *Bolarum* hay the urine was acid. In the latter case there was a higher % of the total excreted Ca and Mg in the urine than when the urine was alkaline. A similar deflexion of Ca and Mg to the urine was found with two other hays giving an acid or almost neutral urine. With theso latter hays the CaO content of the fæces was low. NUTR. ABS.

Origin of urinary ammonia. Action of renal tissue in the presence of glycine. E. MILHEIRO (Compt. rend. Soc. Biol., 1932, **111**, 591—592).—NH_3 was formed from glycine when subjected to the action of kidney tissue of the dog in the presence of buffered solutions. NUTR. ABS.

Photometric method for the analysis of urinary sulphur. E. OBERMER and R. MILTON (Bull. Soc. Chim. biol., 1932, **14**, 1447—1509).—The method of Denis and Reed (A., 1927, 167), with some modi-

fication particularly with regard to the reagent, has been adapted for determination of inorg., aromatic, and total SO_4'' in urine. H. G. R.

Determination of indoxyl compounds in urine. H. SHARLIT (J. Biol. Chem., 1933, **99**, 537—545).—Jolles' method (A., 1913, ii, 892) is satisfactory only as a qual. method for detection of indican in urine, but the technique of a trustworthy quant. modification using $K_2S_2O_8$ (which prevents pigment formation with skatole) as the oxidising agent and extracting the blue thymol pigment with $CCl_3{\cdot}CO_2Et$ formed *in situ* from added $CCl_3{\cdot}CO_2H$, is described. The indican is then determined colorimetrically viewed through a green filter and using 1·5% $CoSO_4,7H_2O$ solution as a standard, the indican equiv. of which is determined. Optimum reaction conditions require only 0·1 c.c. of urine (clarification unnecessary) and detect $< 0{\cdot}0025$ mg. of indican. Under the test conditions none of the other normal urinary constituents produces any colour, nor is glucose, CH_2O, or tryptophan (which interfere in larger concn.) present in sufficient amount to interfere. In 1% concn. all the foreign homo- and hetero-cyclic compounds tested are non-reactive. Determination of 24 hr. indican excretion in normal urine by this method gives vals. (40—150 mg.) much $>$ those previously reported. J. W. B.

Chromogens of indoxyl type in human sweat. C. HERVIEUX (Bull. Acad. méd., 1932, [iii], **107**, 121—126; Chem. Zentr., 1932, ii, 2200).—The same metabolic products, in the same ratios, are excreted in sweat as in urine. A. A. E.

Use of permanganate for clarification in the determination of calcium in fæces. R. GOIFFON (Compt. rend. Soc. Biol., 1931, **106**, 723—724; Chem. Zentr., 1932, ii, 1943).—After boiling with $KMnO_4$, Mn is pptd. by boiling with sugar after addition of AcOH. Ca is determined manganimetrically in the colourless filtrate. A. A. E.

Metal cages and nutritional anæmia. G. B. GERAGHTY, F. A. UNDERHILL, J. M. ORTEN, and R. C. LEWIS (J. Biol. Chem., 1933, **99**, 451—456).—Nutritional anæmia may be induced in rats kept in both Fe-wire and glass cages. H. D.

***Bartonella muris* anæmia. VI. A lipin extract of the spleen that prevents *Bartonella muris* anæmia in splenectomised rats. VII. Protective action of copper and iron against *Bartonella muris* anæmia.** D. PERLA and J. MARMORSTON-GOTTESMAN (J. Exp. Med., 1932, **56**, 777—782, 783—792).—VI. The material was prepared for injection by Et_2O and EtOH extraction of ox spleen. The extract was finally emulsified with distilled H_2O. 1 c.c. was equiv. to 100 g. spleen. No Cu or Fe was found in the final product. The effect of the extract in protecting splenectomised rats of carrier stock against *B. muris* anæmia was investigated and the extract was given twice daily intraperitoneally in amounts of 0·5 c.c. Of 8 male rats, 6—8 weeks old, 3 were completely protected by this means. Of 21 adult male rats, 14 were completely protected.

VII. The effects of adding Cu or Fe, or both, to an adequate diet, in protecting rats of carrier stock against the development of *B. muris* anæmia following splenectomy were studied. The addition to the diet of Cu (0·1 mg. per rat per day), or Fe (1 mg. per day), or both, during a period of two days prior to splenectomy and one month subsequent thereto, failed to give protection to adult albino rats. For a period of ten days prior to splenectomy and one month subsequent thereto, the addition of Cu or Fe, or both, to an adequate diet gave protection in 75, 50, and 75% of cases, respectively. The addition of Cu alone for a period of two months prior to and one month subsequent to splenectomy protected 63% of the rats, whilst the addition of Fe, or of Cu and Fe for similar periods, protected about one third of cases. NUTR. ABS.

Relationship between *Bartonella* anæmia and spleen hormone. M. KOH (J. Chosen Med. Assoc., 1932, **22**, 554—567).—Transplantation of rabbit's or rat's spleen, or subcutaneous injection of a solution of spleen powder, into rats with *Bartonella* anæmia following splenectomy causes the anæmia to disappear. The spleen hormone appears in greater concn. in the splenic vein when the animals are subjected to ultra-violet irradiation. CH. ABS.

Dietary protein in hæmorrhagic Bright's disease. I. Effects on the course of disease with special reference to hæmaturia and renal function. E. H. KEUTMANN and W. S. MCCANN (J. Clin. Invest., 1932, **11**, 973—994). CH. ABS.

Mineral metabolism and "stone." R. MCCARRISON (Current Sci., 1932, **1**, 8—9).—Deficiency of vitamin-*A* is the chief factor in causing urinary calculus, which consists largely of $MgNH_4PO_4$. When Ca is added to diets deficient in vitamin-*A* the stones consist largely of $CaCO_3$ or $Ca(OH)_2$. Addition of PO_4 prevents the excessive elimination of Ca through the urinary tract and lowers the incidence of stone. Addition of Mg produces stones similar in Ca content to those produced with a diet rich in Ca. Addition of CaO to a Mg-rich diet arrests its stone-forming action. CH. ABS.

Calcium carbonate gallstones and their experimental production. D. B. PHEMISTER, L. DAY, and A. B. HASTINGS (Ann. Surgery, 1932, **96**, 595—614).—Ca, but not cholesterol, is derived from the wall of the gall bladder. CH. ABS.

Mechanism of cholesterol gallstone formation. E. ANDREWS, L. E. DOSTAL, M. COFF, and L. HRDINA (Ann. Surgery, 1932, **96**, 615—623).—The stones may result from absorption of bile salts by the diseased gall bladder with consequent pptn. of cholesterol. Cholesterol is not excreted by the gall-bladder mucosa. CH. ABS.

Cytagenin and "mitogenetic radiation" of blood. M. HEINEMANN (Klin. Woch., 1932, **11**, 1375—1378; Chem. Zentr., 1932, ii, 2321).—Injection of cytagenin, prepared from the stroma of red corpuscles, transiently increases the mitogenetic radiation of the blood in cancer. A. A. E.

Properties of the causative agent of a chicken tumour. VII. Separation of the associated inhibitor from tumour extracts. J. B. MURPHY and E. STRUM. **VIII. Effect of testicle extract**

on the rate of growth of chicken tumour-*I*. E. STRUM and F. DURAN-REYNALS (J. Exp. Med., 1932, **56**, 705—709, 711—717).—VII. The inhibiting factor in certain slow-growing strains of chicken tumour-*I* and in -*X* is adsorbed from extracts of the desiccated tumours by $Al(OH)_3$ (Willstatter type *C*) and released in effective quantities by treatment with basic Na_3PO_4.

VIII. No definite effect was observed.

CH. ABS.

Detection and determination of chromium in tumours. A. DINGWALL and H. T. BEANS (Amer. J. Cancer, 1932, **16**, 1499—1501).—Blood-Cr is very low, but the Cr content of certain human tumours is relatively high (0·001—0·25% of ash). A spectrographic technique is described. CH. ABS.

Calcium and phosphorus of saliva in relation to dental caries. R. B. HUBBELL and R. W. BUNTING (J. Nutrition, 1932, **5**, 599—605).—In children of 7—16 years, addition to the diet of milk and tomato juice tended to decrease the incidence of dental caries, but no corresponding change in the Ca or P contents of saliva occurred. A. G. P.

Relation of calcium and phosphorus in the diet to the cause of mottled enamel of human teeth. R. M. LEVERTON and M. C. SMITH (J. Home Econ., 1932, **24**, 1091—1097).—A quant. study of the diet of 19 children in a district where mottled enamel (I) of the teeth was common showed no significant differences in Ca or P intake, or in the Ca : P ratio, between those with and those without (I). The children with severest (I) had the lowest intake of vitamin-*C*. It is concluded that adequate intake of Ca and P during the years of enamel formation will not prevent the development of (I) if the child is exposed to the environmental factors present where (I) is endemic. NUTR. ABS.

Diabetes mellitus. Evidence that the disability is concerned solely with the metabolism of glucose. Mode of action of insulin. L. H. NEWBURGH and D. S. WALLER (J. Clin. Invest., 1932, **11**, 995—1002).—Tolerance in diabetes is not depressed by dietary fat or increased by dietary carbohydrate. Insulin efficiency is related to the amount of glucose on which it acts. When available glucose far exceeds the tolerance, each unit oxidises 6—7 g. of sugar; under ordinary conditions it oxidises only 1—2 g.

CH. ABS.

Diabetes in childhood. I. Ætiology, diagnosis, and prognosis. II. Treatment. III. Coma. IV. Significance of the blood-sugar curve in ketosis. G. B. FLEMING, N. MORRIS, F. J. FORD, and M. L. GILCHRIST (Glasgow Med. J., 1932, **37**, 314—320, 321—334, 335—339, 340—345).—A review.

NUTR. ABS.

Elderly diabetics with cardiovascular disease. Available carbohydrate and blood-sugar level. S. SOSKIN, L. N. KATZ, S. STROUSE, and S. H. RUBINFELD (Arch. Int. Med., 1933, **51**, 122—142).—Administration of insulin produces a cardiac impairment due, probably, to the hypoglycæmia produced; this effect is antagonised by feeding or injecting glucose. H. D.

Treatment of diabetes with diet rich in carbohydrates. O. BANG (Acta med. Scand., 1932, Suppl. 50, 202—205).—On low-carbohydrate diets, in addition to ketonuria, an increase of urobilin (I) is observed in the urine, due to liver dysfunction. (I) falls to normal when higher carbohydrate diets are given and less protein and fat. When the liver begins to function normally, carbohydrate metabolism improves and less insulin is required. NUTR. ABS.

Periodicity in carbohydrate metabolism. J. MOLLERSTROM (Acta med. Scand., 1932, Suppl. 50, 250—257).—Diabetics, even if starved, exhibit waves of increased sugar excretion which tend to recur daily. These waves are due to variations in the blood-sugar levels, which are attributed to rhythmical alternation of function of the liver. This organ has been shown to alternate between storing glycogen and making bile. NUTR. ABS.

Experiences concerning 1000 insulin-treated diabetics. A. NORGAARD (Acta med. Scand., 1932, Suppl. 50, 196—202).—The insulin requirements of diabetics tend to increase over the first few years of treatment to about 60 units per day. Men require rather > women. NUTR. ABS.

Fat deposition in depancreatised dogs and the effect on it of insulin and sugar. S. HOTTA (Tohoku J. Exp. Med., 1932, **20**, 79—92).—In depancreatised dogs, fat rich in saturated and poor in unsaturated fatty acids is accumulated. These changes are not obtained after partial removal of the pancreas and are rapidly reversed on injection of insulin. Intravenous infusion of glucose is as active as insulin in preventing these changes. NUTR. ABS.

Reduction of the urine- and blood-sugar by calcium metasilicate hydrogel. A. VON SZTANKAY (Pharm. Zentr., 1933, **74**, 33—38).—Administration of Ca metasilicate gel to diabetics reduces the blood- and urine-sugar and improves the clinical condition.

W. O. K.

Animal diastases. III. Comparison of different methods of blood-diastase determination. IV. Effect of insulin on blood-diastase in diabetes. V. Blood- and tissue-diastases with reference to the depancreatised dog. E. REID, J. P. QUIGLEY, and V. C. MYERS (J. Biol. Chem., 1933, **99**, 595—605, 607—613, 615—623).—III. Four different methods of blood-diastase determination are compared, the most trustworthy being those of Myers and Killian (A., 1917, i, 369) and Elman and McCaughan (A., 1927, 986). The latter is, however, unsuitable when the vals. are low. The method of Ottenstein (A., 1931, 1447) modified for a 15-min. incubation period is also satisfactory for high vals. Since the Myers–Bailey and the Hagedorn–Jensen methods give the highest vals. for maltose determinations, they are the most suitable for the determination of reducing sugars from starch digestion.

IV. Normally the diastase activity of the blood varies between 18 and 19 units (Myers–Killian method). In diabetic individuals under dietetic treatment alone, blood-diastase is high; under insulin therapy normal levels are maintained. It is

suggested that in diabetes the liver, in order to conserve its glycogen, liberates diastase into the blood.

V. In normal dogs, insulin causes a decrease in blood-, an increase in the liver-, and no change in muscle-diastase. In contrast with the results obtained in IV, the blood-diastase in depancreatised dogs decreases at first and then becomes normal again, increasing after administration of insulin. Withdrawal of insulin causes a fall, normal vals. being reached on resumption of insulin treatment. In normal rabbits insulin causes the blood-diastase to decrease, and when hypoglycæmic convulsions occur, the normal level is sharply reached again.

A. L.

Callus-phosphatase and its participation in the healing of fracture. K. KAMADA (Fukuoka Acta Med., 1932, **25**, 207—267).—Callus tissue contains an enzyme (optimum p_H 8·2) which hydrolyses glycerophosphoric ester, hexosemonophosphoric ester, and blood-org. P compounds. CH. ABS.

Treatment of hyperacidity. P. BOHRISCH (Pharm. Zentr., 1933, **74**, 65—68).—"Gastro-Sil" (SiO_2 66·7%, CaO 17·1%, Na_2O 2·6%, H_2O 13·5%) neutralises HCl less efficiently than $NaHCO_3$, but better than other medicaments used to reduce hyperacidity. W. O. K.

Blood-guanidine in hypertension. O. L. V. S. DE WESSELOW and W. J. GRIFFITHS (Brit. J. Exp. Path., 1932, **13**, 428—434).—Blood-"guanidine" (Minot and Cutler, J. Clin. Invest., 1928, **6**, 369) exceeded the normal upper limit in 9 of 23 cases of hypertension. Large fluctuations are observed. Low vals. are obtained in acute glomerulo-nephritis, pre-eclampsia, and eclampsia. In N retention vals. are not necessarily increased. Arginine-rich food given to rabbits does not lead to appreciably high vals. CH. ABS.

Hyperadrenalinæmia in essential hypertonia and its treatment with atropine. I, II. K. KURE, T. NAKAYA, S. MURAKAMI, and S. OKINAKA (Proc. Imp. Acad. Tokyo, 1932, **8**, 468—470, 471—473).—I. The blood of normal persons and, to a greater extent, that of persons suffering from essential hypertonia and kidney disease, contains a vaso-constrictor substance which is readily destroyed by atm. O_2 at alkaline reactions, is decreased by administration of atropine, and is therefore probably adrenaline. Adrenaline, when tested on the perfused frog's or rabbit's blood-vessel *in vitro*, reacts five times as strongly in saline as in blood-plasma.

II. The application of atropine to the lowering of high blood-pressure is described. F. O. H.

Blood-sugar curve in various forms of icterus. E. MEULENGRACHT (Acta med. Scand., 1932, **79**, 32—75).—In acute and chronic hepatitis there was a tendency to the occurrence of low fasting blood-sugar vals. (range 42—120 mg. per 100 c.c. : average 80); the rise and fall after ingestion of glucose were within normal limits. In patients with cancer of the biliary passages or head of the pancreas the blood-sugar curves varied much; often they tended to be flat without any initial or subsequent hypoglycæmia. In patients with gall-stones causing obstruction there was very great variation of the blood-sugar curve.

NUTR. ABS.

Formation of bile pigment and jaundice. L. ASCHOFF (Klin. Woch., 1932, **11**, 1620—1624; Chem. Zentr., 1932, ii, 2843).—The reticuloendothelial system and the blood are normally sources of bile pigment. In jaundice it is inadequately excreted by the liver. A. A. E.

Bilirubin and the blood-[cerebrospinal] fluid barrier. N. KLEIN and S. SZENTMIHALYI (Deut. Arch. klin. Med., 1932, **173**, 234—240; Chem. Zentr., 1932, ii, 2326).—The cerebrospinal fluid-bilirubin does not depend on the degree of icterus or on the serum-bilirubin, but on the duration of icterus and the condition of the reticuloendothelial system. Cerebrospinal fluid-bilirubin vals. are usually too small to be determined. A. A. E.

Biochemistry and mental disorder. J. H. QUASTEL (Lancet, 1932, **223**, 1417—1419).

L. S. T.

Citric acid content of cerebrospinal fluid in man. B. BENNI (Acta med. Scand., 1932, Suppl. 50, 167—172).—500 cases, mostly neurological, were investigated. The cerebrospinal fluid was found normally to contain $40—50\times10^{-6}$ g. per c.c., the serum $15—30\times10^{-6}$ g. In epilepsy, hydrocephalus, and tumours causing a rise of intracranial pressure $30—40\times10^{-6}$ g. per c.c. were found. In meningitis (all kinds), neurosyphilis, and cerebral vascular lesions, high vals. were found ($50—100\times10^{-6}$ g. per c.c.). The highest val. (150×10^{-6} g. per c.c.) was found in a cerebral cyst. Normal vals. were generally found in the psychoses. NUTR. ABS.

Plasmaphoresis œdema. I, II. D. C. DARROW, E. B. HOPPER, and M. K. CARY (J. Clin. Invest., 1932, **11**, 683—699, 701—715).—I. Dogs were bled, and the cells re-injected after removal of plasma-proteins. Globulin was restored more rapidly than albumin. Œdema occurred at 3·0—3·5% plasma-protein, but more characteristically at 1·5% albumin.

II. Total base and HCO_3' showed no relation to protein concn.; Ca varied directly, and Cl' inversely, with protein. CH. ABS.

Endemic nutritional œdema. II. Serum-proteins and nitrogen balance. J. B. YOUMANS, A. BELL, D. DONLEY, and H. FRANK (Arch. Int. Med., 1933, **51**, 45—61).—Determination of the serum-protein in 31 patients with nutritional œdema showed a slight decrease in the serum-albumin, which rose to normal on a high-protein diet. H. D.

Prevention of poliomyelitis. S. FLEXNER (Science, 1933, **77**, 7—11).—A lecture. L. S. T.

Biology of pregnancy. K : Ca ratio in muscle and liver during pregnancy and its relation to growth processes. H. YOSHIURA (Arch. Gynakol., 1932, **152**, 89—108).—In rabbits during pregnancy there is a progressive slight decrease of the K of muscles and a greater decrease of Ca, so that the K/Ca quotient rises. In the liver the K falls and the Ca rises so that K/Ca is markedly decreased. The fall in tissue-K is due to the demands of the fœtus for K.

NUTR. ABS.

Placental enzymes in various stages of pregnancy. M. ABE (Japan. J. Obstet. Gynæcol., 1932, **15**, 44—52).—Small quantities of pepsin and asparaginase are present in human placenta at every stage; the enzyme which decomposes glycine could not be found. CH. ABS.

Biological investigation of iron metabolism. S. INOUE (Japan. J. Obstet. Gynæcol., 1932, **15**, 53—69).—In the rat, blood-Fe slightly increased in the early periods of pregnancy, gradually decreased from the 15th day, and again increased immediately before parturition, afterwards decreasing to a min. on the 3rd—5th day of puerperium, and recovering from the 7th day. The liver-Fe of the pregnant rat is < that of the non-pregnant rat. The no. and body-wt. of young of mothers with dietary Fe deficiency were subnormal. CH. ABS.

Metabolism of women during reproductive cycle. V. Nitrogen utilisation. H. A. HUNSCHER, E. DONELSON, B. NIMS, F. KENYON, and I. G. MACY (J. Biol. Chem., 1933, **99**, 507—520).—In pregnancy the mother retains an excess of N over the fœtal needs, whilst a loss occurs at parturition which persists for 2 weeks or more. H. D.

Serum-calcium in relation to menstruation in cases with dysmenorrhœa. R. E. BOYNTON and E. M. GREISHEIMER (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1115—1117).—No cyclic variation in serum-Ca was found. Administration of Ca gluconate did not affect the vals. CH. ABS.

Prevention and cure of rickets through irradiated milk. L. J. AUERBACHER (Med. J. and Rec., 1932, **136**, 383—387, 427—431).—A survey. NUTR. ABS.

Phosphoric ester content of red blood-cells and liver in experimental rickets. H. D. KAY (J. Biol. Chem., 1932, **99**, 85—94).—In experimental rickets the acid-sol. phosphoric ester content per unit vol. of the red blood-cells is diminished, returning to normal on addition of therapeutic agents. A similar, although less marked, change occurs in liver tissue. H. G. R.

Basal metabolism in rachitic infants and infants with rickets and tetany. A. NITSCHKE and M. SCHNEIDER (Z. Kinderheilk., 1932, **54**, 1—9). During the determination the infants were asleep following the administration of adalin or somnifen which had no effect on the basal metabolic rate (I). In 6 cases of active rickets (I) was 10—25% below normal (average 17·5%); in 2 cases of healing rickets (I) was reduced 12—34% (average 22%) below normal. Moderate doses of vigantol did not affect (I) in healthy infants, but raised it in rickets and tetany. The fall of (I) occurs early in the development of tetany and rickets and the rise after vitamin-*D* treatment is also early. The val. for the inorg. P of the serum is no indication of the level of (I). Injection of P-substance produces a fall of (I) of the same degree as that found in rickets and tetany. NUTR. ABS.

Effect of irradiated ergosterol preparations in tetany of parathyroidectomy. Internal secretory relationships of the antirachitic and toxic principle. G. POPOVICIU and I. I. NITZESCU (Z. ges. exp. Med., 1932, **81**, 656—677; Chem. Zentr., 1932, ii, 1933).—In normal, and particularly in parathyroidectomised, animals the rise in blood-Ca and -P after administration of irradiated ergosterol is parallel to the content of the toxic, and not to that of the antirachitic, factor. Antagonism between the toxic factor and the parathyroid is indicated. The increased activity of the parathyroid in rickets suppresses the activity of the toxic factor, so that in this condition only the antirachitic factor is significant. A. A. E.

Gastric secretion in hyperthyroidism before and after operation. W. R. BERRYHILL and H. A. WILLIAMS (J. Clin. Invest., 1932, **11**, 753—760). CH. ABS.

Blood-cholesterol in thyroid disease. I. Toxic and non-toxic goitre. L. M. HURXTHAL (Arch. Int. Med., 1933, **51**, 22—32).—The blood-cholesterol (I) in 505 cases of thyroid disease was determined during fasting, and the average vals. for the different classes were compared, being lowest in severe hypothyroidism and highest in chronic thyroiditis. The basal metabolic rate is inversely proportional to (I). H. D.

Effects following thyroidectomy in merino sheep. H. R. MARSTON and A. W. PEIRCE (Austral. J. Exp. Biol., 1932, **10**, 203—213).—Thyroidectomy of adult merino sheep results in a lowering of the basal metabolic rate (I) and a decrease in the growth of wool. Thyroidectomised lambs exhibit decreased growth, low (I), shortness of wool fibres, and mental dullness, but in a considerable proportion regeneration of thyroid tissue occurs, accompanied by a return of the animal almost to normality. W. O. K.

Rapid determination of the gold excretion of patients under sanocrysin treatment. W. S. STANBURY (Tubercle, 1932, **13**, 396—399).—The test depends on the formation of a Pb–Zn couple; addition of KCN in excess ppts. Au as Zn Au cyanide. Conversion into $AuCl_3$ by HCl–HNO_3 is followed by reduction with $SnCl_2$ and colorimetric determination. CH. ABS.

Blood-lipins in acute infectious diseases. S. MARINO (Arch. Farm. sperim., 1933, **55**, 1—27).—In typhoid fever there is a marked fall in free and combined cholesterol and in phosphatides during fever, attributed to effects on the endocrine glands governing lipin metabolism. R. K. C.

Blood-uric acid in disease. E. P. JORDAN and D. GASTON (J. Clin. Invest., 1932, **11**, 747—752). CH. ABS.

Rate of oxygen consumption by fertilised and unfertilised eggs. IV. *Chætopterus* and *Arbacia punctulata*. V. Comparisons and interpretation. D. M. WHITAKER (J. Gen. Physiol., 1933, **16**, 475—495, 497—528).—IV. At 21° the unfertilised eggs of *Chætopterus* use approx. 2 cu. mm. O_2 per hr. per 10 cu. mm. eggs, whilst the fertilised eggs consume only 1·3 cu. mm. per hr. during the first hr., the pre-fertilisation rate being regained 4½—5 hr. after fertilisation. In the case of the eggs of *A. punctulata* the O_2 consumption rises from 0·36—0·5 cu. mm. per

hr. per 10 cu. mm. eggs before fertilisation to 2·0 cu. mm. after fertilisation.
V. A discussion. W. O. K.

Effect of phosphate on tissue respiration. B. KISCH (Biochem. Z., 1933, **257**, 95—112).—The respiration of tissues (retina, heart, kidney, liver, Jensen sarcoma of rat, cat, guinea-pig, sheep, ox) in Ringer solution and in Ringer solution in which phosphate mixture replaces $NaHCO_3$, gradually and regularly falls, but is increased in most cases (for 15—45 min.) by addition of Na pyruvate, Na lactate, glucose, alanine, or serine. The phosphate has pronounced and often surprising effects on the respiration of the various tissues, which are quite differently affected. Thus, the respiration of retina is increased, but that of kidney is decreased. Possibly the effects are partly due to interaction of the phosphate and the substances added. W. McC.

Do basal metabolism and insensible perspiration as predicted by the Benedict–Root method correspond? A. JORES (Klin. Woch., 1932, **11**, 2065—2067).—A comparison of the determined basal metabolism with that calc. from the Benedict–Root law was made in 105 cases. A disagreement of $> 10\%$ was found in only 6 cases, of which 5 had pathological disturbances of metabolism. Calculation, however, offers no advantages over direct determination. NUTR. ABS.

Relation between mobility and metabolism in the spermatozoa of mammals. E. REDENZ (Biochem. Z., 1933, **257**, 234—241).—The movement of mammalian (guinea-pig, bull) spermatozoa suspended in serum under anaerobic conditions is caused by glycolysis and can be increased under aerobic conditions by carbohydrates [glucose, maltose, and (sometimes) glycogen, but not by lactic or pyruvic acid, lactose, sucrose, galactose, hexose-mono- or -di-phosphate]. The metabolism was measured by Warburg's method. W. McC.

Heterogony and the chemical ground-plan of animal growth. C. H. WADDINGTON (Nature, 1933, **131**, 134).—Theoretical. L. S. T.

Physico-chemical phenomena during regeneration. V. Lactic acid content of the regenerating extremities in axolotl. N. OKUNEV (Biochem. Z., 1933, **257**, 242—244; cf. A., 1929, 1332).—The extremities of regenerating limbs in axolotl contain more lactic acid than do the normal extremities. W. McC.

Rôle of liver in the acid–base balance of the body. T. KIN (J. Chosen Med. Assoc., 1932, **22**, 21—37).—After fasting (12 hr.), the blood-p_H is 7·18—7·41 (average 7·29) and the bile-p_H is 7·97—8·25 (average 8·12). Normally the p_H of the blood of portal and hepatic veins is the same in the normal animal. Introduction of acid or alkali into the duodenum alters the p_H of portal, but not of hepatic, vein-blood. Injection of acid or alkali into the ear vein changes the bile-p_H. CH. ABS.

Participation of the carbonates of bone in the neutralisation of ingested acid. L. IRVING and A. L. CHUTE (J. Cell. Comp. Physiol., 1932, **2**, 157—176).—Administration of HCl to rats resulted in a reduction of the CO_3'' and in many cases the Ca'' and P contents of the femurs. The CO_2 content of the muscles was not affected. The bone minerals are not combined in definite proportions. A. G. P.

Effect of acid feeding on the composition of bone. A. L. CHUTE and L. IRVING (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 141—144).—The feeding of 5 c.c. of 2*N*-HCl daily to rats produces a temporary depletion of Ca and CO_3 and a rise in the Ca : CO_3 ratio of the bones. The P and Ca : P levels are not significantly changed, indicating that $CaCO_3$ is withdrawn in preference to $Ca_3(PO_4)_2$. The CO_2-combining power of the blood, but not the CO_2 content of the muscle, is lowered. F. O. H.

Utilisation of calcium and phosphorus by dairy heifers; high- and low-calcium roughages. O. C. CUNNINGHAM, L. H. ADDINGTON, and W. E. WATKINS (New Mexico Agric. Exp. Sta. Bull., 1932, No. 206, 18 pp.).—No differences were observed in the utilisation of P from lucerne and from cane hay; the low intake of Ca from the latter was counterbalanced by the increased % utilisation. A. G. P.

Symptoms shown by young rats on a diet deficient in magnesium. J. LAVOLLAY (Compt. rend. Soc. Biol., 1932, **111**, 545—547). NUTR. ABS.

Sulphur and sulphate balance experiments with cattle. F. J. WARTH (Indian J. Vet. Sci., 1932, **2**, 225—241).—Balance experiments with bullocks show that, with some types of rations, the whole of the inorg. SO_4'' present in the food is not recovered as SO_4'' in the urine. There is no loss of total S, and the missing SO_4-S is present as org. S in the fæces, only negligible traces of S″ being produced. The amount of S″ produced is related to the nature of the fodder rather than to the quantity of SO_4'' in the ration. When fed in small amounts, the org. S of earthnut cake is excreted in the fæces, but when the amount is considerably increased the additional org. S is excreted almost quantitatively as SO_4'' in the urine, this urinary excretion as SO_4'' presumably representing luxury consumption. Ethereal SO_4'' in the urine is present due to sulphuric conjugation of *p*-cresol and other volatile phenols, which can occur only if an excess of SO_4'' is provided. NUTR. ABS.

Sulphur metabolism of the dog. XI. Metabolism of methionine and related sulphides. N. W. PIRIE (Biochem. J., 1932, **26**, 2041—2045).—Methionine is oxidised by the dog to the same extent as is cystine. *S*-Ethylcysteine and *S*-benzylcysteine are not appreciably oxidised. *S*-Methylcysteine is oxidised, but is too toxic to allow an accurate estimate of the extent of its oxidation. S. S. Z.

Quantitative production of benzoic acid and phenols in the animal system. F. J. WARTH and N. C. D. GUPTA (Indian J. Vet. Sci., 1932, **2**, 281—288).—Figures are given for the production of BzOH and phenols from different typical fodders and concentrates. The amount of BzOH produced to 100 g. of fodder consumed is const. for any given fodder with different animals, and the ratio of BzOH to *p*-cresol is const. for each fodder. NUTR. ABS.

Conjugation of benzoic acid by Indian cattle. N. C. D. GUPTA (Indian J. Vet. Sci., 1932, **2**, 289—

293).—With Indian cattle, whether on a normal or a low concentrate ration, the conjugation of BzOH is complete, and this acid is eliminated entirely in the form of hippuric acid. NUTR. ABS.

Liver injury and conjugation of benzoic acid in the dog. A. J. QUICK and M. A. COOPER (J. Biol. Chem., 1933, **99**, 119—124).—The conjugation of BzOH with glycine and glycuronic acid (I) is unaffected by obstructive jaundice induced by ligature and resection of the common duct. $CHCl_3$ anæsthesia produced a temporary decrease in the synthesis of (I).

Significance of highly unsaturated fatty acids in organs. S. HOTTA (Tohoku J. Exp. Med., 1932, **20**, 65—77).—The unsaturated fatty acid content of the organs of rabbits is increased during increased metabolism due to injection of thyroxine, adrenaline, and phloridzin. The highly-unsaturated fatty acids of the organs are not to be regarded as desaturation products of more saturated acids, but are accumulated because they are more resistant to oxidation than the saturated acids. NUTR. ABS.

Vital need of the body for certain unsaturated fatty acids. III. Inability of the rat organism to synthesise the essential unsaturated fatty acids. H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1932, **99**, 231—234).—The Me esters of fats from normal female rats (just weaned) or from rats fed on a complete diet, but not of fats from rats on a fat-free diet, alleviate the characteristic symptoms due to deficiency of essential unsaturated fatty acids (A., 1930, 810; 1932, 646). The degree of unsaturation of the esters is not related to the curative effect. F. O. H.

Unilateral feeding. E. STRACK (Ber. Sachs. Ges. Wiss., Math.-physikal. Kl., 1932, **84**, 129—208; Chem. Zentr., 1932, ii, 2326—2327).—Dogs were fed directly into the small intestine with solutions or emulsions of various nutritive substances. Digestion of olive oil does not take place by simple fission into fatty acid or soap and glycerol (I). Me laurate is partly resorbed as such, and has a narcotic effect. Soap emulsions produce diarrhœa, and hence soaps cannot be present in great quantity in the intestine during the digestion of fats. (I) can be resorbed in large quantities, but is utilised only at a limited rate depending on the body-wt. and the quantity taken. On a continuous fat diet the urinary N is as great as during fasting; with (I)-free esters and free acids the N metabolism is increased. The determination of (I) in urine is described. Up to 1015 c.c. of MeOH in 30 days can be tolerated. Tri-(hydroxyethyl)amine can be administered as the base of soaps. Ketonic substances do not appear in the urine in noteworthy quantities when only fat is administered, but sometimes do so when (I) is replaced by MeOH. A. A. E.

Effect of choline on fat deposition in species other than the white rat. C. H. BEST, M. E. HUNTSMAN, and O. M. SOLANDT (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 175—176).—Oral administration of choline inhibits the deposition of fat in the livers of mice and probably also in chickens and dogs fed on a fat-rich diet. F. O. H.

Function of pancreas in fat absorption. M. NOTHMANN and H. WENDT (Klin. Woch., 1932, **11**, 2137—2139).—A review. NUTR. ABS.

Ketosis during fasting in Eskimos. P. HEINBECKER (J. Biol. Chem., 1932, **99**, 279—282).—The analysis of urine from three Eskimos during a 7-day fast confirms the view that there occurs a smaller degree of ketosis than in inhabitants of temperate zones (cf. A., 1929, 210; 1932, 83). Eskimos can burn considerable amounts of fat to completion without the aid of carbohydrate. F. O. H.

Capacity for food consumption after fasting. V. FAMIANI (Atti R. Accad. Lincei, 1932, [vi], **16**, 357—360).—Pigeons which have lost 20% in wt. by fasting can take food at first only in small quantities, but later in amounts gradually increasing to double the normal ration, this being maintained until or even after normal body-wt. is reached. T. H. P.

Production of oxalic acid by *Tænia*. M. LOEPER and J. TONNET (Compt. rend. Soc. Biol., 1931, **106**, 716—717; Chem. Zentr., 1932, ii, 2074).—During 24 hr. the glycogen content diminishes with simultaneous increase in glucose and $H_2C_2O_4$. A. A. E.

Formation of oxalic acid in tissues containing glycogen. M. LOEPER, R. DEGOS, and J. TONNET (Compt. rend. Soc. Biol., 1931, **106**, 717—718; Chem. Zentr., 1932, ii, 2074).—In rabbit's liver and calf's heart etc. the formation of malic acid is parallel with the autolytic disappearance of glycogen and increase of glucose. A. A. E.

Liver and protein-sugar. H. BIERRY, F. RATHERY, and Y. LAURENT (Compt. rend. Soc. Biol., 1931, **108**, 389—391; Chem. Zentr., 1932, ii, 2842).—Glucose is liberated from the protein-sugar of arterial blood-plasma by the liver. The protein-sugar may also be converted into glycogen. A. A. E.

Influence of bromoacetate on carbohydrate metabolism and lactic acid disappearance. W. HAARMANN (Biochem. Z., 1932, **256**, 326—349).—The formation of lactic acid (I) from carbohydrate in tissue is depressed by addition of $CH_2Br{\cdot}CO_2H$ (II), the acid, both preformed and added, disappearing. Anaerobic disappearance of (I) can be detected in brain without addition of (II) and in skeletal muscle amounts to 0·081% and with addition of (I) to 0·218%. Inhibition of formation of (I) from hexosediphosphate is very incomplete. Glyoxalase is unaffected by (II) and the process whereby $AcCO_2H$ is reduced to (I) is little affected. Higher vals. for (I) are obtained in presence of (II) after addition of succinic, fumaric, malic, or glycerophosphoric acid or $EtCO_2H$ than without these acids. (II) has no effect on the hydrolysis of glycogen, but represses completely the formation of glucose. Hydrolysis of hexose-di- and -mono-phosphates and glycerophosphate under conditions inhibiting the formation of (I) is only slightly affected. A lethal dose of (II) to rabbits is insufficient to affect the metabolism of muscle and brain, but completely inhibits the formation of (I) by liver and kidney. P. W. C.

Comparative investigation of the action of oxalate, fluoride, and bromoacetate in carbo-

hydrate metabolism. W. HAARMANN (Biochem. Z., 1932, **256**, 350—360).—Examination of the formation of lactic acid, of the carbohydrate balance, and of the inhibition of hydrolysis of phosphoric esters in presence of various toxic substances show that $CH_2Br{\cdot}CO_2'$, F', and C_2O_4'' have not the same point of attack in carbohydrate degradation, the sensitivity of the constituent enzymes of the glycolytic system being very different for the different substances. P. W. C.

Influence of different concentrations of glucose on the formation of lactic acid and on the degradation of glycogen. W. HAARMANN and F. W. STRATMANN (Biochem. Z., 1932, **256**, 361—370).—The formation of lactic acid (I) from added glucose by various types of tissue is dependent on the glucose concn. With skeletal muscle the optimal extra-formation of (I) is obtained with concns. of added glucose equal to the normal blood-sugar val.; higher concns. inhibit. With heart-muscle, kidney, and brain the optimum is at higher sugar concns. With skeletal muscle both formation of (I) from glycogen and also degradation of glycogen are inhibited by increasing concns. of glucose. P. W. C.

Degradation of xylose, tetraglucosan, and *d*-sorbitol by surviving tissues. W. HAARMANN and F. W. STRATMANN (Biochem. Z., 1932, **256**, 371—375).—The three substances added to surviving tissue under anaerobic conditions do not lead to the formation of lactic acid. P. W. C.

Carbohydrate metabolism. I. Influence of *d*-glucal, *d*-hydroglucal, and *d*-2-glucodeose on blood-sugar. W. FREUDENBERG. **II. Rate of metabolism of *d*-2-oxyglucal and styracitol in the rabbit.** W. FREUDENBERG [with G. E. FELTON] (J. Biol. Chem., 1933, **99**, 647—655, 657—662).—I. Determinations of apparent and reducing blood-sugar after intravenous injection into rabbits of *d*-glucal (I), hydroglucal, and 2-glucodeose (II) indicate that only (I) is metabolised. (II) is toxic, the lethal dose being $> 0{\cdot}5$ g. per kg. body-wt. Of the three, only (I) is capable of relieving hypoglycæmic convulsions.

II. Intravenous injection of impure 2-oxyglucal prepared by hydrolysis of the Ac_4 derivative with NH_3-saturated MeOH causes a rise in apparent and fermentable blood-sugar; glycosuria, however, results from the injection into hypoglycæmic animals. It is concluded, therefore, that the metabolism of oxyglucal is only partial and that no glucosone is formed. Styracitol under the same conditions is inactive. The organism is therefore apparently able to utilise C(1)·C(2) unsaturated sugars. A. L.

Metabolism of galactose. I. Cutaneous blood-sugars after galactose ingestion. V. J. HARDING and G. A. GRANT (J. Biol. Chem., 1933, **99**, 629—646).—A method of determining glucose (I), galactose (II), and residual reducing substances using 0·5 c.c. of cutaneous blood is described. With normal fasting humans on (II) tolerance tests, after ingestion of 40 g. of (II) the peak of blood-(II) is usually $\not>$ 30 mg. per 100 c.c., and occurs at 30—60 min. after the ingestion. At the end of 2 hr. the val. is $\not>$ a few mg. per 100 c.c. Ingestion of 80 g. of (II) increases these vals. and also that of urinary (II). In most cases blood-(I) rises, but this is not dependent on the amount of (II) intake. Arterial–venous differences in blood-(II) are reported. After carbohydrate- or fat-rich diets there is no material difference in the results of the tolerance tests. Ingestion of 30 g. of (I) with 40 g. of (II) causes decreases in both galactæmia and galactosuria, the hyperglycæmia being $<$ would be expected after 30 g. of (I) alone. Figures showing small blood-(II) levels coinciding with galactosuria indicate that the renal threshold, if it exists, must be very low. A. L.

Effect of acid on post-mortal lactic acid formation in mammalian muscle. L. IRVING and A. E. C. RIGGS (Trans. Roy. Soc. Canada, 1932, [iii], **26**, 121—126).—The formation of lactic acid (I) in dog's or rabbit's gastrocnemii (II) is checked by the addition of Ringer's solution (III), a max. occurring with 1 c.c. for each g. of (II). Addition of very low concns. of HCl to (III) reduces the formation of (I) in incubated (II). This inhibition increases (but not proportionately) with increasing concn. of HCl, but is more pronounced with naturally formed (I). F. O. H.

Changes in hexosephosphate, glycogen, and lactic acid during contraction and recovery of mammalian muscle. G. T. CORI and C. F. CORI (J. Biol. Chem., 1933, **99**, 493—505).—A 5-sec. tetanic stimulation of rat's gastrocnemius produces a 2—3-fold increase in hexosephosphate (I) concn.; return to the resting val. occurs within 10 min. 43% of the glycogen disappearing from muscle after 15 sec. stimulation is accounted for by the accumulation of (I), and the remainder by lactic acid formation. During 20 min. rest a muscle regains 50·8% of its glycogen. H. D.

Change of volume in muscular contraction. O. MEYERHOF (Naturwiss., 1932, **20**, 977—980).—By an improved technique it is shown that the diminution of vol. which occurs in electrically stimulated muscle is simultaneous with the contraction in length. The diminution continues during the stimulus and a slow recovery takes place afterwards. The change in mol. vol. associated with various possible hydrolytic reactions in the muscle and the electrical effect on the muscle-protein probably account for the phenomenon. R. K. C.

Metabolism of tonic and non-tonic bird's muscle. J. MUNDELEIN (Biochem. Z., 1932, **256**, 376—383).—Formation of lactic acid (I) by pigeon's tonic (reacts to acetylcholine) leg muscle is increased by addition of glucose or hexosediphosphate, whilst that by non-tonic breast muscle is inhibited by glucose and the increase is very much smaller with hexosephosphate. Similar differentiation of the two types of muscle is obtained in respect to the conversion of $AcCO_2H$ into (I), the process being completely inhibited by $CH_2Br{\cdot}CO_2H$ with breast muscle and being unaffected with leg muscle. P. W. C.

Glucose utilisation by brain. R. W. GERARD and R. J. SCHACHTER (Proc. Soc. Exp. Biol. Med., 1932, **29**, 525—528).—The metabolism of the brain, as determined by the glucose taken from the blood passing through it, is at least 20 times as intense as that

of resting muscle. In the dog, insulin did not uniquely influence brain-sugar utilisation. CH. ABS.

Significance of bile acids in carbohydrate metabolism. XXIV. Blood-sugar curve under the influence of bile acids and adrenaline with and without spleen extract in splenectomised rabbits. K. FUZIWARA (Biochem. Z., 1932, **256**, 384—397).—Splenectomy in rabbits leads to hyperglycæmia lasting for 20 days, the blood-sugar then returning to normal. The hypoglycæmic action of cholic acid is less with splenectomised than with normal rabbits. The experimental hyperglycæmia of splenectomised rabbits receiving glucose is decreased by both cholic acid and spleen extract, and is reduced to a greater extent by both acting together. Cholic acid increases adrenaline hyperglycæmia of splenectomised rabbits, the action being decreased by addition of spleen extract. The antagonistic action of cholic acid and adrenaline on sugar metabolism is inhibited by splenectomy. P. W. C.

Effect of strenuous exercise of short duration on the blood-sugar. O. M. SOLANDT and G. C. FERGUSON (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 173—174).—Men running for periods of 30—45 sec. or of 5—6 min. experience an increase in blood-sugar. The duration of the hyperglycæmia varies with different individuals. F. O. H.

Effect of exercise on the blood-creatinine of the horse. Y. YASUDA (J. Chosen Med. Assoc., 1931, **21**, 808—816).—The average val. for resting horses was 1·445 mg. [per 100 c.c.?], the quantity being a function of body-wt. After strenuous and prolonged exercise it increased by 0·0328 mg., the increase being parallel with the degree of fatigue. After ordinary exercise the smaller increase is not directly proportional to the degree of fatigue. CH. ABS.

Utilisation of amino-nitrogen in the animal organism. P. MEZINESCO (Compt. rend., 1933, **196**, 291—293).—Previous results (A., 1932, 189) are confirmed for asparagine, NH_2Ac, and succinamide. R. S. C.

[Imino-acids as intermediates in] the synthesis and degradation of amino-acids. C. BLASCHE (Biochem. Z., 1933, **257**, 14—21).—Catalytic hydrogenation (with Pd) of phenyl-pyruvic, -glyoxylic, and -ketobutyric acids in aq. NH_3 yields the corresponding NH_2-acids, but similar reduction of iminodipropionic acid (A., 1916, i, 636) or of its nitrile or Me ester yields no NH_2-acid. When Bottinger's mixture (Annalen, 1881, **208**, 122—141) (which always contains 25% or more of its N as NH_2) is thus reduced no increase in the NH_2 content occurs. It follows that the mixture contains no doubly-bound NH or that no such groups are produced during the synthesis or degradation of NH_2-acids. W. McC.

Biological fission of histidine. M. KIYOKAWA (Z. physiol. Chem., 1933, **214**, 38—41).—*l*-Histidine subcutaneously injected into rabbits is converted into urocanic acid; *dl*- is asymmetrically utilised, *d*-histidine, but no urocanic acid, being isolated from the urine. *Oidium lactis* converts histidine into iminazolylpropionic acid; no iminazolyl-lactic acid could be isolated. J. H. B.

Intermediary metabolism of tryptophan. XII. Mechanism of anthranilic acid formation from tryptophan by micro-organisms. Y. KOTAKE and S. OTANI [with M. KAWASE]. **XIII. Determination of kynurenine in urine and the form of excretion of kynurenine.** Y. KOTAKE and M. KAWASE. **XIV. Is subcutaneously administered tryptophan utilised for nutrition?** G. SHICHIRI and H. SAKATA. **XV. Influence of tryptophan and of its physiological metabolic products on the development of yeast.** J. SAITO. **XVI. Influence of kynurenine on nutrition and experimental anæmia.** N. IWAKURA, S. OTANI, and T. TANIGUCHI. **XVII. (*a*) Modification of the halogen reaction of tryptophan.** Y. KOTAKE. **(*b*) Fate of aminoacetophenone in the animal body.** S. INAGAKI. **(*c*) Effect of configuration in indole formation from indolelactic acid by bacteria.** J. SAITO. **(*d*) Interception of acetaldehyde by means of amino-acids in yeast fermentation.** S. OTANI (Z. physiol. Chem., 1933, **214**, 1—6, 6—13, 14—16, 17—21, 22—25, 25—32).—XII. *B. subtilis* produces anthranilic and kynurenic acids from tryptophan (I) or kynurenine (II), probably by way of aminobenzoylpyruvic acid. Small amounts of (II) are produced from (I).

XIII. (II) is determined by pptn. with acid $HgSO_4$ solution and filtration. The NH_3 liberated from the ppt. by heating with aq. $Ba(OH)_2$ is titrated. The figure obtained is about 5% low. (II) is probably excreted as the acid K salt, kynurenic acid as the Na salt. (II) is probably present in small amount in normal urine. *dl*-(I) is converted into (II) in the animal body, but to a much smaller extent than the *l*-form.

XIV. (I) subcutaneously administered to rats on a (I)-free diet has a favourable effect on body-wt., but does not meet the entire (I) requirement of the animal (cf. A., 1927, 791).

XV. (II) promotes yeast growth; (I), kynurenic acid, and kynurine have no action.

XVI. (II) cannot replace (I) in the diet and is not curative for experimental anæmia.

XVII. (*a*) The solution is acidified with dil. HCl or H_2SO_4, treated with I in KI solution, and heated to boiling. (I) gives a reddish-violet colour with green fluorescence. The pigment is extracted by amyl alcohol and spectroscopically resembles urorosein.

(*b*) *o*-Aminoacetophenone subcutaneously injected into rabbits is converted into anthranilic acid and *o*-aminophenylmethylcarbinol, the latter forming a paired compound with glycuronic acid.

(*c*) *B. coli* converts *dl*- (but not *l*-)indolelactic and indolepyruvic acids into indole.

(*d*) In a yeast (*Willia anomala*) fermentation in presence of (I), the latter acts as interceptor for MeCHO forming *N-ethylidenetryptophan*, m.p. 275° (decomp.), $[\alpha]_D$ −144·9° (in H_2O). The constitution was confirmed by synthesis by heating to 80° MeCHO and (I) in H_2O. J. H. B.

New paired glycuronic acid, tyrosinehydantoinglycuronic acid. K. ICHIHARA and S. TAMURA (Z. physiol. Chem., 1933, **214**, 33—37).—Tyrosinehydantoin fed to rabbits is excreted as *tyrosinehydantoinglycuronic acid* (*K* salt, $[\alpha]_D$ −98°). J. H. B.

Cystine metabolism in sheep. P. V. RAMAIYYA (Current Sci., 1932, 1, 12).—The wool of sheep given 0·07—0·1 g. S daily contained 3% S (controls, 2·7%). CH. ABS.

Mammalian hair growth. I. Sulphur economy of animal fibre production. A. T. KING. **II. The chemico-histological system in follicle activity.** A. T. KING and J. E. NICHOLS (Trans. Faraday Soc., 1933, **29**, 258—271, 272—278).—I. The availability of different sources of S in sheep nutrition is reviewed and the importance of sufficient Fe emphasised.

II. The formation of the hair from the follicle is reviewed. It is suggested that there is a cystine concn. gradient in the papilla which may lead to a similar gradient from the outside to the inside layers of the hair. A. G.

Relation between oxygen tension and protein synthesis in certain tissue extracts. C. VOEGTLIN, M. E. MAVER, and J. M. JOHNSON (Science, 1933, **77**, 92—93).—A decrease in O_2 pressure below atm. increases the degree and rate of proteolysis in certain normal and malignant tissues. Oxygenation of digests of voluntary muscle of albino rats and rabbits, and of rat sarcoma and carcinoma results in a relatively rapid synthesis of protein (I). Conditions favouring synthesis of (I) are high O_2 pressure, a p_H near neutrality, relatively high initial concn. of SH groups attached to (I) or glutathione, and an adequate concn. of suitable decomp. products of (I). Variation in O_2 supply to tissues under normal or pathological conditions in particular may exert a controlling influence on the equilibrium between cleavage and synthesis of tissue-(I). L. S. T.

Comparative value of various protein foodstuffs for growth. E. F. TERROINE and (MLLE.) S. VALLA (Compt. rend., 1933, **196**, 288—290).—The coeffs. of digestibility (absorbed N/undigested N × 100), of retention (retained N/absorbed N × 100), and of "practical utilisation" (retained N/undigested N × 100) for 18 protein foodstuffs, fed to young pigs, are recorded. Large variations are observed, skimmed milk being the most valuable. R. S. C.

Protein requirement of the albino mouse. F. C. BING, W. L. ADAMS, and R. O. BOWMAN (J. Nutrition, 1932, **5**, 571—579).—Feeding experiments in which the level of protein (caseinogen) intake was varied indicate the protein requirement to be > 15·6% of caseinogen. In all cases showing positive growth the content of reduced glutathione remained approx. the same. A. G. P.

Replacement of part of the protein in the food of cows by ammonium hydrogen carbonate. P. EHRENBERG and H. BRIESE (Biochem. Z., 1933, **257**, 194—208; cf. A., 1932, 421).—In suitable circumstances part of the protein in the food of milk-cows can advantageously be replaced by NH_4HCO_3. This replacement has no detrimental effects on the health of the cows or on the quality of their milk, although its amount is slightly reduced. W. McC.

Nutritive value of milk. I. Deficiencies of an exclusive milk diet. W. E. KRAUSS (Ohio Agric. Exp. Sta. Bull., 1931, No. 477, 54 pp.).—Rats fed exclusively on a whole milk diet developed nutritional anæmia and subsequently died. Addition of small amounts of Fe^{III} citrate, chloride, sulphate, colloidal hydroxide, or Mn, alone or with Fe, had no beneficial effect. Small quantities of $CuSO_4$ (0·16 g. of Cu daily) were effective. (The milk used contained 2·4 mg. Fe + 0·5 mg. Cu per litre.) Yeast, caseinogen, agar, and molasses were also beneficial according to their Cu contents. No reproduction occurred with rats fed exclusively on milk. Addition of Cu etc. permitted reproduction, but lactation was poor. A. G. P.

Formation of purines from proteins in endogenous nitrogen metabolism. E. F. TERROINE and (MLLE.) G. MOUROT (Compt. rend., 1932, **195**, 1424—1427).—The sum of the purine-N (including allantoin-N) excreted by rats and guinea-pigs during a period of starvation and of that of their bodies after death is > their purine-N content at the commencement of starvation, deduced from similar controls. This confirms the synthesis of purines from proteins (cf. A., 1931, 647). A. C.

Nucleic acid metabolism. II. Synthesis of uric acid in pupæ of silkworms from metabolites of nitrogenous compounds. A. AKAO (J. Chosen Med. Assoc., 1931, **21**, 762—768).—The fact that the normal female, with vigorous synthesis of purine bases (I), produces less uric acid (II), and the normal male or castrated pupa, with a less active synthesis of (I), produces more (II), indicates that (II) is not a mere final metabolic product of (I). CH. ABS.

Effect of hippuric acid excretion on nitrogen balance. F. J. WARTH and N. C. D. GUPTA (Indian J. Vet. Sci., 1932, **2**, 294—300).—Balance experiments with *Ragi* straw and *Bolarum* hay supplemented with varying amounts of earthnut cake are reported. It is concluded that the N balance was influenced by hippuric acid excretion. NUTR. ABS.

Reconstructive food value of embryos of various cereal and leguminous seeds. V. FAMIANI (Atti R. Accad. Lincei, 1932, [vi], **16**, 360—365).—Wheat or beans have considerably greater food val. when containing, than when devoid of, the embryos (cf. A., 1932, 423, 772). T. H. P.

Bilirubin metabolism. I. Erythropoesis at high altitude. F. VERZAR, A. VON ARVAY, J. PETER, and H. SCHOLDERER. **II. Influence of the spleen on the bilirubin content of the blood-serum.** G. VON LUDANY and F. VERZAR. **III. Disappearance of injected bilirubin from the blood-stream. Action of the spleen on this process. IV. Resorption of bilirubin in the intestine.** H. SCHOLDERER (Biochem. Z., 1933, **257**, 113—129, 130—136, 137—144, 145—150).—1. In so far as they are not due to contraction of the spleen the simultaneous increases in the bilirubin (I) and red corpuscle (II) content of human blood which result from living and exercising vigorously at high altitude (3450 m.) indicate the possibility that (I) in particular and/or other decomp. products of the (II) stimulate increased production of (II).

II. In rabbits the content of (I) of the blood-serum is doubled as a result of extirpation of the

spleen, whilst if this is caused to contract by injection of adrenaline, bleeding, or partial asphyxia, that content always increases. Adrenaline and bleeding cause no increase if the spleen is first removed.

III. (I), intravenously injected into rabbits, disappears very rapidly (90% disappearance after 5 min., 95% after 15 min.) from the blood. The remainder disappears slowly. The rate of disappearance is not appreciably affected by extirpation of the spleen and/or the kidneys, but if the abdominal viscera (including the liver) are excluded from the circulation, disappearance does not result. The rapid disappearance makes detection of (I) impossible in some parts of the circulatory system.

IV. In rats (I), injected into the small intestine, is scarcely, if at all, resorbed, and addition of 2—4% of Na cholate or taurocholate does not stimulate resorption. The extirpated small intestine (dead or surviving) is made permeable to (I) by Na cholate and Na taurocholate in concns. of at least 2%. W. McC.

Relation between bile acids in the fæces and the resorption of fat in children. H. Minnibeck (Biochem. Z., 1933, **257**, 160—170; cf. A., 1931, 1084).—Bile acids undergo little or no bacterial decomp. during passage through the large intestine. The ratio of the bile acid content of the fæces of children to the fat content sometimes approximates to that (1 : 8 to 1 : 24) which prevails in the small intestine, but usually exceeds 1 : 100. W. McC.

Effect of carbon dioxide in presence of varying amounts of hydrogen carbonate on the cleavage rate of the egg of *Arbacia*. C. Haywood and W. S. Root (J. Cell. Comp. Physiol., 1932, **2**, 177—191).—With CO_2 tensions of 0·2—90 mm. Hg, increasing amounts of HCO_3' decreased the effectiveness of CO_2 in delaying the first cleavage of the eggs. With higher CO_2 tensions HCO_3' also increased the no. of eggs ultimately undergoing first cleavage and reduced the no. of abnormally cleaved eggs. A. G. P.

Determination of alcohol in blood. J. Peltzer (Chem.-Ztg., 1933, **57**, 93—94).—Traces of EtOH in blood are detected and approx. (70%) determined by pptg. proteins and carbohydrates, treating with *p*-nitrobenzoyl chloride and alkali, extracting the ester with Et_2O, and weighing it. For more exact determinations the EtOH is converted into EtI with HI, and the I determined. A correction must be applied. A. G.

Anæsthetic action of divinyl oxide on humans. S. Gelfan and I. R. Bell (J. Pharm. Exp. Ther., 1933, **47**, 1—3).—Divinyl oxide appears to be a suitable anæsthetic for man. F. O. H.

Anæsthetic action of divinyl oxide on animals. C. D. Leake, P. K. Knoefel, and A. E. Guedel (J. Pharm. Exp. Ther., 1933, **47**, 5—16).—The action of divinyl oxide (A., 1931, 1033) when inhaled by mice and dogs is more rapid and is attended by less severe physiological effects than that of Et_2O. Comparatively rapid polymerisation on exposure to light and air, however, is a disadvantage. F. O. H.

Fate of chloral hydrate in the organism. B. Olszewski and N. E. Renescu (Bull. Soc. Chim. biol., 1932, **14**, 1510—1530).—The quantity of $CHCl_3$ produced during poisoning with chloral hydrate (I) is negligible and is distributed throughout the whole organism. (I) is found chiefly in the brain, heart, liver, and intestines; the quantity found in the blood is high immediately after injection and then falls very rapidly. Brain fixes (I) rapidly and without any relation to the quantity injected. The amount in the fat and liver increases with the duration of narcosis. It is destroyed rapidly during putrefaction. H. G. R.

Carbazole derivatives. I. Local anæsthetics of urethane type. P. K. Knoefel (J. Pharm. Exp. Ther., 1933, **47**, 69—78).—The local anæsthetic action of various substituted amino-alkyl esters of carbazole-*N*-carboxylic acid was determined. Presence of a methane linking induces subnormal stimulation of the central nervous system and a primary depressor action. The diethylaminoethyl ester ("carbacaine") exhibits pressor activity, is absorbed slowly from subcutaneous tissue, and is detoxified more rapidly than cocaine. F. O. H.

Accelerated production of specific urinary pigments by drug administration. II. Effect of trional on urobilin and urobilinogen formation. F. G. Germuth (Amer. J. Pharm., 1933, **105**, 30—35).—The urobilin content of urine is increased by administration of trional over a period of a week; the urobilinogen content is also affected, but to a smaller degree. P. G. M.

Physico-chemical properties and hypnotic action of substituted barbituric acids. D. L. Tabern and E. F. Shelberg (J. Amer. Chem. Soc., 1933, **55**, 328—332).—The hypnotic efficiencies of various 5 : 5-disubstituted barbituric acids parallel their distribution coeffs. between H_2O and olive oil at 20° and (qualitatively) the % adsorption from aq. solutions by ash-free C, but not the surface tensions of aq. solutions or the stabilities of aq. solutions of their Na salts at 100°. H. B.

Toxicological detection of barbituric acid derivatives; vacuum micro-sublimation. H. Kaiser (Süddeut. Apoth.-Ztg., 1932, **71**, 518—520, 540—542, 547—549, 553—556, 690—693; **72**, 57—59, 65—67; Chem. Zentr., 1932, ii, 747—748).—Physical changes of urine due to veronal poisoning cannot be detected. Satisfactory extraction is accomplished by means of Et_2O+30% light petroleum, and the extract is sublimed in vac. For identification, micro-reactions with $HgCl_2$ are recommended. A. A. E.

Permeability of mammalian salivary glands for organic non-electrolytes. W. R. Amberson and R. Hober (J. Cell. Comp. Physiol., 1932, **2**, 201—221).—High lipoid (Et_2O) solubility and low mol. vol. in acid amides is associated with ease of penetration into excised salivary glands of cats. A. G. P.

Antogonism between camphor and potassium chloride. J. Lévy and A. Beaune (Bull. Soc. pharmacol., 1932, **39**, 217—227; Chem. Zentr., 1932, ii, 2204).

Toxicity of mixtures of poisons. B. A. Southgate (Quart. J. Pharm., 1932, **5**, 639—648).—The

toxic effects on trout (*Salmo irideus*, Gibb.) of the components of mixtures of two poisons are (broadly) either additive and interchangeable, or independent. KCN–*p*-cresol and *p*-cresol–1 : 2 : 6-xylenol mixtures fall in the latter category, *p*-cresol–PhOH in the former, whilst 1 : 2 : 6-xylenol–1 : 3 : 5-xylenol is intermediate. W. S.

Urine examination in chronic injury by benzene and benzene derivatives. H. JOST (Arch. Gewerbepath. Gewerbehyg., 1932, **3**, 791—797).—Among printing operatives, increased urinary excretion of hippuric acid is associated with the inhalation of PhMe and of SO_4'', of glycuronic acid and phenols with that of C_6H_6. A. G. P.

Effect of *Panax ginseng* on serum-calcium and -potassium. I. Rabbit's serum; effect of narcotics. K. IN (J. Chosen Med. Assoc., 1932, **22**, 142—150).—Oral administration of the EtOH extract increases serum-Ca and -K (max. in 1 hr. and 3 hr., respectively). Urethane (I) and chloral hydrate (II) decrease -Ca and increase -K; morphine hydrochloride (III), although variable, has on the average the opposite effect. Ginseng is antagonistic to (I) and (II), but accentuates the effect of (III). CH. ABS.

Effect of the constituents of *Panax ginseng* on blood-sugar. K. KIN (J. Chosen Med. Assoc., 1932, **22**, 221—227).—Subcutaneous injection into the rabbit of panax acid, panax saponin (I), or panacen produces hypoglycæmia; (I) reduces adrenaline hyperglycæmia, but only slightly affects NH_4Cl hyperglycæmia. CH. ABS.

Effect of *Rehmannia lutea* on blood-sugar. K. KIN (J. Chosen Med. Assoc., 1932, **22**, 131—134).—The aq. extract produces hypoglycæmia in the rabbit; it reduces NaCl, but not adrenaline, hyperglycæmia. The EtOH extract is more active; the Et_2O extract is inactive. The active substance is named "rehmanin." CH. ABS.

Blood, cerebrospinal fluid, and [blood-] calcium during the cataleptic state induced by bulbocapnine. Combined effect of bulbocapnine and some other drugs. S. KATZENELBOGEN and M. C. MEEHAN (J. Pharm. Exp. Ther., 1933, **47**, 131—139).—Following injection of bulbocapnine into cats, the blood-non-protein-N is unchanged, the K and cholesterol levels tend to decrease, whilst the Ca level is markedly decreased. The cerebrospinal fluid-Ca, however, is unchanged. The action of the drug is not counteracted by stimulants such as caffeine, adrenaline, or mescaline. F. O. H.

Solanocapsine, a new alkaloid with a cardiac action. J. M. WATT, H. L. HEIMANN, and E. EPSTEIN (Quart. J. Pharm., 1932, **5**, 649—656).—The min. lethal dose of *solanocapsine hydrochloride*, which had been isolated from the poisonous "winter cherry," *Solanum pseudocapsicum*, L., is 0·022 g. per kg. (frog) and 0·01175 g. per kg. (rabbit). The alkaloid has a depressor cardiac effect. W. S.

Cardiotoxic principles of lombiry, *Cryptostegia madagascariensis*. F. MERCIER and J. BALANSARD (Compt. rend., 1932, **195**, 1427—1429).—Some chemical and pharmacological properties of two cardiotoxic glucosides isolated from the roots and stems of this plant are described. One is H_2O-sol., is related to the saponins, and is twice as toxic as the H_2O-insol. glucoside, which is of the digitalis type. A. C.

Relation between the constitution of the opium alkaloids and their action on intestinal movements in rabbits. K. KIN (Keijo J. Med., 1932, **3**, 501—529).—The action of various concns. of the following alkaloids on the rabbit's intestine *in situ* was determined: *apo*morphine, narceine, narcotine, heroin, morphine, codeine, papaverine, thebaine, and pantopon. All possessed both an excitatory and a paralysing action, depending on the concn. and related to the structure of the alkaloid. F. O. H.

Action of sinomenine and parasinomenine on the uterus; comparison with quinine. III. Uterus *in situ*. F. YAGI (Folia Pharmacol. Japon., 1932, **15**, No. 1, 85—92).—All three substances, given intravenously, stimulate the uterus; very large quantities of sinomenine and parasinomenine depress the isolated, living uterus. CH. ABS.

Central blood-sugar regulation. Effect of antipyretics, particularly pyramidone, on blood-sugar. F. HOGLER (Klin. Woch., 1932, **11**, 1191; Chem. Zentr., 1932, ii, 2326).—Subcutaneous injection of large amounts of pyramidone affects the sugar metabolism in the opposite way to that of small quantities. With rabbits 0·046—0·3 g. per kg. produces hyperglycæmia and hypothermy, whilst 0·01—0·03 g. per kg. produces hypoglycæmia and hyperthermy. 0·03—0·06 g. per kg. does not affect blood-sugar or -temp. A. A. E.

Effect of iodoacetic acid on reflex activity, gas exchange, and sugar requirement of the central nervous system. J. VON LEDEBUR (Pflüger's Archiv, 1932, **230**, 229—237; Chem Zentr., 1932, ii, 2074).

Acetylcholine contraction of transversely striped muscle after iodoacetic acid poisoning. J. VON LEDEBUR (Pflüger's Archiv, 1932, **230**, 394—400; Chem. Zentr., 1932, ii, 2075). A. A. E.

Physiological significance of urea. Elasmobranch heart. W. W. SIMPSON and E. ODGEN (J. Exp. Biol., 1932, **9**, 1—5).—Sucrose, $CS(NH_2)_2$, and Na_2SO_4 in iso-osmotic concns. cannot replace urea in maintaining the beating of the excised auricle of the dogfish. CH. ABS.

Action of magnesium on the heart and its behaviour towards potassium and calcium. N. V. GOLJACHOVSKI (Pflüger's Archiv, 1932, **230**, 401—411; Chem. Zentr., 1932, ii, 2075).—Mg intensifies the effect of Ca, but cannot replace it, and is antagonistic to K. A. A. E.

Physiological action of mineral waters. III. Action of hypotonic water on acid–base equilibrium. U. SAMMARTINO (Arch. Farm. sperim., 1933, **55**, 53—68).—No significant changes in the acid–base equilibrium, as determined by the urinary p_H and NH_3-coeff., were observed during periods when drinking-H_2O rich in salts was replaced by hypotonic H_2O. R. K. C.

Effect of prolonged milk–iron–copper diet on rats. F. A. UNDERHILL, J. M. ORTEN, E. R. MUGRAGE, and R. C. LEWIS (J. Biol. Chem., 1933, 99, 469—472).—No pathological changes are observed. H. D.

Electrophoresis of ferrous and ferric iron through undamaged skin. R. JÜRGENS (Klin. Woch., 1932, 11, 586—588; Chem. Zentr., 1932, ii, 1935).—$K_3Fe(CN)_6$ or $K_4Fe(CN)_6$ was injected into a mouse's tail which was made the cathode in a bath containing Fe ions. $Fe^{\cdot\cdot}$ appreciably passes through the skin, particularly as carbonate or sulphate, but skin is practically impervious to $Fe^{\cdot\cdot\cdot}$. It is probable that the active component of chalybeate waters is Fe^{II}. A. A. E.

Influence of copper and manganese on the therapeutic activity of iron. J. H. SHELDON (Brit. Med. J., 1932, ii, 869—872). NUTR. ABS.

Preparation, toxicity, and absorption of bismuth compounds. I. Bismuth salts of fatty acids. W. M. LAUTER, A. E. JURIST, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1932, 21, 1277—1282).—The average absorption of the Bi compounds of 14 fatty acids (injected in olive-oil solution or suspension) over a period of 4—5 weeks was 47% and in all cases was slow and irregular. They were relatively low in toxicity (to rats). E. H. S.

Lead contents of blood and urine in relation to the appearance of clinical symptoms and its diagnostic significance. S. LITZNER and F. WEYRAUCH (Arch. Gewerbepath. Gewerbehyg., 1932, 4, 74—100).—The crit. Pb concn. in blood associated with positive clinical observations of poisoning is 0·06 mg. per 100 c.c. The proportion of Pb in urine bears no direct relationship to that of the blood and is valueless for diagnostic purposes. A. G. P.

Acid–base equilibrium in the dog during experimental uranium nitrate poisoning. L. BALLIF and I. GHERSCOVICI (Compt. rend. Soc. Biol., 1932, 109, 229—231; Chem Zentr., 1932, ii, 2204).—There is acidosis, a decrease in plasma-Cl, a greater decrease in corpuscle-Cl, and an increase in blood-urea and -P. A. A. E.

Electro-catalytic detection of mercury in forensic chemistry. H. SCHMIDT-HEBBEL (Pharm. Zentr., 1933, 74, 83—86).—As little as 0·01 mg. of $HgCl_2$ can be detected in 10 c.c. of beer by electrolysis for 1 hr. between a C anode and an Al cathode. Negative results were obtained in this test on the organs of a mouse and of a hare killed with $HgCl_2$. A. R. P.

Industrial manganese poisoning. Parkinsonian-like condition. D. MOSHEIM (Klin. Woch., 1932, 11, 1989—1990). NUTR. ABS.

Blood-volume in cobalt polycythæmia. J. M. ORTEN, F. A. UNDERHILL, E. R. MUGRAGE, and R. C. LEWIS (J. Biol. Chem., 1933, 99, 457—463).—An increase in blood-vol. per body-wt. occurs when rats have a milk–Fe–Cu diet supplemented by Co, due to an increase in the no. of circulating erythrocytes. H. D.

Manganese in cobalt polycythæmia. J. M. ORTEN, F. A. UNDERHILL, E. R. MUGRAGE, and R. C. LEWIS (J. Biol. Chem., 1933, 99, 465—468).—Addition of Mn to the Co diet produces an increased blood count and lowers the toxicity of Co. H. D.

Cobalt in animal nutrition. F. J. STARE and C. A. ELVEHJEM (J. Biol. Chem., 1933, 99, 473—483).—Co (0·01 mg.) is determined by adding to a solution of the ashed tissue the NO-derivative of Na β-naphthol-3 : 6-disulphonate and NaOAc, warming to 70°, and stirring with dropwise addition of KOH until alkaline. The solution is boiled and conc. HNO_3 added. The red colour which develops if Co is present is compared with a standard. Rats given 0·5—2 mg. Co per day had amounts of Co in their bodies proportional to their daily intake. The presence of 0·04—0·05 mg. Co in the body was sufficient to produce polycythæmia. The tissues of pigs fed with 25 mg. of Co daily showed a widely distributed Co content, being highest in the liver, pancreas, and spleen. The vertebræ and ribs contained much more than the long bones. H. D.

Quantitative changes in the reduced glutathione content of the liver under various experimental conditions. L. BINET and A. ARNAUDET (Compt. rend. Soc. Biol., 1932, 108, 1117—1118; Chem. Zentr., 1932, ii, 2075).—Administration of "Na hyposulphite" increases the glutathione content of the normal animal and arrests its fall in experimental obstruction of the bile duct. A. A. E.

Transient methæmoglobinæmia due to ammonium nitrate. L. TARR (Arch. Int. Med., 1933, 51, 38—44).—Four cases are reported. H. D.

Elimination of bromides from the bloodstream. J. W. PALMER and H. T. CLARKE (J. Biol. Chem., 1933, 99, 435—444).—There is no differentiation between chloride (I) and bromide (II) in blood-cells and plasma. The kidneys excrete (I) preferentially, and the excretion of (II) is not affected by changes in urinary vol. The ratio of the fraction of (II) in the total halide in blood to that in urine is const. during const. intake of (I). H. G. R.

Relation between chemical constitution and action of chemotherapeutic agents. L. BENDA (Angew. Chem., 1933, 46, 85—87).—A review.

Photochemistry of the action of ultra-violet irradiation on human skin. W. FRANKENBURGER [with W. ZIMMERMANN] (Naturwiss., 1933; 21, 116—124).—The absorption spectra curves of phenylalanine, tyrosine (I), and tryptophan in the region of 310—320 mμ resemble the erythema effect–wave-length curve. The curve for alkaline solutions of (I) is displaced from that for neutral aq. (I) by approx. 20 mμ towards the higher wave-lengths. The effective absorption of alkaline (I) in a layer and in a concn. comparable with those of the Malpighian layer indicates that substances containing (I) play an essential part in the biological action of irradiation. The significance of the absorption curves for normal and irradiated histidine (II) is discussed. Irradiation in absence of O_2 does not effect any change in aq. (I), whilst presence of O_2 results in decarboxylation. The theories that (I) functions as the parent substance of the pigments produced by irradiation and (II) of the erythema-producing substance are upheld. F. O. H.

Effect of irradiation on the mineral constituents of blood. S. Malczynski, A. Borysiewicz, and T. Toczyski (Compt. rend. Soc. Biol., 1931, **108**, 165—167; Chem. Zentr., 1932, ii, 2839).—Ultra-violet radiation tends to increase the mineral constituents, particularly Ca and P, of blood. *X*-Radiation has a less characteristic effect; P, K, and Na are scarcely ever affected, whilst Ca is usually diminished. Administration of irradiated ergosterol has an effect similar to that of ultra-violet light. A. A. E.

***X*-Ray investigations on stimulated and paralysed nerve substance.** H. Handovsky (Kolloid-Z., 1933, **62**, 21—22).—The nerve substance of a frog narcotised with $CHCl_3$ gives interference rings which agree with those obtained from Na oleate. It is probable that orientation of fatty acid mols. occurs during narcosis. E. S. H.

***X*-Ray diagram of nerves.** G. Boehm (Kolloid-Z., 1933, **62**, 22—26).—A review, demonstrating how far the fine structure of nerves can be recognised by *X*-ray analysis, and the changes brought about by narcosis and degeneration. E. S. H.

Biological effects of high pressure: resistance of bacteria, enzymes, and toxins to very high pressures. J. Basset and M. A. Machebœuf (Compt. rend., 1932, **195**, 1431—1433).—Bacteria generally survive exposure to a pressure of 3000 atm. in liquid media at p_H 6·9—7·2 for 45 min. *B. prodigiosus*, *S. aureus*, and Koch's bacillus are rapidly destroyed at 6000 atm. Sporing bacilli (*B. subtilis*) resist 17,600 atm. for 45 min. Enzymes are only partly inactivated below 9000 atm. Above this pressure inactivation is rapid. Diphtheria toxin loses 80% of its activity in 45 min. at 13,500 atm. and all at 17,600 atm. Tetanus toxin is slightly more sensitive. Cobra venom and tuberculin are not affected by 13,500 atm. for 45 min. A. C.

Flocculation of colloidal dyes in the organism. M. Piettre (Compt. rend., 1933, **196**, 298—300).—Various electro-positive, colloidal dyes, when injected intravenously into rabbits, are pptd. in various organs, the organ affected being to a certain extent sp. for the dye used. Electro-negative dyes are usually without effect. R. S. C.

New oxidation enzyme. O. Warburg and W. Christian (Naturwiss., 1932, **20**, 980—981).—A summary account of the isolation of a new oxidation enzyme from yeast-juice. The enzyme, consisting of protein coupled with pigment, shows absorption bands at 435, 465 (max.), and 495 mμ. The free pigment, with absorption shifted 15—20 mμ towards the blue, crystallises from H_2O in needles. R. K. C.

Catalytic deamination of amino-acids. B. Kisch.—See this vol., 263.

Quinones as enzyme models. VIII. CO_2/NH_3 quotient in oxidative deamination. B. Kisch and K. Schuwirth (Biochem. Z., 1933, **257**, 89—94).—In the oxidative deamination of glycine (I) and serine in presence of catalysts (pyrocatechol, hydroxyquinol, adrenaline, gallic acid, resorcinol) CO_2 and NH_3 are eliminated in the ratio 1 : 1, but when glycylglycine (II) and glycyltyrosine are similarly deaminated with hydroxyquinol as catalyst no CO_2 is produced. Traces of CO_2 which are produced with (II) and the greater amount obtained with glycine Et ester probably come from small amounts of (I) liberated by hydrolysis. Only traces of CO_2 and NH_3 are obtained with alanine, leucine, and *iso*leucine. In these experiments borate can replace phosphate as buffer. W. McC.

Peroxidases. II. Influence of concentration of substrate (quinol), hydrogen peroxide, and other factors on activity of peroxidase of Chow Chow (*Sechium edule*). B. B. Dey and M. V. Sitharaman (J. Indian Chem. Soc., 1932, **9**, 499—508).—The activity of the enzyme is dependent on the concn. of H_2O_2 and quinol, and p_H, being greatest at p_H 4·8—5·2, and completely suppressed in presence of sufficient HCl. It is very readily poisoned by KCN, but is less sensitive to $HgCl_2$. H. A. P.

Biological hydrogenation of fumaric acid under the influence of cereals. K. P. Jacobsohn and A. da Cruz (Compt. rend. Soc. Biol., 1931, **107**, 94—96; Chem. Zentr., 1932, ii, 1800).—When ground rice, maize, oats, etc. which has been treated with $COMe_2$ and Et_2O is added to 2% aq. fumaric acid neutralised with KOH, emulsified, and kept at 37°, malic acid is gradually formed. A. A. E.

Kinetic study of liquefaction and enzymic saccharification of starch. II. Pancreatic amylase. G. Orestano (Bull. Soc. Chim. biol., 1932, **14**, 1531—1551).—Liquefaction of starch with pancreatic amylase behaves as a unimol. reaction. Saccharification follows this law at high concns. of enzyme only. The rate of liquefaction runs parallel to the amount of enzyme present and is directly proportional to the concn. of the substrate; the rate of saccharification is directly proportional to the amount of the enzyme and is inversely proportional to the concn. of the substrate. H. G. R.

Determination of the starch-liquefying power of amylase. T. Chrzaszcz and J. Janicki (Biochem. Z., 1932, **256**, 252—291).—Determinations of the starch-liquefying power with malt amylase (from rye, wheat, oats, barley) were carried out, using 15 known methods and 21 published modifications thereof. Seven of the methods gave trustworthy results, and the peculiar advantages of each are given. In order to obtain comparable results it is necessary to specify the methods of preparing both starch and enzyme. The liquefying power of amylase from the different cereals is very different. Displacement of the p_H of the starch to 5 increases the sensitivity of all the methods. P. W. C.

Amylolytic fermentations. IV. Influence of diamines and their hydrochlorides on the saccharification of starch by pancreas, saliva, and malt extract. F. Caujolle and P. Roche (Bull. Sci. pharmacol., 1932, **39**, 361—372; Chem. Zentr., 1932, ii, 2666).—Ethylenediamine, putrescine, and cadaverine inhibit the amylolytic action in each case. The hydrochlorides have no effect on that of malt extract, scarcely affect that of pancreas, and increase that of human saliva. A. A. E.

β-Glucosidase. C. NEUBERG and E. HOFMANN (Biochem. Z., 1932, **256**, 450—461).—Enzyme solutions prepared from the lactose fermenters *Saccharomyces fragilis*, *S. Kefir*, and lactose-yeast, Sp. 102, hydrolyse not only β-galactosides in the wide sense (lactose, lactoseureide, lactobionic acid) and β-methyl-, β-ethyl-, and β-phenyl-galactosides, but also the β-glucosides amygdalin, β-methylglucoside, salicin, arbutin, and cellobiose, but do not attack melibiose (which is hydrolysed by emulsin). Enzymic hydrolysis and power to ferment by the fresh yeast do not always run parallel, and the β-glucosidase of these enzyme solutions is different from that of emulsin. P. W. C.

β-Glucosidase of lactose fermenters. E. HOFMANN (Biochem. Z., 1932, **256**, 462—474).—Whereas emulsin lactase is considerably inhibited by glucose and little by galactose, the reverse is true of the lactase of enzyme solutions from *S. Kefir*, and whereas the p_H optimum for the former is 4·4, for the latter it is 7. The rate of hydrolysis with kefir lactase is the same for lactose and for lactoseureide. Optimum hydrolysis of salicin and β-methylglucoside is at p_H 6, activity decreasing rapidly on both sides. Only against amygdalin have both emulsin and the enzyme solutions a wide p_H optimum. The reaction with β-glucosidase of the enzyme solutions is not unimol., as is the action of emulsin on β-glucosides. From the aq. enzyme solutions a dry prep. is obtained, by an EtOH–Et_2O method, which possesses hydrolytic activity of both β-galactosides and β-glucosides. The optimum is 6, and it forms the most active lactase prep. known. P. W. C.

Enzymes of the mammary gland. Presence of glucomaltase. I. S. KLEINER and H. TAUBER (J. Biol. Chem., 1932, **99**, 241—247).—Glycerol extracts of cows' mammary glands contain no protease, salolase, lactase, or amylase. A maltase is present which hydrolyses maltose but not α-methylglucoside or sucrose, and has a p_H optimum of 6·8—7·0. Comparison with other maltases indicates the existence of glucomaltases as distinct from glucosidomaltases (A., 1926, 322, 865). F. O. H.

Reactivation of koji-invertase. N. TAKETOMI and T. HORIKOSI (J. Soc. Chem. Ind., Japan, 1932, **35**, 583B).—The activity of koji-invertase (I) that has been injured by very dil. (*e.g.*, 0·01*N*) acids or alkalis can be gradually and partly restored by cold storage after neutralisation. (I) damaged by strong alkali, acids, or heat does not recover. $HgCl_2$ has a marked action on (I), but the activity is completely restored by passing H_2S through the solution. E. L.

Dismutation of glyoxal. C. NEUBERG and E. SIMON (Biochem. Z., 1932, **256**, 485—491).—The extent of dismutation of glyoxal to glycollic acid is followed, using enzyme solutions prepared from pea seedlings, pig's liver and kidney, rabbit liver, $COMe_2$-dried pea preps., and bottom and top yeast. P. W. C.

Iodoacetic acid, glutathione, and tissue glyoxalase. F. DICKENS (Nature, 1933, **131**, 130—131).—With extracts of rat liver purified by isoelectric pptn. and dialysis, or with undialysed extracts, the action of $CH_2I{\cdot}CO_2H$ (I) in arresting glyoxalase (II) activity is completely reversed by the addition of reduced glutathione (III) to the inhibited extract. In a dialysed extract activated by glutathione (III) the quantity of iodoacetate (IV) required to stop lactic acid formation is approx. equiv. to the (III) added. The (II) activity of the crude extract is unaffected by such a concn. of (IV) and requires a much larger amount before lactic acid formation is arrested or retarded. The results suggest the occurrence of a direct reaction between (III) and (I), which has been observed when dil. neutral solutions of acid and (III) are mixed. HI is liberated and the thiol group of the (III) is attacked. L. S. T.

Chemical biology of growth-promoting substances. I. Enzymes of the extract of the embryo chick. G. BORGER and T. PETERS (Z. physiol. Chem., 1933, **214**, 91—103).—The embryonal extract (I) contains dipeptidase, less aminopolypeptidase, a trace of proteinase, amylase, and lipase. The activity of the dipeptidase falls by about 90% and that of the polypeptidase by about 50% in 50 days at 0°. The yolk membrane in glycerol extract contains about 12 times as much as (I) (glycerol extract), allantois only 1/5. The enzyme content of the incubated egg varies within wide limits. J. H. B.

Nature of emulsin, rennin, and pepsin. H. TAUBER (J. Biol. Chem., 1932, **99**, 257—264).—Emulsin is prepared by extraction of fat-free almond meal with 33% EtOH and pptn. of the extract by addition (1 : 1) of 96% EtOH. The prep. is inactivated by acid ($p_H < 2$), but not by pepsin, trypsin, or pancreatin. Active preps. of emulsin, rennin, and pepsin, however purified, give positive protein tests when sufficiently conc., but not when considerably diluted, a finding which refutes evidence for the non-protein character of these enzymes. F. O. H.

Action of rennin on caseinogen. M. BEAU (Lait, 1932, **12**, 618—640; Chem. Zentr., 1932, ii, 1984).—Rennin is considered to catalyse the polymerisation of caseinogen with the aid of CaO and H_3PO_4. A. A. E.

Enzymic formation of acetoin. II. From proteins. W. CIUSA (Annali Chim. Appl., 1932, **22**, 747—753; cf. A., 1932, 1287).—Acetoin is formed by the action of pepsin, trypsin, or papain on milk, blood-serum, or egg-white, in the last case from the ovomucoid. T. H. P.

Properties of proteolytic protective enzymes. Optimal p_H of their action. Detection of polypeptidase in urine. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1932, **13**, 363—381).—The optimal p_H for the action of the protective enzymes of the urine and serum of pregnancy and of animals previously injected with placental peptone is 7·0 for a protein substrate, 7·5 for *dl*-leucylglycine. With a peptone substrate max. activity is observed both below and above p_H 7·0. The polypeptidase activity of serum and urine is enhanced by the appearance of protective enzyme. Their inactivation by chilling, activation by serum, and specificity distinguish the protective enzymes from other proteases. A. C.

Enzyme systems contained in erepsin- and trypsin-complex. E. ABDERHALDEN and W. ZEISSET.—See this vol., 265.

Behaviour of polypeptides composed solely of *l*(+)-α-aminobutyric acid towards *N* alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN and E. HAASE.—See this vol., 264.

Behaviour towards erepsin and trypsin of polypeptides containing α-amino*iso*butyric acid. E. ABDERHALDEN and W. ZEISSET.—See this vol., 264.

Physical properties of polypeptides composed of *l*(+)-norleucine and their behaviour towards erepsin and trypsin. E. ABDERHALDEN and K. PLOTNER.—See this vol., 264.

Identity of the chloroacetyl-*l*-alanine-splitting component of erepsin solutions with that which hydrolyses chloroacet-*o*-nitroanilide and related compounds. E. ABDERHALDEN, E. VON EHRENWALL, E. SCHWAB, and O. ZUMSTEIN (Fermentforsch., 1932, **13**, 408—432).—Trypsin-free preps. of erepsin which hydrolyse chloroacetyl-*l*-alanine do not hydrolyse chloroacet-*o*-nitroanilide (I). Hydrolysis of the latter, for which p_H 8·0 is optimal, occurs only when trypsin is incompletely removed. The acylase of erepsin (A., 1931, 125) is therefore not identical with the ereptic enzyme described by Balls and Kohler (A., 1931, 521), which hydrolyses (I). Preps. of the latter enzyme are inactive towards chloroacetyl-*dl*-leucine, chloroacetyl-*l*-tyrosine, and benzoyltriglycine. (I) is hydrolysed by enzymes of liver and urine, but not by pancreatic extract. The activity of erepsin and trypsin towards *m*- and *p*-nitroanilides is considerably lower than towards the *o*-isomerides. Erepsin also hydrolyses *chloroacet*-o-*toluidide*, m.p. 111—112°; chloroacetanilide, dl-α-*bromopropion*-o-*nitroanilide*, m.p. 64—65°; *chloroacet*-o-*chloroanilide*, m.p. 75—76°; and o-*nitro-oxanilide Et* ester, m.p. 108°, but not chloroacet-*p*-toluidide, 2 : 2′-*dinitro-oxanilide*, m.p. 326°, N-o-*nitrophenylphthalimide*, m.p. 199°, chloroacetylaminoacrylic acid, phthalylglycyl-, and *phthalyldiglycyl-glycine*, m.p. 239°. A. C.

Influence of thiol compounds on enzymic processes. E. WALDSCHMIDT-LEITZ, A. SCHARIKOVA, and A. SCHAFFNER (Z. physiol. Chem., 1933, **214**, 75—88).—Cathepsin freed from natural activator becomes active towards proteins only in presence of a thiol compound, *e.g.*, cysteine, which likewise activates papain. Arginase is activated by SH and $Fe^{\cdot\cdot}$ salt under conditions in which SH alone inhibits. Cysteine or H_2S specifically inhibits the hydrolysis of H_3PO_4 esters induced by phosphatase, but does not appreciably affect their synthesis; disulphide compounds such as cystine are inactive. This also applies to the elimination of H_3PO_4 from nucleic acid by nucleotidase. SH-compounds inhibit catalase, in part irreversibly, but the degree of inhibition depends on the contact time and is not instantaneous as with HCN. Cystine shows no inhibition. PO_4''', AsO_4''', citrate, and EtOH depress the action of SH compounds on catalase. J. H. B.

Tumour-arginase. II. Activation and inhibition of arginase. III. Action of boiled and native juices from tumour, muscle of the affected animal, and from healthy muscle on arginase from liver and tumours and on extracts from healthy muscle. G. KLEIN and W. ZIESE (Z. physiol. Chem., 1932, **213**, 201—216, 217—225; cf. A., 1932, 1167).—II. The liver-arginase (I) of man and other mammals behaves like calf's liver-arginase towards thiols. In dil. suspensions and extracts cysteine and glutathione behave as inhibitors. Liver- and tumour-arginase (II) from carcinomatous subjects frequently show activation effects. This is not due to a direct effect on the enzyme, but to interaction between the thiols and the other substances present. When these are removed the thiols produce inhibition. The hypothesis of the action of Cu or simple Cu compounds does not satisfactorily explain the facts.

III. Boiled juices of tumour extracts strongly inhibit (I) and (II), but have no action on inactive muscle extracts of healthy animals. Only conc. boiled juices from healthy and diseased muscle inhibit, dil. native extracts slightly activate, and conc. strongly inhibit (I). The inhibitors are degradation products of protein metabolism. J. H. B.

Ammonia production during the histamine–histaminase reaction. E. W. MCHENRY and G. GAVIN (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 321—328).—Histamine (I), when acted on by a histaminase prep. from pig's kidney (A., 1932, 92) in PO_4''' buffer at p_H 7·2 or 8·8 and at 38°, liberates 1 N as NH_3 for each mol. of (I) inactivated. At p_H 5·9 the amount of NH_3 is considerably less. This formation of NH_3 is due to deamination, which at certain reactions is also accompanied by rupture of the glyoxaline ring. Urea is not formed. F. O. H.

Lipases of wheat. I. B. SULLIVAN and M. A. HOWE (J. Amer. Chem. Soc., 1933, **55**, 320—324).—Triacetin (I) is hydrolysed to a greater extent by low-grade flour than by bran or germ in phosphate or phosphate–borate buffers at 37·9° for 24 hr.; optimum activity is at p_H 7·3—8·2. Hydrolysis of the higher glycerides does not occur so readily and the optimum is on the acid side. Germinated wheat has a higher lipase activity towards the higher glycerides, but not towards (I). H. B.

Action of pancreatic extract on glycine in glycerol medium. R. WOLFF and (MLLE.) LAFRANÇAISE (Compt. rend., 1933, **196**, 221—223).—A slow and irregular decrease in the no. of CO_2H groups occurs when a 3% solution of glycine in glycerol is incubated at 37° with pancreatic lipase (hog). In presence of EtOH a marked decrease is observed, reaching 20—30% at p_H 5—9 in several weeks, indicating esterification of glycine. A. C.

Choline-esterase, an enzyme present in the blood-serum of the horse. E. STEDMAN, (MRS.) E. STEDMAN, and L. H. EASSON (Biochem. J., 1932, **26**, 2056—2066).—The enzyme hydrolyses acetyl- and butyryl-choline, Me butyrate (I), and tributyrin (II). It can be purified by fractional pptn. with $(NH_4)_2SO_4$. The activities towards (I) and (II) are much depressed in purified preps. S. S. Z.

Phosphatase. I. Determination of inorganic phosphate. Beer's law and interfering sub-

stances in the Kuttner–Lichtenstein method. A. BODANSKY (J. Biol. Chem., 1933, **99**, 197—206).—The Kuttner–Lichtenstein procedure (A., 1930, 725) is modified by making up the standard Na molybdate solution from molybdic acid and NaOH and by using a $SnCl_2$ solution containing 60 g. in 100 c.c. conc. HCl. The deviation from Beer's law produces a 20% difference between the vals. found for the concns. of the unknown and the standard; a table of corr. vals. may be used. The conditions of the test are standardised to obviate the large errors entering when $CCl_3{\cdot}CO_2H$ or $CCl_3{\cdot}CO_2H$ + glycerophosphate is present as in serum-inorg. P and phosphatase determinations. H. D.

Paradoxical increase of phosphatase activity in preserved serum. A. BODANSKY (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1292—1293).—Blood-serum kept for 1 hr. at room temp. and 23 hr. at 0° showed an increase (7—23%) in phosphatase activity; inorg. P was unchanged. CH. ABS.

Decomposition of adenylpyrophosphate *in vitro*. E. JACOBSEN (Biochem. Z., 1933, **257**, 221—233).—In inactivated, feebly alkaline (p_H 9·2—10) muscle extracts more equivs. of NH_3 than of pyrophosphate are eliminated, whereas in neutral or feebly acid extracts the ratio is 1 : 1. Deamination and dephosphorylation are independent and the former proceeds 20 times as fast with adenylic acid (I) as with adenylpyrophosphate (II). NaF, $CH_2I{\cdot}CO_2Na$, and KCNS (but not KCN) restrict or inhibit the conversion of (I) into (II) as they restrict or inhibit production of lactic acid. W. McC.

Hexose monophosphoric esters: mannose monophosphate. R. ROBISON (Biochem. J., 1932, **26**, 2191—2202).—A third component—*monophosphoric ester* of *mannose*, $[\alpha]^{20}_{61}$ +15·1° (*Ba* salt, $[\alpha]^{20}_{5461}$ + 3·5°; *phenylhydrazine* salt of phenylhydrazone, m.p. 144—145°; *phenylhydrazine* salt of osazone, m.p. 154—155°)—has been isolated from hexose monophosphate produced by fermentation of hexoses with yeast-juice. The Hagedorn and Jensen reducing power of the ester is the same as that of glucose and fructose monophosphate. The I-reducing power is only 60—70% of the val. theoretically required for an aldose monophosphate. It is very slowly hydrolysed by *N*-HCl at 100° ($K=0{\cdot}29\times10^{-3}$). The rate of hydrolysis of the free ester in 0·01*M* solution is the same as in *N*-HCl. Neuberg's fructose monophosphate has been isolated in a purer form as a component of fermentation (A., 1931, 523). In *N*-HCl the val. of *K* for this compound is $4{\cdot}36\times10^{-3}$, but in 0·01*M*-solution of the free ester the initial val. of *K* is $0{\cdot}37\times10^{-3}$. S. S. Z.

Relation of thiol compounds to glucose fermentation. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1932, **26**, 2169—2176).—$CH_2I{\cdot}CO_2H$ reacts with $Na_2S_2O_3$, cysteine (I), and glutathione (II). (I) and (II) markedly affect the relationship between fermentation and respiration of baker's yeast in presence of glucose; (I) inhibits the O_2 uptake, whilst (II) has little effect. Both compounds increase the rate of CO_2 formation, (II) having the greater action. The fermentation of fructose is similarly affected by (I). The O_2 uptake and CO_2 output of yeast in presence of glycerol are only slightly affected by (I). S. S. Z.

Biochemical action of boron. II. Influence of boric acid on alcoholic fermentation and the production of lactic acid by yeast. J. VOÏCU and M. NICULESCU (Bull. Soc. Chim. biol., 1932, **14**, 1290—1328).—The experiments are made using brewer's yeast, baker's yeast, and a commercial yeast prep. introduced into natural and synthetic media containing glucose or sucrose. The greater is the concn. of carbohydrate the less is the inhibition produced by $B(OH)_3$. With 5—10% of carbohydrate the no. of yeast cells after the fermentation is the same in presence of 0·5% $B(OH)_3$ as in the control without $B(OH)_3$; with 1% carbohydrate, however, the no. of yeast-cells in the control is twice that in the medium containing $B(OH)_3$. The inhibiting effect of $B(OH)_3$ varies with the p_H of the media, being greater in acid than in alkaline or neutral solution. In neutral solutions $B(OH)_3$ causes a decrease in EtOH, but an increase in volatile acid and glycerol formation; no MeCHO or $AcCO_2H$ is, however, formed. In the presence of a little grape juice fermentation increases and lactic acid is formed. A. L.

Sterilisation of solutions of glucose and sucrose. W. B. COOK (Iowa State Coll. J. Sci., 1932, **6**, 417—418).—At room temp. yeast grows more rapidly in sucrose than in glucose solutions, probably because at equal *d* the osmotic pressure in glucose is twice that in sucrose solution. At 60° the death rate was higher in sucrose than in glucose solutions of equal *d*, probably because the osmotic pressure of the latter kept the hot H_2O out of the cells. Addition of citric acid (0·02 or 0·04*M*) greatly accelerates the death of the yeast at 60°. CH. ABS.

Chemotaxis of plasmodia of *Myxomycetes*. Y. EMOTO (Proc. Imp. Acad. Tokyo, 1932, **8**, 460—463).—The chemotaxis towards various inorg. and org. substances at different vals. of p_H and concn. was investigated in *Physarum viride* and *P. rigidum*. F. O. H.

Effect of strontium salts on the movements of *Paramecium caudatum*. E. EISENBERG-HAMBURG (Arch. Protistenk, 1932, **77**, 108—124).—The rhythmic movement induced by Sr salts increased in rapidity with increasing concn. up to the toxic point, and declined with still higher concns. The accelerating effect was observed at all p_H ranges examined, but the abs. rapidity of movement in a given concn. of $Sr^{\cdot\cdot}$ was greater in alkaline than in neutral media. Ba, Rb, and Cs salts produced similar but less definite results, and Ca, Mg, Na, K, Fe, and Cd salts were ineffective. An anion effect among the Sr salts is recorded. An antagonism exists between $CaCl_2$ and $SrCl_2$ in this respect. A. G. P.

Action of *X*-rays on *Euplotes Taylori* and associated bacteria. M. G. BROWN, J. M. LUCK, G. SHEETS, and C. V. TAYLOR (J. Gen. Physiol., 1933, **16**, 397—406).—The protozoon, *Euplotes Taylori*, which normally grows only in presence of living bacteria, is killed by irradiation with *X*-rays for about 220 sec. (2110 Röntgen units per sec.). Sublethal doses are sufficient to kill completely the associated

bacteria. Strains of *B. fluorescens* and *B. coli* are killed in 15 and 45 sec., respectively (2530 Röntgen units per sec.). *E. Taylori* fails to grow on dead bacteria whether these have been killed by *X*-rays or otherwise. W. O. K.

Action of certain alkaloids on the development of *Aspergillus niger*. G. Mezzadroli and A. Amati (Atti R. Accad. Lincei, 1932, [vi], **16**, 366—369).—Growth of the mould is favoured by 0·5—3 g. per litre of quinine as sulphate and by 1 g. per litre of strychnine as nitrate, but 0·5 g. per litre of caffeine inhibits it. T. H. P.

Role of " nutrilites " in the nutrition of moulds and other fungi. R. J. Williams and J. M. Honn (Plant Physiol., 1932, **7**, 629—641).—The growth of moulds and certain yeasts was stimulated by certain vitamin-like substances (" nutrilites ") supplied in the form of yeast extracts. Similar although less extensive effects were produced by mixtures of NH_2-acids. Sporulation of some moulds occurred much more freely in nutrient solutions containing NH_2-acids. A. G. P.

Effect of hydrogen cyanide and carbon monoxide on butyric acid fermentation. W. Kempner (Biochem. Z., 1933, **257**, 41—56).—CO and HCN reversibly inhibit $PrCO_2H$ fermentation, which is nearly as sensitive to these substances as is respiration. It follows that the process, like respiration, is catalytic and that the enzyme is a heavy metal compound. The CO compound of the fermentation enzyme is not dissociated by ordinary or ultra-violet light, and hence it is probable that the metal involved is not Fe, but possibly Cu (which occurs in $PrCO_2H$ bacteria). W. McC.

Acetic fermentation and the oxidation of higher alcohols in sugar-free nutrients. H. Mosel (Zentr. Bakt. Par., 1932, II, **87**, 193—229).—EtOH is utilised as a nutrient by *B. aceti* and *B. ascendens* and is partly assimilated and partly transformed by metabolic processes into AcOH. The latter also serves as a nutrient and undergoes further oxidation to an extent which is influenced by the amount of EtOH present. In commercial fermentation practice the use of sugars as sources of C improves the growth conditions of the organisms, accelerates the change EtOH ⟶ AcOH, and retards the further oxidation of AcOH. PrOH is similarly utilised, but to a smaller extent. The production of the corresponding acids from BuOH and Bu$^\beta$OH is small. MeOH, Pr$^\beta$OH, *sec.*- and *tert.*-butyl, *n*-hexyl, and β-phenylethyl alcohols, glycerol, and erythritol are not utilised.

Volatile acids formed from citric acid by *Streptococcus citrovorus* and *S. paracitrovorus*. M. B. Michaelian (Iowa State Coll. J. Sci., 1932, **6**, 455—456).—In addition to AcOH, *S. paracitrovorus* produces a little propionic acid, whilst *S. citrovorus* produces more; as the concns. of acid increase the production of Ac_2 increases. Ch. Abs.

Effect of germanin (Bayer 205) on lactic acid formation. O. Fürth, R. Scholl, and H. Herrmann (Wien. klin. Woch., 1932, **45**, 1012—1013; Chem. Zentr., 1932, ii, 2330).—The formation of acid in muscle and liver was accelerated *in vitro* and *in vivo*. Bacterial production of lactic acid in milk was also accelerated by the substance in small concn. The action of diastase, pepsin, trypsin, and lipase is not arrested. A. A. E.

Fermentation of fructose by *Aërobacillus*. R. Patrick (Iowa State Coll. J. Sci., 1932, **6**, 457—461).—Three species formed EtOH, $COMe_2$, acetoin, CO_2, H_2, lactic acid, succinic acid, AcOH, and HCO_2H from glucose and fructose. MeOH was an intermediate product; βγ-butylene glycol and methylglyoxal were not detected. Ch. Abs.

Fermentation of rare sugars by members of the colon-aerogenes groups of bacteria. I. Trehalose. C. F. Poe and J. T. Field (J. Biol. Chem., 1932, **99**, 283—287).—The fermentation products yielded by members of the *Escherichia* (I) and *Aerobacter* (II) groups grown in a peptone–trehalose medium and the progressive changes in p_H were determined. The ratio AcOH : succinic acid is greater for (II), whereas that of AcOH : lactic acid is greater for (I). (II) but not (I) produces CHAcMe·OH. F. O. H.

Characteristics of oxidation by *Azotobacter*. H. Lineweaver (J. Biol. Chem., 1933, **99**, 575—593).—*Azotobacter vinelandii* is capable of oxidising by means of O_2 such compounds as glucose, lactate, pyruvate, succinate, AcOH, $CH_2(CO_2H)_2$, malate, tartrate, fumarate, EtOH, PrOH, BuOH, CH_2O, and *l*-tyrosine. Not oxidised appreciably are HCO_2H, MeCHO, glycollate, $H_2C_2O_4$, cystine, *l*-cysteine, *l*-leucine. In general, if a substance is oxidised at all, the reaction goes almost, if not completely, to CO_2 and H_2O. Change of p_H in the case of alcohols and an initial loss of CO_2 in that of $CH_2(CO_2H)_2$ indicate the formation of intermediate compounds. The presence of dehydrogenases is shown by the methylene-blue technique and the inhibition caused by narcotics. A study of the velocity of reaction indicates that either intermediate compound or enzyme formation may be involved, and with mixed substrates the velocity is not additive. The Q_{O_2} val. for the various substrates oxidised is high (1000—4000) compared with that for other organisms. The concns. of homologous series of narcotics (EtOH, urea, and urethane) producing 50% inhibition are given. Such inhibition is not dependent on age, and in the case of PrOH and BuOH is reversible. The inhibition produced by HCN and H_2S indicates heavy metal catalysis, and that by the Hecht–Eichholtz reagent suggests that Cu is involved. A. L.

Influence of carbon dioxide on rate of multiplication of bacteria, as judged by viable counts. R. B. Haines (J.S.C.I., 1933, **52**, 13—17T).—Viable counts of the rate of growth of bacteria isolated chiefly from meat in nutrient broth saturated with air and air containing 10—20% CO_2 have shown that the gas in these concns. has little action on *Proteus*, but increases the lag period and lengthens the generation time of *Pseudomonas* and *Achromobacter*. The effect is more marked at low temp., and at 0° 10% CO_2 approx. doubles the time required for a strain of *Achromobacter* to attain max. growth.

The p_H change will not account for the retardation of growth, and the possibility of interference with the dehydrogenating enzymes is indicated.

Carbon dioxide as a factor affecting lag in bacterial growth. H. H. WALKER (Science, 1932, **76**, 602—604).—CO_2 is necessary for the growth of *Esch. coli* in a fluid medium; the time lag in growth may be due to the time required for the culture to build up a concn. of CO_2 essential for growth. The postulation of an essential formation of intermediate substances other than CO_2 in protein synthesis is unnecessary. L. S. T.

Chemical changes accompanying the growth of tubercle bacilli (H 37) on Long's synthetic medium. F. E. HOOPER, A. G. RENFREW, and T. B. JOHNSON (Amer. Rev. Tuberc., 1932, **26**, 179—186).—Results suggest that the bacillus does not produce an enzyme capable of affecting the Cu-reducing power of the culture medium filtrates. The reducing power of the filtrates is increased by hydrolysis. CH. ABS.

Protein fractions of the H 37 (human) strain of tubercle bacillus. M. HEIDELBERGER and A. E. O. MENZEL (Science, 1933, **77**, 24—25).—Lævo-rotation increases, P content decreases, whilst N content remains const. in the fractions separated. L. S. T.

Cellular reactions to lipin fractions from acid-fast bacilli. K. C. SMITHBURN and F. R. SABIN (J. Exp. Med., 1932, **56**, 867—891). CH. ABS.

Antigenic proteins of *Salmonella aertrycke*. F. J. O'HARA and M. E. TAYLOR (Proc. Indiana Acad. Sci., 1932, **41**, 235—243).—Sp. antigenic fractions may be separated from the whole bacterial protein, which is a more powerful antigen than any of the fractions tested. The antigens are probably albumin, conjugated protein, and some undetermined protein or proteins. CH. ABS.

Concentration of pseudoglobulins of anti-pneumococcus serum. M. H. BROWN and W. KNOWLES (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 263—265).—The diluted plasma is saturated with NaCl, filtered, and the filtrate pptd. by addition of half its vol. of saturated aq. $(NH_4)_2SO_4$. The ppt. is dissolved in 1% NaCl, repptd. by 50% saturation of $(NH_4)_2SO_4$, and finally dialysed. Further salting-out at p_H 5·0—5·1 and at p_H 6·6—6·8, followed by dialysis, yields a conc. and purified pseudoglobulin prep. F. O. H.

Relationship between hæmolytic and toxigenic properties of staphylococcus cultures. C. E. DOLMAN (Trans. Roy. Soc. Canada, 1932, [iii], **23**, V, 309—310). F. O. H.

Concentration and purification of diphtheria toxoid. C. SIEBENMANN (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 257).—$BaSO_4$ is added to the acidified toxoid, then removed by sedimentation, washed at p_H 4, and re-suspended in aq. buffer at p_H 8·5. Centrifuging then yields a conc. and purified product. F. O. H.

Assay of the antigenic value of diphtheria toxoid. P. J. MOLONEY and E. M. TAYLOR (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 283—285).—The determination of the degree of immunity imparted by subcutaneous injection of diphtheria toxoid was investigated. F. O. H.

Importance of the antigenic value of anatoxin in antidiphtheritic vaccination. Precipitin reaction and immunisation. G. RAMON and P. NELIS (Ann. Inst. Pasteur, 1933, **50**, 66—78).—The precipitin reaction runs parallel with the immunising power of the anatoxin. P. G. M.

Action of organic compounds on diphtheria toxin. S. SCHMIDT (Dansk Tidsskr. Farm., 1933, **7**, 1—11).—Aliphatic hydrocarbons had no action, but the introduction of halogen usually conferred toxin-destroying power (I). The lower monohydric alcohols have little action, but at C_5H_{11}·OH a sudden development of (I) results; this holds good for C_6H_{13}·OH, but thereafter rapidly decreases. Both the above classes of substances exert a destructive influence on both the toxin and antigenic properties, but CH_2O destroys only the former. MeCHO and the next few members partly destroy the antigenic properties also, but the higher aldehydes from C_9 upwards have no action. Glyoxal and glyoxylic acid behave like CH_2O. The introduction of a halogen into an aldehyde greatly increases its action. In the fatty acid series (I) first becomes evident at C_5, and thereafter increases with the no. of C atoms in the mol. Introduction of halogen causes an acid otherwise indifferent to assume (I). Introduction of OH has no effect, and maleic and fumaric acids are without action, although the higher members, oleic and ricinoleic acids, act rapidly. Other aliphatic compounds (NH_2-acids, ketone alcohols, etc.) showed little effect. Cyclic compounds are generally more active than aliphatic. C_6H_6 and its homologues, and PhCl have no action, but the introduction of one or more OH groups confers marked (I); NO_2 and NH_2 groups have less marked effect than OH groups. Introduction of halogen in the side-chain of C_6H_6 homologues confers marked (I). Introduction of NH_2 into the ring with or without the presence of CO_2H in the side-chain increases the effect, but the introduction of NHMe into the ring with CHO in the side-chain weakens the action. The introduction of a primary alcohol group, CHO, or CO_2H into PhOH generally increases the effect, and cinnam-, salicyl-, and benz-aldehyde act more powerfully than the corresponding acids; furfuraldehyde resembles MeCHO in its effect. H. F. H.

Heat-stable precipitating substance extracted from vaccinia virus. W. SMITH (Brit. J. Exp. Path., 1932, **13**, 434—446).—The thermostable substance which gives a sp. reaction with immune sera contains both protein and carbohydrate. Pptg. antibodies are probably identical with virus-neutralising antibodies. Allergic skin reactions are elicited by inoculation of the extracts into previously vaccinated human subjects. CH. ABS.

Effect of cysteine on vaccine virus. N. E. MCKINNON (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 259—261).—In presence of methylene-blue, addition of 0·1% cysteine (I) to an emulsion of vaccine virus effects a small but definite preserving action during

storage at 2—5° or 18—22°; at 37°, however, the presence of (I) results in a loss of potency greater than that occurring in its absence. F. O. H.

Steam *versus* ether in the separation of acids from bacteriological media. J. B. McNair (Ind. Eng. Chem. (Anal.), 1933, **5**, 62—65).—The medium is extracted in a continuous extraction apparatus for 10 hr. with Et_2O. H_2O is added to the extract and, after evaporation of the Et_2O, the acids are titrated. HCO_2H may be determined as $(HCO_2)_2Hg$. T. McL.

Toxic action of alcohol–acid mixtures. I. G. Lockemann and W. Ulrich (Z. Hyg., 1932, **114**, 584—601).—The germicidal action of aq. solutions of acids is considerably increased by the addition of EtOH and *vice versa*. Organisms not killed by either agent alone may be killed by mixtures of these. A. G. P.

Sensitivity to light and bactericidal action of fading dyes. G. Kogel (Ber. Int. Cong. Phot., 1932, **8**, 363—366; Chem. Zentr., 1932, ii, 2151—2152).—The properties are correlated. A. A. E.

Bactericidal properties of silver chloride. J. Dekker and C. H. Dekker-Koers (Pharm. Weekblad, 1933, **70**, 23).—Saturated AgCl solution, containing $1{\cdot}5\times10^{-6}$ g. of Ag, was added to two samples of gelatin broth, one of which was placed in the incubator immediately, and the other after exposure to light for 1 hr. After 24 hr. at 22°, the former had remained sterile, whereas two colonies had developed in the latter; control plates developed about 70 colonies. H. F. G.

Relationship between hormones and non-specific cell activity, with special reference to phagocytosis and endocrine organs. Y. Muro (J. Chosen Med. Assoc., 1932, **22**, 642—654). Ch. Abs.

Hormones determining the secretion of crop "milk" in pigeons. L. Kaufman (Compt. rend. Soc. Biol., 1932, **111**, 881—883).—In adult male pigeons castrated at different times during the reproductive cycle, the brooding instinct persisted in the castrates for a year, but they secreted "milk" only during the brooding period immediately following castration. Brooding in itself was incapable of provoking secretion, and normal birds taken from the nest during the first few days of brooding did not secrete "milk." Aq. extracts of the testes of a bird which had been mated 22 hours previous to the gonadectomy, injected into brooding castrates, failed to provoke "milk" secretion. A hormone is probably produced by the testes during or immediately after mating which, during the course of brooding, stimulates the secretion by the anterior pituitary of another hormone, the latter provoking the secretion of crop "milk." Nutr. Abs.

Preparation of vagotonin. D. Santenoise and H. Penau (Bull. Acad. Med., 1932, [iii], **107**, 861—867; Chem. Zentr., 1932, ii, 1930).—Detailed directions are given for the prep. of clinically pure vagotonin from pancreas. A. A. E.

Isolation of thymocrescin. D. Asher (Biochem. Z., 1933, **257**, 209—212; cf. A., 1932, 1171).—From the partly purified material previously described a much more active product (I) is obtained by pptn. from aq. solution with $(NH_4)_2SO_4$ (almost to saturation) and extraction of the ppt. with 70% aq. EtOH. (I), which gives peptide reactions, is active in daily doses of 1 mg. W. McC.

Salivary glands. II. Y. Hiki, N. Takizawa, T. Ban, Y. Miyazaki, and K. Akazaki (Trans. Japan. Path. Soc., 1931, **21**, 184—188).—Hyperfunction of the anterior pituitary lobe appeared after extirpation of the parotid gland or the parotid and submaxillary glands. Blood-sugar decreased after ligation of the parotid and/or submaxillary duct. Ch. Abs.

Hormone of the pars intermedia of the pituitary (intermedin). III. B. Zondek and H. Krohn (Klin. Woch., 1932, **11**, 1293—1298; Chem. Zentr., 1932, ii, 1792—1793; cf. A., 1932, 432; this vol., 98).—For the prep. of intermedin (I) the pituitary, immediately after slaughter, is placed in $COMe_2$; after 8—24 hr. it (or anterior and posterior lobes separately) is finely chopped and the mince is extracted several times with $COMe_2$ at room temp. during several days until the $COMe_2$ is colourless. The dried gland powder is boiled three times with 0·25% AcOH for 5—10 min. each time so that in all 30 c.c. of solution are obtained. This is evaporated to dryness and the residue extracted three times with hot abs. EtOH. After centrifuging, the EtOH is evaporated and the residue dissolved in H_2O. After 24 hr. in the cold it is filtered. If the material was only the anterior lobe the solution of (I) is free from oxytocin (II) and vasopressin (III), but posterior lobe gives a better yield of (I). In the latter case NaOH (up to 1%) is added and the solution is neutralised after 24 hr., whereby (II) and (III) are destroyed and (I) suffers less decomp. The last traces of protein are removed with sulphosalicylic acid. (I) may now be pptd. from solution in abs. EtOH by pouring into Et_2O or $COMe_2$. (I) resists boiling; it is completely destroyed by trypsin and 85% destroyed by pepsin. Ultra-violet irradiation destroys it. (I) is easily adsorbed, *e.g.*, on C, Al_2O_3, $Fe(OH)_3$, kieselguhr; it is readily decomposed by HCl, and somewhat less readily by NaOH. The biological action of (I) is exclusively chromatophoric, actual synthesis of pigments appearing to take place. In the body (*e.g.*, injected into rabbits) it is rapidly decomposed. A. A. E.

Chemical fractionation of spinach secretin and a new plant secretin. J. Skuja (Skand. Arch. Physiol., 1932, **65**, 84—91).—The active principle of spinach secretin is quantitatively pptd. by phosphotungstic acid. The histidine fraction, obtained from the phosphotungstate by Steudel's method, contains the secretin in a purer and more active state. A similar secretin occurs in pickled-cabbage juice, but it is not present in the fresh leaves and must be a product of the fermentation. Nutr. Abs.

Parathyroid hormone. W. R. Tweedy and M. Torigoe (J. Biol. Chem., 1933, **99**, 155—164).—A parathyroid prep. is inactivated by (*a*) suspension in CH_2O at p_H 4·6 at room temp. for 2 hr., addition of EtOH to 75%, and pptn. with Et_2O at 0—2°, (*b*) 0·75*N*-HCl in 75% EtOH at room temp., (*c*) 0·1*N*-HCl in MeOH at room temp., and (*d*) treatment with

$NaNO_2$ in AcOH. Reactivation occurs in (*a*) by boiling a suspension in 0·001*N*-HCl for 20 min., in (*c*) by treatment with 0·08*N*-NaOH; the product of (*b*) is not reactivated by alkali. H. D.

Significance of the parathyroid hormone in regulating the calcium economy. II, III. C. Bomskov and G. Moschinski. **IV.** C. Bomskov (Z. ges. exp. Med., 1932, **83**, 326—335, 336—339, 340—346; Chem. Zentr., 1932, ii, 1795).—II. In rabbits injection of Ca salts and parathormone (I) produces a summation of the individual calcæmic effects. Compound formation is postulated.

III. The calcæmia curve during the first hr. after injection of (I) depends on the dose; the max. occurs 15 min. after injection.

IV. When adrenaline is injected into a rabbit with high blood-Ca following injection of Ca gluconate, the blood-Ca rapidly falls in a way similar to that after injection of (I). Hence the latter is presumed to act by increasing the excretion of adrenaline from the adrenals, followed by standardisation of the blood-Ca against the hormone concn., presumably by direct combination of Ca and (I). A. A. E.

Physiology of the parathyroid glands. V. Action of parathyroid extract on the renal threshold for phosphorus. R. Ellsworth (J. Clin. Invest., 1932, **11**, 1011—1017).—In hypoparathyroidism, injection of parathormone caused an immediate increase in P excretion; a fall in serum-P preceded a rise in -Ca. The hormone may affect the renal threshold for P. Ch. Abs.

Extracts of parathyroid glands containing an anti-growth factor. I. C. J. Eastland, N. Evers, and J. H. Thompson (Biochem. J., 1932, **26**, 2123—2128).—Acid EtOH extraction of the glands yields a prep. containing a factor which retards the growth of rats. Removal of fat and salting-out increase the potency of the extracts. Activated C does not affect the activity, but H_2O_2 may partly or completely destroy the factor. S. S. Z.

Effect on metabolism of highly-iodinated or brominated thyroid preparations. I. Abelin (Biochem. Z., 1933, **257**, 213—220).—Highly-iodinated or brominated thyroid preps. are less toxic than is the original material and do not have such pronounced effects on metabolism (in rats). Possibly di-iodo- and dibromo-tyrosine, which act as antagonists of thyroxine, are produced at some stage. W. McC.

Effect of di-iodotyrosine on thyroid action. I. Abelin and C. Wegelin (Klin. Woch., 1932, **11**, 2103—2106).—Oral administration of di-iodotyrosine (I) to guinea-pigs led to thyroid hypertrophy, increase of colloid, flatter epithelium, and reduced vascularity. Intraperitoneal injections of anterior pituitary extract (II) produced greater vascularity of the thyroid, reduction of colloid, and increased size of epithelial cells. Simultaneous administration of (I) and (II) prevented either in part or *in toto* the reduction of colloid and other results of (II). Nutr. Abs.

Spleen hormone. T. Miwa (Trans. Japan. Path. Soc., 1931, **21**, 193—196).—The blood of the splenic vein contains a hypocalcæmic substance which is antagonistic to parathyroid hormone and synergistic with thymic hormone. Ch. Abs.

Interrelationship between non-specific cell activity and hormones with special reference to ultra-violet rays and the spleen hormone. Y. Tokumitu and G. Toyota (Trans. Japan. Path. Soc., 1931, **21**, 191—193).—Increase in blood-platelets after ultra-violet irradiation is probably closely related to the splenic and parathyroid hormones. Ch. Abs.

Hormone of the adrenal cortex. H. Magistris (Klin. Woch., 1932, **11**, 1384—1387; Chem. Zentr., 1932, ii, 1794; cf. A., 1932, 779).—The hormone is gradually inactivated in aq. solution at room temp. Purified preps. are decomposed in 5 min. at 85°, whilst crude preps. tolerate 100°. In abs. EtOH it is stable for 10—12 weeks. The biuret reaction is negative, and the ninhydrin and Millon reactions are positive. The hormone is quantitatively salted out of aq. solution at p_H 7·0 by NaCl and $(NH_4)_2SO_4$. It is dialysable, and not absorbed by C, kaolin, or talc. A. A. E.

Function of the adrenal cortical hormone and the cause of death from adrenal insufficiency. W. W. Swingle, J. J. Pfiffner, H. M. Vars, P. A. Bott, and W. M. Parkins (Science, 1933, **77**, 58—64).—Experiments with adrenalectomised dogs show that the function of the adrenal cortical hormone (I) is the regulation and maintenance of a normal circulating vol. of fluid within the vascular system. In absence of (I), fluid is continually lost from circulation, normal blood-vol. cannot be maintained, and death from circulatory collapse results. The progressive decrease in blood-vol. is accompanied by a direct progressive fall of blood-pressure to death level; these phenomena appear within 24 and 72 hr. after discontinuance of the hormone injections. Hæm concn., increased blood viscosity, and retardation of circulation are chiefly dependent on the decline in plasma-vol. and blood-pressure. Blood-urea and non-protein-N also vary inversely with blood-pressure. Blood-colloids are proportionately increased in adrenal insufficiency, but dilution or compensation does not occur owing to the declining blood-vol. and -pressure. Blood-vol., -pressure, and constituents all return to normal when adequate amounts of (I) are administered to prostrate adrenalectomised animals. Traumatic or secondary shock in man with its analogous symptoms appears to be due to failure of the blood-diluting mechanism, the adrenal cortex, and loss of power to increase blood-vol. L. S. T.

Chemico-toxicological study of adrenaline. G. Venturoli (Boll. Chim.-farm., 1932, **71**, 957—958).—The demonstration of the conversion of administered adrenaline (I) into hydroxyadrenaline (II) in the body (A., 1911, ii, 635) has been extended by showing that after the putrefaction of flesh containing (I) the usual tests are not given, but (II) is recognisable by the Bronardel–Bouty and Jungmann tests. R. K. C.

Colorimetric determination of adrenaline in suprarenal gland extracts. J. H. Barker, C. J. Eastland, and N. Evers (Biochem. J., 1932, **26**,

2129—2143).—$FeCl_3$, NH_4 molybdate, and phosphotungstic acid tests are not sp., although the last is very sensitive and gives good results with fairly pure adrenaline solution under conditions described. The $K_2S_2O_8$ test gives results comparable with those obtained biologically when necessary conditions are observed. Sufficient accuracy can be obtained by applying this test to the determination of adrenaline in the glands themselves. S. S. Z.

Adrenaline, adrenals, and blood-pressure. T. Konschegg (Z. ges. exp. Med., 1932, **81**, 559—627; Chem. Zentr., 1932, ii, 2066).—Tissue- and (particularly) blood-lipins gradually reduce the adrenaline content of solutions. Acids liberate again part of the fixed adrenaline. A lipin–adrenaline complex is present in the blood. A. A. E.

Action of adrenaline on nitrogen metabolism. H. Labbe and M. Rubinstein (Compt. rend., 1932, **195**, 1429—1430).—Injection of 0·5—1·5 c.c. of 1% adrenaline solution into dogs in N equilibrium on a normal diet causes appreciable depression of the urinary N which persists for 3 days. A. C.

Action of adrenaline, insulin, and phloridzin on the urinary ammonia in the dog. M. Polonovski, G. Bizard, and P. Boulanger (Compt. rend. Soc. Biol., 1932, **108**, 1252—1255; Chem. Zentr., 1932, ii, 2067—2068).—Insulin and adrenaline both increase urinary NH_3; hence sugar metabolism does not appear to depend directly on the NH_3 excretion, but the latter reflects the effect of the former on the alkali reserve. Phloridzin had no effect on the NH_3 excretion. A. A. E.

Preparation of insulin. D. A. Scott and H. Parker (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 311—314).—The method previously described (A., 1926, 97) is modified by an additional salting-out with 15% NaCl, followed by isoelectric pptn. at p_H 5·0, pptn. of inactive material by 80% EtOH at p_H 2·0, pptn. of the EtOH solution by EtOH+Et_2O, and a final isoelectric pptn. at p_H 5·0. The method yields 2000 units per kg. ox pancreas with a N content of approx. 0·009 mg. per unit. F. O. H.

Insulin crystals. D. A. Scott (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 275—282).—Insulin crystallised from AcOH–NH_4OAc in aq. $COMe_2$ at p_H 5·2 yields a form [wedge-shaped crystals (I)] different from that separating at p_H 6·2 [rhombohedral (II)] (A., 1931, 1194). The activity of (I) is 24·1—24·3 units per mg. It is readily converted into (II), but the reverse process could not be achieved. The seeding at one particular p_H by crystals obtained at the other p_H has no influence on the final cryst. form. (I) cannot be obtained in phosphate buffer and appears to be due to dimorphism and not to the formation of a compound with $COMe_2$ or AcOH. F. O. H.

Insulin. XI. Chemistry of insulin. K. Freudenberg and H. Eyer. **XII. Action of proteolytic enzymes on insulin and its derivatives.** K. Freudenberg, E. Weiss, and H. Eichel (Z. physiol. Chem., 1932, **213**, 226—247, 248—262; cf. A., 1932, 96).—XI. Aromatic aldehydes do not inactivate insulin directly, but induce oxidation by atm. O_2. BzO_2H is especially active in this respect. HgO, cysteine and other thiols also inactivate, one third of the insulin becoming insol. Na_2SO_3 destroys insulin irreversibly, probably attacking the S·S linking. Inactivity produced by CH_2O can be restored to the extent of 60—70%. Destruction by ultra-violet light needs many light quanta; atm. O_2 is not involved in the inactivation. A quant. study of these reactions leads to a mol. wt. of 20,000 for insulin. Some inactivations are probably due to attack on the protein chain and not on the active group.

XII. Commercial insulin is shown by ultrafiltration to consist wholly of large mols. Acetylinsulin is irreversibly attacked by pepsin and trypsin-kinase. Insulin inactivated by esterification is also hydrolysed by trypsin-kinase. Activated papain destroys all insulin preps., non-activated discriminates; some preps. may contain traces of activator. The alkali-labile group containing 0·16% N is probably removed by papain and trypsin-kinase, but not by pepsin. J. H. B.

Action of methyl iodide on insulin. A. F. Charles and D. A. Scott (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 335—339).—Treatment of insulin (I) in MeOH–HCl with MeI at 56° results in a loss of 95% of the potency. On keeping at 0° for 12 hr. in dil. alkali, the inactivated product (II) recovers 30% of its original potency. Pptn. of (II) by Et_2O gives a product containing 5·08% I, which is reduced to 1·1% by isoelectric pptn., whilst the reactivated product contains 0·92%. Hence (I) appears to form an inactive compound with MeI, the I content of which, however, is not directly related to the accompanying inactivation. F. O. H.

Equilibrium between various monosaccharides and insulin. A. Moschini (Compt. rend. Soc. Biol., 1931, **108**, 270—273); Chem. Zentr., 1932, ii, 1796).—The max. quantity of glucose necessary to produce normal blood-sugar in the insulinised rabbit was 1·26 g. per kg. per hr., injected intravenously. Fructose gave a similar val., but galactose was given in so high doses that the blood-sugar was increased far above the normal, yet there were severe convulsions which were stopped by injection of glucose. A. A. E.

Effect of insulin on reduced glutathione of the blood. E. Zunz (Compt. rend. Soc. Biol., 1931, **108**, 223—225; Chem. Zentr., 1932, ii, 1796).—Intravenous injection of insulin (1—1·5 units per kg.) only moderately increases the blood-glutathione in the dog; after 2—2·5 units the increase is 2—7 mg. per 100 c.c. (arterial). Arterial and venous blood of the choralosed dog contain, respectively, (average) 49·10 and 53·81 mg. reduced glutathione per 100 c.c. Vagotonin, injected intravenously, behaves like insulin, but the rise in reduced glutathione is not clearly related to the low blood-sugar level. A. A. E.

Effect of insulin on the hypercholesterolæmia of the nephritic rabbit. P. Mauriac (Compt. rend. Soc. Biol., 1931, **108**, 54—56; Chem. Zentr., 1932, ii, 1797).—High blood-cholesterol in (U) nephritic rabbits is considerably reduced by injection of insulin. A. A. E.

Insulin and alimentary hyperglycæmia. R. BOLLER and K. UEBERRACK (Klin. Woch., 1932, **11**, 1391—1392; Chem. Zentr., 1932, ii, 1796—1797).—Alimentary hyperglycæmia (I) cannot be suppressed by insulin. The (I) curve after insulin is scarcely affected by ergotamine. After large doses of insulin the (I) curve rises and simulates the diabetic curve. A. A. E.

Blood-sugar curve after injection of insulin and lecithin. E. SKOUGE (Acta med. Scand., 1932, Suppl. 50, 232—237).—Insulin given with lecithin intravenously to normal men had the same action as when given alone; given with lecithin subcutaneously, it had an action more prolonged and less intense than when given alone. The max. action was observed about the 7th hour instead of the 3rd. NUTR. ABS.

Increase in the hypoglycæmic power of insulin by an extract of the lachrymatory gland. D. MICHAIL and P. VANCEA (Compt. rend. Soc. Biol., 1931, **108**, 284—285; Chem. Zentr., 1932, ii, 1796).—Intravenous injection of an extract of the lachrymatory gland causes a fall in blood-sugar in the normal or hyperglycæmic dog. In combination the effect of both is not the sum, but is greatly increased. A. A. E.

Insulin and oxalæmia. M. LOEPER, P. SOULIE, and J. TONNET (Compt. rend. Soc. Biol., 1931, **107**, 589—591; Chem. Zentr., 1932, ii, 1797).—In man, as in other animals and in plants, $H_2C_2O_4$ arises from the incomplete combustion of sugar; injection of insulin causes a fall in blood-$H_2C_2O_4$. A. A. E.

Influence of guanidine derivatives on insulin hypoglycæmia. K. ANDO (Folia Pharmacol. Japon., 1932, **14**, No. 3, 379—422).—Generally, guanidine derivatives produce hypoglycæmia, frequently preceded by hyperglycæmia; smaller doses cause the latter only. Methylcreatine, methylarginine, and dimethylguanidine markedly, and methylguanidine, benzoylarginine, and creatine slightly, increase the effect of insulin. CH. ABS.

Effect of infection on the insulin content of the pancreas. D. W. G. MURRAY and E. T. WATERS (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 169—172).—The pancreas of acutely-infected dogs has a subnormal content of insulin. F. O. H.

Oral administration of insulin derivatives. D. A. SCOTT, A. F. CHARLES, and E. T. WATERS (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 287—293).—Insulin, inactivated by MeOH–HCl (A., 1929, 1495), Ac_2O, MeI, or 0·1*N*-HCl and administered by stomach tube in doses of an original equivalence of 234 units, fails to lower the blood-sugar of normal dogs or to decrease the sugar excretion in depancreatised dogs. F. O. H.

Biology and chemistry of the sexual hormones. A. BUTENANDT (Naturwiss., 1933, **21**, 49—54).—A review of the chemistry of the follicular and testicular hormones.

[With K. TSCHERNING.] New results indicate the formula $C_{19}H_{30}O_2$ or $C_{18}H_{28}O_2$ for the testicular hormone, which probably contains four saturated rings, and the formulæ $C_{19}H_{30}O_2$ and $C_{19}H_{30}(OH)_2$ for the accompanying OH-ketone (m.p. 176·5°) and diol, respectively (cf. A., 1932, 971). The C_{19} substances may be intermediates in the degradation of sterols to hormones. R. K. C.

Biology and chemistry of the sex hormones. B. ZONDEK (Naturwiss., 1933, **21**, 33—39).—A review. R. K. C.

Adoption of a system of international units for the standardisation of folliculin. A. GIRARD (J. Pharm. Chim., 1933, [viii], **17**, 61—76).—A report of a conference on the standardisation of sex hormones, London, July, 1932. The unit is the sp. œstrogenic activity of 0·0001 mg. of a standard prep. of cryst. hormone, and is approx. one third of the rat unit of Allen and Doisy. A. C.

Purification and constitution of theelol. D. W. MACCORQUODALE, S. A. THAYER, and E. A. DOISY. —See this vol., 278.

Interrelationship between pituitary gland, ovaries, and placenta. J. B. COLLIP (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 1—7).—The hypothesis that the pituitary gland (I) is entirely responsible for the maintenance of the normal œstrous cycle is discussed. During pregnancy first the decidua and then the placenta (II) secrete an anterior pituitary-like principle (III), whilst at a later stage œstrin and emmenin are elaborated by (II), the activity of (I) being partly inhibited. The anterior lobe of (I) appears to form a principle inhibitory to (III). F. O. H.

Gonad-stimulating hormones in hypophysectomised animals. J. B. COLLIP, H. SELYE, and D. L. THOMSON (Nature, 1933, **131**, 56).—Administration of the anterior pituitary-like hormone of the human placenta produces a secretion of œstrin from the ovary of the adult hypophysectomised female rat. Hypophysectomy of adult female rats results in failure of milk secretion. L. S. T.

Hormone of the anterior pituitary lobe. S. FUKUI and M. MURATA (Trans. Japan. Path. Soc., 1931, **21**, 152—156).—Extracts of placenta and of the anterior pituitary lobe have the same biological reaction, but differ in resistance to heating, alkali, and acid. CH. ABS.

Hormone content of the human anterior pituitary lobe. A. UENO and M. MURATA (Trans. Japan Path. Soc., 1931, **21**, 149—152).—The content of the hormone which produces puberty phenomena in mice increases with age to the adult stage and decreases during senility; it decreases in chronic diseases and carcinoma and increases during pregnancy. It is present in equal quantities in man and woman. CH. ABS.

Amount of so-called pituitary hormone in the blood and urine in pregnancy. S. IIMURO and M. MURATA (Trans. Japan. Path. Soc., 1931, **21**, 156—159).—The hormone originates in the trophoblasts of the placenta. CH. ABS.

Origin of the comb-growth-promoting substance in male urine. D. R. MCCULLAGH, W. K. CUYLER, and J. T. FRAWLEY (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 183—192).—The similarity of the physiological and physico-chemical properties of the hormone (I) extracted from male urine (A.,

1930, 1321) to those of testicular extracts indicates the identity of the active principles concerned. This is confirmed by the absence of (I) from the urine and body-fluids of eunuchs. (I) appears to form a relatively insol. phenylhydrazone. F. O. H.

Transplantation of the seminal vesicle in the anterior chamber of the eye. W. KAISER (Naturwiss., 1933, **21**, 61).—Transplants of seminal vesicle in the iris of the rabbit's eye show reddening after intramuscular injection of testicular hormone, and the reaction is suggested as a test for the hormone. R. K. C.

Synthetic œstrus-exciting compounds. J. W. COOK, E. C. DODDS, and C. L. HEWETT (Nature, 1933, **131**, 56—57).—When injected into castrated animals 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene induces œstrus of a type similar to that obtained with œstrin. L. S. T.

Sex hormones and cancer-producing compounds. J. W. COOK and E. C. DODDS (Nature, 1933, **131**, 205—206).—Synthetic compounds of known structure possess both carcinogenic and œstrogenic activity. Thus 9 : 10-dihydroxy-9 : 10-di-*n*-butyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene, 5 : 6-*cyclo*penteno-1 : 2-benzanthracene, and 1 : 2-benzpyrene possess œstrus-exciting activity. At present, however, there is no evidence that carcinogenic compounds arise from œstrin in the animal. L. S. T.

Recent research on the vitamins. ANON. (Nature, 1933, **131**, 118—121).—A summary. L. S. T.

Need for standardisation of products containing added vitamins. (MISS) K. CULHANE and S. W. F. UNDERHILL (Chem. and Ind., 1933, 66—68).—The vitamin efficiency of foodstuffs can be improved either by improving the basic material, *i.e.*, the diet of cows, or by addition of vitamins in conc. form. Vitamins should be administered in relative proportions. Rats develop xerophthalmia more readily when there is an abundance of vitamin-*D* and no -*A* than when both vitamins are absent. The effects of vitamin-*D* excess, *i.e.*, urinary calculi, are counteracted by the addition of -*A*. Excessive intake of vitamin-*A* (50,000 times the necessary dose) has no deleterious effect on the health of rats. The therapeutic ratio of vitamin-*D* is $>$ 1000 and toxic effects due to over-dosage are much less apparent than the results of insufficiency. Adequate standardisation of manufactured foodstuffs is urged. E. H. S.

Vitamin content of natural products. A. L. BACHARACH (Chem. and Ind., 1933, 68—71).—In the prep. of foodstuffs containing added vitamins, apart from regular and adequate vitamin assay, it is necessary to choose a raw material having not necessarily a high vitamin content but one that is const. and stable. E. H. S.

Biological determination of vitamins-*A*, -*C*, and -*D* in plant juices. II. C. A. ROJAHN and E. WIRTH (Apoth.-Ztg., 1932, **47**, 838—841, 855—857; Chem. Zentr., 1932, ii, 2840).—Garlic, tomato, spinach, cucumber, radish, carrot, and celery juice (commercial samples) did not contain antiscorbutic quantities of vitamin-*C* or appreciable quantities of vitamin-*A* or -*D*. A. A. E.

Vitamin-*A* content of pasture plants. I. White clover and Kentucky bluegrass under pasturage conditions. E. WOODS, A. O. SHAW, F. W. ATKESON, and R. F. JOHNSON (J. Dairy Sci., 1932, **15**, 475—479).—White clover contained approx. twice as much vitamin-*A* as the blue grass (*Poa pratensis*). A. G. P.

Vitamin-*A* in ether extract of wheat flour. A. DANGOUMAU (Compt. rend. Soc. Biol., 1932, **111**, 796—797).—The Et_2O extract of wheat flour was deeply coloured, probably by carotene. 0·5—1·0 c.c. of the extract produced growth in rats which had become steady in wt. on a diet deficient in vitamin-*A*. NUTR. ABS.

Distribution of vitamin-*A* in the normal animal organism. H. SIMONNET, A. BUSSON, and L. ASSELIN (Compt. rend. Soc. Biol., 1932, **109**, 182—183; Chem. Zentr., 1932, ii, 2200—2201).—Only the liver and kidneys of a dog which had received carotene contained significant amounts of vitamin-*A*; the lung contained much less. The liver serves as test organ for determining changes in the vitamin-*A* content of the organism. A. A. E.

Determination of the vitamin-*A* content of human blood-serum. J. G. MENKEN (Deut. med. Woch., 1932, **58**, 1484; Chem. Zentr., 1932, ii, 2328).—Serum from 20 c.c. of blood was treated with 10 vols. of EtOH and centrifuged, the EtOH fraction then being shaken with light petroleum. This extract was evaporated to 1 c.c., and the carotene determined colorimetrically. After further evaporation and treatment with $SbCl_3$ and Ac_2O the blue colour was measured, and a correction applied for the blue colour originating from the carotene. The vitamin-*A* content varies between 0 and 8·4 blue units; it is absent in childbirth and in the newborn, and low in disease. The carotene content varies between 1·1 and 65 yellow units. A. A. E.

Characteristics of highly-active vitamin-*A*. F. H. CARR and W. JEWELL (Nature, 1933, **131**, 92).—Distillation at approx. 10^{-5} mm. gives a highly-active vitamin-*A*. The fraction (b.p. 136—137°), 83·5% C, 10·6% H, corresponds with the formula $C_{20}H_{30}O$; $SbCl_3$ blue val. 78,000. 0·0006 mg. administered daily to rats cured xerophthalmia and gave a slightly better growth than 1 unit a day. L. S. T.

Comparative studies on the adsorption behaviour of crude vitamin-*A*, carotene, and cholesterol. H. N. HOLMES, V. G. LAVA, E. DELFS, and H. G. CASSIDY (J. Biol. Chem., 1933, **99**, 417—427).—Adsorption curves are given. A high % of vitamin-*A* can be eluted from porous solids on which it has been adsorbed. The use of a special type of Al_2O_3, with petrol as solvent for adsorption and $CHCl_3$ for elution, is most effective. H. G. R.

A new carotene. R. KUHN and H. BROCKMANN. —See this vol., 278.

Heat-stability of the vitamin-*B* factors required by the chick. C. A. ELVEHJEM, O. L. KLINE, J. A. KEENAN, and E. B. HART (J. Biol. Chem., 1932, **99**,

309—319).—Vitamin-B_1 is destroyed when moist (but not dry) yeast is heated at 100° for 24 hr. The rate of destruction decreases with increase of [H·]. Inactivation of B_2 in a dry natural ration at 100° depends on the period of heating. No destruction occurs at 24 hr., one half of the potency is lost at 72 hr., and there is total destruction after 144 hr. Chickens do not require heat-labile B_3 or any other B-factor destroyed by heating at 100° for 24 hr. F. O. H.

Relation of vitamin-B complex to renal enlargement caused by cystine and protein in the diet of the rat. B. B. Longwell, R. M. Hill, and R. C. Lewis (J. Nutrition, 1932, **5**, 539—550).—Addition of vitamin-B to the diet prevents abnormal kidney development induced by excessive feeding of caseinogen or cystine. A. G. P.

Influence of vitamin-B and iodine on calcium and phosphorus metabolism of rabbits with hyperplastic thyroids. M. Sandberg and O. M. Holly (J. Biol. Chem., 1933, **99**, 547—553).—Rabbits given a vitamin-B-deficient diet develop thyroid hyperplasia. Subsequent injection of KI increases the Ca excretion, so that 3 weeks after the injection the Ca : P retention ratio rises to 1 : 216; thereafter it fluctuates considerably. Feeding of vitamin-B produces the same effect except that the fluctuations in the Ca : P ratio are more rapid. H. D.

Sparing action of fat on vitamin-B. IV. Is it necessary for fat to interact with vitamin-B in the alimentary canal to exert its sparing effect? V. Role of glycerides of oleic acid. H. M. Evans and S. Lepkovsky (J. Biol. Chem., 1932, **99**, 235—236, 237—240; cf. A., 1929, 1203).—IV. Addition of fat to the diet causes practically the same improvement of growth in rats whether receiving vitamin-B (I) (from rice-polishings) parenterally or orally. Hence no reaction between fat and (I) occurs in the alimentary tract.

V. The glycerides of purified oleic acid (II) exert a sparing action on (I) equal to that of natural fats and, when the intake of (I) is inadequate, superior to that of commercial (II). With diets both adequate and inadequate in (I) a mixture of the glycerides of commercial (II) and stearic acid promotes more rapid growth than the glyceride of either acid alone. F. O. H.

Possibility of obtaining persistent beriberi phenomena by deprivation of vitamin-B. G. Amantea and V. Famiani (Atti R. Accad. Lincei, 1932, [vi], **16**, 353—357).—Results obtained with hens are similar to those previously found with pigeons (A., 1932, 200). T. H. P.

B-Vitamins. I. Statistical comparison of small and large litters of rats on a normal stock diet. II. Statistical comparison of rat litters on normal stock diets with litters on synthetic diets containing varying amounts of the vitamin-B complex and combinations of -B_1 and -B_2. C. U. Moore, H. B. Plymate, B. J. Andrew, and V. White. **III. Evidence of a third vitamin-B factor in yeast (B_4) as shown by growth curves and clinical symptoms of first and second litter young of mothers raised on synthetic B_1 and B_2 diets.** C. U. Moore, H. B. Plymate, and B. J. Andrew. **IV. Report of litters obtained on a diet in which fæces were supplied as a sole source of vitamin-B.** C. U. Moore, H. B. Plymate, and V. White. **V. Myelin degeneration in the peripheral nerves of rats associated with low vitamin-B content of diet.** C. U. Moore, H. B. Plymate, and B. J. Andrew. **VI. Pyloric obstruction in rats.** C. U. Moore and H. B. Plymate (Amer. J. Physiol., 1932, **102**, 566—572, 573—580, 581—592, 593—597, 598—604, 605—613).—III. The young of mothers on a synthetic diet containing vitamins-B_1 and -B_2 showed clinical symptoms and a cessation of growth, attributed to lack of vitamin-B_4. It was present in mother's milk in amounts adequate to produce normal wt. gains in the young up to weaning (28 days), even when the maternal diet was relatively deficient.

IV. 11 litters (46 young) were obtained over a period of several months from parents raised on a diet in which fæces were the sole source of B-vitamins. The litters had fewer young and a very low birth wt. compared with stock animals. Mortality was 100% in the lactation period (77% in the first week).

V. Myelin degeneration in the peripheral nerves is not a valid criterion of any deficiency of the B-vitamins.

VI. In a period of 14 months, from 41 females raised on a diet in which 1·0 g. daily of autoclaved yeast was the sole source of B-vitamins, only one viable litter was obtained. Three out of four males but none of the females showed gastric dilatation, due, it is suggested, to pylorospasm, probably caused by lack of vitamin-B_1, a concentrate of which effected a complete cure. Nutr. Abs.

Adsorption experiments with vitamins-B (B_1) and -G (B_2). H. C. Sherman and N. Halliday (J. Amer. Chem. Soc., 1933, **55**, 332—335).—Protein-free milk is prepared by addition of dil. HCl to skimmed-milk powder in H_2O (to ppt. caseinogen) and subsequent coagulation of dissolved protein by heat, without appreciable loss of vitamins-B_1 (I) and -B_2 (II). (I) and (II) are adsorbed (from the protein-free milk adjusted to p_H 3 or 4) to the same extent by Lloyd's reagent irrespective of the amount (5—40 g. per litre) used; the resultant activated solids contain about 50% and 33% of (I) and (II), respectively, whilst the filtrate contains no (I) and about 16% of (II). When adsorption is carried out in N_2, the activated solids contain 60—70% of (I). H. B.

Vitamin-B_1 and -B_2 contents of dry skimmed milk and dry whey. R. C. Bender and G. C. Supplee (J. Dairy Sci., 1932, **15**, 445—450).—Roller-dried and spray-dried skim milks had approx. the same vitamin-B_2 contents, but vitamin-B_1 contents were affected by the detail of the drying process adopted. In all dried-milk products the vitamin-B_1 content was relatively lower than that of vitamin-B_2. A. G. P.

Use of the chick in vitamin-B_1 and -B_2 studies. O. L. Kline, J. A. Keenan, C. A. Elvehjem, and E. B. Hart (J. Biol. Chem., 1932, **99**, 295—307).—

The prep. of a diet which can be rendered deficient in vitamin-B_1 by autoclaving at 120°/15 lb. for 5 hr. and in -B_2 by heating dry at 95—100° for 144 hr. is described and its use for the chick recommended. F. O. H.

Irradiation of nucleic acids and uracil. F. F. Heyroth and J. R. Loofbourow (Nature, 1933, **131**, 92; cf. A., 1932, 1294).—Ultra-violet irradiation of yeast-nucleic acids or uracil does not produce vitamin-B_1 or -B_2. L. S. T.

Vitamin-B_2 and protein intake. H. C. Sherman and I. A. Derbigny (J. Biol. Chem., 1933, **99**, 165—171).—Rats fed on a diet containing 12 or 18% protein are more resistant to vitamin-B_2 deficiency than those fed on a 6% protein diet. H. D.

Vitamin-B_2 in root and leaf vegetables. P. L. Day (Southern Med. J., 1931, **24**, 876).—Fresh beet, carrot, potato, and turnip contain a small amount of vitamin-B_2; beet, carrot, and turnip tops are good sources. Winter spinach contains < the other leaves. Ch. Abs.

Vitamin-B_4. H. Barnes, J. R. P. O'Brien, and V. Reader (Biochem. J., 1932, **26**, 2035—2040).—The cryst. *hydrochloride* of a base, $C_4H_4N_4$,HCl,0·5H_2O, with apparently const. vitamin-B_4 content was isolated from yeast by fractional pptn. with Na phosphotungstate and removal of a pentose group from the mol. by acid hydrolysis. S. S. Z.

Vitamin-*C*. F. Micheel (Naturwiss., 1933, **21**, 63).—Vitamin-*C*, $C_6H_8O_6$ (I), and CH_2N_2 yield *dimethylvitamin*-C (II), stable to acid I solution, in which one OMe-group is of ester nature. The action of I on (I) is the oxidation of >CH·OH to >CO. The *di*-p-*nitrobenzoate* of (II), m.p. 172° [K. Kraft], is stable to neutral $KMnO_4$ in $COMe_2$ and Br in AcOH, and, therefore, is not an enol derivative. NH_3 and (II) in MeOH yield a *substance*, $C_6H_7O_4(OMe)_2NH_2$, m.p. 123°. The $COMe_2$-compound of (I) yields with CH_2N_2 a *Me$_2$ ether*, m.p. 99°. The sixth O atom in (I) is present as >CO or in a ring. (I) is unaffected by 1% MeOH–HCl at 100° for 5 hr.; with a concn. of 4% at 100° for 18 hr. it yields the ester; no glucoside is formed, therefore no OH group is in the 4- or 5-position to >CO. Catalytic reduction of (I) at room temp. yields a lactonic substance. The CO group may, therefore, be in the 4-position to the CO_2H group. A furan or *cyclo*pentane structure for (I) is suggested.

Similar results have been obtained by Karrer (Vierteljahrsschrift Naturforsch. Ges. Zürich, 1933, **78**, 9). R. K. C.

Vitamin-*C* and the suprarenal cortex. I. Antiscorbutic activity of ox suprarenal. L. J. Harris and S. N. Ray (Biochem. J., 1932, **26**, 2067—2075).—Raw suprarenal cortex (ox) is three times as active as fresh orange-juice. The vitamin-*C* activity of the suprarenal gland of the guinea-pig is lost with the onset of scurvy. S. S. Z.

Antiscorbutic activity of the cortex of the suprarenal gland of the ox. S. S. Zilva (Biochem. J., 1932, **26**, 2182).—A sample of the cortex was more active than a sample of decitrated lemon-juice tested at the same time and under the same conditions. S. S. Z.

Vitamin-*C* activity of hexuronic acid from suprarenal glands. W. A. Waugh and C. G. King (Science, 1932, **76**, 630).—A biological assay of hexuronic acid from suprarenal glands showed it to be identical with the authors' product prepared from a different type of starting material. The new product was also identical in other properties such as m.p. and [α]. The method of prep. would have removed the *o*-diphenol derivatives of narcotine considered by Rygh (A., 1932, 1294) to be identical with vitamin-*C*. L. S. T.

Antiscorbutic potency of apples. V. M. B. Crane and S. S. Zilva (Biochem. J., 1932, **26**, 2177—2181).—The antiscorbutic potency of a no. of triploid and diploid varieties of apples has been compared. The varieties in each group showed a variation in activity, but the triploid group contained the most active apples. S. S. Z.

Vitamin-*C*. IV—VI. Germination of seeds and vitamin-*C*. III—V. T. Matsuoka (Mem. Coll. Agric. Kyoto, 1932, No. 24, 1—22, 23—36, 37—47).—III. Rice seeds were germinated for 1—10 days at 28—30° under a 1000-watt Mazda lamp. The production of chlorophyll, which began to appear about the third day, corresponded with a considerable increase in the vitamin-*C* (I) content. 10-day-old sprouts fed at the rate of 1 g. per 100 g. of body-wt. prevented the onset of scurvy. There was no quant. relation between the Bezssonoff colour reaction and the results of feeding experiments.

IV. (I) is produced even when germination proceeds in the dark. At 3 days the content is equal to that of seedlings grown under a 1000-watt lamp, but at 10 days it is only about one half. The active material was extracted from dried sprouts with EtOH, and 1 c.c. of the residue (after evaporation at 32°/vac. in CO_2) was equiv. to 2 g. of original sprouts.

V. The production of (I) in sunlight is almost identical with that under a 1000-watt lamp. P. G. M.

Vitamin-*C*. Reaction of plant and animal extracts with 2 : 6-dichlorophenol-indophenol. H. von Euler and E. Klussmann (Svensk Kem. Tidskr., 1932, **44**, 290—294).—1 mg. of hexuronic acid (I), [α] approx. +26°, in 10 c.c. of H_2O reduces 15·36 c.c. of buffered 0·029% aq. 2 : 6-dichlorophenol-indophenol, whilst the titre for 1 c.c. of fresh lemon-juice is 5·5, for 10 mg. of glutathione (II) in 10 c.c. of H_2O 18·3, and for 1 mg. of (II) in 1 c.c. of H_2O nil. Vals. for aq. extracts of animal organs and plants are given and these are correlated with the respective contents of vitamin-*C*. $CuSO_4$ accelerates the oxidation of (I) by H_2O_2. F. O. H.

Nature and value of Bezssonoff's reaction for vitamin-*C*. A. Salvadori (Atti R. Accad. Lincei, 1932, [vi], **16**, 369—371).—This reagent (A., 1921, ii, 608) detects, in all antiscorbutic materials, a reducing factor, which may or may not be identical with vitamin-*C*. T. H. P.

Surface potentials of unimolecular films of ergosterol. Photochemical formation of vita-

min-*D*. R. J. FOSBINDER (Proc. Roy. Soc., 1933, **A**, **139**, 93—104).—With a view to decide whether the active product of irradiation of ergosterol is a ketone or an alcohol, a study has been made of the surface potentials and force–area curves of unimol. films of ergosterol and its irradiation products on the surface of a citric acid–NaOH buffer. The method of determining ΔV was a modification of that devised by Schulman and Rideal (A., 1931, 299). From the semi-reversible nature of the change in ΔV and μ, and the permanent increase in the mol. area of the ergosterol mol. on exposure to ultra-violet radiation, it is assumed that the photochemical formation of vitamin-*D* involves at least two reactions, one of which is reversible. The primary reversible change may be either enolic or ketonic, the evidence being in favour of the former. The irreversible reaction which follows probably involves a steric rearrangement at the CH·OH group. L. L. B.

Photographic recording of line-tests for vitamin-*D*. A. L. BACHARACH, E. ALLCHORNE, V. HAZLEY, and S. G. STEVENSON (Ind. Eng. Chem. [Anal.], 1933, **5**, 12—14).—Technique is described and certain modifications of the method of Stevens and Nelson (cf. A., 1932, 658) are recommended. T. McL.

Administration of irradiated ergosterol to dogs with biliary fistulæ. N. B. TAYLOR, C. B. WELD, and J. F. SYKES (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 29—31).—Intravenous but not oral administration of irradiated ergosterol (I) to dogs with biliary fistulæ is followed by hypercalcæmia, whilst the bile (II) shows antirachitic activity. Hence (II) is necessary for the absorption of (I). The re-entrance of (I) into the duodenum accounts for the prolonged effect of a single dose. F. O. H.

Antirachitic potency of eggs from hens receiving massive doses of activated ergosterol. F. G. MCDONALD and O. N. MASSENGALE (J. Biol. Chem., 1932, **99**, 79—83).—Increasing the amount of irradiated ergosterol administered to pullets 10,000 times resulted in an increase of only 183 times in the vitamin-*D* potency of the egg-yolk oil. H. G. R.

Fate of antirachitic factor in the chicken. II. Effectiveness of the factor administered by mouth and intraperitoneally. W. C. RUSSELL, M. W. TAYLOR, and D. E. WILCOX (J. Biol. Chem., 1933, **99**, 109—118).—Analysis of the bone-ash of chicks fed and intraperitoneally injected with cod-liver oil (I) shows that the degree of assimilation is the same in the two cases. There is a significant difference in the % bone-ash of chicks given (I) and that of birds given irradiated ergosterol. The chicks given the latter were less immune to leg weakness than those treated with (I). Serum-inorg. P vals. were higher in the injected groups. H. D.

Mechanism of calcification in the heart and aorta in hypervitaminosis-*D*. A. W. HAM (Arch. Pathol., 1932, **14**, 613—626).—Intense calcification of the aorta and heart-muscle occurred in rats 48 hr. after giving them large single doses of irradiated ergosterol, but no obvious degenerative changes could be found after 24 hr. The calcification which appeared so rapidly during the second 24 hr. was thus not likely to be secondary to previous degeneration in the tissues, but depended on a sudden saturation of the serum with diffusible $Ca^{\cdot\cdot}$. The mechanism of the toxic action of vitamin-*D* is probably essentially the same as that of its therapeutic action. NUTR. ABS.

Effect of small (therapeutic) doses of irradiated ergosterol on the serum-calcium. N. B. TAYLOR and C. B. WELD (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 13—16).—Subcutaneous administration of irradiated ergosterol to young dogs is followed by a marked fall in the serum-Ca (I), which returns to normal or higher levels in 3—6 days. With parathyroidectomised dogs a single large dose produces a fall in (I) and a rise in serum-P followed by a rise in (I). With humans a latent tetany may become manifest on such administration. F. O. H.

Effect of irradiated ergosterol on the absorption of calcium. N. B. TAYLOR and C. B. WELD (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 9—12).—Administration of small or moderate does of irradiated ergosterol to young dogs on a diet of biscuit and meat was followed generally by a marked increase in Ca excretion. No evidence of increased Ca absorption was obtained. F. O. H.

Effect of irradiated ergosterol on calcium and phosphorus retention in children. C. B. WELD and J. F. SYKES (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 81—88).—Small amounts of vitamin-*D* do not affect Ca or P retention in normal children fed on a diet moderately low in Ca but otherwise adequate. F. O. H.

Ergosterol, irradiated ergosterol, and alcoholic fermentation. F. PIRRONE (Annali Chim. Appl., 1932, **22**, 731—737).—Preliminary experiments indicate the possibility of correlating the antirachitic effect of irradiated ergosterol with its influence on the amount of CO_2 formed during fermentation of glucose. T. H. P.

Ecological and physiological studies of certain aquatic angiosperms. W. S. BOURN (Contr. Boyce Thompson Inst., 1932, **4**, 425—496).—Failure of these plants is attributed to unfavourable light conditions resulting from excessive turbidity of the H_2O and also to the presence of certain injurious organisms. The presence of NaCl and the variation of O_2 and CO_2 contents of the H_2O were not crit. factors. A. G. P.

Chemical course of photosynthesis. A. STOLL (Naturwiss., 1932, **20**, 955—958).—A discussion. Chlorophyll *a* or *b* contains a "supernumerary" double linking outside the conjugated system. Catalytic hydrogenation yields a dihydro-derivative in which the absorption spectrum is not significantly changed and which is readily dehydrogenated. The course of photosynthesis in the leaf is: (i) union of CO_2 with chlorophyll (I), (ii) transformation of CO_2 into a H-acceptor (first photochemical reaction), (iii) dehydrogenation of (I) with stepwise reduction of CO_2, (iv) rupture of the H_2O attached to (I) thus: $H_2O \longrightarrow H + OH (\longrightarrow H_2O_2)$, with rehydrogenation of the (I) (second photochemical reaction), (v) destruction of H_2O_2 by leaf catalase. R. K. C.

Oxygen metabolism of non-succulent plants. P. SCHWARZE (Planta [Z. wiss. Biol.], 1932, **18**, 168—210).—The org. acid content (per unit dry wt.) of non-succulent plants is > that of succulents, but the molar concn. of acid has a similar average val. for both classes. Varying proportions of $H_2C_2O_4$ and malic acid occur in leaves of nearly all non-succulent plants, active forms of the latter being rare. Plants having fruits rich in citric acid usually contain only traces of the acid in their leaves. Variations in the acid contents of a no. of plants resulting from diurnal changes, age, aeration, and temp. are recorded. A. G. P.

Absorption of oxygen by roots when the shoot is in darkness or in light. W. A. CANNON (Plant Physiol., 1932, **7**, 673—684).—Exposure of shoots to daylight tended to decrease, and rapid evaporation from leaves to increase, the O_2 consumption of roots. A. G. P.

Carbon dioxide assimilation in a higher plant. W. H. HOOVER, E. S. JOHNSTON, and F. S. BRACKETT (Smithsonian Misc. Coll., 1933, **87**, No. 16, 19 pp.).—In wheat plants linear relationships over limited ranges were observed between assimilation and the concn. of CO_2 with an excess of light, and between assimilation and light intensity with an excess of CO_2. The intermediate range between regions in which each of the two limiting factors was dominant was wider for higher plants than for algæ. A. G. P.

Apparatus for determining the absorption of carbon dioxide by leaves under natural conditions. A. J. HEINICKE and M. B. HOFFMAN (Science, 1933, **77**, 55—58). L. S. T.

Growth hormone of plants. II. Entry of growth substance into the plant. K. V. THIMANN and J. BONNER (Proc. Nat. Acad. Sci., 1932, **18**, 692—701).—The determination of growth substance (I) in a prep. from *Rhizopus suinus* by the degree of curvature induced in *Avena* coleoptiles (II) was investigated. Application in agar blocks is followed by the passage into (II) of a const. fraction of (I), the val. of which depends on the concn. of (I) in the block. F. O. H.

Relation of western yellow pine seedlings to the reaction of the culture solution. J. HOWELL, jun. (Plant Physiol., 1932, **7**, 657—671).—Seedlings preferred an acid culture medium (p_H 4—5). Ca was absorbed only in small amounts even under alkaline conditions, but its presence in the nutrient was not deleterious. The buffer system of seedlings is dependent on the org. as well as the inorg. constituents of the sap. Other factors affecting growth in soils are discussed. A. G. P.

Nitrogen metabolism of vegetative storage organs in plants. H. RAHN (Planta [Z. wiss. Biol.], 1932, **18**, 1—51).—The crude fibre content of tissues remains const. under conditions involving metabolic changes in or transition of N and carbohydrate constituents. It serves, therefore, as a basis of reference for calculating changes among other plant materials. Apparatus for the determination of fibre by extraction with 21% HNO_3 for 70 min. is described. For the determination of α-NH_2-N (Van Slyke) preliminary pptn. of tannin with $K_2Cr_2O_7$ is necessary. The sprouting of bulbs, rhizomes, etc. is preceded by a transition of insol. to sol. N. N is stored principally in tissues adjacent to the vegetative area and carbohydrates in the peripheral tissues. Prior to sprouting, rhizomes of "acid" plants have a high NH_2-acid content, but in "amide" plants amides and NH_2-acids occur in approx. equal proportions (cf. this vol., 197). The early stages of sprouting involve the utilisation of about half the stored N, which is finally depleted at the flowering stage. The distribution of N during the growth of *Allium cepa*, *Oxalis Deppei*, and *Asparagus officinalis* is recorded. A. G. P.

Mineral and nitrogen contents of the leaves of some forest trees at different times in the growing season. J. S. MCHARGUE and W. R. ROY (Bot. Gaz., 1932, **94**, 381—393).—In a no. of deciduous trees the largest % of K, P, and N occurred in the dry matter of young leaves, and that of total ash, SiO_2, and Ca in old leaves. Cu, Zn, and Mn were present in all cases. In certain trees the Mn content was > that of Fe and leaves of such trees did not show the colour changes typical of the late autumn season. No very definite evidence of the translocation of mineral matter from leaves to stems in the later part of the growing season was observed. A. G. P.

Nitrogen fixation in the genus *Lolium*. R. BROWN (Nature, 1933, **131**, 169—170).—Part of the N requirements of plants of this genus is obtained from the atm. Under certain conditions H_2 appears to stimulate growth. L. S. T.

Comparison of methods for determining ammonia-nitrogen and their adaptability to plant juice. F. S. SCHLENKER (Plant Physiol., 1932, **7**, 685—695).—Five methods compared showed good agreement. Permutit readily absorbs NH_3 from plant juices (Folin), but also a yellow colouring matter which is liberated with NH_3 on subsequent treatment with NaOH. Folin's method is preferably modified by substituting an aeration process for the direct Nesslerisation of the permutit residue after addition of NaOH. A. G. P.

Micro-method for [determination of] nitrogen in plant material. L. D. DONEEN (Plant Physiol., 1932, **7**, 717—720).—The sample of plant-tissue or sap evaporated to dryness should contain approx. 1 mg. N. The sample is mixed with 1—2 c.c. of H_2SO_4 containing 5% salicylic acid, and, after 20 min., heated with 0·3 g. $Na_2S_2O_3$ until fumes appear. 1 c.c. of 60% $HClO_4$ containing 0·1% $CuSO_4$ is added and the solution digested until clear and diluted to about 50 c.c. 5 c.c. of 5% gum arabic solution are added, the solution is neutralised with 10% NaOH, and NH_3 determined by Nessler's reagent. Samples of gum arabic which affect Nessler's reagent may be treated as described by Chiles (A., 1928, 312). A. G. P.

Nitrogen, sulphur, phosphorus, and potassium of leaves of *Prunus laurocerasus* at the time of falling. E. MICHEL-DURAND (Compt. rend., 1932, **195**, 1419—1420).—The N, K, and, to a smaller extent, the S and P contents of fallen leaves of the evergreen,

bay-laurel, are, as in the case of the chestnut, < those of mature leaves. The distributions of S and P alter, the sol. increasing considerably at the expense of the protein fraction. In both types of leaf proteolytic action occurs before falling. A. C.

Manganese essential for the growth of *Lemna major*. J. S. McHargue and R. K. Calfee (Plant Physiol., 1932, **7**, 697—703).—A deficiency of Mn in the nutrient caused retarded growth, failure to reproduce, chlorosis, necrosis, and death of the plant after the utilisation of its residual Mn. Normal growth followed the addition of $MnSO_4$ but not of $Fe(NO_3)_3$. In Mn-deficient nutrients plants had a lower total ash and higher Fe contents. A. G. P.

Distribution of molybdenum. W. A. Roach (Nature, 1933, **131**, 202).—The distribution of Mo in certain parts of apple trees is described (cf. this vol., 140). L. S. T.

Mineral content of Egyptian cereals. P. Schrumph-Pierron (Bull. Inst. d'Egypt, 1932, **14**, 141—151).—The optimum ratio of the mineral constituents (expressed in mol. equivs.) in wheat is $MgO/(K_2O+CaO)=0{\cdot}85$. Egyptian soil is characterised by its natural richness in Mg; the corn commonly grown in Egypt has also more Mg than that grown in countries where chemical manures are used. Tables are given of the salt content of various grains and of vegetables. Nutr. Abs.

Iodine volatilisation by *Laminaria* species. S. Suneson (Z. physiol. Chem., 1932, **213**, 270—272).—The I reaction given by *Laminaria* species gathered on the Swedish west coast fails with specimens collected on the west coast of France, probably owing to the much greater difference between ebb and flood tides which prevails in the latter situation. J. H. B.

Determination of inorganic phosphoric acid and phytinphosphoric acid in phytin preparations. K. Lindenfeld (Biochem. Z., 1933, **257**, 8—13).—Inorg. PO_4''' is determined by pptn. as NH_4 phosphomolybdate and org. P is best expressed as the difference between total and inorg. P. The method of Heubner and Stadler (A., 1914, ii, 690) gives less accurate but satisfactory results if the factor 1·2 is used. W. McC.

Variations in the organic reserves in underground parts of five perennial weeds from late April to November. A. C. Arny (Minnesota Agric. Exp. Sta. Tech. Bull., 1932, No. 84, 28 pp.).—Carbohydrate reserves in roots decline rapidly in spring as growth proceeds, to reach a min. at the flowering period. Subsequently there is a period of rapid increase, during which the proportion of readily-available carbohydrate to the total reserve was small. Carbohydrate accumulation continued until late in the season, but at a reduced rate. A corresponding decline in N reserves takes place as growth advances. The recovery period commences later in the season than in the case of carbohydrates. These changes are discussed in relation to weed eradication by cutting. A. G. P.

Carbohydrate content of tomato fruit. L. G. Saywell and D. P. Robertson (Plant Physiol., 1932, **7**, 705—710).—Tissues of the core contained relatively high proportions of reducing sugars, total solids, and acid-hydrolysable matter. The locular material had lower amounts of these constituents than any other part of the fruit. The fruit resembled the core in composition except in having lower reducing sugar contents. In different varieties the ratio glucose : fructose was quite uniform, fructose averaging 46% of the total reducing sugar. A. G. P.

Carbohydrates of *Raphanus sativus* var. *macropodus*. T. Takahashi (J. Agric. Chem. Soc. Japan, 1932, **8**, 393—399).—Glucose and pectic acid were found in radish juice; the radish contained 57% of cellulose. Starch was detected only microscopically. Ch. Abs.

Sugar content of *Cucurbitaceæ*. R. S. Alexandrova (Bull. Appl. Bot., Russia, 1929, **21**, No. 4, 437—519).—For a given variety of melon the glucose (I), fructose (II), and sucrose (III) vals. may vary by 2% with the degree of maturity. The p_H, (I) : (II) ratio, and (III) content serve as criteria of maturity. The max. sugar content is reached early; later, (I) is converted into (II) and still later (III) increases at the expense of the monosaccharides. The amount of (III) (max. 5·47%) appears to vary directly with the available moisture in irrigated fields. Ch. Abs.

Carbohydrates of some species of the genus *Vinca*, and variation in their proportions during growth. The vincosides. J. Vintilesco and N. I. Ioanid (Bul. Soc. Chim. Romania, 1932, **14**, 12—24).—The content of reducing sugars, polysaccharides hydrolysable by invertase, and glucosides hydrolysable by emulsin in *V. herbacea*, *V. minor*, and *V. major* are determined, and, in the case of the first-named, their monthly variation is studied. Three β-glucosides (*vincosides*) are isolated from *V. herbacea*; one only is cryst., m.p. 120° (block), and yields the same amount of glucose with either aq. H_2SO_4 or emulsin. KNO_3 is also isolated from this species, and the presence of a non-toxic alkaloid similar in reactions to strychnine detected. H. A. P.

Easy method of extraction of certain glucosides. H. Hérissey (J. Pharm. Chim., 1932, [viii], **16**, 513—516). R. S. C.

Composition of bamboo. VI. Water-soluble constituents. S. Oguri and T. Ogura (Bull. Waseda Appl. Chem. Soc., 1932, **17**, 19—27; cf. B., 1931, 1087).—Hot and cold H_2O extraction of *Phyllostachys bambusoides*, Sieb. et Zucc., gave 14·26 and 8·43% of extract, respectively. The extract contained ash 38·82, pentosan 10·06, glucose 12·28, and non-reducing sugars 17·71%. Ch. Abs.

Wood cellulose. IV. The "resistant portion" of Thiriena pulp. D. J. Bell (Biochem. J., 1932, **26**, 1772—1776).—The three dimethylglucoses (2 : 3-, 3 : 6-, 2 : 6-) derived from the fully methylated resistant portion and from the correspondingly methylated non-resistant residue are formed in different relative proportions. Etherification, therefore, does not follow the same course in the two portions. H. W. D.

Jelly of the egg of *Phallus impudicus*. H. COLIN and M. QUILLET (Compt. rend., 1932, **195**, 1313—1315).—The lævorotatory acidic gum in the volva of the fungus is described. It is hydrolysed slowly by boiling H_2O, and more rapidly by 2% H_2SO_4 with production of reducing sugar and a change to dextrorotation. Neutralisation with $BaCO_3$ leads to the isolation of a uronic acid. HCl hydrolysis liberates CO_2, furfuraldehyde, and a reducing sugar, probably mannose. The presence of an ester group is indicated by treatment with HI, and alkaline hydrolysis. The gum is liquefied in a few hr. by an enzyme contained in the leaflets of the volva. A. C.

Flavoxanthin. R. KUHN and H. BROCKMANN (Z. physiol. Chem., 1932, **213**, 192—198).—The xanthophylls of the blossoms of *Ranunculus acer* consist of lutein, xanthophyll-β, and small amounts of taraxanthin and *flavoxanthin* (I), $C_{40}H_{56}O_3$, m.p. 184° (corr.), $[\alpha]_1^{20}$ +190° in C_6H_6. (I) has three active OH groups (Zerevitinov) and adsorption bands at 448 and 421 mμ in EtOH. (I) also occurs in *Senecio vernalis*. J. H. B.

Taraxanthin. R. KUHN and E. LEDERER (Z. physiol. Chem., 1932, **213**, 188—191).—Taraxanthin (as ester) was obtained from the blossoms of *Impatiens noli me tangere*. The xanthophylls of *Leontodon autumnalis* consist of 60% of lutein and 40% of taraxanthin. J. H. B.

Microchemical characteristics of oxyflavone compounds; their localisation in vacuoles. A. GUILLIERMOND and R. GAUTHERET (Compt. rend., 1933, **196**, 369—371).—Comparison of a large no. of microchemical reactions applied both to the extracted oxyflavone derivative and to the vacuoles indicates that the combination of these tests, but not any single one, is trustworthy for the detection of such derivatives in the vacuole, providing tannins are absent. In the presence of the latter only $Pb(OAc)_2$ and, especially, Klein's reaction (gaseous HCl) can be employed. J. W. B.

Occurrence of dehydrodeguelin and dehydrotoxicarol in derris root. E. P. CLARK and G. L. KEENAN (J. Amer. Chem. Soc., 1933, **55**, 422—423).—Mixtures, m.p. 200—225°, of dehydrodeguelin and dehydrotoxicarol, which are sometimes inseparable by fractional crystallisation, have been isolated from samples of derris root containing no rotenone. H. B.

***Gymnocalycium multiflorum* [Hook], Britton, and Rose.** E. H. DUCLOUX (Rev. farm., 1932, 74, 251—261).—The alkaloid content is low. The principal acid constituent is malic acid. The active principle resembles the β-alkaloid of *G. gibbosum* (Haw), Pleiff. CH. ABS.

Exudation of alkaloids of *Lupinus albus*. J. CHAZE (Compt. rend., 1932, **195**, 1315—1317).—An alkaloidal exudate has been detected histochemically on the epidermis of leaves and stems of white lupin. The alkaloid exudes maximally in warm sunlight. A. C.

Indian medicinal plants. I. *Capparis horrida*. S. CHAKRAVARTI and A. VENKATASUBBAN. **II. Leaves of *Pithecolobium bigeminum*.** S. CHAKRAVARTI and K. GANAPATI (J. Annamalai Univ., 1932, **1**, 176—180, 181—185).—I. The isolation of an alkaloid from the root bark of *C. horrida* is described.

II. The leaves contain no alkaloid, but two acids were detected. J. L. D.

A prolamin isolated from a legume seed. A. HASSAN and M. K. A. BASHA (Biochem. J., 1932, **26**, 1843—1845).—A protein ("*helbin*") sol. in hot 70% EtOH has been isolated from the seeds of the legume of fenugreek. It differs from the known gliadins in being insol. in cold, but sol. in hot 70% EtOH. Like the gliadins, this protein is sol. in PhOH and is pptd. from this solution by EtOH, Et_2O, Me_2O, or amyl alcohol. S. S. Z.

Fatty substances of *Cascara sagrada*. A. JERMSTAD (J. Pharm. Chim., 1933, [viii], **17**, 76—83).—The $CHCl_3$-sol. fat of the bark contains rhamnol, m.p. 132—133°, to which the formula $C_{20}H_{36}O$ is given (cf. Jowett, A., 1905, ii, 192), phytosterol, melissic, arachidic, palmitic, oleic, linoleic, and linolenic acids. Contrary to the literature, myristic acid and dodecyl alcohol were not found. A. C.

Content of essential oil during maturation and germination. N. N. IVANOV, V. F. GRIGORIEVA, and A. I. ERMAKOV (Bull. Appl. Bot., Leningrad, 1929, **21**, No. 4, 321—341).—For a particular plant variety and geographical region the quantities and properties of the oils obtained from anise and coriander do not vary at different stages of maturity. Absence of light is also without effect. CH. ABS.

Determination of essential oils in plants. A. S. GINSBERG (Khim. Farm. Prom., 1932, **8**—**9**, 326—329).—Condensed oil falls into a graduated U-tube suspended in the distillation flask. CH. ABS.

Resinous coat of *Sarcocaulon rigidum*, Schinz. P. KARRER and K. SCHWARZ (Vierteljahr. naturforsch. Ges. Zurich, 1932, **77**, 78—82; Chem. Zentr., 1932, ii, 1639).—The wax slightly sol. in EtOH contained principally ceryl ferulate and some ceryl alcohol; the alcoholic mother-liquor contained traces of ferulic acid, amorphous tannin-like substances, a phytosterol, $C_{24}H_{42}O_2$ or $C_{24}H_{44}O_2$, m.p. 253—255°, and a neutral substance, m.p. 98—100°. A. A. E.

Tobacco. VII. The resin of tobacco smoke. A. W. KOPERINA (Biochem. Z., 1932, **256**, 134—144; cf. A., 1931, 1296).—Tobacco contains 5—11% of volatile resin, the larger amounts being found in the better qualities. In poorer qualities the N content of the resin is > in the better qualities. The resin gives the reactions of the phenolic OH and CHO groups and contains (besides nicotine) alkaloid (or alkaloids) volatile in steam. High I vals. of the resin accompany good quality in the tobaccos. W. McC.

Biology of the potato. Potato tuber catalase. M. KLINKOWSKI (Arb. biol. Reichsanst. Land-Forstwirt., 1932, **20**, 91—99; Chem. Zentr., 1932, ii, 2832—2833).—The cortex is more active than the parenchyma. The activity does not depend on the habitat. The activity diminishes on storage. An apparatus for the determination is described.

In an appendix O. LOEW remarks that in injured cells the H_2O_2 is not rapidly decomposed, and the

protoplasm is subjected to oxidation. Complete disappearance of catalase would indicate the death of the cell. A. A. E.

Fluorescence of *Lolium* seedlings in ultra-violet light. P. A. LINEHAN and S. P. MERCER (Nature, 1933, **131**, 202—203). L. S. T.

Organisation of plant-cell membranes. M. LUDTKE (Cellulosechem., 1932, **13**, 169—175, 191—195; 1933, **13**, 1—9). H. B.

Penetration of electrolytes of organic anions and univalent cations into the cells of *Beggiotoa mirabilis*. W. RUHLAND, H. ULLRICH, and G. YAMAHA (Planta [Z. wiss. Biol.]), 1932, **18**, 338—404).—Permeability coeffs. show the more rapid penetration of uni- than of bi-valent, of aromatic than of aliphatic, anions. Among univalent cations penetration decreases with increasing ionic vol. Permeability is largely controlled by the membrane potential. The theory of the penetration of ionic "pairs" is examined and discussed. A. G. P.

Rate of penetration of rubidium into living cells of *Valonia* and its relation to apparent ionic radii. S. C. BROOKS (J. Cell. Comp. Physiol., 1932, **2**, 223—231).—Penetration of $Na^{\cdot}$, $K^{\cdot}$, and $Rb^{\cdot}$ is in the order determined by their apparent ionic radii as in the case for dried collodion membranes. A. G. P.

Penetration of *m*-bromophenol-indophenol and of guaiacol-indophenol into *Valonia ventricosa*. M. M. BROOKS (Proc. Nat. Acad. Sci., 1932, **18**, 691; cf. A., 1926, 647).—Both dyes penetrate into the sap, where they are reduced. The rate of penetration at const. temp. depends on the p_H of the external solution, but is greater for the first dye than for the second. When equilibrium is attained, the concn. of dye in the sap is $<$ that in the external solution. F. O. H.

Permeability of living cells. XIV. Penetration of certain oxidation–reduction indicators into different species of *Valonia*. M. M. BROOKS (Protoplasma, 1932, **17**, 89—96).—Rates of penetration of *o*-chlorophenol- and *o*-cresol-indophenol are recorded. α-Naphthol-2-sulphonate-indophenol does not penetrate. A. G. P.

Relation between green and yellow pigments in chlorotic leaves. J. OSERKOWSKY (Plant Physiol., 1932, **7**, 711—716).—Chlorotic leaves are deficient in yellow pigment as well as in chlorophyll. A. G. P.

Pathological fat-formation in sugar-beet leaves. E. W. SCHMIDT (Ber. deut. bot. Ges., 1932, **50**, 472—474).—Beet leaves infected with *Uromyces betæ* develop oil droplets in cells adjacent to the point of infection. Technique for their detection is described. A. G. P.

Production of toxins by various plant parasites. E. SCHAFFNIT and M. LUDTKE (Ber. deut. bot. Ges., 1932, **50**, 444—463).—Plant toxins occur in the culture media of various fungi and are volatile substances, capable of decomp. by enzymes. Toxins are not sp. in their action, but produce wilting of growing plants and retardation or inhibition of germination in seeds. Certain amines have a similar action. A. G. P.

Effect of parasiticides on assimilation by plant leaves. G. GASSNER and G. GOETZE (Ber. deut. bot. Ges., 1932, **50**, 517—528).—The assimilation rates of leaves were not appreciably affected by dusting with S, but were reduced by treatment with $CaCN_2$ dust and by Cu preps. (notably by $CuCl_2$). Treatment of seed wheat with uspulun or germisan did not alter the assimilation rates of the plants. Addition to soil of sub-toxic amounts of $HgCl_2$ caused a small decrease in assimilation. Tho effect was more marked in sand cultures. A. G. P.

New medium for conserving dermatophytes (pleomorphism, acquired character, tissue specificity). L. GRIGORAKI (Compt. rend., 1933, **196**, 60—62).—On a medium containing gelatin, peptone, and calf spleen, certain parasitic fungi grow well and do not show the pleomorphic changes which take place on media commonly used. W. O. K.

Photo-electric cells and their applications in biological chemistry. A. LESURE, A. THOMAS, and J. LAVAGNE (J. Pharm. Chim., 1933, [viii], **17**, 5—21, 49—61).

Micro-determination of iodine in organic material. G. PFEIFFER (Biochem. Z., 1932, **256**, 214—227; cf. A., 1932, 102).—Further details and improvements of apparatus and method previously described are given. Schwaibold's procedure (A., 1932, 102) is unsatisfactory. W. McC.

Distillation apparatus for the Kjeldahl method. M. SIOIRI and A. OKUDA (J. Imp. Agric. Exp. Sta. Nishigahara, 1932, **2**, 33—38; Proc. Internat. Soc. Soil Sci., 1932, **7**, 274).—The Pregl micro-apparatus is adapted for use with plant materials. A. G. P.

Colorimetric determination of phosphorus in the presence of interfering substances. D. R. DAVIES and W. C. DAVIES (Biochem. J., 1932, **26**, 2046—2055).—Pyrophosphoric (I), glycerophosphoric (II), citric, oxalic, pyruvic, tartaric, lactic, and glycollic acids form complexes with NH_4 molybdate and thus interfere with the determination. The max. amounts of these compounds which may be present without vitiating the determination have been established. (I) and (II) also undergo hydrolysis with the production of H_3PO_4. S. S. Z.

Determination of sodium in biological material. E. KAHANE and M. R. DUMONT (Bull. Soc. Chim. biol., 1932, **14**, 1257—1272).—The material is treated with HNO_3 and $HClO_4$, PO_4''' is eliminated by double pptn. with $CaCO_3$, $KClO_4$ removed from the conc. filtrate after addition of EtOH, and Na determined as Mg U Na acetate. A. L.

Analysis of individual carbohydrates. V. J. HARDING, T. F. NICHOLSON, G. A. GRANT, G. HERN, and C. E. DOWNS.—See this vol., 260.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1933.

General, Physical, and Inorganic Chemistry.

Continuous spectra of the hydrogen molecule. L. GOLDSTEIN (J. Phys. Radium, 1933, [vii], 4, 44—53).—Mathematical. The intensity distribution of the continuous H_2 bands is calc. N. M. B.

Excitation functions of atomic hydrogen. L. S. ORNSTEIN and H. LINDEMAN (Z. Physik, 1933, 80, 525—533).—Excitation functions are given for the Balmer lines of H. A. B. D. C.

Dispersion and absorption of helium. J. A. WHEELER (Physical Rev., 1933, [ii], **43**, 258—263).—Mathematical. The strength of the absorption continuum below the 507 Å. series limit and of the resonance line at 584 Å., and the at. absorption coeff. for *X*-rays, are calc. and discussed. N. M. B.

Dependence of the excitation of the spectral lines of helium and mercury on pressure under a high-frequency discharge. E. MATUYAMA (Sci. Rep. Tohoku, 1932, **21**, 928—935).—The intensities of spectral lines of Hg and He under high-frequency oscillatory discharge have been measured under various pressures. The results are discussed in relation to the excitation probabilities of these lines, the velocity of electrons, and other conditions of excitation. J. W. S.

Effect of gradient of potential of alternating current on the glowing potential of inert gases and air in discharge tubes. W. SPIELHAGEN (Physikal. Z., 1933, **34**, 164—168).—For both inert gases and air the glowing potential decreases with increasing potential gradient, and reaches a const. val. A. J. M.

Glowing potential of discharge tubes (nitrogen) with varying electrode separation. I. Straight tubes. H. FRICKE (Physikal. Z., 1933, **34**, 168—172). A. J. M.

Characteristics of metallic spectra excited by active nitrogen. H. HAMADA (Sci. Rep. Tohoku, 1932, **21**, 554—563).—In the metallic spectra excited by active N (cf. A., 1929, 615) no evidence is found of the resonance enhancement of the lines due to collisions between the metallic atoms and either the metastable atoms (2·37 and 3·56 volts) or the metastable mols. (8·2 volts) in the active N. The concns. of such metastable species must therefore be small. The half-val. width of the *D* line excited by active N was found to be 0·07 Å., and hence the mean translational energy which the Na atom and the N_2 mol. receive during the triple collisions is $\geq$ 0·35 volt O. J. W.

Spectrum of the corona discharge in air, oxygen, and nitrogen. A. C. YOUNG and A. G. CREELMAN (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 39—42).—The spectra of corona discharges in air, O_2, and N_2 are of mol. origin, no at. spectra being observed (cf. A., 1930, 5; 1931, 1103). The results indicate that this discharge gives a low degree of excitation. J. W. S.

Spectrum of the discharge through oxygen and hydrogen mixtures. A. S. ROY (Phil. Mag., 1933, [vii], **15**, 421—426).—The Balmer lines H_β and H_γ are enhanced in Geissler discharges through O_2 containing H_2; this is attributed to excitation and ionisation of H atoms by O^+ or O_2^+. H. J. E.

Continuous spectrum of sodium. H. HAMADA (Phil. Mag., 1933, [vii], **15**, 574—592; cf. A., 1932, 1193).—The intensity distribution in the continuous spectrum of a discharge in Na vapour has been measured. The origin of the continuum is discussed. H. J. E.

Interaction of configurations: sd—p^2. R. F. BACHER (Physical Rev., 1933, [ii] **43**, 264—269).—Mathematical. The possibility of the presence of singlets below their triplets as observed in the two-electron spectrum of Mg I is demonstrated. N. M. B.

Arc spectrum of sulphur. R. FRERICHS (Z. Physik, 1933, 80, 150—160).—The arc spectrum of S was measured between 4000 and 11,000 Å. A. B. D. C.

Quantitative intensity determinations in the spectra of normal and of singly-ionised vanadium V I and V II. G. R. HARRISON (Physical Rev., 1931, [ii], **38**, 1921).—The relative intensities of lines of V I and V II between 5200 and 2500 Å. have been determined under different conditions of excitation in the vac. arc. L. S. T.

Interferometer measurements in the extreme ultra-violet region of copper. J. C. MCLENNAN and (MISS) F. M. QUINLAN (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 19—24; cf. this vol., 2).—The wave-lengths of the lines in the ultra-violet spectrum of Cu are suggested as standards for the region 2300—2000 Å. J. W. S.

Spectra of bromine: Br V, VII, and IV. A. S. RAO and K. R. RAO (Nature, 1933, **131**, 170).—The chief multiplets belonging to the higher spark spectra of Br have been identified. L. S. T.

Deviations from the sum rule in the spectrum of strontium. W. KAST (Z. Physik, 1933, **80**, 414).—Correction of an earlier paper (this vol., 200). A. B. D. C.

Optical constants of transparent silver. H. MURMANN (Z. Physik, 1933, **80**, 161—177).—The optical consts. of Ag were determined from reflexion and transmission measurements on layers deposited by sublimation on transparent substances. Anomalies appear similar to those known for cathodic and chemical layers. Variation of the consts. with thickness shows that beyond 15 mμ the layer is identical with massive Ag. A. B. D. C.

Relative intensity of spectral lines in indium and gallium. R. PAYNE-SCOTT (Nature, 1933, **131**, 365—366).—Results for the doublet $2p_{3/2}$—$2s_{1/2}$ and $2p_{1/2}$—$2s_{1/2}$ are given for each element. L. S. T.

Absorption bands of iodine vapour at high temperatures. E. SKORKO (Nature, 1933, **131**, 366).—Details of the absorption bands of I vapour in the region 2900—5000 Å. at 800—1050° are recorded. L. S. T.

Effect of foreign gases on the relative intensities of the mercury triplet $2^3P_{0\,1,2}$—2^3S_1 under conditions of optical excitation. R. T. MACDONALD and G. K. ROLLEFSON (Physical Rev., 1933, [ii], **43**, 177—180).—Anomalous effects on the intensity ratio of 5461 to 4358 or 4046 Å. were found when N_2 or N_2–CO_2 mixture was introduced. N. M. B.

Atomic energy levels and Zeeman effect. D. R. INGLIS and N. GINSBURG (Physical Rev., 1933, [ii], **43**, 194—196).—Results of applying the theory of complex spectra are compared with experimental data. N. M. B.

Line groups and fine structure. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss., 1932, **32**, 502—513).—The configurations of line groups with narrow coarse structure and simultaneous fine structure are discussed. A. J. M.

Broadening of spectral lines. W. LENZ (Z. Physik, 1933, **80**, 423—447).—A crit. review is given of present theories of broadening, displacement, and asymmetry of spectral lines, and a general theory is developed by statistical mechanics. It is applied to the particular cases of disturbance due to foreign gases, the gas itself, and to the presence of ions; comparison with experiment is made for A, H_2, N_2, O_2, CO_2, and H_2O. A. B. D. C.

Integrals required for the theory of pressure broadening of spectral lines. H. JENSEN (Z. Physik, 1933, **80**, 448—450). A. B. D. C.

Spectra emitted during the early stages of a condensed discharge through nitrogen at low pressure. H. HAMADA (Sci. Rep. Tohoku, 1932, **21**, 549—553).—The second positive and the negative bands begin to be emitted after $0{\cdot}4\times10^{-8}$ sec. from the beginning of the discharge, and the intensity is greatest during $1{\cdot}7\times10^{-8}$ sec. The first positive bands are emitted mainly $>7\times10^{-7}$ sec. after beginning of the discharge. O. J. W.

Electrical discharge in gases at normal pressures and temperatures. J. D. STEPHENSON (Phil. Mag., 1933, [vii], **15**, 241—262).—Theories of discharge are reviewed in the light of three fundamental experimental equations for the crit. conditions for discharge with the principal types of electrode shape and field distribution. A new theory is proposed showing the dependence of the breakdown strength on the electron mean free path. N. M. B.

Variations in visible solar light during submarine measurements. C. L. UTTERBACK (Science, 1933, **77**, 118—119).—Marked variations in the intensity of visible solar light measured beneath the surface of ocean waters are recorded. L. S. T.

Long-wave part of the visible spectrum of the night sky. L. A. SOMMER (Z. Physik, 1933, **80**, 273—276).—Long wave-length lines reported by Vegard (*ibid.*, 1932, **77**, 574) in Northern lights have the same wave-lengths as lines in the spectrum of the night sky, but the relative intensities of the lines are different. A. B. D. C.

Efficiency effect of *X*-ray *K*-fluorescence radiation for light elements. M. HAAS (Ann. Physik, 1933, [v], **16**, 473—488).—The efficiency effect (ratio of no. of excited atoms to no. of emitted atoms) for the *K*-fluorescence radiation from Mg, Si, S, Cl, Ca, and Cr was measured. A. J. M.

Weak lines in the *K*-spectra of 42 Mo and 47 Ag. E. CARLSSON (Z. Physik, 1933, **80**, 604—609). A. B. D. C.

***X*-Ray satellites.** H. C. WOLFE (Physical Rev., 1933, [ii], **43**, 221—223).—Calc. energies and frequencies for the 5 $K\alpha$ satellites of K based on Druyvestyn's theory are in agreement with observed vals. N. M. B.

***M* series of tantalum obtained by means of an ionic tube.** V. DOLEJSEK and (MLLE.) D. FILCAKOVA (Compt. rend., 1933, **196**, 388—389).—Using an improved form of Dolejsek's ionic tube at 3400 volts, the Ta lines M_IN_{III} 5385, $M_{III}O_I$ 5820, and $M_{IV}N_{III}$ 8875 X, corresponding with the W lines found by Lindberg (cf. A., 1928, 1078), and also the lines M_VO_{III} (7280 for Ta, and 6990 X for W) have been measured. C. A. S.

Properties of *X*-radiation. C. G. BARKLA (Nature, 1933, **131**, 166).—The present position with regard to the *J*-phenomenon is discussed. L. S. T.

Theory of *X*-ray absorption by molecular gases. II. H. PETERSEN (Z. Physik, 1933, **80**, 258—266; cf. A., 1932, 892).—Kronig's theory of fine structure of absorption edges due to mol. gases is more fully worked out. A. B. D. C.

Spectral composition of an *X*-ray radiation determined from its filtration curve. L. SILBERSTEIN (Phil. Mag., 1933, [vii], **15**, 375—394).—Theoretical. H. J. E.

Ionisation of solid dielectrics on *X*-irradiation. M. BENDER (Z. tech. Physik, 1932, **13**, 431—432; Chem. Zentr., 1932, ii, 3206).—Ionisation of S and paraffin on *X*-irradiation was observed. Ohm's law was obeyed. A. A. E.

Higher ionisation potentials of atoms according to the Thomas–Fermi model. A. SOMMERFELD (Z. Physik, 1933, **80**, 415—422).—An earlier

calculation (*ibid.*, 1932, **78**, 283) is corrected, and calculations of the second and third ionisation potentials are given for atoms between Li and Cs. A. B. D. C.

Ionisation and scattering accompanying positive ion impact in gases. C. A. FRISCHE (Physical Rev., 1933, [ii], **43**, 160—168; cf. Mouzon, A., 1932, 1184).—Ionisation and scattering curves and data are given for the ionisation produced by K^+ ion impact in A, Ne, He, N_2, CO, H_2, and Hg for the range 0—4000 volts. N. M. B.

Photo-electric and metastable atom emission of electrons from surfaces in the rare gases. C. KENTY (Physical Rev., 1933, [ii], **43**, 181—193).—The causes, and relative effects under various conditions, of conductivity at considerable distances beyond the end of a discharge in Ne, He, and A were investigated for the pressure range 0·5—2 mm. N. M. B.

Conservation of energy and the impulse in the photo-electric effect. J. KUNZ (Physikal. Z., 1933, **34**, 218).—Mathematical. A. J. M.

Classical distribution of electrons in the photo-electric effect with *X*-rays. J. KUNZ (Physikal. Z., 1933, **34**, 219—220).—Mathematical. A. J. M.

Adsorbed films of cæsium on tungsten. I. Space charge sheath and the image force. I. LANGMUIR (Physical Rev., 1933, [ii], **43**, 224—251).—Mathematical. For a W-walled heated enclosure containing Cs vapour in thermal equilibrium the image force in the sheath close to the surface acting on an electron, and the image force on a given electron due to electrons near the surface which have a Fermi distribution, are calc. by a perturbation method. N. M. B.

"Electric diffusion" of ions in gases with unipolar charge. N. VOLODKEVITSCH (Ann. Physik, 1933, [v], **16**, 431—467).—The theory and method for the production of a unipolar charged air stream are given, and an instrument (the ionometer) for determining the charge density is described. A. J. M.

Electron diffraction by films of grease. G. P. THOMSON and C. A. MURISON (Nature, 1933, **131**, 237).—The patterns produced by films of grease and waxes when used to reflect electrons are discussed. L. S. T.

Electron emission by metals under the influence of monochromatic *X*-rays. H. HASE (Z. Physik, 1933, **80**, 670—689).—Electron emission from the incident side was determined for Fe, Cu, Mo, Ag, Sn, Ta, W, Au, Pb, and Bi, and from the exit side for Cu, Sn, and Au. Electrons emitted by the heavier metals are almost all of the third kind. A. B. D. C.

Positive ion emission from oxide catalysts. C. F. POWELL and L. BRATA (Nature, 1933, **131**, 168).—Positive ion sources of Tl and In have been produced by evaporation on to an Fe oxide base (cf. A., 1932, 670). For a given metal the emission characteristic of the saturated surface increases rapidly with a rise in temp. until the Fe oxide sinters, when emission becomes unstable. The bearing of the results on the catalytic action of the Kunsman source in the production of NH_3 is discussed. L. S. T.

Energetics of the reciprocal effect in corpuscular impact. R. DOPEL (Ann. Physik, 1933, [v], **16**, 1—38).—The excitation of He by H canal rays was investigated between 2 and 40 kv. Other experiments were carried out with H impact on Hg, Na, K, and He charged with H^+. A simple mechanical-elastic theory of the collision is discussed. W. R. A.

Investigation of negatively-charged hydrogen atoms by light emission in the photographic range. R. DOPEL (Physikal. Z., 1933, **34**, 199—200).—An attempt was made to show the existence of H atoms by photographs of their light emission. No sign of light emission due to this cause was found, and it is concluded that if a negatively-charged H atom produces light, discrete or continuous, within the wave-length range 7111 Å. to the Lyman region, it is $<1\%$ of that due to neutral H atoms in this range. A. J. M.

Ionisation by positive ions. J. S. TOWNSEND and F. L. JONES (Phil. Mag., 1933, [vii], **15**, 282—294).—Experiments are described to determine separately the effects of the ionisation of gas mols. or atoms by collisions of positive ions, and the setting free of electrons from the negative electrode by positive ions, in currents between parallel plates at a gas pressure corresponding with the min. sparking potential. N. M. B.

At. wt. of cæsium. G. P. BAXTER and J. S. THOMAS (J. Amer. Chem. Soc., 1933, **55**, 858—859).—Determinations of the CsCl : Ag ratio using specially pure CsCl lead to the at. wt. 132·91, which is consistent with vals. from mass-spectrographic data. J. G. A. G.

Relative abundance of the carbon isotope, C^{13}. F. A. JENKINS and L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1212—1219).—The relative intensities of the 1,0 bands of $C^{12}C^{13}$ and $C^{12}C^{12}$ indicate an abundance ratio of 106 : 1 for $C^{12} : C^{13}$, corresponding with an at. wt. of 12·010. Lines due to $C^{13}N$ in the CN band at 3883 Å. have been detected in the C arc in air. D. R. D.

Isotopes (oxygen, neon, and chlorine). H. KALLMANN and W. LASAREV (Z. Physik, 1933, **80**, 237—241).—Mass-spectrograph measurements on CO, H_2O, and O_2 gave the intensity ratio $O^{18} : O^{16}$ as 1 : 630; Ne gave $Ne^{23} : Ne^{20}$ as 1 : 2000, and HCl gave Cl^{40} and $Cl^{39} : Cl^{36}$ as 1 : 6000. A. B. D. C.

Masses of O^{17}. W. D. HARKINS and D. M. GANS (Physical Rev., 1931, [ii], **37**, 1671—1672).—New vals. are discussed (cf. A., 1931, 783). L. S. T.

Existence of barium isotopes 136 and 137. R. C. GIBBS and P. G. KRUGER (Physical Rev., 1931, [ii], **38**, 1921).—The satellites of the Ba II lines 4554 and 4934 Å. may be due to Ba^{137} and the parent line to Ba^{136} and Ba^{138} (cf. A., 1932, 979). L. S. T.

Zero-point energy and the separation of isotopes. H. EYRING (Proc. Nat. Acad. Sci., 1933, **19**, 78—81).—Theoretical. It is shown that the higher zero-point energy of the lighter isotope of H makes it the more reactive of the two in the special case of

processes involving adsorption and desorption at electrode surfaces. The bearing of this on isotope separation is discussed. M. S. B.

Nuclear moments of the gallium isotopes 69 and 71. J. S. CAMPBELL (Nature, 1933, **131**, 204).—An examination of the hyperfine structure in the visible lines of the Ga II spectrum has shown the patterns due to the individual isotopes to be separated by a difference in the magnetic moments of the nuclei. From this the mechanical moments have been separately determined as $i=3/2$ for both isotopes. The ratio of the $g(i)$ factors from the hyperfine separations is 1·27, isotope 71 having the greater magnetic moment. The abundance ratio c_{69}/c_{71} is 1·5/1. The only other example of isotopes with equal spins and unequal hyperfine separations is that of Tl. L. S. T.

Mass defect of helium. E. WIGNER (Physical Rev., 1933, [ii], **43**, 252—257).—Mathematical. A connexion between the mass defect of H_2, the width and depth of a simple potential hole, and the mass defect of He and higher nuclei is obtained. N. M. B.

Artificial disintegration. D. VAN DER VEEN (Chem. Weekblad, 1933, **30**, 66—75, 146).—A review of recent work on at. disintegration by α-particle bombardment and by means of H canal rays. H. F. B.

Mobilities of molecular aggregates in gases containing radon. E. L. HARRINGTON and E. O. BRAATEN (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 177—186).—The mobilities of mol. aggregates in gases containing radon have been studied by two methods employing an ultramicroscope and also a modified Erikson apparatus. The results show a wide range of mobilities and suggest the importance of ionic winds and inconstancy of ionic charge in the study of mobilities. J. W. S.

Influence of distillation on the grouping of radioactive atoms. (MLLE.) M. I. ARCHINARD (J. Chim. phys., 1933, **30**, 56—60).—The nature of the radioactive layers condensed on a cold surface from Po or active Th deposit volatilised under various conditions was investigated photographically. N. M. B.

Amplification of the ionisation produced by radioactive sources. J. A. C. TEEGAN (Nature, 1933, **131**, 277—278). L. S. T.

Energy distribution of β-rays from atoms of known age. B. W. SARGENT (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 205—216).—By collecting Th-*C''* atoms from a Th-*B*+*C* prep. under the action of an electric field on a moving Cu strip, atoms of known age have been obtained and the absorption of the β-rays emitted by these atoms at ages of 21 sec. to 10·7 min. for papers of various thicknesses has been measured. No dependence of energy distribution on the age of the atoms could be detected. J. W. S.

Scattering of β-rays. I. B. W. SARGENT and A. J. O'LEARY (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 217—232).—The average angles of scattering of β-rays from Ra-*E* by gases and vapours are 60° and 90°. For gaseous compounds of H, C, N, and O the intensities of the scattered β-rays are proportional to their mol. scattering nos., in accordance with theory. For gaseous compounds of S, Cl, Br, and I the intensities relative to CO_2 are in some cases > theoretical, suggesting plural scattering. Scattered β-rays are the more penetrating the higher is the at. no. of the scattering atoms. J. W. S.

Absorption of β-rays by, and molecular structure of, organic compounds. G. FOURNIER and M. GUILLOT (Compt. rend., 1933, **196**, 412—414).—The mass absorption coeffs. (μ/ρ) of 19 hydrocarbons calc. additively from those of C and H deduced from the authors' formula (cf. A., 1932, 210) compared with the coeff. determined experimentally show differences of 1·0—2·3 units. The difference increases with length of chain whether principal or lateral, is decreased by an ethylenic linking (C_6H_6 behaves as if it contained three such linkings), and approx. double as much by an acetylenic linking. The differences in saturated hydrocarbons are similar to that for C in diamond, in unsaturated hydrocarbons to that for C in graphite (cf. A., 1917, ii, 437). C. A. S.

Magnetic spectra of the β-rays emitted by thorium-*B*+*C*+*C'*+*C''* and actinium-*B*+*C*+*C'*+*C''*. S. SHIH-YUAN (Ann. Physique, 1933, [x], **19**, 59—85; cf. A., 1932, 443).—Using the method described previously, H and intensity have been measured for the β-rays emitted by the active deposits of Th and Ac, and the corresponding energy levels deduced. The energies of the γ-rays emitted in the changes Th-*C* ⟶ Th-*C'* and Ac-*C* ⟶ Ac-*C'* are equal to the differences in energy between the groups of α-rays from Th-*C* and Ac-*C*, respectively. J. W. S.

γ-Radiation from Th-*C* and Th-*C'* and fine structure of the α-rays. L. MEITNER and K. PHILIPP (Z. Physik, 1933, **80**, 277—284).—γ-Lines belonging to the transitions Th-*C*⟶Th*C''* and Th-*C''*⟶Th-Pb were distinguished; the results fit Gamow's relation of α-ray fine structure to γ-ray emission. 21 β-ray groups were measured for Th-*C''*. A. B. D. C.

γ-Rays emitted on disintegration of lithium. H. R. VON TRAUBENBERG, A. ECKARDT, and R. GEBAUER (Z. Physik, 1933, **80**, 557—558).—Li disintegrated with protons emits γ-rays. A. B. D. C.

γ-Radiation of radium. E. STAHEL and W. JOHNER (Helv. phys. Acta, 1932, **5**, 310—311; Chem. Zentr., 1932, ii, 3197).—Ionisation measurements show that the no. of γ-quanta emitted by Ra is 1·3%. The no. of secondary β-rays is 5%; hence 100 disintegrating Ra atoms emit 6·3 γ-quanta. A. A. E.

Neutron, atomic nucleus, and mass defect. W. D. HARKINS (J. Amer. Chem. Soc., 1933, **55**, 855—857).—Theoretical. The energies of union of 13 atoms with either a proton, neutron, or H^2 nucleus are recorded. The mass defect per α-particle increases rapidly with the no. of α-particles up to mass 52 and then decreases slowly. J. G. A. G.

Conditions of emission of neutrons by the action of α-particles on light elements. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1933, **196**, 397—399).—The relation between the radiation

(neutrons) emitted by Be, B, and Li under the influence of α-particles from Po and the energy, $w\alpha$ (expressed in $eV\times10^6$), of the α-particles, has been determined by means of the ionisation produced in CH_4. For Be excitation begins when $w\alpha=1{\cdot}3$, is a max. for $w\alpha=2{\cdot}6$, and a min. for $w\alpha=3{\cdot}2$; corresponding figures for B are 2·0, 2·2, and 2·85, figures near to those for excitation of γ-rays (cf. A., 1932, 895, 1073). The radiation from Li is much less, and extends from $w\alpha$—3 to 5; emission of γ-rays before neutrons is explicable by transmutation without capture of an α-particle. Under similar conditions Al emits feebly, CaF_2 very, penetrating radiation, the latter due to F, and in both cases consisting mainly of neutrons, so that Al^{27} and F^{19} are able to emit both protons and neutrons (cf. A., 1931, 142). C. A. S.

Possibility of spontaneous emission of neutrons from certain non-radioactive elements. W. Swientosławski and A. Dorabialska (Rocz. Chem., 1933, **13**, 1—4).—The existence of certain isotopes cannot be explained solely on the basis of α-, β-, and *H*-radiation from predecessors, but requires the postulation of neutron radiation, to which the thermal radiation found by Dorabialska (A., 1932, 927) for certain elements is tentatively ascribed. R. T.

Emission of neutrons by aluminium under action of α-particles. P. Auger and G. M. Herzen (Compt. rend., 1933, **196**, 543; cf. preceding abstracts).—500 photographs of the rays emitted by powdered Al, obtained by the Wilson method, showed two trajectories due to rapid and two to slow protons, indicating emission of neutrons by Al, although much more rarely than by Be under similar conditions. C. A. S.

Experimental proofs of the existence of the neutron. (Mme.) I. Curie and F. Joliot (J. Phys. Radium, 1933, [vii], **4**, 21—33).—Evidence of the existence and properties of radiations of particles of unit mass and zero charge in the transmutation of Be, B, and Li by α-rays was obtained by the cloud-track method and by the ionisation of A–He and N_2–He mixtures and absorption in Pb. N. M. B.

Diffusion of neutrons. J. Solomon (Compt. rend., 1933, **196**, 607—609).—The applicability of Born's first approximation (cf. A., 1926, 1078) to the equation $V(r)=Ze^2e^{-r/p}/r$ (cf. A., 1932, 443, 672) for the interaction energy of an electron and a neutron is shown to be limited to the case of H. C. A. S.

Chemical nature of the neutron. P. Achalme (Compt. rend., 1933, **196**, 614—616).—Assuming that the negative charge of the electron is double the positive charge of the proton (cf. A., 1912, ii, 322) it is suggested that the neutron is identical with para-H, and consists of two protons and one electron; and further that X_3 (cf. A., 1913, ii, 820) and α-particles consist of one electron and three and four protons, respectively. C. A. S.

Neutrons. D. Meksyn (Nature, 1933, **131**, 366).—Theoretical. An electron and a proton are held together in a neutron by combined forces of attraction and repulsion which are in statical equilibrium. The size of the neutron is $r=1{\cdot}4\times10^{-13}$ cm. and the binding energy is $mc^2\sim5\times10^5$ electron-volts. L. S. T.

Structure of atomic nuclei. III. W. Heisenberg (Z. Physik, 1933, **80**, 587—596; cf. A., 1932, 1074).—The Thomas–Fermi method is applied to neutrons and protons constituting at. nuclei. γ-Ray scattering is treated on lines developed for Raman scattering, and finally the anomaly of β-ray emission without exchange energy of electrons within the nucleus is discussed. A. B. D. C.

Models of atomic nuclei. E. N. Gapon (J. Gen. Chem. Russ., 1932, **2**, 862—863).—Models of the structure of nuclei are given, based on the assumption that α-particles are composed of 2 neutrons and 2 protons. R. T.

Theory of atomic nuclei. I—IV. E. N. Gapon (J. Gen. Chem. Russ., 1932, **2**, 837—842, 843—848, 849—850, 851—861).—I. See this vol., 111.

II. Variations in the velocity of β-particles are ascribed to the mass defect of intra-nuclear electrons. The law of conservation of energy applies to β-particles.

III. Mass defect is ascribed to entrance into protons of electrons of negative wt.

IV. Mass defect and mechanical moment of at. nuclei are discussed with reference to a theory of the structure of the at. nucleus, based on Rutherford's model. R. T.

Theory of superconductivity. II. R. de L. Kronig (Z. Physik, 1933, **80**, 203—216; cf. this vol., 15).—A three-dimensional electron lattice must traverse very high potential barriers in passing through a crystal; this difficulty is obviated by assuming that the electrons form a one-dimensional lattice which melts at the superconductive temp. A. B. D. C.

Electron spin. S. Shimasaki (Sci. Rep. Tokyo Bunrika Daigaku, 1933, **1**, 251—273).—Mathematical. Treating the impulse in a linear form and the spin angular momentum as a vector gives a result similar to that of the perturbation theory, and leads to the Dirac fine structure for the H_α spectrum. N. M. B.

Most probable values of the atomic constants, *e* and *h*. R. Ladenburg (Ann. Physik, 1933, [v], **16**, 468—472).—The vals. regarded as most probable are $e=4{\cdot}770\pm0{\cdot}004\times10^{-10}$ and $h=6{\cdot}547\pm0{\cdot}009\times10^{-27}$. A. J. M.

Earth's magnetic effect and corpuscular nature of cosmic ultra-radiation. IV. J. Clay (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1282—1290).—The variation of intensity with magnetic latitude suggests that cosmic rays consist primarily of a charged corpuscular radiation. D. R. D.

Electronic theory of metals. R. Peierls (Ergebn. exakt. Naturwiss., 1932, **11**, 264—322; Chem. Zentr., 1932, ii, 2923).—A discussion. A. A. E.

Uncertainty relations and volume of photons. D. Meksyn (Phil. Mag., 1933, [vii], **15**, 592—601).—Theoretical. H. J. E.

Physical proof of existence of Gurwitsch radiation by means of a differential arrangement.

W. W. SIEBERT and H. SEFFERT (Naturwiss., 1933, **21**, 193—194).—An experiment is described for this purpose. A. J. M.

Band spectra and dissociation of molecules. R. SAMUEL (Proc. Muslim Assoc. Adv. Sci., 1932, **2**, 55—67).—An address.

Spectro-photometry in the ultra-violet. H. ARENS (Z. Physik, 1933, **80**, 629—635).—Methods are given for sensitising plates for the extreme ultra-violet, and the sensitivity of AgI emulsions in relation to AgI absorption bands is discussed. A. B. D. C.

Total radiation of oxides and mixtures of oxides. K. HILD (Mitt. Kaiser-Wilh.-Inst. Eisenforsch., 1932, **14**, 59—70; Chem. Zentr., 1932, ii, 3055).—The total radiation at 800—1400° of Al_2O_3, MgO, CaO, SiO_2, Cr_2O_3, Fe_2O_3, and ZnO in relation to particle size, and of mixtures in relation to composition, was investigated. A. A. E.

Continuous absorption spectrum of some polyatomic molecules. I. Y. HUKUMOTO (Sci. Rep. Tôhoku, 1932, **21**, 906—927).—A continuous absorption spectrum without a neighbouring band spectrum and convergence limit is accounted for by the excited electronic state of the mol. being unstable or much less stable than the normal state.

The continuous absorption spectra of this type of a no. of alkyl halides which have been investigated in the ultra-violet region are very similar, excepting that the absorption regions are displaced towards the long-wave side in the order RCl, RBr, RI. I-compounds show some selective absorption. J. W. S.

Chappuis bands of ozone and the boric acid spectrum. E. WALLES (Z. Physik, 1933, **80**, 267—272).—The H_3BO_3 spectrum is identical with Chappuis' bands of O_3. A new spectrum in the red was obtained from the C arc in O_2. A. B. D. C.

Absorption spectra of cobaltous chloride in alcoholic solutions. O. SPECCHIA (Nuovo Cim., 1932, **9**, 164—167; Chem. Zentr., 1932, ii, 3362—3363).—The fundamental frequencies of the vibration components of the $COCl_2$ band at 6950—6100 Å. and the multiplicities are, respectively; MeOH 416, 36—40; EtOH 417, 36—41; PrOH, 472, 32—36; Bu$^{\beta}$OH 371 cm.$^{-1}$, 39—44. A. A. E.

Absorption spectra of complex salts of Cr, Mn, Ru, Rh, Pd, Re, Os, Ir, and Pt. R. SAMUEL and A. R. R. DESPANDE (Z. Physik, 1933, **80**, 395—401).—Absorption curves are given for 13 complex cyanides and chlorides of the above metals in the region 650—200 mμ. A. B. D. C.

Line absorption spectra of chromium complex salts. G. JOOS and K. SCHNETZLER (Z. physikal. Chem., 1933, **B**, **20**, 1—10; cf. A., 1932, 983).—Most of the salts examined exhibit sharp absorption lines, showing that the differences in the Cr$^{\cdots}$ ion in the various salts are merely quant. In the hexa-cyano- and -thiocyano-complexes, however, there is a qual. change in the electron envelope of the central ion, for these salts give no lines. The introduction of a charged group into aquo-, ammino-, or en-complexes displaces the absorption by about 500 cm.$^{-1}$ towards the red. R. C.

Effect of crystal symmetry and chemical composition on the energy levels of solids. F. H. SPEDDING and G. C. NUTTING (J. Amer. Chem. Soc., 1933, **55**, 496—504).—Absorption spectra of 6 Gd$^{\cdots}$ salts have been determined. The lines arise from electronic transitions from the $^8S_{7/2}$ level to excited levels which are non-degenerate through the influence of the fields of neighbouring ions. The degree of splitting depends on the symmetry and separation of the ions in the lattice. J. G. A. G.

Ultra-violet absorption spectra of simple benzene derivatives. II. F. W. KLINGSTEDT (Z. physikal. Chem., 1933, **B**, **20**, 125—141; cf. A., 1928, 1304).—Absorption measurements down to 2000 Å. have been made in hexane solution. With PhBr there are regions of selective absorption at 2800—2420 and 2240—2100, and a third commences at about 2075 Å., resembling those of PhCl displaced about 50 reciprocal Å. towards longer wave-lengths. PhI has a structureless flat band at about 2680—2460 Å., and a region of strong absorption at 2420—2170 Å., the former being ascribed to the nucleus. p-$C_6H_4Br_2$ has a region of selective absorption at 2900—2560 Å. and a superimposed region extending to 2170 Å.; the vibration frequency of the nucleus averages 1035 cm.$^{-1}$ The excitation energy of mono-substituted C_6H_6 and PhMe derivatives increases fairly regularly with the nuclear charge of the element directly attached to the nucleus. R. C.

Ultra-violet absorption of hydroxyazo-compounds in aqueous solution and its relation to p_H. I. T. UYEMURA (Bull. Tokyo Univ. Eng., 1932, **1**, 327—347).—The effect of various groups was examined. Me has little effect. NO_2 *para* to the azo-group is bathochromic; when *o*- or *m*- it shows similar absorption spectra. The position of OH relative to the azo-group is important. The band due to Ph is absent in *p*-cresol, possibly owing to the effect of the position of OH. In general, absorption bands are shifted towards longer wave-lengths with increase in p_H. CH. ABS.

Spectrographic study of phloridzin and its derivatives. Ultra-violet absorption. A. LAMBRECHTS (Compt. rend., 1933, **196**, 295—297).—In H_2O phloridzin has a band max. at 2852 Å. (ε, 16,250) at 1·7, and bands with max. at 3225 (ε, 27,000) and 2300 Å. at p_H 10·04, whilst at p_H 7·5 both bands appear as small max. in a more general absorption. In EtOH only the band at 2852 Å. is seen. These effects are duo to keto–enol tautomerism. R. S. C.

Pleochroism of calcite in the infra-red. P. LE ROUX (Compt. rend., 1933, **196**, 394—396; cf. A., 1928, 934).—K_0, K_0', the coeffs. of absorption of calcite for propagation parallel and perpendicular to the axis for λ 2·2—4·4 μ, are respectively 0·6—30·7 and 0·7—34·8, K_0 being always slightly $< K_0'$. C. A. S.

Infra-red absorption spectrum of nitrogen dioxide. C. R. BAILEY and A. B. D. CASSIE (Nature, 1933, **131**, 239).—At room temp. the absorption spectrum of $N_2O_4 \rightleftharpoons 2NO_2$ shows bands at 15·6, 13·4, 7·92, 6·17, 5·75, 3·22, and 2·91 μ. At 100°, the max. of radiation emission characteristic of this temp. is

beyond 20 μ; all bands except those at 15·6 and 6·17 μ disappeared. These two bands are ascribed to NO_2, the mol. of which is thus probably rectilinear and symmetrical. The N–O force const. is approx. 7×10^5 dynes per cm., the deformation force const. is approx. 6×10^{-12} dyne per cm., and the moment of inertia is 60×10^{-40} g.-cm.^{2} with an interat. separation of 1·1 Å. This structure is confirmed by the Raman spectrum of inorg. nitrites in aq. solution which show an intense line at 1303 cm.$^{-1}$, a val. of the same order as that calc. from the above. L. S. T.

Envelopes of infra-red absorption bands. S. L. Gerhard and D. M. Dennison (Physical Rev., 1933, [ii], **43**, 197—204).—The intensity formulæ for the fine-structure absorption lines of mols. of the symmetrical rotator type are approximated to determine line intensities or envelopes. Application of results gives for the moment of inertia perpendicular to the symmetry axis for MeF, MeCl, MeBr, and MeI, vals. $\times10^{40}$, 32, 61, 89, and 99, respectively. N. M. B.

Vibration spectra and molecular structure of methyl and ethyl alcohols. R. Tittéica (Compt. rend., 1933, **196**, 391—394).—The infra-red spectra of MeOH and EtOH in the low-pressure gaseous condition have been measured for λ=2·10—14·70 μ, and compared with previous results (cf. A., 1925, ii, 351; 1929, 236) and the Raman spectra. For MeOH eight fundamental frequencies (four single, four double) are inferred, leading to a structure in which C–H=1·08, C–O=1·46, O–H=0·96 Å., and the angle of H–C–H= 106° (cf. A., 1932, 670); in EtOH C–O=C–C=1·53 Å., and the angle of C–C–O=108° 16′. C. A. S.

Raman effect of the ions SO_4'' and SO_3'' and the electrolytic dissociation of sulphuric and sulphurous acids. P. Fadda (Nuovo Cim., 1932, **9**, 168—179; Chem. Zentr., 1932, ii, 3363).—Saturated aq. Na_2SO_4, irradiated with λ 4358 Å., gave Raman frequencies: 460, 617, 984, 1104 cm.$^{-1}$ 25% H_2SO_4 gives 984; more conc. H_2SO_4 gives frequencies of HSO_4' (421, 574, 1047), H_2SO_4 (912, 1522), and SO_2 (1166). The H_2SO_4 frequencies diminish rapidly in intensity on dilution. The SO_3'' frequencies in saturated aq. Na_2SO_3 (471, 602, 984 cm.$^{-1}$) do not appear in the Raman spectrum of H_2SO_3, which indicates that H_2SO_3 contains chiefly free SO_2 (1142), together with some HSO_4' (569, 1047) formed by atm. oxidation. The line 1199 may be due to HSO_3'. A. A. E.

Polarisation of light-scattering. II. S. Venkateswaran (Phil. Mag., 1933, [vii], **15**, 263—282; cf. A., 1932, 898).—Polarisation measurements of vibrational Raman lines are reported, and results are discussed in relation to mol. structure for the following 27 liquids: H_2S, HCN, H_2O_2, SO_3, HNO_3, PCl_3, CS_2, MeOH, HCO_2H, MeCl, MeBr, MeI, MeSH, $CHCl_3$, $CHBr_3$, CCl_4, C_5H_{12}, $(C_3H_5)_2S$, C_6H_6, $PhNO_2$, PhCl, PhBr, mesitylene, salol, C_5H_5N, C_4H_4S, and C_4H_4NH. Raman lines from transverse oscillations are highly depolarised, all showing the limiting depolarisation val. 6/7. N. M. B.

Raman effect in liquids. A. Carrelli and J. J. Went (Z. Physik, 1933, **80**, 232—236).—Investigation of the Rayleigh continuum shows that there is no relation between depolarisation and optical anisotropy of mols. Broadening of Raman lines was studied for C_6H_6, CCl_4, H_2O, and glycerol. A. B. D. C.

Raman effect. T. Cujumzelis (Praktika, 1932, 7. 242—247; Chem. Zentr., 1932, ii, 3202).—The following frequencies were detected: C_6H_6, $\Delta\nu$ 1038; PhCHO 2971, PhMe 1237, and two anti-Stokes lines. Three PhMe lines reported by Pringsheim and Rosen as excited by 5461 Å. were not confirmed. A. A. E.

Raman effect of methyl esters of silicic acid. R. Signer and J. Weiler (Helv. Chim. Acta, 1933, **16**, 115—121; cf. this vol., 23).—Raman frequencies of $Si(OMe)_4$, and of the di-, tri-, and deca-polymerides, are given and compared with those of quartz and of crown glass. The results are discussed. F. L. U.

Normal vibrations of the SiO_4 group. J. Weiler (Z. Physik, 1933, **80**, 617—628).—Raman spectra of the polymerides of $Si(OMe)_4$ gave four fundamental frequencies near 1200, 1070, 800, and 500 cm.$^{-1}$ for the SiO_4 group, and combinations of these frequencies give the bands of cryst. quartz. A. B. D. C.

[Raman spectra of] α-ethylene oxides. R. Lespieau and (Mlle.) B. Gredy (Compt. rend., 1933, **196**, 399—401).—The Raman spectra of α-mono- and -di-substituted ethylene oxides have been determined. The α-ethylene oxide group is characterised by a line near 1250 cm.$^{-1}$; the spectra of most of the derivatives are similar, but the presence of Pr^β or of a halogen introduces a difference. C. A. S.

Raman effect in the terpene series. III. Products of sulphuric acid isomerism of pinene. G. Dupont and R. Gachard (Bull. Soc. chim., 1932, [iv], **51**, 1579—1594; cf. A., 1932, 1076).—The following constituents of terebene have been recognised: cymene, camphene, limonene, α-terpinene, γ-terpinene, terpinolene, 1 : 4-cineole, and four unidentified substances for which Raman data are given. E. S. H.

Raman spectra and chemistry. Anon. (Nature 1933, **131**, 263—265).—A summary. L. S. T.

Temperature effect of the molecular polarisation of gases and vapours. R. Sänger, O. Steiger, and K. Gachter (Helv. phys. Acta, 1932, 5, 200—210; Chem. Zentr., 1932, ii, 2949—2950).

Negative polarisation in fluorescence. K. S. Krishnan and S. M. Mitra (Nature, 1933, **131**, 204—205).—Vavilov's experiments (Z. Physik, 1929, **55**, 690) on the polarisation of fluorescence of dyes in glycerol when excited by radiations of different wave-lengths have been repeated and the general conclusions confirmed. L. S. T.

Inhibitory action of certain ions on fluorescence of uranine. J. Rouchard (Compt. rend., 1933, **196**, 485—487; cf. A., 1927, 609).—The intensity of fluorescence in NaOH solution is inhibited by ions in the order $S''>CNS'>I'>S_2O_4''>S_nO_n''>NO_2'>HAsO_3''$; NO_3', Cl', Br', F', CN', CO_3'', SO_3'', SO_4'', AsO_4''', PO_4''', and AcO' are inactive. The active salts are all antioxygenic. C. A. S.

Triboluminescence in mercury vapour. S. de Walden (Acta phys. Polonica, 1932, **1**, 223—236;

Chem. Zentr., 1932, ii, 3203).—The spectrum of the triboluminescence of Hg in a SiO_2 vessel with carefully cleaned walls was studied at 90—400°. Arc lines first appeared, followed at >115° by the band spectrum. At 200—300° spark lines appeared. At >200° the Steubing band at 2345 Å. was observed. The spectrum of the electrodeless discharge in Hg at 100° resembles the triboluminescence spectrum, without spark lines. A. A. E.

Investigations of the ultra-violet rays. L. ZEHNDER (Z. Physik, 1933, **80**, 699—700).—A weak radiation observed by the author (1899) is now confirmed in the mitogenetic rays, and methods of spectral analysis are suggested. A. B. D. C.

Potential curves for mercury hydride. R. RYDBERG (Z. Physik, 1933, **80**, 514—524; cf. A., 1932, 104).—This method is applied to HgH, which is shown to dissociate by rotation. A. B. D. C.

Existence of a barrier layer photo-effect for lead sulphide? E. TIEDE and G. BRÜCKMANN (Z. Physik, 1933, **80**, 302—304).—Only thermo-electric e.m.f. could be obtained from thin PbS layers. A. B. D. C.

Spectral sensitivity of cæsium oxide photo-electric cathodes. G. DÉJARDIN and R. LATARJET (Compt. rend., 1933, **196**, 470—473).—The Cs_2O–Ag cell is prepared by treating a Ag plate oxidised superficially with Cs vapour at >200° in a closed vessel, which may or may not contain A, excess Cs being absorbed by Pb glass at the base of the vessel at 350°. It is stable, the sensitivity being a min. at 5000 Å., a max. at 8000, and then decreasing to 12,000 Å. (the threshold). If insufficiently heated the sensitivity varies with time, becoming const. after about 7 weeks; excessive heating decreases sensitiveness uniformly (cf. B., 1933, 26). C. A. S.

Reversal of current in rectifier photo-cells. J. GUILD (Nature, 1933, **131**, 327—328; cf. this vol., 209).—The Cu_2O–Cu junction is the essential factor in producing reversal in Au–Cu_2O–Cu cells of the Auger type. Cells with no Cu backing to the Au–Cu_2O layer show reversal in ultra-violet light, but not near 0·6 μ. A silvered Cu_2O cell without Cu backing shows reversal at the blue end of the visible spectrum. L. S. T.

Distinction between electronic and photo-chemical effects in photo-voltaic elements. R. AUDUBERT (Compt. rend., 1933, **196**, 475—477).—An oxidised Cu plate heated at 1000° in N_2 becomes coated uniformly with Cu_2O. In an oxidising electrolyte, *e.g.* aq. Na_3BO_3, this gives a negative photo-potential, indicating absence or at least insignificance of the photolytic effect (cf. A., 1930, 173) in comparison with the intense photo-electronic process whereby the electrons under the action of light pass from the semi-conducting Cu_2O into the metal. The essential difference between the two processes is supported by the fact that the photo-voltaic characteristics of such a plate for light of different wave-lengths are or are not concurrent according as X=KI or Na_3BO_3 in the cell Cu|Cu_2O|X.*m*|100|KCl sat. Hg_2Cl_2|Hg in which it has been polarised. C. A. S.

Thermodynamic analysis of electromotive forces. J. VILLEY (J. Phys. Radium, 1933, [vii], **4**, 10—20).—Theoretical. N. M. B.

Theory of conductivity of polarisable media. G. JAFFÉ (Ann. Physik, 1933, [v], **16**, 217—248, 249—284).

Conductivity of highly insulating oxides and nitrides at very high temperatures. E. PODSZUS (Z. Elektrochem., 1933, **39**, 75—81).—Data are given for Al_2O_3, MgO, CaO, ZrO_2, ThO_2, and BN from 1700° to 2400° abs., in vac. and in N_2 and H_2. The conductivity, *k*, varies with the pressure and nature of the gas and the time of heating, and falls with increasing energy of formation of the compound. Normally, gases cause rise in *k*, but the val. for BN is depressed by N_2, probably owing to its chemical identity with the anion. When the materials are pure, the variation with temp. is given by $k=Ae^{-B/T}$. D. R. D.

Electrical conductivity of tridymite and cristobalite at their transformation temperatures. S. SHIMIZU (Sci. Rep. Tôhoku, 1932, **21**, 882—905).—The conductivity of SiO_2 plates changes abruptly in a direction parallel to the optical axis during the change β-quartz ⟶ tridymite, but in a direction at right angles it shows only continuous change. The conductivity of cristobalite is discontinuous at 225—245° in heating, but not in cooling, whilst that of tridymite changes abruptly in the range 175—202°. J. W. S.

Liquid crystal character of dipole liquids at the m.p. L. S. ORNSTEIN, W. KAST, and P. J. BOUMA (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1209—1212).—The electrical conductivity of *p*-azoxyanisole is abnormally high throughout the temp. range within which it is in the liquid crystal state, passing through a max. in this region. A similar phenomenon occurs with $COPh_2$, but extends over a range of only 2°. D. R. D.

Existence of limiting resistance in mixed crystals having a disordered atom arrangement. U. DEHLINGER and R. GLOCKER (Ann. Physik, 1933, [v], **16**, 100—110). W. R. A.

Recovery of electrical resistance and the hardness of copper, silver, gold, platinum, and palladium after cold working. G. TAMMANN and K. L. DREYER (Ann. Physik, 1933, [v], **16**, 111—119). W. R. A.

Method of determining dielectric constants of powders. K. HØJENDAHL (Z. physikal. Chem., 1933, **B**, **20**, 54—64).—At the temp. at which a condenser filled with the powder with the air between the grains displaced by a pure liquid has the same capacity as when filled with the liquid, the dielectric consts. of the liquid and powder are equal. C_6H_6 is recommended as the liquid. The dielectric consts. of solid alkali halides, Cu_2O, and Ag_2O have been measured. R. C.

Dipole moment of hydrogen peroxide. W. THEILACKER (Z. physikal. Chem., 1933, **B**, **20**, 142—144; cf. this vol., 8).—The observed dipole moment agrees with that deduced from the formula HOOH if the angle between the O–O–H valencies is 110° and there is free rotation of the OH groups about the O–O axis. R. C.

Electric moments of hydrazine and its derivatives. L. F. AUDRIETH, W. NESPITAL, and H. ULICH (J. Amer. Chem. Soc., 1933, **55**, 673—678).—Dielectric consts. of dil. solutions in C_6H_6 were determined in the range 17·5—20°. The following dipole moments ($\times 10^{-18}$ e.s.u.) were evaluated: N_2H_4 1·83—1·85, NHPh·NH_2 1·65—1·79, NPhMe·NH_2 1·79, NPh_2·NH_2 1·87, NHPh·NHPh 1·53 (cf. Bergmann *et al.*, A., 1931, 82), CHPh:N·NHPh 1·97, CHPh:N·N:CHPh 1·0. J. G. A. G.

Possibility of dipole rotation in crystalline solids. S. E. KAMERLING and C. P. SMYTH (J. Amer. Chem. Soc., 1933, **55**, 462—465; cf. this vol., 209).—Dielectric consts. at 0·2—50 kilocycles were determined in the range —91° to 36°. Neither *n*-heptyl bromide, *p*-$C_6H_4(OMe)_2$, or anisole mols., nor their polar groups turn in the applied field. Traces of impurities may account for effects attributable to such turning in PhOH and BzCl. J. G. A. G.

Dipole moment and structure of organic compounds. XII. A. WEISSBERGER and R. SANGEWALD (Z. physikal. Chem., 1933, **B**, **20**, 145—157; cf. A., 1932, 718).—CPh·CPh has zero dipole moment. In *p*-xylylene dichloride the CH_2Cl groups are apparently freely rotatable. The dipole moments of the meso- and *dl*-forms of *p*-di-(α-chlorobenzyl)benzene differ only slightly, showing that the interposition of the C_6H_6 ring between the CHPhCl groups has decoupled them, permitting practically free rotation. In the monochlorodiphenyls the polarisation of the C_6H_4Ph residue varies with the position of the substituent relative to the diphenyl linking, as is shown by the differences in the dipole moments. A similar effect probably operates in the dichlorodiphenyls. R. C.

Dipole moments of stannic chloride and some derivatives. M. E. SPAGHT, F. HEIN, and H. PAULING (Physikal. Z., 1933, **34**, 212—214).—$SnCl_4$ in CCl_4 and in C_6H_{14} has zero dipole moment (cf. A., 1932, 793), showing the tetrahedral structure of this mol. $SnEt_4$ gives the same result. For the ratio of dipole moments of singly- and doubly-substituted compounds the val. 1 : 1·12 was found (theoretical, 1 : 1·15). In contrast to C compounds, there is no marked deformation of the tetrahedral angle. A. J. M.

Dependence of dipole moment of αß-dichloroethane on the temperature and solvent. S. MIZUSHIMA and K. HIGASI (Proc. Imp. Acad. Tokyo, 1932, **8**, 482—485).—The dielectric const. of Et_2O solutions of CH_2Cl·CH_2Cl was measured between 20° and —60°. The dipole moment increases with rise of temp. The rotation of the CH_2Cl groups in the mol. about the axis joining them is considered, and it is shown that the only case corresponding with the observed temp. effect is when interaction between the groups is not weak, but not strong enough completely to stop rotation. An expression is derived connecting the dipole moment with temp. on this assumption, giving satisfactory vals. A. J. M.

Polarity in hydrocarbon vapours. K. B. MCALPINE and C. P. SMYTH (J. Amer. Chem. Soc., 1933, **55**, 453—462).—Dielectric consts. have been determined at pressures between 10 and 1100 mm. in the temp. range 226—486° abs. The electric moments are C_6H_6 0, PhMe 0·37, C_3H_8 0, propylene $0·35 \times 10^{-18}$ e.s.u. The absence of temp. coeffs. of the polarisation of C_6H_6 and C_3H_8 indicates that those observed in liquid paraffins are due to decrease in intermol. action. The moments found for PhMe and propylene are attributed to inductive effects in the mols. J. G. A. G.

Dispersion experiments with undamped ultra-short waves. M. SEEBERGER (Ann. Physik, 1933, [v], **16**, 77—99).—Three methods for the direct determination of the refractive index of liquids were investigated. Measurements were carried out with undamped waves of 12·6, 13·6, 14, 19, and 24 cm. The refractive and absorption indices, and the dielectric consts. of H_2O and aq. NaCl, $CuSO_4$, $ZnSO_4$, $Pb(OAc)_2$, and glucose were determined at room temp. and 14 cm. Several alcohols were also measured. W. R. A.

Molecular theory of the simultaneous optical effects of rotatory magnetic polarisation and of magnetic birefringence. G. DUPOUY and M. SCHÉRER (Ann. Physique, 1933, [x], **19**, 5—46; cf. A., 1931, 787).—The mathematical theory is developed for the optical effects when a beam of polarised light is passed through a liquid in a magnetic field. J. W. S.

Compact molecules. J. J. VAN LAAR (Chem. Weekblad, 1932, **29**, 763—764).—A criticism of Backer's views (this vol., 211). H. F. G.

New theory of chemical compounds. M. REBEK (Coll. Czech. Chem. Comm., 1933, **5**, 36—48).—The theory is based on the electronic conception of the atom. The system distinguishes between polar and non-polar combination, but avoids the use of those secondary valencies the nature and application of which are not clear. M. S. B.

Electronic structures of polyatomic molecules and valency. IV. Electronic states, quantum theory of the double linking. R. S. MULLIKEN (Physical Rev., 1933, [ii], **43**, 279—302; cf. A., 1932, 1190).—Types of electronic states of polyat. mols. are tabulated. The determination of possible electronic states corresponding with any given electron configuration for any type of symmetry, and the selection rules for transitions between electronic states of mols. is shown. Mols. having all their electrons in closed shells or electron-pair linkings, and the approx. construction of mol. orbitals as linear combinations of at. orbitals are discussed. The quantum theory of the double linkings is illustrated and extended. N. M. B.

New photo-magnetic effect. D. M. BOSE and P. K. RAHA (Z. Physik, 1933, **80**, 361—375).—Light absorption by solutions increases the paramagnetic susceptibility of the ions $Cr^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, and $Cu^{\cdot\cdot}$, but leaves unchanged $Ti^{\cdot\cdot\cdot}$ and $Ce^{\cdot\cdot\cdot}$. The increase is attributed to the absorbed light destroying the *l*-coupling of the ion to its associated H_2O mols. A. B. D. C.

Absorption centres in crystals containing paramagnetic ions, and the mechanism of their

light absorption. D. M. Bose and S. Datta (Z. Physik, 1933, **80**, 376—394).—It is shown that in aq. solutions and in crystals containing H_2O, the absorption centre is the complex $[M,nH_2O]^{m+}$, and that this also causes the paramagnetic effects. The effect of *l*-coupling within the complex (cf. preceding abstract) is discussed, and it is shown that the energy required to destroy the *l*-couplings displaces the absorption frequency to higher wave nos. NH_3, N_2H_4, CN, etc. may replace H_2O in the complex, and if the coupling energy be increased, the magnetic moment is decreased and the absorption displaced to the violet. Rise of temp. increases the energy of the complex, tending to destroy the *l*-couplings and so affect the phenomena. A. B. D. C.

Diamagnetic susceptibility of inorganic compounds. III. Oxyacidic salts and chlorides. K. Kido (Sci. Rep. Tohoku, 1932, **21**, 869—881; cf. A., 1932, 1077).—Measurements have been made of the magnetic susceptibility of salts of the oxyacids and of the chlorides and oxychlorides of the elements of groups IV, V, VI, and VII, and the susceptibilities of the oxyacidic ions calc. The susceptibility of an ion with a similar co-mol. structure decreases with increase of the nuclear charge on the central atom in the same group and increases with increase of the nuclear charge on the central atom in the same series. J. W. S.

Diamagnetic susceptibility and refractivities according to wave mechanics. B. Mrowka (Z. Physik, 1933, **80**, 495—505).—The susceptibility of H_2 is given in terms of universal consts. Ionic susceptibilities are deduced from ionic refractivities for Cl′, Br′, I′, Li˙, Na˙, K˙, Rb˙, Mg˙˙, Sr˙˙, and Ba˙˙. A. B. D. C.

Magne-crystallic action. I. Diamagnetics. K. S. Krishnan, B. C. Guha, and S. Banerjee (Phil. Trans., 1933, A, **231**, 235—262).—The magnetic anisotropy of 13 inorg. and 12 org. crystals was determined by oscillating them about different axes in a uniform magnetic field. Results are tabulated for quartz, calcite, aragonite, strontianite, witherite, $NaNO_3$, KNO_3, $KClO_3$, S, barite, celestite, anhydrite, and gypsum (the nitrates and carbonates showed large anisotropy, the sulphates were almost completely isotropic); $C_{10}H_8$, anthracene, β-naphthol, acenaphthene, Ph_2, $(CH_2Ph)_2$, $COPh_2$, benzil, salol, azo- and hydrazo-benzene. Except for the two last-named, for which the mean val. is lower, these follow the Pascal additive relations. The susceptibility of $COPh_2$ decreases 2½% in the fused state. A correlation of the magnetic consts. of a crystal with those of its individual mols. by means of magnetic birefringence and light-scattering data, leading to a determination of the orientations of the mols. in the crystal lattice, is examined. N. M. B.

Paramagnetic properties of rare-earth crystals. I. H. A. Kramers (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1272—1281).—The author's theoretical views (A., 1930, 401; 1931, 287) have been modified and extended. D. R. D.

Paramagnetism of rhenium. N. Perakis and L. Capatos (Compt. rend., 1933, **196**, 611—612).—The coeff. of magnetisation of Re at 20°, −23°, and −79° is alike $0{\cdot}369\pm0{\cdot}006\times10^{-6}$, giving an at. coeff. of $68{\cdot}7\times10^{-6}$ (cf. A., 1931, 153). C. A. S.

Ferromagnetism of trigonal ferric oxide. V. Danilov, G. Kurdjumov, E. Pluschnik, and T. Stellezky (Naturwiss., 1933, **21**, 177).—By heat treatment of some alloys containing Fe_2O_3, the latter may be converted from the para- into the ferromagnetic state. The lattice of the Fe_2O_3 is unaltered by this change in magnetic properties, remaining trigonal. The change takes place only when the Fe_2O_3 is present in an alloy. A. J. M.

Interpretation of Weiss' law. H. Fahlenbrach (Physikal. Z., 1933, **34**, 204—207).—Explanations alternative to those of Gorter (A., 1932, 900) are given. A. J. M.

Interpretation of Weiss' law. E. Vogt (Physikal. Z., 1933, **34**, 207).—An addition to the paper of Fahlenbrach (cf. preceding abstract). A. J. M.

Preliminary photographs of emission and absorption spectra with bent crystals as transmission gratings. A. Sandstrom and E. Carlsson (Z. Physik, 1933, **80**, 597—603).—Emission spectra Mo-*K* and Ag-*K* were obtained in four orders, and absorption spectra of *K*-edges of Br and Mo were obtained with bent gypsum crystals. A. B. D. C.

Correction calculations for *X*-ray spectrometers. M. Siegbahn (Z. Physik, 1933, **80**, 413—414).—Polemical against Seemann (this vol., 108). A. B. D. C.

Calculation of *X*-ray spectrographs. I. D. Borisov (Ukrain. Chem. J., 1932, **7**, [Sci.], 84—93).—Mathematical. R. T.

Direct determination of the indices and locations of the spots in a Laue pattern of calcite. G. F. H. Harker (Phil. Mag., 1933, [vii], **15**, 512—527).—A calculation from first principles, assuming the lattice type and the lattice consts. H. J. E.

Errors due to photographic development in spectrograms, particularly in measurement of band edges. H. Seemann (Z. Physik, 1933, **80**, 506—513).—Errors introduced by photographic development have been reinvestigated using a microphotometer. A. B. D. C.

Improvement of *X*-ray quantitative chemical analysis. F. Voges (Z. Physik, 1933, **80**, 542—556).—Measurement of intensity by ionisation combined with the Küstner monochromator (A., 1931, 993) gives quant. chemical analysis accurate to within a few parts per thousand, the time required for one measurement being 2—3 hr. A. B. D. C.

Bitter's striations with an iron-silicon plate. R. Becker and H. W. F. Freundlich (Z. Physik, 1933, **80**, 292—298).—A study of the deposition of a colloidal suspension of Fe_2O_3 particles on to the surface of magnetised Si-Fe. The particles are deposited in regular patterns in the form of striations. A. B. D. C.

Co-operative phenomena. F. Zwicky (Physical Rev., 1933, [ii], **43**, 270—278).—Phenomena due to the interaction over large distances of elementary particles, a generalisation of thermodynamics from

static to stationary systems, the existence of crystals and their secondary structure, and ferromagnetic substances are discussed. N. M. B.

Deposits of metallic mercury by high-frequency discharge. D. BANERJI and R. GANGULI (Phil. Mag., 1933, [vii], **15**, 676—681).—The deposits are explained in terms of the space potential distribution. H. J. E.

Fusion of carbon. A. EGERTON and M. MILFORD (Nature, 1933, **131**, 169).—Under certain conditions in the C arc C is deposited as small spherules of graphite, *d* 2·25, indicating that the C has existed for a finite time in the molten state. L. S. T.

Electron diffraction photographs of microcrystalline carbon. R. FRISCH (Naturwiss., 1933, **21**, 173—177).—The method previously described (A., 1932, 980) was used, employing spider's web as basal substance instead of Au foil. Investigation of the photographs obtained with various preps. of "amorphous" C shows these to be microcryst. A. J. M.

Change of lattice constant and conductivity of palladium by electrolytic charging with hydrogen. F. KRÜGER and G. GEHM (Ann. Physik, 1933, [v], **16**, 174—189).—The lattice const. and resistance of Pd charged with H_2 by an electrolytic method were simultaneously determined as a function of the H_2 concn. In the concn. range 0·03—0·77H/Pd, two phases exist, both showing an extended Pd lattice. The conclusion was confirmed by resistance measurements. The two phases are two solid solutions of H_2 in Pd. A. J. M.

Dependence of lattice constants and electrical conductivity of electrolytically charged palladium–silver alloys on the hydrogen concentration. F. KRÜGER and G. GEHM (Ann. Physik, 1933, [v], **16**, 190—202).—As concn. of H_2 increases there is an extension of the Pd lattice up to 0·1H/Pd. For greater concns. two lattices are present, one weak, the other strong, in H_2. In this range there are two phases, which may be regarded as solid solutions of H_2 in the alloy. Resistance measurements confirm this conclusion. With increase of Ag concn., the lattice consts. approach each other, and ultimately coexist; limiting concn. for this is 45% Ag. Discrepancies in the previous work on the solubility curve of H_2 in Pd–Ag alloys are explained. A. J. M.

Precision measurements of crystal parameters. E. A. OWEN and E. L. YATES (Phil. Mag., 1933, [vii], **15**, 472—488; cf. A., 1932, 557, 990).—Parameters of the following elements, showing cubic symmetry, were measured: Au 4·0699, Pt 3·9158; Pd 3·8824; Rh 3·7957; Pb 4·9396 Å. (all ±0·0003); Ir $3·8312 \pm 0·0005_5$ Å.; Fe $2·8607_5$; Al $4·0406_5$; Cu $3·6077_5$; Ag $4·0772_4$ Å. (all ±0·0002). Crystal densities at 0° and 20° were calc. H. J. E.

***X*-Ray investigation of molten metals and alloys. I.** F. SAUERWALD and W. TESKE (Z. anorg. Chem., 1933, **210**, 247—256).—*X*-Ray data are given for molten Hg in H_2 and in vac., Tl in vac., Sn in vac., Pb in H_2, Hg_5Tl_2 in N_2, and KHg_2 in A. Observations with the pure metals support the view that within a small region above the m.p. the melts contain structures similar to those observed in the solid state. The existence of intermetallic compounds is recognised in the longer periods of the alloys. E. S. H.

Metals and alloys. VII. Crystal structure of indium. VIII. Crystal structure of β-lanthanum. IX. Alloy phases of the type $NaPb_3$. E. ZINTL and S. NEUMAYR (Z. Elektrochem., 1933, **39**, 81—84, 84—86, 86—97).—VII. In has a face-centred tetragonal structure with *a* 4·583, *c* 4·936 Å., 7·308.

VIII. Mixtures of rare-earth metals with NaCl or KCl, suitable for *X*-ray investigation, may be prepared by action of Na or K vapour on their anhyd. chlorides. In some cases formation of mixed crystals (*e.g.*, Ce–K) causes error. Hence, La was first prepared electrolytically, converted into the β-form by heating for some days at 350°, and then mixed mechanically with KCl. β-La forms face-centred cubes with *a* 5·296, *r* 1·872 Å.

IX. The following are cubic: $CaPb_3$ (*a* 4·891 Å.), $CePb_3$ (4·864), $CaTl_3$ (4·794), $CaSn_3$ (4·732), $CeSn_3$ (4·711). $SrPb_3$ is tetragonal with *a* 4·955, *c* 5·025 Å. D. R. D.

Effect of lattice distortion and fine grain on the *X*-ray spectra of metals. W. A. WOOD (Phil. Mag., 1933, [vii], **15**, 553—562; cf. A., 1932, 1193).—A method is given for differentiating between the broadening of *X*-ray diffraction lines due to fine grain and to lattice distortion, and is applied for electrodeposited Ni, for which both factors must be considered. H. J. E.

Recrystallisation power and shear hardening in aluminium single crystals. W. G. BURGERS (Nature, 1933, **131**, 326—327).—Recrystallisation of stretched Al single crystals indicates that for the same amount of shear the no. of crystallites formed under identical conditions of heat treatment is the smaller the greater is the no. of slip-planes involved in the distortion. L. S. T.

Preparation and crystal structure of lithium hydroxide. T. ERNST (Z. physikal. Chem., 1933, **B**, **20**, 65—88).—LiOH has a layer lattice with the space-group D_{4h}^3 and *d* 1·462, *Z* 2, *a* $3·549 \pm 0·004$, and *c* $4·334 \pm 0·008$ Å. *n* has been measured for various wave-lengths. R. C.

Crystal structure of manganous sulphides and their mixed crystals with zinc sulphide and cadmium sulphide. H. SCHNAASE (Z. physikal. Chem., 1933, **B**, **20**, 89—117; cf. A., 1932, 986).—The Mn sulphides pptd. from aq. solution are all forms of MnS. The green sulphide has NaCl structure, and *a* $5·212 \pm 0·002$ Å. The rate of transformation of the red forms into the stable green form is appreciable at about 200°. Whilst the red forms are completely miscible in the solid state with CdS, there is apparently a gap with ZnS. R. C.

Determination of the structure of the hexafluorides of sulphur, selenium, and tellurium by the electron diffraction method. L. O. BROCKWAY and L. PAULING (Proc. Nat. Acad. Sci., 1933, **19**, 68—73).—The diffraction patterns obtained when a beam of electrons intersects a jet of gas (cf. Mark and Wierl, A., 1930, 1336; 1931, 13, 665) give the

following separations for the elements in SF_6, SeF_6, and TeF_6: S–F 1·58±0·03 Å.; Se–F 1·70±0·03 Å.; Te–F 1·84±0·03 Å. These agree very well with the vals. expected for an ionic structure. M. S. B.

Crystal structures of fluorides. II. HgF, HgF_2, CuF, and CuF_2. F. Ebert and H. Woitnek (Z. anorg. Chem., 1933, **210**, 269—272).—Lattice consts. have been determined: HgF, *a* 3·66, *c* 10·9; HgF_2, *a* 5·54; CuF, *a* 4·26; CuF_2, *a* 5·40. E. S. H.

Planar structure of platinous complexes. F. Rosenblatt and A. Schleede (Naturwiss., 1933, **21**, 178).—After repeated recrystallisation, the third isomeride of $Pt(NH_3)_2Cl_2$ (Drew *et al.*, A., 1932, 562) gave the Debye diagram of the *trans*-compound. It can be obtained by crystallising together the *cis*- and *trans*-compounds. The more easily sol. *cis*-compound is found in greater amount in the mother-liquor; since the crystals give the Debye diagram of the new isomeride, it is concluded that this is a new cryst. form of *trans*- with some *cis*-compound. A. J. M.

Linear thermal expansion of a single crystal of sodium nitrate. J. B. Austin and R. H. H. Pierce, jun. (J. Amer. Chem. Soc., 1933, **55**, 661—668; cf. A., 1931, 1359).—The linear expansion accompanying the gradual transition between 150° and 278° was most marked in the direction of the *c* axis and was not detected along the *a* axis. This indicates a separation of the layers of NO_3 ions resulting from the increasing amplitude of the oscillations and transition to rotation of these ions. The phenomena are reversible except along the *a* axis when the crit. point has been passed. At 280°, $\alpha=45°\ 34'$. J. G. A. G.

Vacant positions in the iron lattice of pyrrhotite. G. Hägg (Nature, 1933, **131**, 167—168).—*X*-Ray measurements support the assumption that the excess of S is due to vacant positions in the Fe lattice. L. S. T.

***X*-Ray studies of fatty acids and of mixtures of fatty acids.** E. Ott and F. B. Slagle (J. Physical Chem., 1933, **37**, 257—258).—The spacings observed with mixtures show a linear relation with composition, in accordance with the usual behaviour of mixed crystals. Only one definite combination spacing may be observed in an equimol. mixture of nine fatty acids. The spacings recognised in highly polymerised substances may indicate an average chain-length. E. S. H.

Magnetostriction of ferromagnetic crystals. R. Gans and J. von Harlem (Ann. Physik, 1933, [v], **16**, 162—173).—Mathematical. The Heisenberg principle can be applied to magnetostriction. A. J. M.

Cross-sectional magnetostriction. W. Fricke (Z. Physik, 1933, **80**, 324—341).—Magnetostriction hysteresis and remanence were established using the cross-section of cylindrical rods of Fe, Co, and Ni. The saturation magnetostriction for Ni agreed with Becker's theoretical val. A. B. D. C.

Kerr effect in Rochelle salt. H. Muller (Physical Rev., 1931, [ii], **38**, 1922). L. S. T.

Change in the thermal power during the recovery of metals from cold work. G. Tammann and G. Bandel (Ann. Physik, 1933, [v], **16**, 120—128).—Changes for Ag, Cu, Au, Mg, Fe, Ni, Pt, and Pd and the influence of the amount of cold work are discussed. W. R. A.

Change in resistance of bismuth crystals in magnetic fields. O. Stierstadt (Z. Physik, 1933, **80**, 636—665).—A method was used which gave change in resistance with any orientation of the crystal; change in resistance was found, in directions normal to the principal axis of the crystal, which was very sensitive to structural changes in the crystal. This might be applied to determination of crystal form. A. B. D. C.

Electrical Barkhausen effect with crystals of sodium potassium tartrate. M. Kluge and H. Schonfeld (Naturwiss., 1933, **21**, 194).—The analogy between the dielectric properties of the salt and the magnetic properties of Fe is shown. De-electrification of the crystal shows an effect similar to the Barkhausen effect for Fe. A. J. M.

Magnetism of the metals. E. Vogt (Ergebn. exakt. Naturwiss., 1932, **11**, 323—351; Chem. Zentr., 1932, ii, 2935).—A discussion of the magnetic properties of metals in relation to the quantum states of the atoms in the crystal lattice. A. A. E.

Strength properties of moistened salt crystals. IV. Commencement of plasticity in rock-salt rods wholly subjected to water. K. H. Dommerich (Z. Physik, 1933, **80**, 242—251). A. B. D. C.

Tensile strength of synthetic rock-salt crystals at low temperatures. W. Burgsmuller (Z. Physik, 1933, **80**, 299—301).—An investigation of the tensile strength and plasticity of synthetic rock-salt between −190° and 90°. A. B. D. C.

Effect of water on the plasticity of rock-salt. R. B. Barnes (Naturwiss., 1933, **21**, 193).—By investigating the absorption bands in the ultra-violet of a rock-salt crystal made plastic by H_2O it is possible to show that the plasticity is due to entrance of H_2O into the crystal, as stated by Polanyi and Ewald, and not to a surface phenomenon (Joffe *et al.*). A. J. M.

Plasticity and tensile strength of rock-salt crystals stretched under water. L. Piatti (Nuovo Cim., 1932, **9**, 102—124; Chem. Zentr., 1932, ii, 2786).—Plastic deformability differs not only in different crystals, but also in the parts of the same specimen. There is no clear relation between elastic limit, plastic extension, and tensile strength. A. A. E.

Isomeric compounds and their mixtures as solvents for micro-mol. wt. determination by the method of molar depression of f.p. J. Pirsch (Ber., 1933, **66**, [*B*], 349—355; cf. this vol., 172).—The val., $E=58·7$, for *iso*bornyl bromide (I) falls into line with those determined previously. In the neighbourhood of its m.p., (I) is isomerised to a slight extent to camphene hydrobromide. With mixtures of (I) and bornyl bromide (II) the val of *E*

increases as a nearly linear function of the percentage of (II). H. W.

Electrical conductivity of mercury at high temperatures. W. BRAUNBEK (Z. Physik, 1933, **80**, 137—149).—The electrical conductivity of Hg was determined up to 900° and 300 atm.; the pressure coeff. of conductivity was determined between 300 and 600 atm. up to 600°. A. B. D. C.

Absorption of sound in polyatomic gases. H. O. KNESER (Ann. Physik, 1933, [v], **16**, 337—349). W. R. A.

Dispersion theory of sound. A. J. RUTGERS (Ann. Physik, 1933, [v], **16**, 350—359).—Mathematical. W. R. A.

[Dispersion theory of sound.] H. O. KNESER (Ann. Physik, 1933, [v], **16**, 360—361).—Polemical against Rutgers (cf. preceding abstract). W. R. A.

Physical properties of high-melting compounds. K. BECKER (Physikal. Z., 1933, **34**, 185—198).—A summary of the physical properties of high-melting compounds, especially carbides, nitrides, and borides, either singly, or in alloys. The physical properties of alloys of WC and Co, and TaC and metals of the Fe group are specially considered. A. J. M.

Thermal conductivity of air. H. S. GREGORY and C. T. ARCHER (Phil. Mag., 1933, [vii], **15**, 301—309).—Previous work (cf. A., 1926, 231) is amplified and discussed in relation to the investigations of Curie and Lepape on the rare gases (cf. A., 1932, 13). N. M. B.

Surface energy of molecules, and their physico-chemical properties. II. Surface energy and b.p. of members of homologous series. S. G. MOKRUSCHIN. **III. Surface energy and b.p. of homologues of acyclic series.** S. G. MOKRUSCHIN and E. I. KRILOV (J. Gen. Chem. Russ., 1932, **2**, 911—915, 916—920).—II. The b.p. T of liquids belonging to a homologous series are given by $T=\omega n+\phi n^2+\pi$, where n is the no. of atoms in the mol. of liquid, and ω, ϕ, and π are consts.

III. The formula derived theoretically $T=\alpha(M/d)^{2/3}+b$, where α and b are consts., M is the mol. wt., and d the density of a member of a homologous series, gives results in good agreement with experiment. R. T.

Physical constants of 20 organic compounds. J. TIMMERMANS and (MME.) HENNAUT-ROLAND (J. Chim. phys., 1932, **29**, 529—568).—Collection of physical consts., including b.p., f.p., density, refractive indices, viscosity, and surface tension, for the following substances: di*iso*butyl, CH_2Cl_2, CH_2Br_2, CH_2I_2, allyl chloride and alcohol, PhI, *n*-amyl alcohol, $CHEt_2\cdot OH$, $CHMePr\cdot OH$, $CMe_2Et\cdot OH$, $COEt_2$, $PrCO_2H$, *n*- and *iso*-valeric acids, HCO_2Et, $PrCO_2Et$, NEt_3, $MeNO_2$, and allylthiocarbimide. A. S. C. L.

Specific heat of oxygen at high temperatures from ozone explosions and the energy of the $^1\Delta$ level of the neutral oxygen molecule. B. LEWIS and G. VON ELBE (J. Amer. Chem. Soc., 1933, **55**, 511—519; cf. this vol., 16).—The sp. heat of O_2 in the range 1400—2500° abs. has been determined by exploding O_3–O_2 mixtures in a const.-vol. bomb. The discrepancy between the theoretical vals. calc. from the known vibration–rotation levels of O_2 and the experimental vals., corr. for dissociation, is explained by the existence of the hitherto unknown $^1\Delta$ state of the neutral O_2 mol. at a level $0{\cdot}75\pm0{\cdot}05$ volt, or $17{,}200\pm1000$ g.-cal., above the ground state. Sp. heats, C_v, in the range 200—3000° abs. are recorded. J. G. A. G.

Temperature variation of the specific heat (C_p) of carbon dioxide at 65·3 kg./cm.^{2} pressure; specific heat of helium as a function of pressure. E. J. WORKMAN (Physical Rev., 1931, [ii], **38**, 587).—The ratio C_p at 65·3 kg. per sq. cm. to C_p at 1 atm. is 1·87, 1·58, 1·38, and 1·27 at 45°, 50°, 80°, and 100°, respectively. At 180 kg. per sq. cm. the ratio may increase to 10 or 12 between 40° and 50°. C_p for He at 50° does not vary with pressure over the range 10—120 kg. per sq. cm. L. S. T.

Temperatures of sublimation of twelve amino-acids. (MISS) J. W. BROWN (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 173—175).—When heated in vac. NH_2-acids begin to sublime at temp. (which are tabulated) about 50—165° below the m.p. The sublimates collected on microscope slides 4 mm. above the surface of the substance form characteristic crystals, photographs of which are given. J. W. S.

Electrical differential method for measuring C_v in gases. V. C_v for carbon dioxide. M. TRAUTZ and H. BLUM (Ann. Physik, 1933, [v], **16**, 362—375).—Modifications in the technique of measurement are described and the dependence of the measured C_v vals. on temp. and the initial heating current intensity were investigated. For CO_2 the vals. of C_v are 6·77, 6·79, and $6{\cdot}80\pm0{\cdot}02$ g.-cal. per mol. at 15·3, 18·0, and 19·0°, respectively. W. R. A.

Accurate determination of specific heats at high temperatures: the Neumann–Joule–Kopp–Regnault law concerning the additivity of the atomic heats of elements in chemical compounds. IV. F. M. JAEGER and J. A. BOTTEMA (Rec. trav. chim., 1933, **52**, 89—111).—The sp. heat of mixed crystals of Au and Ag is almost exactly equal to the sum of the at. heats of the elements, but this is not true for the compounds PtSn, AuSn, and $AuSb_2$, except in the case of γ-$AuSb_2$. The deviations, which usually increase with rise of temp. and sometimes exceed 60%, may be positive or negative and show no correlation with the vol. changes on compound formation. Determinations of the crystal structure of AuSn, PtSn, and γ-$AuSb_2$ (A., 1927, 815; 1928, 574, 1079) have been confirmed. $AuSb_2$ is trimorphous, transition temp. γ—β 355·2°, β—α 405°. Sb is dimorphous, transition temp. β—α 413°. The sp. heats of α- and β-$AuSb_2$ and α-Sb change rapidly with temp. D. R. D.

Heat capacity data for durene, pentamethylbenzene, stilbene, and dibenzyl. J. D. FERRY and S. B. THOMAS (J. Physical Chem., 1933, **37**, 253—255).—The sp. heats (in the solid and liquid states) and heats of fusion have been determined. E. S. H.

Calorimetric evidence for a term separation in gadolinium sulphate. N. KURTI and F. SIMON

(Naturwiss., 1933, **21**, 178—179).—Using the method of Simon *et al.* (A., 1930, 282), the determination of sp. heat at low temp. has been used as an indication of small term separations in $Gd_2(SO_4)_3$. The sp. heat decreases between 10° and 6° abs. as T^3, followed by a rapid rise, so that at 1·6° abs. the val. is 500 times normal. This gives 0·2° abs. as the characteristic temp. There is thus fairly complete equilibrium between all states at 1·3°. Neither susceptibility nor magneto-caloric effect shows any deviation from the Curie–Langevin law. Different results are, however, obtained if adiabatic demagnetisation of $Gd_2(SO_4)_3$ is used for the attainment of very low temp. By using strong fields it is possible to reach temp. below those obtainable with liquid He. A. J. M.

Physico-chemical measurements on hydrogen fluoride. K. FREDENHAGEN (Z. anorg. Chem., 1933, **210**, 210—224).—Densities of the saturated vapour have been determined between −78° and 19·5°, and of the unsaturated vapour at atm. pressure between 20° and 80°. Heat of vaporisation of 20 g. of liquid to saturated vapour is 1704·6 g.-cal. at 4·40° and 1751 at 15·76°. V.p. between 15° and 25° are given by $\log p = -1345·3/T$ (abs.) + 7·48. The association factor at the b.p. is 3·5, and has a max. 4·27 at −34°. The same degree of association obtains in the liquid phase. F. L. U.

Vapour pressures of BaO, SrO, CaO, and their mixtures from measurements of velocity of evaporation. A. CLAASSEN and C. F. VEENEMANS (Z. Physik, 1933, **80**, 342—351).—Formulæ are given relating the v.p. of the three oxides with temp., and observations for mixtures suggest that the three are completely miscible. A. B. D. C.

Vapour pressures of CF_4 and NF_3 and the triple point of CF_4. W. MENZEL and F. MOHRY (Z. anorg. Chem., 1933, **210**, 257—263).—CF_4 has b.p. $-128·0\pm0·1°$; NF_3 has b.p. $-129·0\pm0·3°$. The heats of vaporisation have been calc. Trouton's consts. are, respectively, 20·3 and 19·9. The triple point of CF_4 is $-183·6\pm0·2°$. E. S. H.

Vapour pressure of crystalline benzene and *cyclo*hexene. V. R. DEITZ (J. Amer. Chem. Soc., 1933, **55**, 472—475).—Data obtained by means of a modified Knudsen procedure for the range 165—200° abs. are recorded. J. G. A. G.

Value of for elements, in correlation with the periodic system. J. A. M. VAN LIEMPT (Rec. trav. chim., 1933, **52**, 123—128).—The following relationships hold approx. for homopolar compounds: $\alpha = 3·6r^5 \times 10^{-24}$, $R = 9·3r^5$, $\sqrt{a}/b$ lies between 30 and 50 (mean 38·5), p_c between 33 and 93 atm. (mean 55), and T_c between 0·7 and 2·0× ×10^5, where α=polarisability, r=at. or ionic radius in Å., R=mol. refractivity, and a and b are van der Waals consts. D. R. D.

Kinetic theory of liquids. R. O. HERZOG and H. C. KUDAR (Z. Physik, 1933, **80**, 217—231).—A kinetic hydrodynamic method is used to deduce the mean free path, the diffusion coeff., and the empirical viscosity formula of Batschinski. The results are applied to dipole-free liquids, to metals and salts. A heat of fluidity is introduced. A. B. D. C.

Viscosity of nitrobenzene. W. M. COX and J. H. WOLFENDEN (J.C.S., 1933, 118—119; cf. A., 1932, 329).—The previously recorded decrease in viscosity of $PhNO_2$ with time is shown to depend on the absorption of H_2O vapour, in the absence of which no change is observed. The viscosity is unaffected by thermal pretreatment, thus rendering improbable the existence of internal equilibria (cf. A., 1931, 148, 899). F. L. U.

Single crystals of the intermediate compound antimony–tin. H. S. VAN KLOOSTER and M. O. DEBACHER (Met. and Alloys, 1933, **4**, 23—24).—A single crystal of SbSn 5 cm. long was obtained by cooling the molten alloy from 480° to 300° in 15 hr. The compound has a simple cubic structure, 4 mols. in unit cell, a 3·061 Å.; d_{calc} 6·918; d^{20}_{obs} 6·9104+ 0·005. C. A. K.

Thermal and electrical conductivity of some magnesium alloys and their behaviour towards the Wiedemann–Franz law. R. KIKUCHI (Sci. Rep. Tohoku, 1932, **21**, 585—593).—The thermal (λ) and electrical (χ) conductivities of Mg and Fe are: Mg, $2·31\times10^5$, 0·382 at 18·1°; Fe, $0·96\times10^5$, 0·158 at 16·4°. The corresponding vals. for binary alloys of Mg with Ag, Al, Cu, Ni, Sn, and Zn, and for electron metal, Dow metal, and nichrome are also recorded. The addition of the second metal lowers both λ and χ in the case of Mg; the effect decreases in the order Al, Sn, Zn, Ag, Ni, Cu. The alloys show considerable deviations from the Wiedemann–Franz law. O. J. W.

Atomic arrangement and magnetic behaviour in the copper–gold, copper–palladium, and copper–platinum systems. H. J. SEEMANN (Z. Metallk., 1932, **24**, 299—301).—The diamagnetic susceptibility of the analogous phases Cu_3Au, Cu_3Pd, and Cu_3Pt increases when the at. arrangement becomes regular on annealing, whereas that of CuAu decreases. Compared with the susceptibilities of the alloys with random orientation of the atoms the changes are +20, +50, +25, and −20%, respectively. A. R. P.

Binary systems cobalt–tungsten and cobalt–molybdenum. W. KOSTER and W. TONN (Z. Metallk., 1932, **24**, 296—299).—The reactions have been investigated by dilatometric, magnetometric, and micrographic methods. The solubility of CoW in Co (*a*) falls from 39% at the eutectic temp. (1480°) to 14% at room temp., the transformation temp. of ε-Co into γ-Co is raised by addition of W to 1040° at 28·5% W (*b*), where it ends in the 3-phase reaction: γ+CoW — ε solid solution, and the magnetic transformation of Co at 1140° takes place at progressively lower temp. with addition of W until at 16% W (*c*) it merges into the γ change. Alloys in the miscibility gap between ε and CoW undergo a magnetic transformation at 825° (*d*). The Co–Mo system is similar, but the corresponding temp. and compositions are as follows: (*a*) 25% (1320°)—8% Mo (20°); (*b*) 20% Mo, 920°; (*c*) 10% Mo; (*d*) 750°. Quenching of Co alloys with > 14% W or > 8% Mo from the homogeneous γ-range followed by ageing at 800—900° results in an increase in hardness which exceeds 600 Brinell units with 28% Mo or 40% W. A. R. P.

X-Ray investigations of BaO–SrO mixtures when heated to redness. W. G. BURGERS (Z. Physik, 1933, **80**, 352—360).—Mixtures of $BaCO_3$ and $SrCO_3$ when heated to redness yield completely mixed BaO and SrO with a lattice const. which is a function of the mixture. Anomalies in the velocity of evaporation are due to the fact that the velocity of diffusion of the oxides into one another is < the velocity of evaporation of BaO. A. B. D. C.

Binary liquid systems and the mixture rule. W. MACFARLANE and R. WRIGHT (J.C.S., 1933, 114—118).—Various physical properties of mixtures of chemically similar liquids have been determined and plotted against the composition expressed as (*a*) wt.-, (*b*) vol.-, and (*c*) mol.-%. The results indicate that (*b*) should be used for density or refractive index, and (*c*) for surface tension. None of the three is satisfactory in the case of viscosity. F. L. U.

[Magnetic] susceptibility of mixtures of substances of high electric moment. J. E. GARSSEN (Compt. rend., 1933, **196**, 541—543).—The diamagnetic susceptibility of mixtures of $COMe_2$ with $PhNO_2$ and with p-$NH_2{\cdot}C_6H_4{\cdot}NO_2$ (I) is not a linear function of the concn., the deviation being approx. 12% for a 50 : 50 (mol.) mixture of $COMe_2$ and $PhNO_2$, and 11% for a 15 : 85 mixture of $COMe_2$ and (I), due possibly to changes in the degrees of association. C. A. S.

M.p. of mixtures of ethyl alcohol and ether. A. LALANDE (Compt. rend., 1933, **196**, 402—404; cf. this vol., 247).—M.p. of 21 mixtures of EtOH and Et_2O are given; the m.p. of EtOH, Et_2O, and of the eutectic (57·85 wt.-%) are respectively $-116{\cdot}3_2°$, $-114{\cdot}5_0°$, and $-125{\cdot}0_5°$. C. A. S.

Examination of binary liquid mixtures. W. A. WRIGHT (J. Physical Chem., 1933, **37**, 233—243).—Apparatus designed to give more complete data for the pressure–temp.–composition relations of binary liquid mixtures is described. Results are given for the system PhMe–EtOH over a wide range of pressure and temp. The data obtained permit the prediction of equilibrium conditions and the calculation of heats of vaporisation. E. S. H.

Binary systems of *m*-nitrotoluene and *p*-nitrotoluene with naphthalene, *p*-toluidine, and *o*-toluidine. H. D. CROCKFORD and N. L. SIMMONS, jun. (J. Physical Chem., 1933, **37**, 259).—The temp.–composition diagrams do not reveal the existence of compounds or solid solutions. The logarithm of the mol. fraction of solvent varies linearly with the reciprocal of abs. temp., showing that the systems are ideal. The calc. heats of fusion, eutectic temp., and eutectic compositions are given. E. S. H.

F.p.–solubility relations of geometrical isomerides. II. Dynamic isomerism of the anisaldoximes. E. L. SKAU and B. SAXTON (J. Physical Chem., 1933, **37**, 197—207; cf. A., 1928, 1328).—The f.p.–composition diagram for *cis*- and *trans*-anisaldoxime is described, and has been adapted to the analysis of unknown mixtures. Either form, when heated at or above 100°, undergoes a reaction involving the formation of a *compound*, which has been isolated, but not identified. The "natural f.p." of the simple binary system is $58{\cdot}4\pm0{\cdot}2°$, corresponding with 12·3% of the *cis*-form. The equilibrium composition does not vary perceptibly with temp. up to 90°. E. S. H.

Errors inherent in the usual determination of the binary f.-p. diagram. E. L. SKAU and B. SAXTON (J. Physical Chem., 1933, **37**, 183—196).—When the f.p.–composition diagram for the system β-chlorocrotonic acid–β-chloro*iso*crotonic acid (constructed without correcting for the amount of solid crystallising) is compared with accurate data, it is shown that the errors involved cause a shift of the observed eutectic along the temp. and composition axes. In some cases false indications of compound formation may be given. Cooling curves have shown that it is possible to follow a branch of the temp.–composition diagram to temp. below the eutectic. The causes of increased errors near the eutectic point are discussed. E. S. H.

Binary azeotropic mixtures. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1933, **13**, 16—19).—A classification of azeotropic mixtures is given. R. T.

Systems of four immiscible liquid layers. E. L. SMITH (Nature, 1933, **131**, 167).—Mainly a reply to criticism (cf. this vol., 120). The system previously described (A., 1931, 159) plus Hg still separates into five layers even after repeated shaking during a period of 2 years. L. S. T.

Solubility of potassium ferrocyanide. E. FABRIS (Gazzetta, 1932, **62**, 909—912).—Data are given for temp. between 70° and 87·3° (the transition temp.) and for the stable and metastable forms at temp. up to 104° and 95·5°, respectively. H. F. G.

Solubility. IV. Solubilities of slightly soluble organic compounds in water. P. M. GROSS, J. H. SAYLOR, and M. A. GORMAN (J. Amer. Chem. Soc., 1933, **55**, 650—652).—Data for 16 compounds at 30° are recorded. J. G. A. G.

Solubility of nitrates in anhydrous acetic acid. A. W. DAVIDSON and H. A. GEER (J. Amer. Chem. Soc., 1933, **55**, 642—649).—The data refer to the nitrates of Ag, Na, NH_4, and Ba in the range 16·45—167·5°. The NH_4NO_3 solutions deviate widely from Raoult's law. J. G. A. G.

Effect of lecithin and sodium chloride on the solubility of fatty acids in salts of bile acids. O. FURTH and R. SCHOLL (Biochem. Z., 1933, **257**, 151—159; cf. A., 1930, 1212; 1931, 1084; 1932, 871).—The solubility of oleic or linoleic acid in solutions of bile acids is increased by lecithin (from eggs, brain, or liver) and by small amounts of NaCl, KCl, or Na_2SO_4. Much NaCl causes pptn. 100 c.c. of a 5% Na taurocholate solution dissolve 4·5 g. of oleic acid if 0·8% of lecithin and 0·9% of NaCl are present. W. McC.

Optical antipodes and velocity of crystallisation: non-existence of racemic form in liquid state. G. RUMEAU (Compt. rend., 1933, **196**, 410—412; cf. A., 1932, 22).—The velocity of crystallisation (v) at 28° of the α_1-form [apparently α_2 of the previous paper] of d-Me_2 tartrate has been raised by purification from 3·20 to 3·95 (1·05 at 33°), that of the

β-form [apparently α_1 of previous paper] at 33° to 0·35 mm. per min. The effects on v of additions of various substances have been examined, those for H_2O and l-Me_2 tartrate explaining the difficulty of obtaining concordant results, since heat causes partial racemisation and the esters are very hygroscopic. d-, l-, and r-Me_2 tartrates and l- and r-malic acids have respectively identical effects on v of Me_3 citrate, indicating that racemates do not exist in the liquid state. Variation of v with time after addition of a foreign substance is a delicate method of detecting chemical action. C. A. S.

Influence of X-rays on formation of crystal nuclei. D. SAMUICAS (Compt. rend., 1933, **196**, 418—420).—Supersaturated solutions of S and P in CS_2 and fused betol and santonin, when rapidly cooled, produce crystal nuclei in much greater no. (3—7 times), and much more rapidly (about 1/15th the time), when irradiated with X-rays ($K\alpha$ and $K\beta$ of Fe) than when not so irradiated. C. A. S.

Rhythmic precipitates. T. ISEMURA (Bull. Chem. Soc. Japan, 1933, **8**, 11—14).—Optimum conditions are described for the formation of rhythmic ppts. of CaC_2O_4, SrC_2O_4, $Cu(OH)_2$, and $PbCrO_4$ in SiO_2 gel, and of Ag_2CrO_4 in gelatin. J. W. S.

Periodic precipitation of ferrous carbonate. R. J. HARTMAN, E. W. CANNING, and F. J. GALLION (J. Physical Chem., 1933, **37**, 229—232).—Conditions favouring the formation of periodic structures of $FeCO_3$ have been elucidated. The bands are formed readily in SiO_2 gels prepared by bubbling CO_2 through aq. Na_2SiO_3, but only with difficulty in gelatin gels, using a salt of Fe" as diffusing agent. The results support the theory advanced to explain the formation of geological deposits (cf. A., 1932, 596). E. S. H.

Action of radiations on Liesegang rings. T. KOFMAN (J. Chim. phys., 1932, **29**, 586—598).—Neither radiations from Ra nor X-rays affect the formation of Liesegang rings. The influence of ultraviolet light and mitogenetic rays (from onion) is described and discussed. A. S. C. L.

Liesegang rings. E. S. HEDGES (Nature, 1933, **131**, 169).—A reply to criticism (this vol., 122). L. S. T.

Adsorption from the gas phase by solid adsorbents. F. KLEIN (Metallbörse, 1932, **22**, 1021—1022, 1085—1086, 1118—1119, 1182—1183, 1277—1278; Chem. Zentr., 1932, ii, 3374).—A review. A. A. E.

Influence of temperature and pressure on the adsorption of hydrogen by nickel. I. J. SMITTENBERG (Rec. trav. chim., 1933, **52**, 112—122).—Isotherms, isobars, and velocity curves are given for 15—300° and 10—760 mm. D. R. D.

Adsorption and amount of adsorbent. I. A. RABINERSON (Kolloid-Z., 1933, **62**, 157—162).—The amount of adsorbed Ba" or Ca", x, varies with the amount of adsorbent (Na- or H-kaolin, Na-permutite), m, in accordance with $x=Km^{1/n}$, where K and n are consts. The dependence of sp. adsorption, X, on m is given by $X/m=Km^{1/p}$, where $p=-n$. Kroeker's equation is applicable as a first approximation to exchange adsorption. An anomalous rise in the curve connecting X/m with m occurs in the system Na-kaolin+$BaCl_2$, but not in H-kaolin+$BaCl_2$. The anomaly is attributed to a diminution of H_2O adsorption by Ba" exchange and to coagulation of small amounts of kaolin by excess of Ba". E. S. H.

Adsorption measurements with streaming gases. H. REMY [with W. HENE] (Kolloid-Z., 1933, **62**, 154—157).—The results differ from those reported for the same adsorbent C, using a static method of measurement (cf. this vol., 120). The ratio of the adsorbabilities of SO_2 and CO_2 is also different. The discordance may be due to different H_2O contents of the C. E. S. H.

Specific surface and adsorbent properties of lead sulphate. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1933, **55**, 851; cf. A., 1922, ii, 618, 619).—The constancy of the sp. surface shows that $PbSO_4$ adsorbs neither Pb" from dil. $Pb(NO_3)_2$ solution nor SO_4" from dil. Na_2SO_4 solutions. Since $PbSO_4$ adsorbs only dye ions from solutions of the Na salt of ponceau-4R, it would seem that SO_4" ions on the surface are replaced by ponceau ions. J. G. A. G.

Sorption of gases, vapours, and mists. H. REMY (Angew. Chem. 1933, **46**, 101—104).—The amount of the solid phase removed from a NH_4Cl mist by $CaCl_2$ and cotton-wool may be calc. additively from the results obtained with the two absorbents separately. The relation between the vols. V_1 and V_2 of two gases adsorbed by a given material at temp. T_1 and T_2 such that in the liquid state the two substances have the same v.p., is given by $V_1=V_2+10^{(T_1-T_2)/a}-1$, where a is a const.; if T_1 and T_2 do not differ greatly, $V_1=V_2$. Adsorption from a stream of gas is considerably less than from stationary gas. The total quantity of gas adsorbed from a binary mixture is approx. equal to the mean of the quantities of each adsorbed at the pressure of the mixture, especially if the adsorbent possesses approx. the same power of adsorption for the two gases; it is not directly related to the partial pressures of the components. H. F. G.

Adsorption of nitrophenol and iodine on calcium fluoride films. J. H. DE BOER (Z. physikal. Chem., 1933, **B**, **20**, 11—16; cf. A., 1932, 689).—A CaF_2 film can take up as many p-nitrophenol mols. as I atoms. It seems certain that I cannot form a multimol. adsorbed layer, but such a layer may perhaps be formed with nitrophenol. R. C.

Inner adsorption in crystal salts. V. D. BALAREV (Kolloid-Beih., 1933, **37**, 180—214; cf. A., 1932, 332).—A review of published work on numerous aspects of crystal growth supports the author's theory. E. S. H.

Extension of phase rule for adsorption under equilibrium and non-equilibrium conditions. I. LANGMUIR (J. Chem. Physics, 1933, **1**, 3—12).—A surface phase rule is based on the postulate that all the intrinsic properties of a surface phase possess $C+E+1$ degrees of freedom, even under non-equilibrium conditions (C=no. of components in surface phase, E=degree of freedom corresponding with an inde-

pendently variable external electric force). When the val. of these variables is chosen, all other properties such as contact potential, rates of evaporation, surface spreading force, etc. are fixed. A condition of validity is mobility of the atoms in a surface phase. The rule holds for transient states only when their duration is large compared with the time of relaxation of surface mobility. A no. of cases are discussed and illustrated by experiments with Cs on W filaments. F. L. U.

Application of the Gibbs adsorption theorem to solid–liquid interfaces. F. E. BARTELL, F. L. MILLER, and E. G. ALMY (J. Amer. Chem. Soc., 1933, **55**, 466—471; cf. A., 1929, 999).—Adhesion tensions against SiO_2 and interfacial tensions against H_2O have been determined for binary mixtures of Et_2CO_3 (I) with C_6H_6 (II), 1-$C_{10}H_7Br$ (III), and $NPhMe_2$ (IV). The adsorption of (I) from the solute decreases in the order (II), (III), and (IV), both for H_2O and SiO_2 interfaces, and the calc. areas of the adsorbed mols. of (I) for the six cases are concordant. J. G. A. G.

Chemical action of electrolytes in changing surface energy at the boundaries: metal–mineral oil–aqueous salt solution. I. M. S. GOLOMBIK, D. S. LEV, and N. N. PETIN (J. Gen. Chem. Russ., 1932, **2**, 880—888).—Mineral oil is best removed from metal surfaces by immersion in solutions of phosphates, with the addition of alkali or of Na silicates; the process is accelerated by agitation, increase in concn. of salts, and higher temp. No close parallelism is observed between depression of surface tension at the boundary oil–water, and degreasing action. The facility of removal of oil diminishes with its duration of contact with the metal surface. R. T.

Adhesion forces brought into play in freezing. A. SELLERIO (Physikal. Z., 1933, **34**, 180—181).—Three methods for measuring the adhesive force between a metal surface and ice are described. The variation of the adhesive force with temp. has been measured for S on Al. A. J. M.

Permeability of quartz and Pyrex and other glass to helium. J. C. MCLENNAN and J. O. WILHELM (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 119—122).—Comparative experiments with a series of discharge tubes show that the permeability is in the order quartz>Pyrex glass>soft glass. The rate of transmission is not increased at low temp. J. W. S.

Kinetics of penetration. V. Kinetics of a model as related to the steady state. W. J. V. OSTERHOUT (J. Gen. Physiol., 1933, **16**, 529—557).—In a system consisting of (*A*), aq. solution of K guaiacoxide, (*B*), a non-aq. layer containing 70% guaiacol and 30% *p*-cresol, and (*C*), an aq. layer through which CO_2 is bubbled (A., 1932, 1180) K moves from (*A*) through (*B*) to (*C*), and this is followed by migration of H_2O in the same direction. Quant. observations with regard to (*C*) and its K content made while all three layers were effectively stirred fit a formula obtained on the assumption that two distinct processes are proceeding. The first is the entry of K into (*C*), the vol. remaining unchanged, the second is the entry of H_2O into (*C*) in consequence of the high osmotic pressure resulting from the increased concn. of K, and both processes are assumed to follow exponential laws. W. O. K.

Electro-osmosis and electrophoresis. II. N. SCHONFELDT (Z. Elektrochem., 1933, **39**, 103—116).—A review and bibliography. D. R. D.

History of modern solution theories and the theory of adhesion pressure. J. TRAUBE (Kolloid-Beih., 1933, **37**, 119—153).—Theories of solution are criticised. The adhesion pressure theory attributes osmotic pressure to the different adhesion intensities of the solute mols. from those of the solvent. This view is discussed in relation to interfacial tension, solubility, colloidal behaviour, adsorption and distribution, electro-potential, and mol. vol. The conclusions reached are applied to biological problems, especially permeability, narcosis, and the sp. effects of ions. E. S. H.

Cryoscopy of paraldehyde, acetone, and ether in solutions of ammonium and magnesium sulphates. F. BOURION and (MLLE.) O. HUN (Compt. rend., 1933, **196**, 480—482; cf. this vol., 223).—Further f.-p. data are recorded; paraldehyde depolymerises with increased dilution. C. A. S.

Cryoscopic studies on the transition points of the compounds of organic solvents with salts. II. H. OOSAKA (Sci. Rep. Tokyo Bunrika Daigaku, 1933, **A**, **1**, 241—249).—The lowering of the transition point of NaI,3MeOH (I) by addition of NHPhAc, BzOH, $COMe_2$, camphor, $PhNO_2$, and H_2O has been investigated, the mean val. for the mol. depression being 20·0 for polar and 18·3 for non-polar compounds. This is attributed to the difference in the influence of polarity of the solute on the activity of the alcohol. The heat of fusion of (I) calc. from the cryoscopic const. is 7276 g.-cal. per mol. or 29·6 g.-cal. per g. J. W. S.

Diffusion of electrolytes. R. J. DAVIES (Phil. Mag., 1933, [vii], **15**, 489—511).—Diffusion coeffs. of $MgSO_4$ and $CdSO_4$, determined by measuring n (cf. A., 1924, ii, 523), show min. vals. at 1·4N and 1·8N, respectively, attributed to complex ion formation. The results indicate ionic solvation. H. J. E.

Equation relating density and concentration. W. C. ROOT (J. Amer. Chem. Soc., 1933, **55**, 850—851).—The equation $D=D_0+c_1N+c_2N^{3/2}$, where c_1 and c_2 are additive consts., D_0 is the density of H_2O, and N the normality of the solution, holds for solutions of alkali and alkaline-earth halides up to 10N, and for H_2SO_4 up to 25N. J. G. A. G.

Viscosity of aqueous solutions as a function of concentration. G. JONES and S. K. TALLEY (J. Amer. Chem. Soc., 1933, **55**, 624—642).—Full details are given for determining to within 0·01 sec. the time of flow of the liquid in a viscosimeter of the Ostwald type by means of a photo-electric cell. Viscosities of 0·0002—0·2M aq. solutions of $KClO_3$, KCl, KNO_3, $KBrO_3$, $CsNO_3$, NH_4Cl, sucrose, and $CO(NH_2)_2$ have been determined at 25°. The results are in agreement with the Jones and Dole equation (A., 1929, 1385) for the viscosity of solutions of electrolytes, and confirm the prediction that all salts increase the viscosity of

H_2O if measured at sufficiently low concn., including those salts which give a diminishing viscosity at moderate concn. The theoretically predicted absence of the square-root term in the equation for non-electrolytes is confirmed for sucrose and $CO(NH_2)_2$. J. G. A. G.

Determination of mass of electrolytic ions. P. DEBYE (J. Chem. Physics, 1933, **1**, 13—16).—The dynamical reactions due to the masses of electrolytic ions when subjected to periodic acceleration are calc. They may be expected to give rise to electric oscillations of the order 10^{-6} volt under suitable experimental conditions. F. L. U.

Solvation. Determination of radii of ions in solution. R. FLATT and A. JORDAN (Helv. Chim. Acta, 1933, **16**, 37—53).—An expression which takes account of the charge and size of the ions, and of the dielectric const. of the solvent, has been deduced for the relative solubilities of a completely ionised binary electrolyte in different solvents. Measurement of the solubilities of $CsClO_4$, $RbClO_4$, $KClO_4$, KCl, NaCl, and $NaBr,2H_2O$ in H_2O and aq. EtOH, in conjunction with this expression, indicate that all the ions in question, excepting $Na^{\cdot}$, have the same radius in solution as in the cryst. salts. It is therefore concluded that they are not hydrated. F. L. U.

Exceptional tendency of the sodium ion to form hydrates, and its significance in the theory of combination of water of crystallisation. M. A. RAKUSIN (Ukrain. Chem. J., 1932, **7**, [Sci.], 65—74).—A discussion. R. T.

Investigation of influence of solute on solvent by means of infra-red absorption spectrum. I. Effect of dissolved salts on state of association of solvent water. R. SUHRMANN and F. BREYER (Z. physikal. Chem., 1933, **B**, **20**, 17—53; cf. A., 1931, 1211).—In presence of alkali halides and various other salts which do not absorb in the short infra-red the absorption bands of H_2O in this region become steeper and are displaced towards shorter waves. Both cations and anions contribute to this effect, which in general increases with the ionic radius, and is to be ascribed to depolymerisation of the H_2O mols. Ionic hydration, however, superimposes on the displacement of the bands towards shorter waves a displacement in the opposite direction, the influence of the cation in this connexion usually preponderating over that of the anion. $MgCl_2$ and some other salts cause a flattening of the H_2O bands, which is attributed to chemical effects. The relations between depolymerisation effects, as revealed by spectroscopy, hydration pressure, contraction of the H_2O in the solution, and chemical influences of solute on solvent, are surveyed. R. C.

Absorption of light by aliphatic carboxylic and amino-acids in presence of neutral salts. F. LEUTHARDT [with M. PFISTER] (Helv. Chim. Acta, 1933, **16**, 228—232; cf. A., 1932, 573).—The absorption curve of AcOH is unaffected by the addition of neutral salts, but that of the Na or K salts of AcOH, $CH_2Cl{\cdot}CO_2H$, $CCl_3{\cdot}CO_2H$, and $PrCO_2H$ is displaced towards shorter wave-lengths by addition of $MgCl_2$. The effect is considered to be due to attachment of $Mg^{\cdot\cdot}$ to the $\cdot CO_2'$ group. F. L. U.

Is hydrotropy a special property of organic salts? F. V. VON HAHN (Kolloid-Z., 1933, **62**, 202—207).—The so-called hydrotropic salts show no essential difference from alcohols, aldehydes, acids, etc. in their influence on the solubility of sparingly sol. substances. E. S. H.

Colloidal sulphur. O. VON DEINES (Kolloid-Z., 1933, **62**, 145—151).—The systems obtained by acidifying solutions of $Na_2S_2O_3$ etc. or by interaction of H_2S and H_2SO_3 consist of solutions of S in highly dispersed persulphides of H. True sols of S are obtained by dispersion methods or by pouring an EtOH solution of S into H_2O. E. S. H.

Highly concentrated fluoride sols. W. BACHMANN and P. PINNOW (Kolloid-Z., 1933, **62**, 131—145).—The prep. of conc. sols of CaF_2, with or without the presence of MgF_2, is described. The viscosity of these sols decreases slightly at first during dialysis, but at a later stage increases strongly; addition of HCl produces a rapid fall in viscosity. Thixotropy is highly developed. The particles are positively charged, and their mobility and size have been determined by several methods. The coagulating influence of univalent anions is small; that of bivalent anions is greater, but the Schulze–Hardy rule is not followed strictly. E. S. H.

Active oxides. LX. Dispersoid analysis of precipitates of zinc oxalate dihydrate prepared in different ways. G. F. HUTTIG and E. HERRMANN (Kolloid-Z., 1933, **62**, 151—153; A., 1932, 1211).—Sedimentation analysis of ppts. of $ZnC_2O_4,2H_2O$ prepared under different conditions shows that small particles are favoured by low pptn. temp. and rapid mixing. With slow pptn. at high temp. or rapid pptn. at low temp. the particles of ppt. produced from $Zn(NO_3)_2$ are smaller than those from $ZnCl_2$. E. S. H.

Mol. wt., viscosity, and conductivity of hydrous silicic acid. W. D. TREADWELL and W. KONIG (Helv. Chim. Acta, 1933, **16**, 54—69; cf. A., 1930, 1537).—The f.-p. depression, viscosity, and electrical conductivity of purified sols of SiO_2 have been measured at various ages of the sol. From the results it is inferred that gelatinisation begins with polymerisation of simple mols. accompanied by a decrease in the no. of free H ions, the polymerised mols. afterwards coagulating to form a network which immobilises the whole of the liquid. F. L. U.

Emulsion systems containing phenols, water, and gelatin. R. M. WOODMAN (J.S.C.I., 1933, **52**, 44—46T).—Aq. solutions of gelatin yield dual emulsions with phenols and hydrogenated phenols. The mechanics of dual emulsion formation are discussed.

Dispersion of Hertz waves in solvated colloids. J. ERRERA (J. Chim. phys., 1932, **29**, 577—585).—The time of relaxation is discussed in relation to the orientation of dipoles. Dielectric consts. have been measured with wave-lengths from 2 to 30,000 m. Results are given for several colloids with λ 2—30 m. A. S. C. L.

Optical anomalies and fine structure. Double refraction of paracrystalline (especially organic), colloidal materials. Shrinkage effects in albu-

min. F. RINNE (Kolloid-Z., 1933, **62**, 216—226).—A review of published work. E. S. H.

Diffusion of colloidal electrolytes; sodium oleate. M. E. L. MCBAIN (J. Amer. Chem. Soc., 1933, **55**, 545—551; cf. A., 1931, 301).—The diffusion coeffs. of Na oleate (0·025—0·5*N*) through a sintered glass membrane into 0·0015*N*-NaOH at 20° and 25° are < those of K laurate, although the primary particles of the latter are only slightly smaller. The viscosity and gelatinising power of Na oleate are due to loose linking of primary particles, and this does not appreciably affect the rate of diffusion. J. G. A. G.

Method of separating different disperse systems by cataphoresis. H. BENNHOLD (Kolloid-Z., 1933, **62**, 129—131).—Apparatus and technique are described, and examples of application to hydrophilic colloids are given. E. S. H.

Cataphoresis. Improved cylindrical cell. S. MATTSON (J. Physical Chem., 1933, **37**, 223—227).—Modifications are described (cf. A., 1928, 1323). E. S. H.

Electrokinetic phenomena. X. Electric mobility and charge of proteins in alcohol–water mixtures. J. DANIEL (J. Gen. Physiol., 1933, **16**, 457—474).—The electrophoretic mobility of quartz particles covered with a film of gelatin, ovalbumin, or gliadin in EtOH–H_2O mixtures (up to 60%) is independent of the field strength. The mobility of gelatin-covered quartz particles in EtOH–H_2O mixtures is independent of size and shape, and is equal to the electro-osmotic mobility of the same EtOH–H_2O mixture in contact with protein-covered quartz surfaces. The electrophoretic mobility corrected for viscosity, and hence the charge, of gelatin-covered quartz particles, in 35% and 60% EtOH is proportional to the combining power of the gelatin. In aq. EtOH (up to 35%), the charge calc. by means of the Debye–Henry approximation employing the dielectric const. and the viscosity of the medium in bulk is, in the neighbourhood of the isoelectric point, proportional to the combining power of the gelatin. Hence the bulk, dielectric const., and viscosity may be employed in the application of the Debye–Henry equation. In presence of aq. EtOH, the isoelectric point of gelatin is shifted to a higher p_H val., the shift being approx. proportional to the change in the dielectric const. of the medium. W. O. K.

Electrochemical investigations on gum arabic sol. W. PAULI and E. RIPPER (Kolloid-Z., 1933, **62**, 162—175).—Potentiometric and conductometric measurements have been made on highly-purified sols of gum arabic and gum tragacanth, and the effect of adding electrolytes has been studied. In the pure acidoid sols the conductivity calc. from $H^·$ activity is much greater than the obs. conductivity. Activities of the compounds of the sols with $Ag^·$ have been determined. With rising temp. the conductivity of the acidoid sols passes through a max., whilst a linear relation is observed in neutral sols. E. S. H.

p_H of gelatin solutions. J. G. MALONE and M. G. MALONE (J. Physical Chem., 1933, **37**, 219—221).—The electrometric method is preferred to the colorimetric method (cf. A., 1932, 700). E. S. H.

Absorption and scattering of light by gelatin. J. H. F. CUSTER, J. H. DE BOER, and C. J. DIPPEL (Rec. trav. chim., 1933, **52**, 195—213).—The true absorption coeff., k, of isoelectric gelatin sols at 40° is independent of the concn., but the scattering coeff., σ, falls with increase in concn. For gels at room temp., k and σ both fall with increasing concn. The sols and gels have similar but not identical absorption spectra. Dil. sols when cooled to room temp. give spectra of the gel type and show increased scattering. These results support the view that gelatin exists in two forms, an *A*-form stable at high temp. and a *B*-form stable at low temp.; gelation occurs only with the latter (cf. A., 1919, i, 179; this vol., 125). At 40°, k is independent of p_H between 2·5 and 8·6, whereas σ passes through a max. at the isoelectric point. When $p_H > 8·6$, k varies with p_H, but the change to the *B*-form still occurs on cooling. The isoelectric point, which is the same for both *A*- and *B*-forms, corresponds with min. optical rotation of the former and max. rotation of the latter. D. R. D.

Structural viscosity in some lyophilic sols. I. Flocculation of gelatin and casein by agar. II. Rubber sols. W. GALLAY (Canad. J. Res., 1932, **7**, 662—670, 671—676).—I. Comparative measurements have been made of the viscosities of mixtures of 0·2% agar and 1% gelatin sols at varying pressures, using the overflow viscosimeter. Wide deviations from Poiseuille's law occur, structure effects and turbulence effects being in evidence at low and high rates of flow, respectively. A min. viscosity is observed for 20—40% agar sol, indicating a dehydrating effect of the agar on the gelatin. In a corresponding series with 0·25% agar and 2% basic casein sol this effect is masked by the greater difference in relative viscosity. Structural turbulence is observed in the structure region. The velocity of flow and pressure are related by a parabolic equation.

II. Relative viscosities of sols of natural and purified rubber of different concn. in C_6H_6 have been measured at varying pressures. The limiting concns. above which structure is evident are in agreement with those calc. theoretically by Staudinger (A., 1932, 619). Regions of structure and turbulence are observed at all concns. Exposure to ultra-violet light lowers considerably the viscosity of a purified rubber sol. J. W. S.

Lyophilic colloids. XVII. Influence of neutral salts on gelatin sols. H. R. KRUYT and H. P. GALEMA (Kolloid-Beih., 1933, **37**, 154—179; cf. A., 1929, 1381).—The viscosity of gelatin sols is influenced by all the ions investigated, which differ in effect from $H^·$ and OH' only quantitatively. The usual influence of valency is observed, suggesting a capillary-electric process. Some peculiarities noted with starch sols (cf. A., 1932, 1087) are also observed. Differences in viscosity under isoelectric conditions are attributed to ion hydration of the bound electrolyte. This explanation is supported by EtOH-pptn. experiments. E. S. H.

Intermicellar combination and hydration in gelatin gels. J. H. DE BOER and C. J. DIPPEL (Rec.

trav. chim., 1933, **52**, 214—224).—When a gelatin gel is kept for some time at 25° an elevation of the apparent m.p. is observed. This is related to changes in the viscosity of gelatin sols (A., 1903, ii, 721; 1915, ii, 752), but not to the transformation from *B*- to *A*-gelatin (see this vol., 349). An electrostatic explanation is offered of the swelling, gelatinisation, etc. of gelatin. D. R. D.

Change of solvation medium in gelatin sols. A. SARLUY (Kolloid-Z., 1933, **62**, 176—180).—The relative viscosities of gelatin sols in PhOH–H_2O mixtures have been determined at 70°. As the amount of PhOH is increased the viscosity falls, remains steady up to about 25%, and then rises sharply; the viscosity in anhyd. PhOH is very high. The high viscosities at extreme compositions are attributed to solvation by PhOH or H_2O, whilst coacervation occurs in the intermediate region. E. S. H.

Complex coacervation. XIV. Autocomplex flocculation of sodium nucleate (yeast) sols. H. G. B. DE JONG and F. A. MENALDA (Biochem. Z., 1933, **257**, 62—77).—A study of the flocculation produced by 6-, 3-, and 2-valent cations. H. W. D.

Complete growth functions, particularly photographic. L. HAMBURGER (Chem. Weekblad, 1933, **30**, 115—138).—A discussion of growth phenomena in colloidal systems, with special reference to the similarity between animate and inanimate systems. A general equation is developed for both individual and collective growth, in which various well-known laws are embodied as special cases. The case of the photographic plate is considered at length, as regards both the growth of the separate nuclei and the increase of the no. of nuclei. H. F. G.

Thixotropic viscosity of cellulose esters. S. A. GLIKMAN (Plast. Massi, 1932, No. 2—4, 16—23).—The phenomenon is observed with sols approaching gelatinisation and is attributed to the disturbance, by mechanical action, of the orientation of the mols. of the solvent by the vectorial forces of the field produced by mols. of the disperse phase. T. H. P.

Structure of cellulose gel. IV. Mechanism of sorption of vapours by cellulose gels. K. ATSUKI, H. SOBUE, and K. KITAJIMA (J. Soc. Chem. Ind. Japan, 1932, **35**, 584—587B).—A study of the mechanism of the sorption by normal and hydrated celluloses of vapours of H_2O, alcohols, ketones, esters, ethers, and acids. Sorption and saturated v.p. run parallel. The sorption of vapours by cellulose is due to sorption and swelling; the former is governed by v.p., surface tension, and density, the latter by the polarity of the OH groups and bridge O in the cellulose mol. V. E. Y.

Radiographical introduction to the cellulose symposium [Delft, May, 1932]. J. R. KATZ (Chem. Weekblad, 1933, **30**, 26—44).—A review of the theory and practice of the *X*-ray method of investigating the structure of cellulose, and of the results obtained, with an extensive bibliography. H. F. G.

Cellulose from the viewpoint of colloid chemistry. H. R. KRUYT (Chem. Weekblad, 1933, **30**, 24—26).—A discussion of the nature of cellulose, particularly in the light of the behaviour of such materials as stannic acid. H. F. G.

Thermal equilibrium between oxygen molecules and atoms. G. VON ELBE and B. LEWIS (J. Amer. Chem. Soc., 1933, **55**, 507—511; cf. this vol., 229).—Vals. of the equilibrium const. of the reaction $2O \rightleftharpoons O_2$ and the degree of dissociation at 1 atm. in the range 1400—5000° abs. have been evaluated from optical and sp. heat data. At the higher temp. the contribution to the sp. heat of mol. O_2 in the $^1\Delta$ state becomes significant. J. G. A. G.

Deacon equilibrium and the entropy of chlorine. A. R. GORDON and C. BARNES (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 171).—See A., 1932, 997. J. W. S.

Chemical equilibria of reactions between hydrocarbons. IV. A. A. VEDENSKI (J. Gen. Chem. Russ., 1932, **2**, 826—828).—The v.p. of methyl*cyclo*hexane is given by $\log P = -1460/T + 1{\cdot}75 \log T + 0{\cdot}0011T + 1{\cdot}7040$, where T is the abs. temp. The vals. of P for PhEt found by Woringer (A., 1900, ii, 709) are confirmed. R. T.

Dissociation constant of acetic acid from 0° to 60°. H. S. HARNED and R. W. EHLERS (J. Amer. Chem. Soc., 1933, **55**, 652—656; cf. A., 1932, 695).—An extension of previous work. The dissociation const., K, is given by $\log K = -1500{\cdot}65/T - 6{\cdot}50923 \log T - 0{\cdot}0076792T^2 + 18{\cdot}67257$ and the heat of dissociation, ΔH, by $\Delta H = 6871{\cdot}0 - 12{\cdot}9436T - 0{\cdot}035161T^2$. J. G. A. G.

Equilibrium between lactic and pyruvic acids. R. WURMSER and (MME.) N. MAYER-REICH (Compt. rend., 1933, **196**, 612—614; cf. A., 1932, 809).—More detailed investigation shows that the normal potential of the system $OH{\cdot}CHMe{\cdot}CO_2' \rightleftharpoons AcCO_2' + H_2$ at 37° is −0·196 volt at p_H 7·3 and +0·252 volt at p_H 0, whence $\Delta F = +11{,}600 \pm 100$ g.-cal., or 58% of the heat of reaction at const. pressure (+20,000 g.-cal.). C. A. S.

Hydrolysis of acetonesemicarbazone. J. E. W. RHODES (J.C.S., 1933, 204—208).—Partial pressures of $COMe_2$–H_2O mixtures have been measured by a transpiration method. Henry's law is not obeyed over the range 0·16—76·6 g. per litre at 30° and 50°. From the partial pressure of $COMe_2$ over aq. solutions of acetonesemicarbazone the degree of hydrolysis has been calc. The val. of the hydrolysis const. is 0·00398 at 30·8° and 0·00974 at 49·7°, whence the heat of reaction is calc. to be 9179 g.-cal. F. L. U.

Equilibrium constants in terms of activities derived from cryoscopic data: dissociation of pyridine *o*-chlorophenoxide in benzene. H. M. GLASS and W. M. MADGIN (J.C.S., 1933, 193—198).—The equilibrium const. for this dissociation (AB ⇌ A+B), when calc. with activities instead of concns., shows remarkable consistency, whereas vals. of [AB]/[A][B] are widely divergent. Determinations were made at different concns. The activities were derived from independent cryoscopic measurements. F. L. U.

Rapid derivation of thermodynamic relations. A. N. Shaw (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 187—204).—Theoretical. J. W. S.

Equations for the application of the law of homogeneous chemical equilibrium. E. Denina (J. Chim. phys., 1933, **30**, 47—55).—Theoretical. N. M. B.

Internal effect in thermodynamic transformations. V. Njegovan (Arh. Hemiju, 1933, **7**, 23—29; cf. A., 1932, 1206).—Mathematical. A modification of the Clausius-Clapeyron and Helmholtz equations explains certain apparent anomalies in the Nernst theorem. N. M. B.

Higher-valency ions and activity. II. Theoretical discussion on the basis of the Poisson-Boltzmann equation. J. B. Chloupek, V. Z. Daneš, and B. A. Danešova (Coll. Czech. Chem. Comm., 1933, **5**, 21—35).—The solubility data (this vol., 26) for $Ce(IO_3)_3$ in aq. solutions of various salts cannot be represented quantitatively by any of the existing theories. M. S. B.

Debye-Huckel ion size parameter in terms of individual ionic radii. Activity coefficient of lead chloride in solutions of cadmium nitrate. H. D. Crockford and H. C. Thomas (J. Amer. Chem. Soc., 1933, **55**, 568—574).—The e.m.f. of the cell Pb-Hg|0·002—0·016*M*-$PbCl_2$, 0·002—0·017*M*-$Cd(NO_3)_2$|AgCl-Ag, with $[PbCl_2]/[Cd(NO_3)_2]$ const., has been determined at 25°. The vals. of the activity coeff. of $PbCl_2$ in $Cd(NO_3)_2$ solutions are consistent with the mean distance of closest approach of ions in dilute solutions of strong electrolytes derived mathematically as a function of quantities which depend on the valency types of the dissolved compounds and the size of individual ions. J. G. A. G.

Reaction between osmium tetroxide and hydrobromic acid. I. Equilibrium. H. D. Kirschman and W. R. Crowell (J. Amer. Chem. Soc., 1933, **55**, 488—495).—When the concns. are expressed in mols. per 1000 g. H_2O the val. of $[Os^{VII}][Br_3']^{\frac{1}{2}}/[Os^{VIII}][H^{\cdot}][Br']^5{}^{,2}\gamma^2$ at 100° is $4{\cdot}5\times10^{-6}$, γ being the activity coeff. of the HBr. At high [HBr], Os^{IV} is probably formed. The reaction mechanism is discussed. J. G. A. G.

System manganese-nitrogen. R. Schenck and A. Kortengraber (Z. anorg. Chem., 1933, **210**, 273—285).—Equilibrium isotherms below 800° are characterised by two rising branches connected by a horizontal portion. The latter diminishes with rising temp. and disappears at about 800°. In the horizontal region two solid solutions co-exist in equilibrium with N_2; these become completely miscible at the crit. temp. 800°. *X*-Ray analysis establishes a N-rich, hexagonal ζ-phase and a face-centred cubic ε-phase, containing less N. Only the ε-phase is ferromagnetic. The dissociation pressures of Mn-Fe alloys (10% Fe) in equilibrium with N_2 are higher than those observed under the same conditions in the Mn-N_2 system. Horizontal portions of the isotherms are not observed. E. S. H.

Equilibrium diagram of the system chromium-carbon. K. Hatsuta (Tech. Rep. Tohoku, 1933, **10**, 186—194).—Four carbide phases exist, viz., Cr_4C (cubic), Cr_7C_3 (trigonal), Cr_3C_2 (orthorhombic), and, probably, CrC. The eutectic between the α-phase (solid solution) and Cr_4C lies at 1485° and 3·7% C. The peritectic temp. of the change Cr_7C_3+melt ⟶ Cr_4C is 1530°, and that of the change Cr_3C_2+melt ⟶ Cr_7C_3 is > 1600°; Cr_7C_3 separates in the form of primary crystals in the range 4·5—8·5% C. Cr_3C_2 probably has the max. m.p. (about 1800°) on the liquidus curve, and it forms a eutectic with CrC at about 17·5% C. A transition takes place in the Cr_3C_2 phase at about 1505°. H. F. G.

Thermal study of the systems KCl-$BaCl_2$ and KCl-LiCl. E. Elchardus and P. Laffitte (Bull. Soc. chim., 1932, [iv], **51**, 1572—1579).—An automatic apparatus for registering the thermal behaviour of systems is described. The system KCl-$BaCl_2$ has a eutectic at 340° (42·75 mol.-% $BaCl_2$) and a transition point at 347° corresponding with the compound $KCl,3BaCl_2$. No evidence for the compound $KCl,2BaCl_2$ was obtained. The system KCl-LiCl has a eutectic at 180° (41·7 mol.-% KCl). E. S. H.

Dissociation of cubic ferric oxide. A. Girard and G. Chaudron (Compt. rend., 1933, **196**, 406—408; cf. A., 1932, 133).—The amount of FeO formed when samples of cubic Fe_2O_3 prepared in various ways are heated in vac. to 300—600°, and magnetisation-temp. curves have been determined. The irregular results are thought to point to formation of solid solutions of the various oxides. C. A. S.

Thermal dissociation of certain oxides and peroxides. V. Magnesium, strontium, and barium peroxides. M. Blumenthal (Rocz. Chem., 1933, **13**, 5—15).—The dissociation pressure of MgO_2 is given by $\log P=12{,}000/4{\cdot}57T+1{\cdot}75\log T+2{\cdot}8$. For anhyd. MgO_2 $P=760$ mm. at 160°; for $MgO_2,1{\cdot}14H_2O$ the temp. is 46°. Decomp. of MgO_2 yields successively $2MgO_2,3MgO$, $MgO_2,2MgO$, $MgO_2,4MgO$, and finally MgO. The thermal dissociation of MgO_2, but not of SrO_2, is an irreversible reaction. O_3 reacts with MgO to yield an ozonide, different from MgO_2, and with SrO to yield ordinary SrO_2. For SrO_2 $\log P=13{,}500/4{\cdot}57T+1{\cdot}75\log T+2{\cdot}8$, and for anhyd. BaO_2 $\log P=-16{,}960/4{\cdot}57T+1{\cdot}75\log T-0{\cdot}0053T/4{\cdot}57+2{\cdot}8$; for hydrated BaO_2 P is considerably higher. The heats of dissociation of MgO_2, SrO_2, and BaO_2 are respectively +12, +13·5, and +16·96 kg.-cal. R. T.

Free energy of formation of iodine monobromide in carbon tetrachloride solution. D. M. Yost, T. F. Andersen, and F. Skoog (J. Amer. Chem. Soc., 1933, **55**, 552—555).—The partial pressures of IBr above solutions in CCl_4 at 25° are given by p_{IBr} (mm.)/mol. fraction $_{IBr}=114$. The free energy changes at 25° are $\frac{1}{2}I_2$ (in CCl_4)+$\frac{1}{2}Br_2$ (in CCl_4)=IBr (in CCl_4) −1746 (equilibrium const. 19·0) and $\frac{1}{2}I_2(s)$ +$\frac{1}{2}Br_2(l)$=IBr (in CCl_4) −221 g.-cal. J. G. A. G.

Beryllium. VI. Reactions of sulphur dioxide with organic beryllium compounds. H. S. Booth and V. D. Smiley (J. Physical Chem., 1933, **37**, 171—181; cf. this vol., 267).—Examination of the pressure-concn. relations in the systems SO_2-Be

acetylacetonate and SO_2–Be Et acetoacetate at 25° has shown that in each case 1 : 1 compounds are formed. The structure of these compounds is discussed. E. S. H.

Equilibrium in the system calcium–sulphur–oxygen. II. R. SCHENCK and F. HAMMERSCHMIDT (Z. anorg. Chem., 1933, **210**, 305—312; cf. A., 1929, 399).—Equilibrium data are given for the reaction $CaS+2SO_2 \rightleftharpoons CaSO_4+S_2$ at 1 atm. and 851—1075°. E. S. H.

Equilibrium in the systems strontium–sulphur–oxygen and barium–sulphur–oxygen. R. SCHENCK and F. HAMMERSCHMIDT (Z. anorg. Chem., 1933, **210**, 313—315; cf. preceding abstract).—In the general reaction $M^{II}S+2SO_2 \rightleftharpoons M^{II}SO_4+S_2$ the equilibrium partial pressure of S increases in the order Ca, Sr, Ba. E. S. H.

X-Ray studies of the system nickel–oxygen–water. I. Nickelous oxide and hydroxide. II. Compounds containing tervalent nickel. R. W. CAIRNS and E. OTT (J. Amer. Chem. Soc., 1933, **55**, 527—533, 534—544; cf. A., 1931, 549).—I. The existence of more than one form of NiO could not be confirmed. The lattice const. is a_0 4·1684±0·001 Å. The lattice consts. of hexagonal $Ni(OH)_2$ are a_0 3·114, c_0 4·167±0·005 Å. Hydrates of $Ni(OH)_2$ do not exist. The two cryst. forms of anhyd. $NiSO_4$ differ only in habit.

II. X-Ray diffraction patterns of Ni_2O_3,H_2O and $Ni_2O_3,2H_2O$ have been obtained. The modes of decomp. of these *compounds* show that they are not true hydrates, but contain the H_2O bound as OH groups. Analogous "*hydrates*" of the hypothetical oxides Ni_3O_4 and Ni_6O_7 have been isolated. The results of Hüttig and Peter (A., 1930, 700) are criticised. J. G. A. G.

Ternary systems. XVII. Sodium iodide, potassium iodide, and water. XVIII. Sodium iodide, sodium iodate, and water. A. E. HILL, H. S. WILLSON, and J. A. BISHOP (J. Amer. Chem. Soc., 1933, **55**, 520—522, 522—526).—XVII. The data refer to 8°, 25°, and 40°. The solid phases are KI and $NaI,2H_2O$ only.

XVIII. The data refer to 8°, 25°, and 40°. The solubility of $NaIO_3$ is greatly decreased by NaI, and solid solutions of the type $(NaIO_3,5H_2O)_n,(NaI,2H_2O)_m$, where $n:m$ varies from 1 : 1 to 1 : 2, are shown to exist over a wide range of concn. J. G. A. G.

Ternary systems mercuric chloride–water–alkaline-earth chloride or cupric chloride. H. BASSETT, G. W. BARTON, A. R. FOSTER, and C. R. J. PATEMAN (J.C.S., 1933, 151—164).—The systems have been studied at 25°, and that containing Cu also at 35°. Complex salts of the types $MCl_2,HgCl_2,xH_2O$, $MCl_2,3HgCl_2,xH_2O$, and $MCl_2,6HgCl_2,xH_2O$ have been found. The $SrCl_2$ system shows a region of mixed crystals of $SrCl_2,3HgCl_2,8H_2O$ and $SrCl_2,2H_2O$, whence it is inferred that the latter is $(SrCl_2,2H_2O)_4$. Probable structures of the various complex salts, and the solubility curves, some of which are of an unusual type, are discussed. A new form of $CaCl_2,4H_2O$ has been obtained. F. L. U.

Liquidus and solidus studies. II. Ternary system KNO_3–NH_4NO_3–$Pb(NO_3)_2$. H. M. GLASS, K. LAYBOURN, and W. M. MADGIN (J.C.S., 1933, 199—202; cf. A., 1932, 468, 1205).—F.p. of ternary mixtures, and compositions of conjugate phases relating to the 150°, 160°, and 190° isotherms have been determined. There is a ternary eutectic of f.p. 127·5°. KNO_3 and NH_4NO_3 form a discontinuous series of mixed crystals with a break between 8 and 35% KNO_3. F. L. U.

The equilibrium FeO+Ni $\rightleftharpoons$ NiO+Fe in the melt. W. JANDER and H. SENF (Z. anorg. Chem., 1933, **210**, 316—324).—Analyses have been made at temp. between 1560° and 1790°. With rising temp. the equilibrium is displaced towards the left. The temp. variation of the equilibrium const. is logarithmic. E. S. H.

Dissociation pressures of magnesium ammonium phosphate hexahydrate and related substances. VII. S. J. KIEHL and H. B. HARDT (J. Amer. Chem. Soc., 1933, **55**, 605—618).—A method for determining the partial pressures of two volatile dissociation products is described. Dissociation pressures for the systems: (1) $MgNH_4PO_4,6H_2O$, $MgNH_4PO_4,H_2O,H_2O$ (below 60°), (2) $MgNH_4PO_4,6H_2O$, $MgNH_4PO_4,H_2O$, $MgHPO_4,3H_2O$, H_2O, NH_3 (above 60°), (3) $MgNH_4PO_4,H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O, (4) $MgHPO_4,3H_2O$, $MgHPO_4,H_2O$, H_2O, and (5) $MgHPO_4,7H_2O$, $MgHPO_4,3H_2O$, H_2O, have been determined. In a vessel exposed to the atm., all volatile material is rapidly removed from these substances at 250°. J. G. A. G.

Thermal dissociation of serpentine minerals. (MLLE.) S. CAILLERE (Compt. rend., 1933, **196**, 628—630).—The cooling curves for various serpentine minerals show in all cases absorption of heat due to dehydration at about 650°. Some show no other irregularity, but others show also an evolution of heat at about 750°, whilst a chrysotile from Quebec shows absorption at 650° and at 400°, the latter being due to dehydration of contained brucite. The results afford a means of classifying these minerals, but their classification does not fall into line with that based on their optical properties. Seven complete analyses are given, all agreeing fairly well with the formula $H_4Mg_3Si_2O_9$. C. A. S.

Gradation of heat of dilution at great dilution. E. LANGE and J. MONHEIM (Naturwiss., 1933, **21**, 24).—The heat of dilution of $CdSO_4$ is greater than that of $ZnSO_4$ even at a dilution of 0·001*M*. This is a reversal of the usual order. The heat of dilution in the series $ZnSO_4$, $CdSO_4$, $CuSO_4$, shows no uniform increase with increasing radius of the cation, as would be expected from the assumptions of Debye and Hückel. The anomalous behaviour is shown in other properties. A. J. M.

Determination of integral heats of dissolution. XIII. N. A. KOLOSOVSKI and E. V. GRISCHKUN (J. Gen. Chem. Russ., 1932, **2**, 906—910).—Kolosovski and Meshinin's method (A., 1932, 115) for the determination of latent heat of vaporisation has been applied to saturated solutions; the integral heat of dissolution L is derived from Kirchhoff's formula:

$L=M(\lambda-\lambda_0)$, where M is the mol. wt. of H_2O, and λ and λ_0 are respectively the latent heats of vaporisation for saturated solution and for pure H_2O. The results obtained for NaCl, NH_4Cl, and $CO(NH_2)_2$ are in good agreement with those given by direct measurement. R. T.

Diffusion in liquids. J. ZIRKLER (Z. Physik, 1933, **80**, 412).—The results of Sitte (this vol., 17) for the % association of LiCl, NaCl, and KCl are discussed in relation to the heat of hydration of ions. A. B. D. C.

Thermodynamic data on zinc chloride and cadmium chloride. F. ISHIKAWA, G. KIMURA, and T. MUROOKA (Sci. Rep. Tohoku, 1932, **21**, 455—473).—The e.m.f. of the cell $Zn(Hg,10\%)|ZnCl_2$, saturated solution, HgCl|Hg from 25° to 42·5 is given by $E=0{\cdot}82378+0{\cdot}0001409(t-30)-0\ 00000039(t-30)^2$. For $ZnCl_2+400H_2O=ZnCl_2,400H_2O$ $\Delta H_{291}=-16{,}706$ g.-cal., and for $Zn+Cl_2=ZnCl_2$ $\Delta H_{298}=-98{,}415$ g.-cal. For $Hg+0{\cdot}5Cl_2=HgCl$, $\Delta H_{298}=-31{,}300$ g.-cal. Recorded v.p. at 25° are: $CdCl_2,2{\cdot}5H_2O$–saturated solution 19·64 mm., $CdCl_2,2{\cdot}5H_2O$–$CdCl_2,H_2O$ 16·94 mm., $CdCl_2,H_2O$–$CdCl_2$ 1·7 mm. The composition of the saturated solution is $CdCl_2,9{\cdot}203H_2O$, and its heat of dilution to $CdCl_2,400H_2O$, $\Delta H_{291}=37$ g.-cal. For α-$Cd+Cl_2=CdCl_2$ $\Delta H_{298}=-92{,}149$ g.-cal. Other recorded data are: ΔF_{298}, $ZnCl_2$, −88,256, $CdCl_2$ −81,857 g.-cal.; S_{298}, HgCl 24·1, $ZnCl_2$ 29·6, $CdCl_2$ 31·2. O. J. W.

Thermodynamic studies of zinc bromide. F. ISHIKAWA and T. YOSHIDA (Sci. Rep. Tohoku, 1932, **21**, 474—483).—The e.m.f. of the cell $Zn(10\%Hg)|ZnBr_2$, saturated solution in EtOH, HgBr|Hg is given by $E=0{\cdot}68133+0{\cdot}00013897(t-25)-0{\cdot}000000334(t-25)^2$ between 20° and 45°, and that of the cell $Zn(10\%\ Hg)|ZnBr_2,2H_2O$, saturated solution in H_2O,HgBr|Hg from 20° to 35° by $E=0{\cdot}68741-0{\cdot}0004584(t-25)-0{\cdot}000001533(t-25)^2$, and by $E=0{\cdot}68328+0{\cdot}0001348\times(t-40)+0{\cdot}000001739(t-40)^2$ above 35° (transition point $ZnBr_2,2H_2O\longrightarrow ZnBr_2$). V.-p. data for the system $ZnBr_2$–H_2O are also given. The following thermodynamic data have been calc.: $Zn+Br_2(l)=ZnBr_2$, ΔF_{298} −74,142 g.-cal., ΔH_{298} −78,470 g.-cal.; $ZnBr_2+2H_2O(l)=ZnBr_2,2H_2O$, ΔF_{298} −3093 g.-cal.; $Zn+2HgBr=ZnBr_2+2Hg$, ΔS_{298} 6·41 g.-cal./per degree; entropy of $ZnBr_2$=35·04. O. J. W.

Thermodynamic study of cadmium hydroxide. F. ISHIKAWA and E. SHIBATA (Sci. Rep. Tohoku, 1932, **21**, 499—510).—The activity product $[Cd^{++}][OH^-]^2$ has been derived from (*a*) e.m.f. measurements of the cell $Cd(10\%\ Hg)|Cd(OH)_2$, 1·0*N*-NaOH, HgO|Hg, $E_{298}=0{\cdot}8598$ volt, (*b*) electrometric titration of $CdSO_4$ solutions with NaOH, and (*c*) conductivity measurements of $Cd(OH)_2$ solutions. The results do not agree, but method (*a*), which is the most trustworthy, gives $1{\cdot}17\times10^{-14}$, according to which the solubility of $Cd(OH)_2$ is $1{\cdot}4\times10^{-5}M$ at 25°. The following thermodynamic data have been obtained: $Cd(s)+H_2$ (1 atm.) $+O_2$ (1 atm.) $=Cd(OH)_2(s)$, ΔF_2 −112,469 g.-cal.; $Cd(s)+HgO(s)+H_2O(l)=Cd(OH)_2(s)+Hg(l)$, ΔF_{298} −42,100 g.-cal.; $Cd(OH)_2(s)+H_2$(1 atm.)$=Cd(s)+2H_2O(l)$, ΔF_{298} −949 g.-cal O. J. W.

Heats of combustion of salicylic acid and of naphthalene with a view to their possible use as a second calorimetric standard. L. J. P. KEFFLER (Bull. Soc. chim. Belg., 1932, **41**, 607—621).—Mainly polemical against Beckers (A., 1932, 125), and a discussion of methods used in the determination of heats of combustion. The val. 5235+2 g.-cal. at 15° is proposed as the standard val. for salicylic acid. O. J. W.

Heats of combustion. M. BECKERS (Bull. Soc. chim. Belg., 1932, **41**, 621—629).—A reply to Keffler (cf. preceding abstract). The adoption of a mean val. for the heat of combustion of salicylic acid is considered to have no significance. O. J. W.

Organic thermochemical measurements. Velocities and heats of saponification of amides. E. CALVET (J. Chim. phys., 1933, **30**, 1—26; cf. A., 1932, 344).—The theory of the Tian microcalorimeter is discussed. The solubilities of five aliphatic amides in NaCl and KNO_3 are recorded. The concn. of amide and electrolyte for max. reaction velocity has been determined. N. M. B.

Free energies of formation of aqueous *d*-alanine, *l*-aspartic acid, and *d*-glutamic acid. H. BORSOOK and H. M. HUFFMAN (J. Biol. Chem., 1933, **99**, 663—676).—Vals. are calc. for the entropy, heat, and free energy of formation of the NH_2-acids and their ions at 25°. The free energy change calc. for the reaction *l*-aspartate$'''\rightleftharpoons$fumarate$''+NH_4^+$ agrees with the equilibrium which is attained in presence of micro-organisms (A., 1929, 850); the data indicate that the enzyme acts as a perfect catalyst. F. O. H.

Transport numbers of solid alkali halides. W. JOST and H. SCHWEITZER (Z. physikal. Chem., 1933, **B**, **20**, 118—124).—Transport no. measurements with NaCl at 550—700° have confirmed the theory that the share of the cation and anion in the conduction can be represented by the terms of a two-term conductivity formula (A., 1926, 231; Joffe, Z. Physik, 1930, **62**, 730). Measurements have also been made with KI and KBr. R. C.

Electrical conductivity of aqueous solutions of sodium and potassium hydroxides and the limiting mobility of the hydroxyl ion at 25°. G. H. JEFFERY and A. I. VOGEL (Phil. Mag., 1933, [vii], **15**, 395—408).—Conductivities at 25° below 0·01*N* are recorded. The limiting mobility of OH′ at 25° is 211·9±0·1%. H. J. E.

Electrolytic solutions. II. Evaluation of Λ_0 and K for incompletely dissociated electrolytes. R. M. FUOSS and C. A. KRAUS (J. Amer. Chem. Soc., 1933, **55**, 476—486).—The equations connecting the conductance and concn. of solutions of incompletely dissociated binary electrolytes are solved on certain assumptions. The validity of the method is confirmed for ion concns. as large as 0·002*N*. J. G. A. G.

Properties of mixtures of electrolytes. II. V. K. SEMENTSCHENKO, B. V. EROFEEV, and V. V. SERPINSKI (J. Gen. Chem. Russ., 1932, **2**, 893—905).—A modification of Shedlovsky's method (A., 1930, 862) gives results for the conductivity of

0·00025—2*N*-KCl solutions accurate to within 0·02%, which agree with those of Shedlovsky, and with those calc. from Onsager's formula (A., 1927, 517). R. T.

Effect of small water additions on the conductivity of electrolytes in non-aqueous solvents. O. L. HUGHES and (SIR) H. HARTLEY (Phil. Mag., 1933, [vii], **15**, 610—637).—Additions of H_2O up to 1% decrease the conductivity of KCl, $AgNO_3$, and NEt_4ClO_4 (I) in MeOH, of (I) in EtOH, and of (I), $HClO_4$, and KCNS in $COMe_2$, but increase that of Ag picrate, NaCNS, $AgNO_3$, NH_4CNS, LiCNS, and of picric acid in $COMe_2$. The effect in each case is proportional to the concn. of H_2O. Its influence on the association and solvation of the ions is discussed. Viscosity measurements for the mixed solvents, and the densities of $COMe_2$–H_2O mixtures, are recorded. H. J. E.

Connexion between complex formation, solvation, and formation of electrically conducting systems. V. S. FINKELSTEIN and M. S. ASCHKINAZI (J. Gen. Chem. Russ., 1932, 2, 790—799).—Electrolysis in the system NH_2Ac–$PhNO_2$–Br_2 is due to complex formation and ionisation represented by $NH_2Ac + Br_2 \longrightarrow NH_2AcBr_2$ $(NH_2AcBr)^+ + Br^-$. R. T.

Electrochemistry of ethereal solutions. VII. Arsenic tribromide–methyl ethyl ether. VIII. Arsenic trichloride–ethyl ether. IX. Acetic acid–ethyl ether. X. Phosphorus trichloride–ethyl ether. P. G. ROZENTRETER (J. Gen. Chem. Russ., 1932, **2**, 864—867, 868—874, 875—877, 878—879).—VII. The sp. conductivity and its temp. coeff. are at a max. for solutions which contain about 50 mol.-% of $AsBr_3$, indicating that the electrolyte is $AsBr_3$,MeOEt.

VIII. The viscosity (η)–composition and conductivity (C)–composition isotherms show that for a given concn. $\eta = Ae^{B/T}$, where T=abs. temp. and A and B are consts. Max. vals. for C are obtained for mixtures which contain 80 mol.-% $AsCl_3$; in view of the negative temp. coeff. of C this result is ascribed to a compound, $AsCl_3$,Et_2O, which readily decomposes on dilution and with rising temp.

IX. Conductivity and viscosity measurements indicate the absence of compound formation in the system AcOH–Et_2O.

X. Viscosity measurements suggest the absence of compound formation in the system PCl_3–Et_2O. R. T.

Anomalous electrolytes. I. Electrical conductivity of solutions of iodine and cyanogen iodide in pyridine [at 25°]. L. F. AUDRIETH and E. J. BIRR (J. Amer. Chem. Soc., 1933, **55**, 668—673).—The conductivity of the solutions increases to max. vals. on keeping. Solvent and solute first form a non-conducting additive compound which slowly changes to a true quaternary pyridonium salt. The mol. conductivity of the I_2 solution at infinite dilution is 130 and this high val. is attributed to ternary salt formation. J. G. A. G.

Calcium electrodes of the third order. J. VELÍSEK and A. VASÍCEK (Coll. Czech. Chem. Comm., 1933, **5**, 10—20).—Previous data for Ca electrodes of the third order are discussed and other electrodes are investigated, but none is found to be entirely satisfactory. It is unlikely that a satisfactory method will be found for determining [$Ca^{\cdot\cdot}$] electrometrically. The electrode studied in most detail was $Hg|Hg_3(PO_4)_2,Ca_3(PO_4)_2|Ca^{\cdot\cdot}$. For [$Ca^{\cdot\cdot}$] between 0·2 and 0·01*N* the hypothetical normal potential of Ca against the normal H electrode is approx. const. =0·6100, but increases below these concns. owing to the solubility of the depolariser $Ca_3(PO_4)_2$. The solubility of the latter corresponds with 0·003*N*-$Ca^{\cdot\cdot}$. There is a slow increase of potential with time due to decomp. of $Ca_3(PO_4)_2$ by H_2O to form $Ca(OH)_2$ and also to the reduction of the $Hg^{\cdot\cdot}$ salt. It cannot be used in physiological solutions because of the presence of Cl' and PO_4'''. M. S. B.

Diffusion in standard cells. G. A. HULETT and R. B. ELLIOTT (J. Physical Chem., 1933, **37**, 245—252).—The concn. of $Hg_2^{\cdot\cdot}$ in standard cells may be explored at any point in the electrolyte or paste by means of an amalgamated Pt point electrode. The cathode systems of Cd cells are shown not to be equilibrium systems. The concn. gradient of $Hg_2^{\cdot\cdot}$ varies with the age of the cell; 4—18 years are required to establish a steady state of diffusion. Diffusion is greater when the depolariser is cryst. Hg_2SO_4 than when electrolytically pptd. Hg_2SO_4 is used. Attention is directed to the importance of diffusion of $Hg_2^{\cdot\cdot}$ in determining the e.m.f. E. S. H.

E.m.f. and temperature coefficient of cell $Cu|CuSO_4|Hg_2SO_4|Hg$ at 25°. (MLLE.) M. GUINTIN (Compt. rend., 1933, **196**, 473—475, 538—540, 652).—The e.m.f. of the cell Cu amalgam (two phases)|$CuSO_4$(*c*)|Hg_2SO_4(solid)|Hg, special care being taken to exclude O_2, has been determined at 25° for c=1·1300—0·00113.

The temp. coeffs. ($\Delta E/\Delta t \times 10^4$) for c=0·525, 0·105, 0·02625, 0·0105, 0·00525, and 0·00105 are respectively −4·0, −3·3, −2·1, −1·2, +0·3, and +0·5. C. A. S.

Lead–mercurous acetate voltaic cell with acetic acid as solvent. G. TARBUTTON and W. C. VOSBURGH (J. Amer. Chem. Soc., 1933, **55**, 618—624; cf. this vol., 126).—The e.m.f. of cells with the solid phases $Pb(OAc)_2,3H_2O$, $Pb(OAc)_2,0{\cdot}5H_2O$, and $Pb(OAc)_2,0{\cdot}5AcOH$, and with solvents for which the wt. ratio, $AcOH/H_2O$, ranges from 0·1969 to 90 has been determined between 16° and 50°. For cells with almost pure AcOH the e.m.f. is const. and reproducible. The temp. coeff. changes from negative to positive as the $AcOH/H_2O$ ratio is increased. The heat of formation of $Pb(OAc)_2,0{\cdot}5H_2O$ is 271·35 kg.-cal. J. G. A. G.

Potential [at metallic electrodes] in electrolytes with foreign ions. III, IV. A. SCHMID, W. WINKELMANN, and P. VOGELE (Helv. Chim. Acta, 1933, **16**, 20—22, 22—28; cf. A., 1930, 705; this vol., 28).—III. C.d.–potential curves for amalgamated Al in Na_2SO_4 and for Cu in NaCl and NaBr show that polarisation occurs which is determined, not by the concn. of ions of the electrode material, but by the concn. and nature of the foreign ions present.

IV. Experiments on the evolution of H_2 by amalgamated Al in various foreign electrolyte solutions

indicate that the purely chemical reaction is essentially different from the corresponding electrochemical change, the electrolyte acting in opposite senses in the two cases. F. L. U.

So-called heats of transfer (Q^* values) in Peltier heats. E. LANGE and T. HESSE (J. Amer. Chem. Soc., 1933, **55**, 853—855; cf. A., 1932, 814).—Preliminary. The Peltier effects at 25° for the system $Ag|AgCl|Cl'$ in presence of K^*, H^*, Li^* vary with the cation, and thus the existence of heats of transfer is established. The conclusions of Bruzs (*ibid.*, 1000) are criticised. J. G. A. G.

Electrolysis of glass at high temperatures. R. SCHWARZ and J. HALBERSTADT (Z. anorg. Chem., 1933, **210**, 286—288; cf. A., 1932, 230).—Conduction of electricity in glass up to 1000° is purely electrolytic. A Cu anode dissolves as Cu^* above 700° and as a mixture of Cu^* and Cu^{**} at lower temp. The Na liberated at the cathode forms a blue sol in the glass. E. S. H.

Influence of organic substances on the deposition of metallic ions at the dropping mercury cathode. G. DEVOTO and A. RATTI (Gazzetta, 1932, **62**, 887—893).—The deposition potentials of Ni and Co from 0·01—0·1*M* solutions of the sulphate or chloride are depressed by 0·1—0·2 volt if 0·3 g. per litre of C_5H_5N is added to the electrolyte, and the form of the c.d.–voltage curves is somewhat modified. With Zn the effect is observed only at relatively high c.d. Deposition of Cd from a $CdSO_4$ solution is retarded if the electrolyte is saturated with COPhMe, probably because of adsorption of the ketone on the Hg surface. H. F. G.

Electrochemistry of polonium. M. HAISSINSKY (J. Chim. phys., 1933, **30**, 27—46; cf. this vol., 128).—The crit. anodic deposition potential in acid solution varies with the acidity and the nature of the electrode, but this is not the case for the crit. cathodic potential. Po shows a strong tendency to form complex ions with the anions. The crit. cathodic potential is due in non-reducing media to the discharge of Po^{****} ions, in reducing media to the discharge of Po^{***} ions, and in alkaline media to the electrolytic reduction of PoO_3 ions. Anodic deposition in alkaline solution is due to discharge of PoO_3 ions with formation of a peroxide, whilst in acid solution this peroxide is formed by nascent O. N. M. B.

Initial electrolytic over-voltage of evolution of hydrogen over mercury. R. DUFOUR (Compt. rend., 1933, **196**, 483—485).—Observations on the cell $Hg|N\text{-}H_2SO_4|Pt$ are recorded. C. A. S.

Passivity phenomena during the dissolution of copper in a mixture of nitric and sulphuric acids. A. KUTZELNIGG (Z. Elektrochem., 1933, **39**, 67—73).—Cu becomes passive on immersion in a mixture of conc. HNO_3 and H_2SO_4, owing to deposition of a layer of $CuSO_4,5H_2O$. When present in high concn. HCl inhibits passivation, especially in presence of soot. D. R. D.

Reaction cells in chain reactions. A. R. UBBELOHDE (Nature, 1933, **131**, 328).—Theoretical. L. S. T.

Upper pressure limit in the explosive chain reaction between hydrogen and oxygen. C. N. HINSHELWOOD and G. H. GRANT (Nature, 1933, **131**, 361—362).—The upper limit is governed by ternary collisions in the gas phase and the particles which recombine or are deactivated in this process must be much more massive than pairs of H atoms. A theory which accounts quantitatively for many known facts concerning the upper limit is developed. L. S. T.

Combustion of an inflammable gas mixture by a hot wire. J. D. MORGAN (Phil. Mag., 1933, [vii], **15**, 440—442).—Dil. coal-gas–air or Et_2O–air mixtures reacting on hot wires of Pt, Fe, or Cu will not discharge an electroscope until the mixture inflames. Ionisation is a consequence and not a cause of inflammation. H. J. E.

Ignition of explosive gaseous mixtures by small flames. J. M. HOLM (Phil. Mag., 1933, [vii], **15**, 329—359; cf. A., 1932, 915).—Measurements were made on the change of flame velocity with tube diam., the limiting diams. for H_2–air and Et_2O–air mixtures, the effect of inert diluents on the limiting diam., and the extinction of moving flames by partitions in tubes. The previous theory of the cause of extinction of flames has been developed. H. J. E.

Oxidation of carbonyl sulphide. C. E. H. BAWN (J.C.S., 1933, 145—151).—The influence of pressure, surface of vessel, method of mixing, etc. on the ignition temp. of COS–O_2 mixtures has been investigated. The explosion gives rise to CO_2, CO, SO_2, SO_3, S, and possibly CS. There is an induction period, decreased by drying, during which a surface reaction occurs. Branched reaction chains are initiated and destroyed at the walls of the vessel. It is suggested that they are initiated by the formation of COS,O_2 on the walls. Addition of O_2 to a mixture COS–$2O_2$ depresses the ignition temp., whereas COS, He, N_2, and A have the reverse effect, and H_2O is without influence. The action of the inert gases is attributed to their cooling effect on the walls. Irradiation with ultra-violet light does not facilitate reaction, possibly owing to the opacity of the S deposited on the walls. D. R. D.

Oxidation of carbonyl sulphide. H. W. THOMPSON, F. L. HOVDE, and A. C. H. CAIRNS (J.C.S., 1933, 208—216).—This investigation covers the same field as that described in the preceding abstract. Data are also given for the upper limiting pressure. In general, the results agree, but N_2 and A are found to produce a depression of the lower explosion limit. SO_2 and CO_2 act similarly in low concn., but at higher concns. they have the opposite effect. Similar results have been obtained with CS_2. No appreciable reaction occurs in the absence of an explosion. D. R. D.

Explosion of mixtures of carbon disulphide and nitric oxide. I. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1933, **52**, 160—168).—Explosion limits have been determined for total pressures up to 400 mm. No explosion occurs if $p < 35$ mm. For a given mixture, the quantity of light emitted $\propto p^2$ (approx.). For a given pressure,

the light intensity is greatest when CS_2 : NO lies between 2·25 and 2·75. The ignition temp. is of the order of 1900°. D. R. D.

Explosion limits and ensurement of safety in the propagation of gas explosions. E. Beil and K. Barth (Z. Elektrochem., 1933, **39**, 73—75).—Explosion limits are given for mixtures of air with coal gas, C_2N_2, C_2H_2, CS_2, Et_2O, EtOH, C_6H_6, and $COMe_2$ vapours. A glass filter diaphragm serves to prevent backward propagation of an explosion. D. R. D.

Explosion pressure of air–benzene mixtures in a closed vessel. Y. Laure (Compt. rend., 1933, **196**, 385—387).—Pressure-time curves have been determined for explosions of the same 'air–C_6H_6 mixture in a sphere and three cylinders of vols. 288, 432, 500, and $729\times\pi$ c.c., but all having the same ratio of surface to vol. (0·5 cm.$^{-1}$). Duration of reaction increased and max. pressure decreased in the above order, but delay in ignition was const. Curves relating max. pressure to richness of mixture were all superposable. The effect of introducing metal plates into the bombs depended on their position. C. A. S.

Homogeneous unimolecular decomposition of mixtures of gaseous aliphatic ethers. E. W. R. Steacie (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 103—110).—In the homogeneous unimol. decomp. of mixtures of Et_2O and Me_2O on a Pt filament at 478°, the efficiency of energy transfer between mols. of the two substances is zero in so far as production of activated mols. is concerned. The rates of decomp. of the separate reactants are therefore additive. J. W. S.

Energy transfer between complex gas molecules and solid surfaces. E. W. R. Steacie and H. A. Reeve (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 75—85).—The homogeneous unimol. decomp. of EtOH, $COMe_2$, PrCHO, and MeOH on a heated Pt filament has been investigated. The reactions occur in the gas layer surrounding the filament and are not catalysed. For EtOH and $COMe_2$ the gas layer is in thermal equilibrium with the filament and the apparent heat of activation calc. from the temp. coeff. of the reaction agrees with that for a homogeneous reaction. The apparent heat of activation of PrCHO and MeOH is much > that of the homogeneous reaction. This is explained by assuming that the accommodation coeffs. for these gases are low and hence thermal equilibrium with the filament is not attained by colliding gas mols. J. W. S.

Dithionates. I. Sodium dithionate. II. Velocity of decomposition of sodium dithionate and potassium dithionate. F. Ishikawa and M. Oku (Sci. Rep. Tohoku, 1932 **21**, 727—746, 747—771).—I. The solubility of $Na_2S_2O_6$ has been measured at temp. between 100° and −1·14° (the cryohydric point). The following hydrates exist: $Na_2S_2O_6,2H_2O$; $Na_2S_2O_6,6H_2O$; $Na_2S_2O_6,8H_2O$, the transition points being 9·1—9·2° and 0°, respectively. The velocity of dehydration of $Na_2S_2O_6,2H_2O$ at 50° as measured by both dynamic and static methods suggests that both mols. of H_2O of crystallisation are equally bound to the $Na_2S_2O_6$ mol. and that the dehydration is controlled by the diffusion velocity of the H_2O vapour. The v.p. of $Na_2S_2O_6,2H_2O$ has also been measured, the changes in heat content and free energy for the hydration process being calc.

II. The velocity of decomp. of these compounds has been measured by determining the vol. of SO_2 evolved. Its course cannot be explained on Langmuir's interfacial theory alone, as the effect of the disintegration of the particles must be taken into account. J. W. S.

Velocity of decomposition of dithionic acid and its volumetric determination. F. Ishikawa and H. Hagisawa (Sci. Rep. Tohoku, 1932, **21**, 484—498).—Velocity measurements in aq. solution at 60—100° show that the reaction $H_2S_2O_6=H_2SO_4+SO_2$ is unimol., the temp. coeff. varying between 3 and 4. The reaction is greatly accelerated by HCl. $H_2S_2O_6$ can be determined by heating with conc. HCl in a sealed tube and titrating with I the H_2SO_3 formed. O. J. W.

Velocity of reaction of potassium cyanide with thiosulphate or tetrathionate. F. Ishikawa, T. Murooka, and H. Hagisawa (Sci. Rep. Tohoku, 1932, **21**, 511—526; cf. A., 1927, 1147).—The reaction $S_2O_3''+CN'=SO_3''+CNS'$ is bimol. at 25° and 70°, and the velocity coeff., k, varies linearly with initial total KCN concn. and with added NaOH concn., *i.e.* $k=0{\cdot}0269+0{\cdot}06[KCN]$ and $k=0{\cdot}0461+0{\cdot}033[NaOH]$. The velocity of the reaction S_4O_6'' $-CN'+2OH'=S_2O_3''+CNS'+SO_4''+H_2O$ at 70° is controlled by the velocity of the secondary reaction $S_2O_3''+CN'=SO_3''+CNS'$, which is accelerated by the KCNS formed in the primary reaction. O. J. W.

Regularities in acid and salt effects in alcoholic aqueous solutions. II. Oxidation of ethyl alcohol by chromic acid. M. Bobtelski and R. Cohn (Z. anorg. Chem., 1933, **210**, 225—240; cf. A., 1931, 1245).—In absence of acids or in presence of weak acids, reaction between EtOH and CrO_3 occurs at measurable speed only when the concn. of EtOH is > 60 vol.-%. In general, the influence of acids or salts depends on the concn. of EtOH and three regions are recognised, according as the latter is < 30, 30—60, or > 60 vol.-%. In the upper region, $CH_2Cl{\cdot}CO_2H$, $CHCl_2{\cdot}CO_2H$, and $CCl_3{\cdot}CO_2H$ accelerate the reaction in the ratio 1 : 2 : 6 for equiv. concns. The acceleration is also proportional to the concn. of acid. Sp. differences in the effect of the acids are shown particularly when the EtOH concn. is > 60%. Al''' has a marked accelerating effect, especially in absence of strong acids; the velocity is proportional to the concn. of Al''' at high concns. of EtOH. Mn'', Cl', and Br' exert an exhibiting influence on the reaction. E. S. H.

Velocity of liberation of hydrocarbons by the action of indene on aliphatic organo-magnesium compounds. Method of measuring the attraction between alkyl radicals and the magnesyl group. D. Ivanov and I. Abdoulov (Compt. rend., 1933, **196**, 491—493).—The velocity of the reaction between indene and RMgX is determined by measuring the vol. of the hydrocarbon RH liberated. This is an inverse measure of the affinity between R and MgX. This affinity decreases in the order Bu^{β}, Me,

Bu$^{\alpha}$, *sec.*-Bu, Pr$^{\alpha}$, Et, Pr$^{\beta}$, which is similar to that deduced from the reaction between RMgX and $CH_2Ph{\cdot}CO_2MgCl$ (A., 1932, 816). A. C.

Invertase action as a heterogeneous reaction. T. A. WHITE (J. Amer. Chem. Soc., 1933, **55**, 556—568).—Kinetic expressions are developed on the assumption that sucrose and H_2O are adsorbed by invertase, the inversion occurs in the adsorbed layer, and adsorption of the products inhibits the reaction. Consistent with theory, it is found that the velocity is const. for the first 10% of hydrolysis and then decreases. The unimol. coeff. decreases with increase of p_H from 4·7 to 7·4, and passes through a max. at a definite % of hydrolysis which decreases with decrease of initial sucrose concn., increase of p_H and temp., and is independent of enzyme concn. The existence of a max. initial velocity with 6% sucrose is interpreted as corresponding with the optimum ratio of adsorbed sucrose to adsorbed H_2O. J. G. A. G.

Combustion of graphite in a current of gas. V. SIHVONEN (Suomen Kem., 1932, 5, 51B).—The combustion of graphite in cold and preheated O_2, CO_2, and steam has been studied. In O_2 either of two first-order reactions may occur, according to the condition of the surface; the one occurs at 800—1400° at the normal porous surface, and results in the formation of CO_2+2CO, and the other at 900° at the surface modified by the action of CO, the product being pure CO. With preheated steam the reaction is initiated by O resulting from dissociation. In cold steam vigorous combustion does not occur below 1500°, whilst at temp. > 1600° the rate of reaction diminishes owing to a change of the surface and decrease of adsorption of the steam. Cold (*i.e.*, undissociated) CO_2 does not react with graphite below 1500°. H. F. G.

Action of chlorine on metal oxides. W. KANGRO and R. JAHN (Z. anorg. Chem., 1933, **210**, 325—336).—The rate of reaction of Cl_2 with BeO, ZnO, CdO, Al_2O_3, TiO_2, V_2O_5, Nb_2O_5, MoO_3, WO_3, and U_3O_8 has been determined at high temp. The oxides of Ta and B do not react with Cl_2. Regularities in the temp. at which chlorination begins are observed only when the product is completely volatile at that temp. Under these conditions the chlorination temp. rises with increasing at. no. in each group of elements. E. S. H.

Law of combustion of mixtures of powders. H. MURAOUR and G. AUNIS (Compt. rend., 1933, **196**, 478—480).—Substitution of part of the powder of a charge by another powder of different velocity of combustion had no effect on $fpdt$ for a density of loading of 0·2 owing to the small variation in t (cf. Appl. Chem. Rep., 1930, **15**, 677), but for lower densities the expected increase in $fpdt$ has been experimentally demonstrated, the $fpdt$–t curve being a straight line inclined to the axes. C. A. S.

Rate of absorption of nitrous gases by sulphuric acid. II. L. SZEGO and M. LOMBARDI.—See B., 1933, 188.

Dynamics and catalysis of the thermal decomposition of hydrogen carbonates in aqueous solution. VIII. Decomposition of sodium hydrogen carbonate. R. STUMPER (Z. anorg. Chem., 1933, **210**, 264—268; cf. A., 1932, 1095).—The decomp. in boiling aq. solutions (0·005—0·05N) is unimol., both with and without application of a CO_2-free air stream. Fe, dextrin, starch, and agar accelerate the decomp. The thermal decomp. of $Ca(HCO_3)_2$ is accelerated by many finely-divided solids, which act as nuclei, but inhibited by hydrophilic colloids. E. S. H.

Chronic poisoning by oxalic acid. Volatilisation of oxalic acid from aqueous solution. C. D. HOWARD (J. Ind. Hyg., 1932, **14**, 283—290).—Volatilisation occurs at the b.p. at a rate dependent on the rate of boiling and concn. In a glass vessel, Cu and Al increase the rate, which is low if a Cu flask is used or when steam is passed through the solution. In presence of Al, HCO_2H, H_2, and CO_2, and in presence of Cu only CO_2, are formed. CH. ABS.

Heavy metal catalysts. II. Influence of cystine on artificial peroxidases. T. OMORI (J. Biochem. Japan, 1932, **16**, 483—497; cf. A., 1932, 346).—Addition of cystine (I) to systems containing H_2O_2 and Fe or Cu (but not Mn, Ni, or Co) accelerates the oxidation of the substrate (starch). The acceleration is proportional to the concn. of (I) and is effective at concns. > M/19,200. The p_H optimum for the system (I)–H_2O_2–Fe–starch is 3·3; outside the range 1·0—5·6 there is no action. Citrates and narcotics inhibit the reaction. (I) can be replaced by tyrosine and, in the Fe-containing systems, by glutathione or thioglycollic acid, but not by caseinogen or ovalbumin. F. O. H.

Comparison of organic inhibitors in chain reactions. K. K. JEU and H. N. ALYEA (J. Amer. Chem. Soc., 1933, **55**, 575—588).—The photopolymerisation of vinyl acetate, the thermal autoxidation of Na_2SO_3, and the photolysis of H_2O_2 are first-order chain reactions. The results in the presence of inhibitors are represented by the general equation $(1/t)\log_e 1/(1-x)-K/(k_2+kC)$, where x is the fraction reacting during time t, K includes the number of chains initiated at $t=0$ and the probability of continuing the chains, whilst k_2+kC is the probability of breaking the chains by a const. factor, k_2, or by an inhibitor of concn. C and inhibiting power k. Relative vals. of k for 16 inhibitors are approx. identical for the first two reactions, but bear no relation to those obtained in the photolysis of H_2O_2. Chain lengths agreeing with experimental vals. were calc. from vals. of k_2. Many org. substances photosensitise the polymerisation of vinyl acetate to visible light. J. G. A. G.

Theory of ammonia catalysis. II. Kinetics. W. FRANKENBURGER (Z. Elektrochem., 1933, **39**, 97—103).—A discussion. D. R. D.

Influence of traces of a salt of tin in acid solution on the rate of corrosion of mild steel. T. N. MORRIS and J. M. BRYAN.—See B., 1933, 231.

Interface catalysis in the reduction of metallic oxides. A. R. UBBELOHDE (Trans. Faraday Soc., 1933, **29**, 532—534).—The possibility of interface

catalysis, or the catalysis of a reaction in the solid phase by the presence of one of the resultants, is discussed in connexion with the reduction of metallic oxides. Thermochemical data indicate that interface catalysis is to be expected in the reduction of oxides of Cu, Ni, Pt, Pd, and Pb. Experimental data confirm this for Cu, Ni, and Pt. M. S. B.

Mechanism of chemical reactions. IV. Specific hydrogenation with combined hydrogen. K. KINDLER and W. PESCHKE (Annalen, 1933, **501**, 191—198; cf. A., 1932, 944).—4-Methyl- and 4-methoxy-cinnamic acids, Me 4-methoxy- (I), 3 : 4-methylenedioxy- (II), and 3 : 4-dimethoxy-cinnamates are reduced to the corresponding propionic acid derivatives (in almost quant. yield) by Pd-black and boiling dihydrophellandrene (III); in all these cases, the same amount of H_2 is evolved as with Pd-black and (III) alone. It is suggested that the affinity of the acceptor and catalyst is small; an adduct is produced which is able to add the donator [*i.e.*, (III)], thereby forming a system in which part of the H of (III) and the reducible portion of the acceptor are activated. Cinnamic acid (IV), Et *p*-nitrocinnamate, and Me, Et, and *iso*amyl cinnamates are not reduced by Pd-black and (III); little H_2 is evolved. In these cases, the affinity of the acceptor and catalyst is great; the adduct formed is unable to add the donator. No reduction of (I) and (II) occurs when they are admixed with an equimol. amount of (IV). 3 : 4-Dimethoxymandelonitrile benzoate is reduced by Pd-black and (III) to 3 : 4-dimethoxyphenylacetonitrile; reduction of mandelonitrile benzoate is slower (less H_2 is evolved). H. B.

Corrosion and local current. F. TODT (Z. Elektrochem., 1933, **39**, 146—147; cf. A., 1930, 1125).—A reply to criticisms by Eckell (A., 1932, 231). F. L. U.

Electro-reduction of perrhenic acid. W. F. JAKÓB and B. JEZOWSKA (Ber., 1933, **66**, [*B*], 461—462).—Reduction of K perrhenate in 6*N*- or 8*N*-HCl takes place with poor current yield and marked cathodic polarisation. In these solutions or those containing KI a sudden fall in potential marks the completion of the change, $Re^{VII}+2\ominus=Re^{V}$. The isolation of the *salt* $K_2[Re(OH)_2Cl_5]$ is described. With thiocyanates it yields an intensely green compound, sol. in Et_2O. With alkalis, the black *oxide* $ReO(OH)_3$,xH_2O, rapidly oxidised by air, is pptd. H. W.

Behaviour of mercuric halides during anodic oxidation. G. ILLARI (Gazzetta, 1932, **62**, 1166—1176).—HgI_2 is oxidised almost quantitatively to $Hg(IO_3)_2$ at a Pt anode in HNO_3 solution, and this forms a convenient method of preparing the latter salt. $HgBr_2$ is oxidised to bromate, which undergoes decomp. by the HNO_3 with evolution of Br. $HgCl_2$ is not oxidised anodically. O. J. W.

Electrodeposition of nickel with insoluble anodes. V. I. LAINER and others.—See B., 1933, 194.

Electrolytic separation of lead as peroxide in non-ferrous alloys. I. Determination of small amounts of lead in copper and copper-rich alloys. B. JONES.—See B., 1933, 193.

Electrodeposition of iron–cobalt alloys. II. S. GLASSTONE and J. C. SPEAKMAN.—See B., 1933, 231.

Electrochemical behaviour of palladium. I. Electrolytic deposition of palladium and palladium–silver alloys from solutions of complex salts. G. GRUBE and D. BEISCHER (Z. Elektrochem., 1933, **39**, 131—139).—Ag and Pd can be deposited simultaneously from a bath containing $KAg(CN)_2$+$K_2Pd(CN)_4$ with a current yield of 5—6%. The deposit is greyish-black and non-coherent. From a bath of the corresponding (CNS) compounds similar deposits are obtained, containing S in addition to org. substances. Satisfactory deposits of Ag could not be obtained from NH_3–$AgNO_2$ baths. The process $[Pd(NH_3)_2(NO_2)_2]+2NH_3\longrightarrow[Pd(NH_3)_4](NO_2)_2$ has been followed by conductivity measurements. F. L. U.

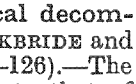
Anodic oxidation of benzene. R. M. ARCHIBALD (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 69—73).—Electrolysis of a solution of C_6H_6 in AcOH using an anode of Ni, Pt, Cu, or Fe yields an equilibrium mixture of PhOH and higher oxidation products. The PhOH concn. is highest when a relatively high voltage (>15 volts) is used, when a diaphragm is used between the electrodes, and in presence of traces of salts such as $CuSO_4$ and NH_4VO_3. The max. yield of PhOH (1·76%) was obtained in 5% solution. The use of a.c., alone or superimposed on the d.c., results in lower yields. Large concns. of salts also lower the yield. Rapid oxidation for a short period is preferable to slower oxidation over longer periods. The voltage–current curve with C_6H_6–AcOH solutions is smooth over the range 0—5 volts, indicating the absence of a definite decomp. potential. Electrolysis of suspensions of C_6H_6 in aq. NaOH or EtOH–H_2SO_4 yielded no PhOH. J. W. S.

Dissociation of nitrous oxide in the glow discharge. E. A. STEWARDSON (Nature, 1933, **131**, 364—365).—With a high-frequency discharge and fields of average peak intensity of 100—400 volts/cm. and initial pressures of 0·1—3·0 mm. results in substantial agreement with those of Hinshelwood and Hutchison (A., 1928, 30) have been obtained. At the lowest discharge intensity the initial rate varies little with the initial pressure, but at the highest p.d. there is a small pressure range over which dissociation is unimol. Beyond this region the rate of dissociation increases for 3—4 sec. after initiation, rapidly attains a max., and then proceeds normally in a manner dependent on pressure. A similar effect has been observed with NO_2. L. S. T.

Effect of water on the photosynthesis of hydrogen chloride. G. K. ROLLEFSON and J. C. POTTS (J. Amer. Chem. Soc., 1933, **55**, 860—861; cf. this vol., 34).—Experiments at 145—200° abs. indicate no decrease in reaction velocity when the v.p. of H_2O becomes $<10^{-5}$ mm. With fall of temp., the relation velocity $\propto I_{abs.}$ probably changes to velocity $\propto I^{\frac{1}{2}}_{abs.}$. Baker's experiments (*ibid.*, 132) are criticised. J. G. A. G.

Reaction of hydrogen atoms with oxygen and the hydrogen–chlorine reaction. J. R. BATES (Proc. Nat. Acad. Sci., 1933, **19**, 81—85).—Theoretical. The part played by the reaction between H and O_2

in the HCl reaction is discussed on the basis of results obtained from the photo-oxidation of HI (this vol., 237). M. S. B.

Primary photochemical processes. II. Absorption spectrum and photochemical decomposition of diazomethane. F. W. KIRKBRIDE and R. G. W. NORRISH (J.C.S., 1933, 119—126).—The absorption spectrum of CH_2N_2 is similar to that of Me·N_2·Me and supports the structure  The photochemical decomp. of CH_2N_2 is a unimol. reaction of quantum efficiency approx. 4 at 365 and 436 mμ. The main products are N_2, C_2H_4, C_3H_6, and a non-volatile liquid (possibly a pyrazoline derivative). In presence of H_2, much CH_4 is formed and the liquid N compound is absent. In presence of O_2, liquid compounds, believed to be oxidation products of CH_2, are obtained, but no oxides of N. These observations support the view that the primary process is $CH_2N_2+h\nu=CH_2+N_2$. D. R. D

Influence of *X*-rays on the oxidation of graphite by oxygen at very low pressures. V. SIHVONEN (Suomen Kem., 1932, **5**, 51B).—When graphite reacts with O_2 (at $3{\cdot}6—15{\cdot}7\times10^{-3}$ mm. pressure) which is subjected to *X*-ray irradiation, the product is CO_2+2CO. If, on the other hand, the *X*-rays fall directly on the graphite, a considerable excess of CO_2 is formed; at low pressures ($5—12\times10^{-3}$ mm.) this excess is not formed from O_2 in the gas phase, but appears to be derived from the breakdown of adsorption complexes on the graphite surface, whereas at higher pressures ($25—32\times10^{-3}$ mm.) part of the excess arises from reaction of the graphite with the gas phase. H. F. G.

Silver nucleus theory of the latent image. II. Size and nature of [latent image] nuclei and [primary silver] nuclei in silver bromide emulsions. W. REINDERS and L. HAMBURGER (Z. wiss. Phot., 1933, **31**, 265—284; cf. A., 1932, 821).—Theoretical. Primary Ag nuclei [" sensitivity specks " (Sheppard), " prokeime "] formed during ripening of AgBr emulsions become developable when aggregates of 3 or 4 atoms are produced. The Ag is replaceable by Ag_2S and other S-containing complexes. The proportion of such aggregates, among the primary Ag adsorbed on the surface of grains of a normal AgBr emulsion, is very small. Ag formed on exposure is preferentially deposited on these nuclei, which form weak spots in the crystal lattice. The desensitising action of methylene-blue is also discussed. J. L.

Photochemical studies. III. C. WINTHER (Z. wiss. Phot., 1933, **31**, 285—293).—Various types of sensitisation are discussed, and simple experiments illustrating their chief features are described. J. L.

Herschel effect as a result of simultaneous forward and reverse reactions. K. M. JOEHNCK and J. M. BLAIR (J. Opt. Soc. Amer., 1933, **23**, 67—69).—The Herschel effect is explained on the basis of Blair and Leighton's hypothesis (cf. A., 1932, 1006) that the formation of the latent image is the equilibrium of two opposed reactions. Then for light of given wave-length and intensity, the max. developable Ag is const., and a higher latent density (obtained by previous exposure to a stronger light) is reducible to this const. by prolonged exposure. Experiments showing these effects are described. J. L.

Blue and green sensitivity of photographic emulsions in absolute measure. M. BILTZ (Physikal. Z., 1933, **34**, 200—204).—The determination of the blue and green sensitivity of a series of Agfa films gave for the blue sensitivity 77—4 sq. cm. per erg. The ratio of the green to blue sensitivity for unsensitised emulsions was 0·006, but for sensitised emulsions it could be increased to about 100 times this val. A. J. M.

Mechanism of hypersensitisation. B. H. CARROLL and D. HUBBARD.—See B., 1933, 252.

Photochemical reaction between quinine and dichromic acid. II. Kinetics of the reaction. G. S. FORBES, L. J. HEIDT, and F. P. BRACKETT, jun. (J. Amer. Chem. Soc., 1933, **55**, 588—596; cf. A., 1932, 480).—The reaction in the system 0·00016—0·003*M*-$K_2Cr_2O_7$ 0·0—1·7*M*-H_2SO_4, 0·00001—0·02*M*-quinine has been investigated at temp. between 5° and 29° with monochromatic light of seven wave-lengths between 405 and 208 mμ. The reaction proceeds by way of clusters and is of zero order with respect to quinine, approx. first order with respect to H_2CrO_4 (or 0·5 for $H_2Cr_2O_7$), and 0·07 with respect to H_2SO_4. At 208 mμ, $H_2Cr_2O_7$ may be photosensitive also. The absorption band of 0·0001*M*-quinine is shifted 200 cm.$^{-1}$ towards the red by increasing the concn. of H_2SO_4 from 0·004 to 4*M*. On one view, the temp. coeff. accords with a bimol. reaction between activated quinine and H_2CrO_4 (or $H_2Cr_2O_7$) without additional energy of activation. J. G. A. G.

Photo-active emanations from some irradiated organic substances. C. SERONO and A. CRUTO (Gazzetta, 1932, **62**, 1203—1209; cf. A., 1928, 1071).—Lecithin, which has been exposed for a few min. to ultra-violet radiation, affects a photographic plate. The emission of radiation is related to the absorption of O by the lecithin during the irradiation. Similar results are described for oleic acid. O. J. W.

Haber-Willstatter chain mechanism of organic and enzymic processes. H. S. TAYLOR and A. J. GOULD (J. Amer. Chem. Soc., 1933, **55**, 859).—Preliminary. In agreement with the theory (A., 1932, 352), OH produced by photo-decomp. of H_2O_2 sensitises the interaction of O_2 with EtOH and MeCHO. The oxidations are chain reactions sensitive to inhibitors. J. G. A. G.

Chemical and biological effects of ultra-sonic radiation. A. SZENT-GYORGYI (Nature, 1933, **131**, 278).—Ultra-sonic radiation decomposes sucrose into monosaccharides, but has no effect on Ph_2O, succinimide, etc. Judged by a fall in viscosity, starch, gum arabic, and gelatin are depolymerised. L. S. T.

Action of potassium nitroacetate on some metallic salts. A. DANSI (Gazzetta, 1932, **62**, 1177—1183).—The products obtained by the action of Hg and Cu salts on nitroacetic acid are very

unstable. With $HgCl_2$ and $Hg(NO_3)_2$ the final product contains Cl or NO_3, respectively, and either one or both Hg atoms are joined directly by a single linking to the C atom. With the corresponding Cu salts basic salts are obtained which contain no org. group. The pure neutral Ag nitroacetate could not be obtained (cf. A., 1924, i, 254). O. J. W.

Coprecipitation. III. Water content of calcium oxalate monohydrate. E. B. SANDELL and I. M. KOLTHOFF (J. Physical Chem., 1933, **37**, 153—170; cf. A., 1932, 457).—$CaC_2O_4,3H_2O$ is pptd. at room temp. from 0·1*N*-$Ca^{"}$ solutions, but is transformed completely into CaC_2O_4,H_2O (I) when left in contact with the mother-liquor for 1—2 days. This transformation is accelerated by rise of temp. and by excess of C_2O_4''. The higher hydrates are converted into (I) rapidly at 100° and more slowly at room temp.; the ppt. formed from boiling solutions consists of (I) alone. Ppts. formed under any conditions always contain adsorbed H_2O. This H_2O is contained in internal capillaries in the crystals, and adsorption and desorption are not quite reversible, as the H_2O tends to become trapped with the ageing of the crystals. (I) is not an ideal form in which to weigh Ca, even after drying at 110°. The least hygroscopic ppt. is formed from relatively conc. solutions, digesting the mixture for about 20 hr. at 90° before filtering. (I) sometimes loses H_2O of hydration on prolonged drying at 115—125°, especially when the ppt. is formed in neutral or ammoniacal solutions, and at 100°. E. S. H.

Dissolution of fluorite. W. KLEBER (Neues Jahrb. Min., 1932, **65**, A, 447—478; Chem. Zentr., 1932, ii, 2948).—The effect of concn. and temp. on dissolution by HCl was determined. A new end-form, probably due to the slight solubility of $CaSO_4$, was obtained with H_2SO_4. A. A. E.

Basic salts. II. Simple basic chlorides of bivalent heavy metals. E. HAYEK (Z. anorg. Chem., 1933, **210**, 241—246; cf. A., 1932, 914).—In general, bivalent heavy metals can form compounds of the type $M^{II}(OH)_2,M^{II}Cl_2$. The prep. of such compounds is described in the cases where M^{II}= Mn^{II}, Sn^{II}, or Fe^{II}. The *compounds* $3CdCl_2,ZnCl_2,8H_2O$ and $2HgCl_2,5ZnCl_2,12H_2O$ are described. E. S. H.

Chloro-complex salts of bivalent copper. H. REMY and G. LAVES (Ber., 1933, **66**, [*B*], 401—407).—The following salts have been prepared by admixture of solutions of their components in hot H_2O: $[NH_3Me]_2[CuCl_4]$, m.p. (indef.) 248°; $[NH_3Et]_2[CuCl_4]$, m.p. 249°; $[NH_3Pr^{\alpha}]_2[CuCl_4]$, m.p. (indef.) 242°; $[NH_3Bu]_2[CuCl_4]$, m.p. 250—251°; $[NH_2Me_2][CuCl_3]$, $[NH_2Me_2]_2[CuCl_4]$, and $[NH_2Me_2]_3[CuCl_5]$; $[NHMe_3][CuCl_3],2H_2O$ and $[NHMe_3][CuCl_3]$, m.p. about 158°; $[NHMe_3]_2[CuCl_4]$, m.p. 201°; $[NHMe_3][CuCl_4]$; $[NHMe_3]_3[Cu_2Cl_7]$; $[NMe_4]_2[CuCl_4]$; $[NH_3Pr^{\beta}][CuCl_3]$, m.p. about 190° (decomp.); $[NH_3Pr^{\beta}]_2[CuCl_4]$, m.p. about 154° after darkening at 55—60°. The region of existence is greatest for the salts with the complex for which the max. energy of formation is calc. H. W.

Changes in properties of chemical compounds due to complex formation. VIII. Compounds of boron fluoride and the synthetic application of boron fluoride. H. MEERWEIN (Ber., 1933, **66**, [*B*], 411—414).—$BF_3,2H_2O$, b.p. 46°/1 mm., f.p. 4·6—5°, is obtained by passing BF_3 (1 mol.) into H_2O (2 mols.). It is strongly acidic, dissolves metals, their hydroxides and carbonates, and decomposes $CHN_2{\cdot}CO_2Et$ explosively. It adds olefines and is characterised by cryst. *dioxan*, $BF_3,2H_2O,C_4H_8O_2$, m.p. 142°, and *cineole*, $BF_3,2H_2O,(C_{10}H_{18}O)_2$, m.p. 59·5—61°, salts. It adds BF_3 yielding BF_3,H_2O, f.p. 5·4—6°, not volatile without decomp. The following compounds with aliphatic alcohols are described: $BF_3,2MeOH$, b.p. 58—59°/4 mm., $BF_3,2EtOH$, b.p. 51—52°/1·5 mm.; $BF_3,2Pr^{\alpha}OH$, b.p. 56°/2 mm.; $BF_3,2BuOH$, b.p. 64—65°/3 mm.; $BF_3,2CH_2Cl{\cdot}CH_2{\cdot}OH$, b.p. 59°/2 mm.; $BF_3,OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, m.p. 40—42°. Compounds with primary alcohols are volatile in vac. without decomp.; those with sec. alcohols yield $BF_3,2H_2O$ and partly polymerised olefine. The dialcoholates are strongly acidic and conduct electricity in $PhNO_2$. In the cold they absorb BF_3, giving compounds BF_3,ROH, not volatile without decomp. Salts BF_3,ROX are obtained by addition of BF_3 to alkali alkoxides. With acids, BF_3 yields the types $BF_3,2RCO_2H$ (those derived from the simple acids of the acetic series are liquid and distillable in vac.) and BF_3,RCO_2H, solid and losing half the combined BF_3 when heated. Stability of the compounds decreases with increasing strength of the org. acid; $CH_2Cl{\cdot}CO_2H$ loses its combined BF_3 completely at 80°/vac., whilst $CHCl_2{\cdot}CO_2H$ absorbs BF_3 only below −15°, and loses it completely at room temp., and $CCl_3{\cdot}CO_2H$ does not unite with BF_3. BF_3 and cold Ac_2O afford the *compound* $(CHAc_2{\cdot}CO)_2O,3BF_3$, m.p. 192—193°, smoothly transformed by warm water into CO_2 and CH_2Ac_2. With $(EtCO)_2O$, $(PrCO)_2O$, and $(CHMe_2{\cdot}CO)_2O$ production of diacyl derivatives recedes in favour of the monoacyl compounds, $(COR{\cdot}CHR{\cdot}CO)_2O,3BF_3$, which yield mainly monoketones with relatively small amounts of β-diketones. In many respects the action of BF_3 resembles that of $AlCl_3$. Thus PhMe, PhOMe, and PhOH with Ac_2O and BF afford $COMe{\cdot}C_6H_4Me$ (*p*), $COMe{\cdot}C_6H_4{\cdot}OMe$, and $COMe{\cdot}C_6H_4{\cdot}OH$, respectively. $CHMe(OAc)_2$ and PhOMe give αα-dianisylethane. PhOH and AcOH or EtOAc yield $COMe{\cdot}C_6H_4{\cdot}OH$. COMePh and Ac_2O afford CH_2AcBz in 85% yield. *cyclo*Hexanone and Ac_2O yield 2-acetyl*cyclo*hexanone. Me styryl ketone and Ac_2O give α-phenyl-Δ^{α}-hexene-γε-dione. BF_3 causes the benzidine transformation, conversion of diazoamino- into aminoazo-benzene, of PhOAc into $COMe{\cdot}C_6H_4{\cdot}OH$, and the Beckmann change. H. W.

Preparation of metallic praseodymium. G. CANNERI and A. ROSSI (Gazzetta, 1932, **62**, 1160—1163).—A max. yield of Pr was obtained by the electrolysis of a fused mixture (m.p. 535°) of 55% $PrCl_3$, 27% NaCl, and 18% KCl, using a W cathode and Acheson graphite anode. The temp. must be kept < 600° to avoid polarisation and formation of PrO_2. The Pr contains <0·2% of other rare-earth metals and only traces of Si and C; *d* 6·765±0·008, m.p. 932±2°. O. J. W.

Thallium iodides. R. LYDEN (Finska Kem. Medd., 1932, **41**, 34—53).—TlI reacts with I in EtOH giving TlI_3 (sol. in presence of excess of I) and ppts. Tl_3I_4 (Tl_6I_8?) alone or mixed with TlI. In H_2O Tl_3I_4 is formed as black a ppt. TlCl (or K_3TlCl_6) and aq. I ppts. higher Tl iodides of varying composition, and forms in solution I and K_3TlCl_6. K_3TlCl_6 is decomposed partly by H_2O giving I and higher Tl iodides, but is stable in presence of excess of I. Higher Tl iodides and KI give I and K_3TlCl_6.

R. P. B.

Ammines of lower chlorides of titanium. W. C. SCHUMB and R. F. SUNDSTROM (J. Amer. Chem. Soc., 1933, **55**, 596—604; cf. A., 1923, ii, 868).—Anhyd. $TiCl_3$ is dimorphous. Anhyd. $TiCl_2$ decomposes slowly in vac. at 475° forming $TiCl_4$ and Ti. Contrary to Meyer and others (A., 1923, ii, 769), $TiCl_2$ is non-volatile in the range 300—600°. $TiCl_3$ combines with NH_3 at low temp. to form a white *hexammine* which loses $4NH_3$ at 300°, giving a black residue, probably a *diammine*, which ignites on exposure to air. At low temp., $TiCl_2$ forms with NH_3 a pearl-grey *tetrammine* which, at 300°, loses NH_4Cl leaving a black nitride (?). J. G. A. G.

Phosphorescence of zirconium oxide preparations. K. HOLZINGER.—See B., 1933, 188.

Preparation of HNO or $[HNO]_n$. P. HARTECK (Ber., 1933, **66**, [*B*], 423—426).—NO is passed at the temp. of liquid air into a stream of H_2 at 0·5 mm. split into atoms to the extent of 60%, whereby, when wide vessels are used to avoid explosions, the product (H : N : O—1 : 1±10% : 1) separates as a pale yellow, translucent deposit on the walls; it is precisely similar to that formed from NH_3 and O, so that identity is assumed. When the temp. is very gradually raised, the deposit becomes white; decomp. commences at −95°, and thence to room temp. is accompanied by evolution of N_2O with traces of H_2 and NO. Small local explosions occasionally caused marked evolution of the latter gases. Analysis shows the product to be mainly hyponitrous acid, accompanied, however, by nitroamide. H. W.

Additive compound of vanadium tetrachloride and sulphur tetrachloride. G. CANNERI and R. SALANI (Gazzetta, 1932, **62**, 1164—1165).—By the action of dry Cl_2 on V_2S_3 or on a mixture of SCl_2 and VCl_4 black crystals of the *compound* VCl_4,SCl_4, m.p. 32° (approx.), are obtained. O. J. W

Autoxidation. III. Initial act in autoxidation. H. N. STEPHENS (J. Physical Chem., 1933, **37**, 209—217).—Theoretical. A crit. discussion of published work indicates that the formation of the intermediate peroxide in autoxidation reactions does not consist of two stages, but is a single act.

E. S. H.

Oxidation of sodium hyposulphite by free oxygen. M. NICLOUX (Compt. rend., 1933, **196**, 616—618).—$Na_2S_2O_4$ acts as a reducer in three ways: (*a*) $2Na_2S_2O_4+O_2+2H_2O=4NaHSO_3$; (*b*) $Na_2S_2O_4+O_2+H_2O=NaHSO_3+NaHSO_4$; and (*c*) $2Na_2S_2O_4+3O_2+2H_2O=4NaHSO_4$. (*a*) occurs when it removes O from a substance containing it, (*b*) when in contact with free O_2, and (*c*) when treated with an energetic oxidiser. (*b*) applies also to the action of $Na_2S_2O_4$ on oxyhæmoglobin, and enables its amount to be determined (cf. A., 1873, 936; 1903, ii, 225).

C. A. S.

Aqueous solutions of thiocyanate–SO_2 complexes. C. J. HANSEN (Ber., 1933, **66**, [*B*], 447—450).—Thiocyanates, including HCNS, add SO_2 in H_2O, the mol. proportion rising to about 1 : 2 near the f.p. of the solution. The compounds are very freely sol. in H_2O. The solutions have marked SO_2 tension and, when evaporated, leave the homogeneous thiocyanate. Thiocyanate solutions are suitable for the absorption of SO_2 from the gases obtained by roasting sulphides. The thiocyanate–SO_2 solutions very readily remove H_2S from its mixtures with pptn. of S. The behaviour of NH_4, K, Na, Ca, Ba, and H thiocyanates is described in detail. H. W.

Preparation of molybdic oxide and some sulphides (molybdenum, tellurium, arsenic) in the crystalline state. L. DEBUCQUET and L. VELLUZ (Bull. Soc. chim., 1932, [iv], **51**, 1571—1572).—Cryst. MoO_3 is obtained by igniting $MoS_3,C_4H_{10}N_2,H_2S$ (cf. this vol., 401). Cryst. MoS_3, TeS_2, As_2S_3, or As_2S_5 is obtained when the corresponding compound with piperazine is treated with cold, dil. HCl or AcOH.

E. S. H.

Polyhalides. IV. Reactions in absence of a solvent. H. W. CREMER and D. R. DUNCAN (J.C.S., 1933, 181—189).—The action of various gases and vapours on solid polyhalides has been investigated. In some cases the polyhalide reacts as such; in others, dissociation into monohalide and halogen or halogen halide occurs prior to reaction (cf. action of NH_3, A., 1931, 182). The reactions between polyhalides and halogens or halogen halides are explained on this basis. O_3 acts on $KIBr_2$ thus: $KIBr_2+O_3=KIO_3+Br_2$. Amines form additive compounds with polyhalides. The action of a halogen or halogen halide on a monohalide may follow one of three courses: (1) reversible direct addition (*e.g.*, CsBr+IBr $\rightleftharpoons$ $CsIBr_2$); (2) irreversible direct addition (*e.g.*, CsI+Br_2 → $CsIBr_2$); (3) irreversible replacement, often followed by a reversible additive reaction (*e.g.*, $2KI+Br_2 \longrightarrow 2KBr+I_2$; $I_2+Br_2 \rightleftharpoons 2IBr$; KBr+IBr $\rightleftharpoons$ $KIBr_2$; all the iodides investigated, except CsI, reacted in this way). The formation of any polyhalide from its dissociation products follows course (1), the reaction $CsBr+Cl_2 \longrightarrow CsBrCl_2$ follows course (2), and $KI+2Cl_2 \longrightarrow KICl_4$, $KI+2ICl \longrightarrow KICl_2+I_2$, and $RBr+2ICl \longrightarrow RICl_2+IBr$ (R=Cs or K) follow course (3). Velocity data are given and certain generalisations deduced. None of the reported cases of isomerism ($CsICl_2$, $CsIBr_2$, and $RbBrCl_2$, cf. A., 1892, 773; 1917, ii, 531) can be confirmed.

D. R. D.

Working up iodine residues. G. A. STUTTERHEIM (Chem. Weekblad, 1933, **30**, 166).—The Cu_2O recovered in van Voorst's method (A., 1931, 448, 1022) is preserved out of contact with air and re-used to work up fresh residues. S. C.

Reduction and oxidation of manganese silicates. B. BOGITCH (Compt. rend., 1933, **196**, 414—416; cf. A., 1929, 400, 1409).—Mn silicates at 1300° in presence of a reducing (*e.g.*, CO, H_2) or

neutral (*e.g.*, CO_2, N_2) gas are reduced to Mn^{II} silicates which are colourless with $< 4\%$ MnO and with more are green. In presence of O_2 a violet Mn^{III} silicate is formed, the tint being the deeper the greater is the excess of O. Na silicates fused with Mn_3O_4 evolve O_2 at the moment of fusion, forming a frothy mass, but the O_2 is reabsorbed on cooling, the amount of O_2 retained being the smaller the higher is the temp. and the greater the duration of fusion. Na silicates rich in Mn when powdered absorb O_2 rapidly above 200°; on fusion these retain the less O_2 the less Mn is present, the higher the temp. of fusion, and the less is the O_2 in the atm. C. A. S.

Formation of alkali-soluble substances in the carbon monoxide reaction on iron. T. BAHR (Ges. Abhandl. Kenntn. Kohle, 1932, **10**, 160—163; Chem. Zentr., 1932, ii, 2805—2806).—The C deposited at 400—600° contains substances similar to humic acid. A. A. E.

Magnetic iron oxide and its hydrate. O. BAUDISCH (Biochem. Z., 1933, **258**, 69—75; cf. A., 1932, 709).—Improved methods of preparing γ-Fe_2O_3 and its hydrate from purest Fe (from Fe carbonyl) and purest HCl ($FeCl_2$ and $FeCl_3$) by pptn. with C_5H_5N and the magnetic and other physical properties of these compounds are described. Dehydration of the hydrate at 250—270° gives a strongly magnetic oxide, but if heating at this temp. is continued for 12—24 hr. the magnetic property disappears. W. McC.

Determination of hydrogen by combustion. A. J. ANTHONY (Z. Biol., 1933, **93**, 405—406).—Combustion is effected in a 1-c.c. glass chamber containing a Pt spiral, 10—12 mm. long, of 0·2 mm. diam. wire. When a small current is passed through the wire the KOH level in the final absorption vessel, to which the combustion chamber is sealed by capillary tubing, falls owing to expansion of the gas, and then rises as combustion begins. The current is then increased until the spiral glows, and the gas is allowed to pass. By following in this manner the initiation of the combustion, the danger of explosion is greatly reduced. H. F. G.

Stick antimony electrode for the measurement of hydrogen-ion concentration. T. UEMURA and H. SUEDA (Bull. Chem. Soc. Japan, 1933, **8**, 1—10).—The stick Sb electrode in an unstirred solution in contact with air gives trustworthy p_H vals. for p_H 1—9 and approx. vals. for p_H 9—12, the e.m.f. against a Hg_2Cl_2 electrode being approx. $(53{\cdot}8p_H - 0{\cdot}7) \times 10^{-3}$ volt. The e.m.f. increases with rise of temp. The surface of the electrode turns black in solutions of p_H 1—8 and whitish in solutions of p_H 9—12. Some time is required in order to establish equilibrium with the solution. The concn. of Sb_2O_3 has only a slight effect on the e.m.f. J. W. S.

Potentiometric analysis. W. HILTNER (Chem. Fabr., 1933, **6**, 111—113).—Details are given of a thermionic valve potentiometer in which a double grid valve is employed. The potential to be measured is applied across the two grids and the reading of a milliammeter connected across the two plates is observed, the reading when a Weston cell is connected to the grids being taken as standard. Suitable electrodes are described. H. F. G.

Detection of hydrogen peroxide by means of spot reactions. F. FEIGL and E. FRAENKEL (Mikrochem., 1933, **12**, 303—306).—Formation of Prussian-blue from Fe^{III} ferricyanide solution detects $0{\cdot}08 \times 10^{-6}$ g. H_2O_2. Bleaching of Ni oxides (used as paste of Ni_2O_3 and $BaSO_4$) detects $0{\cdot}01 \times 10^{-6}$ g. Yellow coloration with alkali vanadate paper detects 3×10^{-6} g. Warming with a drop of 0·01% $AuCl_3$ gives red or blue colloidal Au, sensitive to $0{\cdot}07 \times 10^{-6}$ g. Warming with acidified 5% NH_4SCN gives an orange ppt. or coloration, sensitive to $0{\cdot}7 \times 10^{-6}$ g. J. S. A.

Gravimetric separation of chlorine, bromine, and iodine. G. BURGER (Z. anal. Chem., 1933, **92**, 19—23).—The halogens in one portion of the sample are all pptd. and weighed as Ag salts. I′ is removed from another portion by oxidation to I with KIO_3 in presence of H_2SO_4 and Cl′ and Br′ are then pptd. as Ag salts and weighed. This mixture is next transformed into AgBr or AgI by calcining with the corresponding NH_4 salt and again weighed. From these data the proportion of the different Ag salts in the mixture, and hence of halogens in the original product, may be determined indirectly. A "cella" filter is recommended. M. S. B.

Determination of periodic acid in presence of iodic acid. P. FLEURY and J. LANGE (J. Pharm. Chim., 1933, [vin], **17**, 107—113).—(1) 5—25 c.c. aq. IO_4' neutral to phenolphthalein, representing not more than 5—6 c.c. 0·1*M*-HIO_4, is mixed with 5—10 c.c. of saturated aq. $NaHCO_3$, 15 c.c. of 0·1*N*-H_3AsO_3 containing $NaHCO_3$, and 1 c.c. of 20% aq. KI to act as catalyst. After 15 min. at room temp. the excess of H_3AsO_3 is titrated with 0·1*N*-I. HIO_4 only, and not HIO_3, is reduced. (2) 10 c.c. of the neutralised HIO_4 and HIO_3, solution, equiv. to $>$ 3 g. 0·1*N*-HIO_4, is mixed with 3 c.c. of 14·3% aq. $Na_2CO_3{,}10H_2O$ and 10 c.c. of 1% aq. $MnSO_4$, the ppt. is centrifuged, the liquid decanted, and the oxidised Mn ppt. washed by centrifuging, using 5% aq. Na_2SO_4 to prevent peptisation. 2 c.c. 20% aq. KI and 0·4—0·5 c.c. 20% H_2SO_4 are added to the ppt., which dissolves, liberating I and CO_2. The former is titrated with 0·1*N*-$Na_2S_2O_3$ without addition of starch. 3% should be subtracted from the result. M. S. B.

Reagent for determination of oxygen. V. I. PANASIUK (Ukrain. Chem. J., 1932, **7**, [Sci.], 94—97).—Pyrogallol is replaced by a solution of 35·4 g. of $FeSO_4$ in 120 c.c. of H_2O, to the filtrate from which 10 g. of tartaric acid and 45 c.c. of 25% aq. NH_3 are added. R. T.

Determination of ozone by absorption measurements, using the photoelectric cell. R. RUYSSEN (Natuurwetensch. Tijds., 1933, **15**, 6—13, and Bull. Acad. roy. Belg., 1932, [v], **18**, 1085—1094).—The max. in the visible absorption band of O_3 coincides approx. with the *D* line. Apparatus for determining O_3 at concns. of 2—5% by measuring the absorption of a 100 cm. layer by means of a Na lamp and a K photoelectric cell is described. The absorption coeff. for the *D* line is $3{\cdot}94 \times 10^{-4}$, the max. deviation being about 2%. H. F. G.

Potentiometric determination of sulphates by indirect titration with benzidine. I. A. ATANASIU and A. J. VELCULESCU (Z. anal. Chem., 1932, **90**, 337—340; cf. A., 1932, 955).—A standard solution of benzidine in dil. HCl is added in excess to a solution of the sulphate, and the excess of benzidine in the filtrate is determined potentiometrically by titration with KNO_3. The error is within 0·0006 g. in 0·01—0·12 g. H_2SO_4. F. L. U.

Volumetric and potentiometric determination of tri- and tetra-thionate by means of silver nitrate. F. ISHIKAWA and T. MUROOKA (Sci. Rep. Tohoku, 1932, **21**, 527—536).—Reaction between $AgNO_3$ and a tri- or tetra-thionate takes place quantitatively: (1) $S_xO_6'' + 2Ag^{\cdot} = Ag_2S_xO_6$, and (2) $Ag_2S_xO_6 + 2H_2O = Ag_2S + 2H_2SO_4 + (x-3)S$, where $x=3$ or 4, respectively. These reactions can be used for the volumetric and potentiometric titration of the polythionates. O. J. W.

Dumas technique for substances difficult to burn. J. F. CROUCH (J. Amer. Chem. Soc., 1933, **55**, 852—853).—The substance is mixed with a large excess of CuO and packed into a Cu tube 15 cm. long and 1 cm. in diameter, and the whole is placed in the position usually occupied by the combustion boat. J. G. A. G.

Antimony electrode. V. Electrometric micro-determination of "formol"-titratable nitrogen with the antimony electrode. A. ROCHE and J. ROCHE (Arch. Phys. biol. Chim.-Phys., 1932, **9**, 273—276; Chem. Zentr., 1932, ii, 2489).—The neutral solution is brought to p_H 8·3 with slightly alkaline CH_2O, when $(CH_2)_6N_4$ and NH_2-acids are formed from the NH_3, but visual titration cannot be employed in presence of hydrolysed protein-N compounds or when only traces of N are present. By means of the Sb electrode $\leq$ 0·05 mg. N can be determined ($\pm$1% for $>$ 1 mg., $\pm$1—2% for 0·1—1 mg., $\pm$3—4% for 0·1—0·05 mg.). A. A. E.

Acidimetric determination of alkali nitrites. B. STEMPEL (Z. anal. Chem., 1933, **91**, 413—415).—A measured excess of standard aq. N_2H_4,H_2SO_4 is heated with the neutral nitrite solution. The excess is then titrated with NaOH in presence of CH_2O (see below). F. L. U.

Potentiometric investigation of the oxidimetric determination of hydrazine. O. STELLING (Svensk Kem. Tidskr., 1933, **45**, 4—9).—N_2H_4 and $KMnO_4$ do not react quantitatively according to the equation $N_2H_4 + O_2 = N_2 + 2H_2O$ (cf. Kolthoff, A., 1924, ii, 871). In dil. aq. H_2SO_4 less, in HCl more, $KMnO_4$ than the theoretical reacts. Side reactions are prevented by adding KI in acid solution before titrating, when three sudden potential changes are found, corresponding with $N_2H_4 \longrightarrow N_2$, $I^- \longrightarrow I$, and $I \longrightarrow ICl$. After correcting the $KMnO_4$ titre for the amount used by the KI, quant. results are obtained. KBr has no effect, and titration in alkaline solution cannot be used. N_2H_4 and I react quantitatively in $NaHCO_3$ solution (cf. Gilbert, A., 1925, ii, 239) and the reaction can be followed potentiometrically. $KBrO_3$ reacts quantitatively with N_2H_4 in hot HCl solution and the reaction is specially suited to potentiometric titration. N_2H_4 and KIO_3 give I in H_2SO_4 solution and ICl in HCl solution. R. P. B.

Formaldehyde titration of hydrazine sulphate. B. STEMPEL (Z. anal. Chem., 1933, **91**, 412).—N_2H_4,H_2SO_4, when titrated with NaOH in presence of neutral CH_2O, behaves as a dibasic acid. Neutral EtOH produces the same effect. F. L. U.

Determination of phosphorus in aluminium. K. STEINHAUSER and J. STADLER.—See B., 1933, 194.

Rapid determination of boric acid in arsenic-free borosilicates. W. MYLIUS (Chem.-Ztg., 1933, **57**, 173—175, 194—195).—The powdered sample (0·5 g.) is heated with KOH+NaOH at about 500° for 6—7 min., and the melt is dissolved in 75 c.c. of H_2O. The solution is rendered slightly acid (Congo-red), and saturated aq. $Ba(OH)_2$ is added to ppt. CO_3'', SiO_2, Al''', Zn'', etc.; the ppt. is redissolved and repptd. twice, to free it from B_2O_3, and the combined filtrate is titrated with $Ba(OH)_2$ after addition of fructose. If the sample is a Zn borosilicate, $K_3Fe(CN)_6$ should be used to ensure removal of all the zinc. The error is $\pm$0·05% on the wt. of the sample. H. F. G.

Determination of potassium by titration of the cobaltinitrite with potassium permanganate. P. L. HIBBARD and P. R. STOUT (J. Assoc. Off. Agric. Chem., 1933, **16**, 137—140).—The material (0·2—2·0 mg. K) is freed from org. matter and the K pptd. as $K_3Co(NO_2)_6$ from AcOH solution. After 12—15 hr. the ppt. is collected on a talc-covered filter, washed, and added to excess of acidified $KMnO_4$, the excess of which is reduced with standard $Na_2C_2O_4$ and titrated back with $KMnO_4$. J. W. S.

Recovery of platinum in potash determinations. L. D. HAIGH and A. R. HALL (J. Assoc. Off. Agric. Chem., 1933, **16**, 147—148).—Residues are treated with conc. NH_4Cl; the $(NH_4)_2PtCl_6$ is collected and combined with K_2PtCl_6 residues. These ppts. are dissolved in hot H_2O, 5 vol.-% of conc. HCl is added, and pieces of mossy or granular pure Zn are added until no more Pt is pptd. Base metals are removed with HCl and the Pt is dissolved in aqua regia and converted into H_2PtCl_6 in the usual way. J. W. S.

Conductometric and electrometric titration of mixtures of sodium hydroxide and carbonate. M. AUMÉRAS and J. MARCON (Bull. Soc. chim., 1932, [iv], **51**, 1594—1605).—Titration with HCl by the conductometric method indicates the neutralisation points of NaOH, Na_2CO_3, and $NaHCO_3$, and gives satisfactory results in dil. solutions. The influence of dissolved CO_2 has been examined and the observations provide a means of determining small amounts of free CO_2. The electrometric method, using the H electrode, is less accurate and is suitable only when the concn. of the solution is $>0{\cdot}01N$. E. S. H.

Photographic sensitivity of lines of alkali metals in the oxy-acetylene flame. R. BOSSUET (Compt. rend., 1933, **196**, 469—470; cf. A., 1932, 825).—The method previously described is rendered more sensitive by using rapid panchromatic plates and a Bourguel spectrograph. The most sensitive line and min. amount of the chloride detectable are :

for Li 6708, 3×10^{-7} mg.; Na 5890 and 5896, traces: K 4044, $1{\cdot}3\times10^{-3}$ mg.; Rb 4216, 10^{-3} mg.; Cs 4555, 10^{-3} mg. C. A. S.

Potentiometric determination of free alkali hydroxide in phenoxides. V. A. KARGIN and M. I. USANOVICH.—See B., 1933, 215.

Quantitative analysis of calcite–aragonite mixtures by *X*-rays. E. G. COX and T. H. GOODWIN (Chem. and Ind., 1933, 172).—Relative intensities of calcite and aragonite lines in *X*-ray photographs of the mixture by the powder method give the proportions with an accuracy of $\pm\frac{1}{2}\%$ to 2%, according to the composition. H. J. E.

Volumetric determination of calcium oxide in lime. I. TANANAEV.—See B., 1933, 226.

Determination of calcium oxide in magnesium compounds. P. ACKERMANN.—See B., 1933, 226.

Rapid determination of calcium in phosphorite and limestone. S. N. ROSANOV and A. G. FILIPPOVA (Z. anal. Chem., 1932, **90**, 340—350).—For routine analysis the methods of Chapman (B., 1929, 142) and of Passon (A., 1898, ii, 642; 1899, ii, 246) are shown to be suitable and nearly as accurate as the standard methods. F. L. U.

Separation of the cations of the alkali, alkaline-earth, and ammonium sulphide groups. A. P. KRESCHKOV (Z. anal. Chem., 1933, **92**, 92—95).—A strongly ammoniacal solution of the cations is treated with $(NH_4)_3PO_4$, when ppts. are obtained of $FePO_4$, $AlPO_4$, $CrPO_4$, $Mn(NH_4)PO_4$, $Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ba_3(PO_4)_2$, and $Mg(NH_4)PO_4$, whilst $[Ni^{II}(NH_3)_6]^{\cdot\cdot}$, $[Co^{II}(NH_3)_6]^{\cdot\cdot}$, $[Zn^{II}(NH_3)_6]^{\cdot\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, and $NH_4^{\cdot}$ remain in solution. The latter are separated in the usual way. A solution of the ppt. in a little dil. HCl is almost neutralised, NaOAc and $FeCl_3$ are added until it is reddish-brown, and it is diluted, boiled, and filtered. This removes $PO_4^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$, and these, and the cations in solution, can be separated by any method. J. W. S.

Precipitation and determination of calcium in the presence of Ag, Hg, Pb, Cu, Bi, Cd, As, Sb, Sn, Co, Ni, Fe, Al, Mn, and Zn. E. ERDHEIM (Rocz. Chem., 1933, **13**, 64—69).—25 c.c. of a solution of 100 g. of citric acid and 350 c.c. of aq. 25% NH_3 in 650 c.c. of H_2O are added to the acid solution under examination, followed by 10 drops of aq. NH_3. The vol. is made up to 250 c.c., and 1 g. of $(NH_4)_2C_2O_4$ is added to the boiling solution, pptd. CaC_2O_4 is dissolved in H_2SO_4, and the solution is titrated with $KMnO_4$. Under these conditions, salts of the above heavy metals do not interfere; $Cr^{\cdot\cdot\cdot}$, if present, should first be removed, and $Fe^{\cdot\cdot}$ should be oxidised to $Fe^{\cdot\cdot\cdot}$. The experimental error is $>1\%$. R. T.

Occlusion by precipitates. B. TEŽAK (Bull. Soc. Chim. Yougoslav., 1932, **3**, 147—156).—The $BaCl_2$ content of $BaSO_4$ pptd. from aq. Na_2SO_4 by $BaCl_2$ varies periodically with the concn. of Na_2SO_4; this effect is ascribed to differences in adsorptive power for $BaCl_2$ of particles of $BaSO_4$ in different stages of aggregation. R. T.

Semi-micro- and micro-determination of magnesium. A. BLANCHETIERE and M. ARNOUX (J. Pharm. Chim., 1933, [viii], **17**, 97—107).—A white cryst. ppt. of $MgI_2,10H_2O,2(CH_2)_6N_4$ is obtained by the action of $(CH_2)_6N_4$ on aq. $MgSO_4$ in presence of excess of KI after all other cations except alkalis and alkaline earths have been removed. The solution must be neutral or slightly acid with AcOH, and $PO_4^{\cdot\cdot\cdot}$ must be absent. Pptn. must take place at a low temp., about 8°, as solubility increases fairly rapidly with rise of temp. After filtering on a microfilter, washing with $COMe_2$ saturated with the product, and then with $CHCl_3$, the compound is redissolved in H_2O and the amount determined either by (1) titrating I' with $AgNO_3$ by adding excess and titrating the excess with NH_4CNS, or (2) boiling with an excess of H_2SO_4 to decompose $(CH_2)_6N_4$ and titrating the excess acid with NaOH using K alizarinsulphonate as indicator. The latter method gives more consistent results. The concn. of Ca must not exceed 0·2 mg. per c.c. of solution to be analysed. M. S. B.

Volumetric determination of lead. A. TRAVERS and LU (Compt. rend., 1933, **196**, 548—549).—Determination of Pb as $PbSO_4$ in presence of Bi or Ba is unsatisfactory; a satisfactory method is to bring the Pb into neutral solution and boil with aq. NaOCl, whereby the Pb is pptd. as PbO_2, which is determined iodometrically. To analyse a Pb–Bi or Pb–Bi–Cd alloy the Bi is separated as basic formate (cf. A., 1928, 388), and the Cd remaining with the Pb is converted into $Cd(OH)_2$ by the NaOCl, and then dissolved out by aq. NH_3 free from CO_2 (cf. A., 1931, 453). Pb is quantitatively separated from Ba as PbS by saturating the solution under pressure with H_2S, and then heating for 2 hr. at 100°. C. A. S.

β-Naphthol test for copper. C. C. FULTON (Amer. J. Pharm., 1933, **105**, 62—63).—The pink colour of a solution of β-$C_{10}H_7{\cdot}OH$ in ammoniacal aq. EtOH becomes cloudy yellowish-green in presence of Cu. 3×10^{-6} pt. of Cu can be detected. E. H. S.

Precipitation of copper and tin groups using hydrogen sulphide. I. Influence of increasing concentrations of ammonium chloride on the complete precipitation of lead and cadmium sulphides at 0·3*N*-HCl. II. Metals other than lead and cadmium. III. Effect of ammonium salts. L. LEHRMAN. L. LEHRMAN and H. WEISSBERG (J. Chem. Educ., 1933, **10**, 50—53, 53—54, 54—55).—CaS and PbS are incompletely pptd. when H_2S is passed into a strongly acid (HCl) solution afterwards diluted to 0·3*N*-HCl, the quantity unpptd. being greater if much NH_4Cl is present. Sn^{IV} when present alone in 0·3*N*-HCl is incompletely pptd. by H_2S to the extent of a few mg., but when all the elements of the group are present, <1 mg. escapes pptn. NH_4 salts other than NH_4Cl do not prevent pptn. of Pb, Cd, and Sn^{IV}; two methods for removing Cl' are described. CH. ABS.

Micro-volumetric analysis using diphenylcarbazide and diphenylcarbazone as indicators (mercurimetry). J. V. DUBSKY and J. TRTILEK (Mikrochem., 1933, **12**, 315—320).—Hg ions give an intense violet-blue coloration with diphenylcarbazide (I) and diphenylcarbazone (II). Chlorides may be titrated in dil. acid solution with 0·01*N*-$Hg(NO_3)_2$,

using (I), or better (II), as indicator, in consequence of formation of non-ionised $HgCl_2$. Heavy metals have little disturbing effect; in presence of Cu results were 0·5% low. J. S. A.

Acetates as a means of separating the yttrium group rare-earth elements from each other. J. A. HARRIS and A. H. CAMERON (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 61—62).—On fractional crystallisation of the acetates of the Y group, Er concentrates in the head fraction and Nd and Sm in the most sol. fraction. J. W. S.

Comparison of the efficiencies of bromates and nitrates in the separation of the rare-earth elements from one another. J. A. HARRIS and (MISS) D. E. WYLIE (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 63—68).—The order of the solubilities of the BrO_3' salts differs from that of the NO_3' salts. Bromates are recommended for the rapid separation of Er or of Nd and Sm from a mixture of the Y group. The nitrates afford a means for the rapid concn. of Eu, Tb, and Gd from a general mixture. J. W. S.

Analytical behaviour of gallium. E. S. VON BERGKAMPF (Z. anal. Chem., 1932, **90**, 333—335).—Details with regard to separation of Ga from its alloys with Al, and to its pptn. by "cupferron," are given. The limits of p_H within which Ga can be pptd. as $Ga(OH)_3$ are 3·4 and 9·7. F. L. U.

Test for aspirin, salicylic acid, and manganese. C. C. FULTON (Amer. J. Pharm., 1933, **105**, 59—61).—Aspirin or salicylic acid treated with H_2O_2, NH_3, and a dil. solution of a $Mn^{\cdot\cdot}$ salt develops a pink or red colour changing to brown. By suitable modification Mn may be detected in concns. of from 5×10^{-6} to 5×10^{-4}. E. H. S.

Determination of manganese, iron, and titanium by B. Lange's photo-electric colorimeter. M. BENDIG and H. HIRSCHMULLER (Z. anal. Chem., 1933, **92**, 1—7).—A colorimeter is described in which a Se half-conductor photo-cell, giving sufficient current to affect an ordinary pointer galvanometer, is used for detection. The sensitivity is increased by using colour filters of the same colour as the solution when this is strongly coloured and of the complementary colour for a weakly coloured solution. A special "substitution" method is employed for great precision. Mn is determined as MnO_4' obtained by oxidation with $(NH_4)_2S_2O_8$ in presence of $AgNO_3$. The concn. of H_2SO_4 is kept const. at 10%. KCNS is used for the determination of Fe. A green filter is used for concns. up to 1 mg. Fe_2O_3, and a red filter for higher concns. Ti is determined by oxidation to TiO_3 by H_2O_2. If Fe is present it must be decolorised by addition of H_3PO_4. Since this also affects the colour due to Ti, a suitable standardisation curve must be prepared to allow for this. If monochromatic light is used, the relation between extinction and concn. is linear, and so facilitates the determination of the standardisation curve. M. S. B.

Determination of metallic iron, ferrous oxide, and ferric oxide in mixtures. F. KAUFMANN (Chem.-Ztg., 1933, **57**, 122—123).—The finely powdered material (2·5 g.) is dissolved in freshly prepared "bromoacetate" solution (60 c.c.) (cf. Mathesius, Stahl u. Eisen, 1914, 868) and after subsequent gentle boiling for 10—15 min., the cooled solution is filtered. After removing Br by boiling in H_2O under CO_2 for 5 min., the insol. material is dissolved in conc. HCl (50 c.c.) and HF (1 c.c.), when the difference between its Fe^{II} and total Fe content gives the Fe^{III} content of the material. The total Fe content of the original material is determined in the usual way and the metallic Fe by the $HgCl_2$ method. D. F. T.

Determination of cobalt in cobaltammines. W. M. MCNABB (Z. anal. Chem., 1933, **92**, 7—11).—The SO_4'' method for the determination of Co cannot be applied in the analysis of complex ammines which are salts of a non-volatile acid. A modification of the method for the determination of Co in steel is therefore used. Co^{II} is oxidised to $Co(OH)_3$ by heating with NaOH and H_2O_2. After filtering by suction and washing with hot H_2O the ppt. is dissolved in H_2SO_4 in presence of KI. Co^{III} is thus reduced to Co^{II} again and the liberated I is titrated with $Na_2S_2O_3$. The method cannot be used for $C_2H_4(NH_2)_2$ salts because they are not completely decomposed with NaOH and H_2O_2. M. S. B.

Microacidimetric determination of nickel. J. V. DUBSKÝ and E. HAUER (Mikrochem., 1933, **12**, 321—326).—Ni dicyanodiamidine (I) is readily sol. in dil. acid. For the determination of Ni, excess of dicyanodiamidine sulphate is added to the solution of Ni, and (I) pptd. by neutralisation with KOH. The washed ppt. is titrated with 0·1*N*-HCl, using Me-red as indicator. J. S. A.

Qualitative analysis with small quantities. III. Analysis of the ammonium sulphide group in presence of phosphate. A. SCHEINKMANN (Z. anal. Chem., 1933, **91**, 415—418; cf. A., 1932, 1223).—A method of procedure based on addition to the filtrate from the H_2S ppt. of excess of $(NH_4)_2HPO_4$, aq. NH_3, and $(NH_4)_2S$, and subsequent digestion of the resulting ppt. with 2*N*-AcOH, whereby Mn, Mg, Ca, Sr, and Ba go into solution, is described. F. L. U.

Sodium sulphide in qualitative analysis; modified Fresenius–Vortmann method. A. SOLDI (L'Ind. Chimica, 1933, **8**, 159—162).—The difficulties encountered in the qual. analysis of mixtures containing Co and Ni, and PO_4''' etc. are discussed. In the scheme described, Pb, Ag, and Hg are pptd. as chlorides, org. matter is oxidised with $Br–H_2O$, and NH_3 is removed from the filtrate by boiling with NaOH. Na_2S is added to the cooled mixture, and the resulting ppt. is extracted with HCl (1 : 1), leaving a residue of Pb, Bi, Cu, and Cd sulphides, which are separated by the usual procedure. The filtrate from the Na_2S ppt. is treated with NH_4Cl and the Al and Hg are removed, the As, Sb, and Sn remaining in solution. The HCl extract is diluted and treated with Na_2S to remove traces of Bi and Pb, conc., treated with solid Na_2CO_3 in excess, and boiled; PO_4''', BO_3', etc. remain in solution, and the ppt. is separated by the standard methods into groups containing Fe, Cr, and Mn, Zn, Co, and Ni, and Ca, Sr, and Ba, respectively. H. F. G.

8-Hydroxyquinoline for the determination of tungsten. S. HALBERSTADT (Z. anal. Chem., 1933, **92**, 86—89).—A dil. alkaline or neutral solution containing the W as WO_4'' is treated with excess of a 4% solution of 8-hydroxyquinoline in EtOH, heated nearly to boiling, and acidified with AcOH. The solution is then boiled and the yellowish ppt. of $WO_2(C_9H_6ON)_2$ collected, washed until the washings are colourless, dried at 120°, and weighed (1 g.= 0·3650 g. W). J. W. S.

Quantitative complete microanalysis of uraninites. F. HECHT and W. REICH-ROHRWIG (Mikrochem., 1933, **12**, 281—292).—A detailed account of procedure, using 25—40 mg. of material. J. S. A.

Colorimetric determination of titanium. R. SCHWARZ (Z. anorg. Chem., 1933, **210**, 303).—The coloration produced when $TiOSO_4$ and H_2O_2 react in presence of H_2SO_4 is probably due to $[TiO_2(SO_4)_2]H_2$. E. S. H.

Simple and complex iodates of titanium. A correction. P. R. RAY (Z. anorg. Chem., 1933, **210**, 304).—Cf. A., 1932, 1099. E. S. H.

Determination of zirconium in steel. Selenious acid method. S. G. SIMPSON [with W. C. SCHUMB].—See B., 1933, 231.

Sensitive test for gold with α-naphthylamine hydrochloride. H. HOLZER and W. REIF (Z. anal. Chem., 1933, **92**, 12—15).—5 c.c. of filtered aq. α-$C_{10}H_7\cdot NH_2$,HCl and 2—3 c.c. EtOAc are shaken with 5—10 c.c. of aq. $AuCl_3$ which is either neutral or slightly acid with HCl. After a short time a violet- to rose-red additive *product*, $AuCl,C_{10}H_7\cdot NH_2$,HCl, is formed in the EtOAc layer. The reaction may be obtained with 0·008 mg. of Au diluted to 1 in 10^6. A similar colour is formed with $FeCl_3$, but it is due to oxidation of the α-$C_{10}H_7\cdot NH_2$,HCl, and the disturbing influence of Fe can be prevented by tartaric acid or Na K tartrate. The sensitivity of the test is reduced, but 1 part of Au in 700 parts of Fe can still be detected. The additive compound formed with $PdCl_2$, $Pd[C_{10}H_7\cdot NH_2]_2Cl_2$, is orange-yellow. M. S. B.

Analysis of platinum minerals. I—VIII. INSTITUT DE PLATINE, B. G. KARPOV, and A. N. FEDEROVA.—See B., 1933, 232.

Detection of free metal particles in dust etc. T. J. WARD.—See B., 1933, 194.

Use of potassium hydroxide as a fusion agent. P. F. THOMPSON.—See B., 1933, 194.

Coiled-filament resistance thermometers. C. H. MEYERS (Bur. Stand. J. Res., 1932, **9**, 807—813).—The strain-free coiled windings of a 25-ohm thermometer are wound in a space 5 mm. diam. and 2 cm. long, which is hermetically sealed, and filled with He to reduce lag. C. W. G.

Accuracy of freezing-point determination by means of the Beckmann thermometer. H. C. S. SNETHLAGE (Rec. trav. chim., 1933, **52**, 139—150).—The sources of error are discussed and methods described for obtaining an accuracy of ±0·0005°. D. R. D.

Determination of specific heats of liquids. Specific heats of aniline and benzene over the approximate range 20—50°. A. FERGUSON and J. T. MILLER (Proc. Physical Soc., 1933, **45**, 194—207).—The electrical power necessary to maintain the calorimeter and its contents at various temp. is measured. The sp. heat of NH_2Ph is $0{\cdot}495_0+0{\cdot}000275(T-20)+0{\cdot}0000035(T-20)^2$ and of C_6H_6 is $0{\cdot}395_8+0{\cdot}00125(T-20)$. C. W. G.

Glass autoclave to facilitate observation of reactions at high temperature and pressure. O. GERNGROSS, K. M. HOFFMANN, and G. KLEIN (Chem. Fabr., 1933, **6**, 93).—A vertical cylinder of special glass is closed above and below by end-plates, the joints being made with asbestos and tightened evenly by a screw working on 10 rods. An upper cover plate is separately held by a screw and bow with another asbestos joint, and only the latter need be removed to withdraw a sample of the contents of the autoclave. The capacity of this is 750 c.c. and it can be used up to 170° and 7 atm. An agitator can be fitted if required. C. I.

Measurement of low-voltage *X*-ray intensities. L. S. TAYLOR and C. F. STONEBURNER (Bur. Stand. J. Res., 1932, **9**, 769—780).—The ionisation produced by 3—12 kv. rays is measured in a very small guarded field ionisation chamber. C. W. G.

Colorimetry. F. L. HAHN (Z. anal. Chem., 1932, **90**, 330—332; cf. A., 1931, 54).—A criticism of a paper by Pestov (A., 1932, 920). F. L. U.

Photo-electric absorption measurement of coloured and cloudy solutions. R. SEIFERT (Pharm. Zentr., 1933, **74**, 97—102).—The comparison and adjustment of the intensities of two colours or turbidities may be carried out photo-electrically. With the aid of the circuit and apparatus described the relationships between the current and the light absorption at varying concns. can be expressed graphically and an equation developed which enables accurate vals. for the concn. to be calc. from any galvanometer reading. E. H. S.

Colour filters for altering colour temperature. Pyrometer absorption and daylight glasses. H. P. GAGE (J. Opt. Soc. Amer., 1933, **23**, 46—54).—Analysis of the Wien equation gives formulæ applicable to colour filters suitable for transforming light of one colour temp. to another. The formulæ for daylight glasses are also calc. J. L.

Self-registering spectrometer. C. LEISS (Physikal. Z., 1933, **34**, 172—175).—The apparatus and its use are described. A. J. M.

Innovations in photomicrography with ultra-violet light. A. KOHLER (Naturwiss., 1933, **21**, 165—173).—A new monochromator for ultra-violet light is described. A. J. M.

Multi-range potentiometer and its application to the measurement of small temperature differences. H. B. BROOKS and A. W. SPINKS (Bur. Stand. J. Res., 1932, **9**, 781—798).—The "second method" of Poggendorff is used. C. W. G.

Universal direct-reading hydrogen-ion potentiometer. C. MORTON (J.S.C.I., 1933, **52**, 6—ST).—

A universal H· potentiometer, reading directly in p_H units, is described. The instrument is applicable to all reversible electrode systems (including glass electrode systems) at any temp. between 10° and 30°. Alternative ranges of 0—14 p_H units and 0—1400 mv. are provided on the same scale, readings being obtained directly to 0·01 p_H unit and 1 mv., respectively. Using the glass electrode, readings are obtained directly in p_H units with an accuracy of $\pm$0·01 p_H over the range p_H 2—10. Erroneous results are obtained with the Sb electrode, the e.m.f.–p_H relationship of which is non-linear.

Metal-connected glass electrode. M. R. Thompson (Bur. Stand. J. Res., 1932, **9**, 833—853).—Glass electrodes with direct metallic connexion can be constructed with substantial walls and have satisfactory accuracy and sensitivity. C. W. G.

Temperature coefficient of the standard Weston cell. P. Vigoureux and S. Watts (Proc. Physical Soc., 1933, **45**, 172—179).—The difference in microvolts from the e.m.f. at 20° can be represented by $363—1·5(t—3)^2+1·68\times10^{-2}(t—3)^3—1·5\times10^{-4}(t—3)^4$. C. W. G.

Simple electrolytic generation of hydrogen and oxygen. D. von Klobusitzky (Biochem. Z., 1933, **257**, 478—479).—A simple cell using Ni and 20% NaOH is described. P. W. C.

Apparatus for cathode sputtering. J. A. Darbyshire (J. Sci. Instr., 1933, **10**, 83—85).—The danger of over-heating has been eliminated. C. W. G.

Magnet for α-ray spectroscopy. J. D. Cockcroft (J. Sci. Instr., 1933, **10**, 71—75).—Fields up to 18,000 gauss can be obtained, using 300 watts. Groups of α-particles having an energy difference of 5000 electron volts can be separated and their relative energies measured by bending the tracks into semicircles. C. W. G.

Use of sintered Jena glass filters in gravimetric microanalysis. Application to gravimetric determination of sulphur as benzidine sulphate and of carbamide as dixanthylcarbamide. R. Guillemet (Bull. Soc. chim., 1932, [iv], **51**, 1611—1615).—Practical notes are given. E. S. H.

Gas-volumetric method. E. Elion (Z. anal. Chem., 1933, **92**, 89—92).—The gas is drawn into an aspirator, the vol. of H_2O displaced from the aspirator being measured, whilst the pressure of the gas can be observed by means of a two-bottle regulator attached to a side tube. J. W. S.

Wet-and-dry bulb hygrometry: relation to theory of the experimental researches of Awbery and Griffiths. F. J. W. Whipple (Proc. Physical Soc., 1933, **45**, 307—309).—August's formula holds from 30° to 100°. C. W. G.

Receiver for fractional distillation in vacuum. A. Hanak (J. pr. Chem., 1933, [ii], **136**, 202—204).—The receiver described has one tap with three independent borings. R. S. C.

Distillation apparatus for water with feed-water regulator and preheater. F. Friedrichs (Chem.-Ztg., 1933, **57**, 123).—The apparatus includes a special H_2O-jacket between the main condenser and the flask, which serves as the preheater, and an overflow regulator for supplying the heated H_2O to make good the evaporation losses. Steady continuous distillation is thereby ensured. D. F. T.

Apparatus for washing with boiling water. H. Reidt (Woch. Brau., 1933, **50**, 59).—The efflux tube of a wash-bottle is lengthened so as to act as a siphon, and is provided with a pinch-cock. E. S. H.

Measurement of the viscosity of liquids; new universal viscosimeter. F. Höppler (Chem.-Ztg., 1933, **57**, 62—63).—A general account is given of viscosity and its measurement. In a new falling-sphere type of instrument, the sphere is maintained in contact with the wall of the tube by inclining the latter at 80° to the vertical; as a result, errors due to variation of the distance between the sphere and wall are obviated. The tube is surrounded by a const.-temp. H_2O-jacket. Results are accurate to within 0·1%, and may readily be converted into abs. units. By using a sphere of diam. only slightly < that of the tube, the viscosity of gases also may be determined to within 0·1%. It is possible with the apparatus to demonstrate the difference between the viscositics of distilled and conductivity H_2O. H. F. G.

Equilibrium forces acting on free drops in irregular capillaries. H. Mouquin and S. Natelson (Mikrochem., 1933, **12**, 293—302).—A method for measuring surface tension by measurement of the length of drops in open, non-uniform capillary tubes is described. J. S. A.

Capillary depressions of mercury in cylindrical tubes and some errors of glass manometers. W. Cawood and H. S. Patterson (Trans. Faraday Soc., 1933, **29**, 514—523).—Measurements have been made of the capillary depressions of Hg in cylindrical glass tubes of various sizes. These must be thin-walled to eliminate refraction errors. Measurements agreeing to within < 0·01 mm. are thus obtained. A table shows the relationship between capillary depression and meniscus height for tubes varying in diam. from 10 to 19 mm. and for meniscus heights from 0 to 1·8 mm. The refraction errors in cylindrical glass tubes have been investigated and considered in relation to the design of glass manometers. M. S. B.

Adjustable greaseless [gas] valve. L. Wolf and S. von Reichel (Z. Elektrochem., 1933, **39**, 143—145).—The action of the valve depends on the passage of gas through a porous porcelain cone, any desired fraction of which can be Hg-sealed by a simple mechanism. A full description and diagram are given. F. L. U.

Extractor for large quantities of organic material. J. J. T. Graham (J. Assoc. Off. Agric. Chem., 1933, **16**, 148—149).—An inverted bell-jar closed with a desiccator top is used. Solvent vapour from a flask enters by the side opening of the bell-jar, whilst a ∽-shaped tube furnishes a return tube from the bottom of the extractor to the flask. The charge to be extracted is supported by a layer of absorbent cotton on a porcelain desiccator plate. J. W. S.

Recording pressure and time in gas explosions. B. LEWIS and G. VON ELBE (J. Amer. Chem. Soc., 1933, **55**, 504—507).—The construction of a hysteresis-free Ni steel diaphragm indicator of const. sensitivity for determining pressures developed in explosions is described. Calibration by a dynamic method *in situ* affords results in accord with vals. determined statically. J. G. A. G.

Electrical heating equipment in Pregl's method of microanalysis: (*a*) combustion furnace, (*b*) bomb for micro-Liebig [determination]. R. GUILLEMET (Bull. Soc. chim., 1932, [iv], **51**, 1615—1619).—Apparatus and procedure are described. E. S. H.

Flow of liquid suspensions. E. G. RICHARDSON and E. TYLER (Proc. Physical Soc., 1933, **45**, 142—151).—A hot-wire anemometer is used to measure the velocity of a liquid between a rotating cylinder and a concentric fixed cylinder. In a suspension the velocity gradients are abnormal and can be explained in terms of a viscosity which is a function of the velocity gradient. C. W. G.

Vacuum work [in the laboratory]. P. HARTECK (Chem. Fabr., 1933, **6**, 104—106).—Inflammable gases which are not readily liquefied can be burnt by admitting a regulated O_2 supply and passing over Pt foil in a sufficiently wide SiO_2 tube. The H_2O and CO_2 are then condensed with liquid air. O_2 can be removed by the inverse process. A gas holder with floating gas bell and Hg seal for pure gases can be fitted with a check valve which is Hg-tight but not gas-tight. The use of gas for washing out the last traces of air can then be avoided. Amongst other devices mentioned are flexible tubes to replace wide glass tubes, a Hg seal to reduce pressure when removing gases from a bomb to high vac., and a Hg-vapour trap for use with Hg jet pumps. C. I.

Practical laboratory improvements. G. GOLLNOW (Chem. Ztg., 1933, **57**, 163—164).—Burettes, a micro-filter, a shaker, a rubber pipette-bulb, and a grease pencil are described and illustrated. P. G. M.

Cause of fire in the laboratory. H. FINK (Woch. Brau., 1933, **50**, 59).—A wash-bottle filled with H_2O acts as a lens in strong sunlight, and may cause ignition of CS_2, Et_2O, etc. E. S. H.

Neutralisation diagram. M. SETA (L'Ind. Chimica, 1933, **8**, 11—13).—The vol. of acid is plotted against the vol. of alkali of equiv. concn. Any point on a line at 45° to the axes and passing through the origin represents stoicheiometric neutrality, whereas for an acid and a base of different strengths, points of ionic neutrality (p_H 7) lie on a line inclined at an angle to the axes which may be calc. from the ionisation consts. concerned. Various typical cases are discussed in relation to the indicator which should be used in each case. H. F. G.

Scientific work of Joseph Priestley. J. R. PARTINGTON (Nature, 1933, **131**, 348—350). L. S. T.

Geochemistry.

Fulminating matter: expansion on decomposition at atmospheric pressure and constant temperature. E. MATHIAS (Compt. rend., 1933, **196**, 455—458; cf. A., 1932, 358).—From an observation of globular lightning it is inferred that the fulminating matter which caused the manifestation expands to approx. eight times the initial vol. on destruction, temp. and pressure remaining unchanged. C. A. S.

Carbon dioxide in the sea. L. H. N. C. (Nature, 1933, **131**, 282—283). L. S. T.

Gold in sea-water. A. GOURÉVITCH (Chim. et Ind., 1933, **29**, 284).—Rags, after being mordanted with tannin, were steeped in a solution of $SnCl_2$. 1 g. of such material is capable of fixing 0·0005 mg. Au per mg. in 1 ton of sea-water. Tests 0·5 km. from the coast of Brittany gave a negative result. W. J. W.

Radium content of ocean-bottom sediments. C. S. PIGGOT (Amer. J. Sci., 1933, [v], **25**, 229—238).—Ra contents of ocean-bottom sediments, mainly from the Pacific, have been determined, and their origin is discussed. C. W. G.

Origin of Chile saltpetre. C. T. KAUTTER (Chem.-Ztg., 1933, **57**, 133—134).—A recapitulation of the evidence for Stoklasa's theory of the volcanic origin of the nitrate deposits. The presence of KIO_3 is explained by the "fog" theory of formation, whereby the I is derived from the air in contact with the sea-surface. P. G. M.

Julienite. V. CUVELIER (Natuurwetensch. Tijds., 1933, **15**, 17—20).—Julienite is free from Cu and Ni; it consists of almost pure $Na_2Co(CNS)_4,8H_2O$. The $Co(CNS)_4''$ ion forms a blue compound with $NHPh_2$. H. F. G.

Metamorphism of the Deeside limestone, Aberdeenshire. A. G. HUTCHISON (Trans. Roy. Soc. Edin., 1932, **57**, 557—592).—From numerous observations on microscopic sections and a few chemical analyses of rocks, the mineral transformations occurring in a group of limestones have been traced and are described in detail. Interchange of mineral constituents has occurred between the pegmatite intrusions and the ground rock, resulting in extensive metamorphosis. Certain unstable associations are observed which probably result from the relief of static pressure during the growth of the lime-silicate minerals. W. O. K.

Occurrence of rubidium, cæsium, and thallium in some Western Australian micas. D. G. MURRAY and F. E. CHAPMAN (J. Roy. Soc. W. Australia, 1930—1931, **17**, 151—155). CH. ABS.

Vogtite, isomorphous with wollastonite. N. L. BOWEN (J. Washington Acad. Sci., 1933, **23**, 87—94).—Vogtite $(Ca,Fe,Mn,Mg)SiO_3$, is probably a wollastonite solid solution. C. W. G.

Thermal dissociation of serpentine minerals. S. CAILLERE.—See this vol., 352.

Crystals of iron-rich pyroxene from a slag. N. L. BOWEN (J. Washington Acad. Sci., 1933, **23**, 83—87).—An analysis and optical and crystallographic details are given. C. W. G.

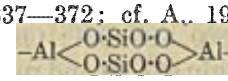
Crystal structure of silicates. E. SCHIEBOLD (Ergebn. exakt. Naturwiss., 1932, **11**, 352—434; Chem. Zentr., 1932, ii, 2925).—Mineralogical relationships of structural types are considered. The structures and physical consts. of the most important rock-forming silicates are tabulated. A. A. E.

Study of contact metamorphism by means of the heavy minerals. L. BERTHOIS (Compt. rend., 1933, **196**, 493—495).—The investigation of the exo- and endo-morphic changes due to metamorphism caused by intrusion of granite etc. is greatly facilitated by examination of the heavy minerals separated from the powdered rock by, *e.g.*, $CHBr_3$, or from the sand formed therefrom. The method enables a much larger amount to be examined than that of thin sections. C. A. S.

Fibrous sepiolite from Madagascar. (MLLE.) CAILLERE (Compt. rend., 1933, **196**, 416—418).—Cryst. sepiolite occurs, associated with gypsum and calcite, in a bed of mica at Ampandrandava, as flexible silky yellow fibres resembling chrysotile, and also as an asbestiform mass. Either form when heated evolves H_2O, mainly at 150°, but in smaller amounts at 440° and 800°. Analysis: SiO_2 52·50, Al_2O_3 0·60, Fe_2O_3 2·99, FeO 0·70, CaO 0·47, MgO 21·31, H_2O+ 12·06, $-$ 9·21%, corresponding with $H_8Mg_2(SiO_4)_3$; $n_\gamma-n_\alpha$ 0·012, n (mean) 1·4997, d 2·08; after heating at 1100° n_γ becomes 1·59 and d 2·78. C. A. S.

Difference between mica and clay as regards possible orientation of crystals growing thereon. L. ROYER (Compt. rend., 1933, **196**, 552—554; cf. this vol., 213).—The micas, clintonites, and chlorites (group *a*) and talc, kaolin, and pyrophyllite (group *b*) are all geometrically similarly constructed of thin parallel planes, but differ in that in (*a*) these planes are alternately electrically positive and negative, but in (*b*) uniformly neutral. Numerous substances when cryst. on a mineral of group (*a*) exhibit epitaxy, but in no case on one of group (*b*). This indicates that for epitaxy not merely must there be geometrical agreement, but also similarity of polarity of the particles that replace one another at the points of union. C. A. S.

Formation of "anomalous mixed crystals" as the cause of geochemical "enclosure" and luminescence. H. SEIFERT (Naturwiss., 1933, **21**, 194).—The presence of foreign substances in the crystal lattice of a mineral may take the form of submicroscopic crystals oriented in certain planes, to which the name "anomalous mixed crystals" is applied. The application of this principle can explain the "enclosure" of certain substances in the crystal lattices of other minerals, *e.g.*, the presence of $NaIO_3$ in $NaNO_3$, etc. Numerous artificial phosphors have their origin in the same cause. A. J. M.

Chemical study of alumosilicates. W. VERNADSKY (Z. Krist., 1933, **84**, 337—372; cf. A., 1901, ii, 249).—A ring structure,  , in which Al has one supplementary valency, is suggested as the fundamental kaolin nucleus, the general formula of which is $Al_2Si_{2+n}O_{7+2n}$, with possible addition of H_2O, M^I_2O, or $M^{II}O$ to form kaolinic acid, $H_2Al_2Si_2O_8$, and its derivatives. To this group are ascribed chromophoric properties to explain the colour of the "additive products," *e.g.*, sodalite, $Na_2O,Al_2Si_2O_7,NaCl$, in which neither "nucleus" nor "radical" (NaCl) is coloured. The colour of ultramarine, hauyne, garnet, epidote, beryl, cordierite, etc. is thus explained. The application of these views to the micas is discussed, as also is the replacement of Si by Al and of Al by Mg, it being held that, *e.g.*, sillimanite, $Al_2Si_2O_5$, is not a silicate of Al, but a complex acid anhydride, thus explaining the formation of an aluminosilicate by the action of K_2CO_3 thereon, and the stereochemical identity of Al and Si; Mg can replace Al only in the "radical." C. A. S.

Measurement of reflecting powers of natural tellurides by the photo-electric method. P. FASTRE (Compt. rend., 1933, **196**, 630—632).—The reflecting powers for monochromatic light (λ 5890, 5270, and 4659 Å.) of coloradoite, petzite, altaite, hessite, nagyagite, sylvanite, calaverite, and krennerite characterise the minerals (cf. B., 1927, 15). C. A. S.

Trends of differentiation in basaltic magmas. W. Q. KENNEDY (Amer. J. Sci., 1933, [v], **25**, 239—256).—The two primary basaltic magmas are olivine-basalt and tholeiitic-basalt, which give rise respectively to the alkaline rock suite and the calc-alkaline suite. No common source of the two primary magmas can be found, nor is there any evidence that one is derived from the other. C. W. G.

Movement of gases through soil as a criterion of soil structure. T. F. BUEHRER (Arizona Agric. Exp. Sta. Tech. Bull., 1932, No. 39, 57 pp.).—Apparatus is described for determining the rate of flow of air of controlled temp. and humidity through soils under standardised pressure conditions. From results obtained the "structural const." is calc. Its use as a single-val. const. is discussed. A. G. P.

Descriptive soil map. A. TILL (Z. Pflanz. Düng., 1933, **27 A**, 402—407).—A system of notation representing the principal characteristics of soils and of parent rocks in soil maps is described. A. G. P.

Soil structure and pan formation with examples from soil maps of the Palatinate. K. SCHLACHT (Z. Pflanz. Düng., 1933, **27 A**, 303—385).—The nature and distribution of soil types of this area are recorded and formation of pans in each type is examined. Ground H_2O levels and the nature of the clay fraction are important factors. No apparent relationship exists between pan formation and the CaO or humus contents of the soils. Cropping, notably with lucerne and potatoes, tends to break up the pan, which may, however, re-form in some cases within 1—2 years. A. G. P.

Formation and transformation of coal. K. LEHMANN and E. HOFFMANN (Glückauf, 1932, **68**, 793—800, 818—821; Chem. Zentr., 1932, ii, 3035).

Origin of coal and mineral oil. R. POTONIE and C. WICHER (Angew. Chem., 1932, **45**, 802—803).—A crit. discussion of the views of Stadnikov (Brennstoff Geol., 1930, No. 5/6). H. F. G.

Origin and environment of petroleum source sediments. M. E. KELLY (J. Inst. Petrol. Tech., 1933, **19**, 117—141).—A review.

Organic Chemistry.

Reaction mechanism rule and its application to the action of fused alkali hydroxides on carbon compounds. H. S. FRY and R. J. BUTZ (Rec. trav. chim., 1933, **52**, 129—138).—The reactions of C compounds with fused NaOH–KOH which have been studied previously (A., 1924, i, 1277; 1926, 710; 1928, 615) are summarised and show (with certain exceptions) that with compounds containing H·C·O and Me·C·O, the H and Me are liberated as H_2 and CH_4, respectively (by combination with H from the alkali hydroxide). The reactions also involve the formation of $Na_2(K_2)CO_3$. The exceptions to this "rule" are $(CH_2{\cdot}OH)_2$, which reacts as MeOH+CH_2O, and glycerol, which reacts partly as MeOH+$2CH_2O$ and partly (by an oxidation–reduction process) as EtOH+HCO_2H. The amounts of H_2 and CH_4 formed from lactic and glycollic acids, $H_2C_2O_4$, $Me_2C_2O_4$, HCO_2Et, EtOAc, Et lactate, Et_2CO_3, and $Et_2C_2O_4$ agree with the predicted vals. H. B.

Tautomerism in the light of recent investigations. R. F. HUNTER (Proc. Muslim Assoc. Adv. Sci., 1932, **2**, 1—41).—A review.

Reactivity of aliphatic and alicyclic hydrocarbons. A. SCHAARSCHMIDT and M. MARDER (Angew. Chem., 1933, **46**, 151—154).—In homogeneous solution, $SbCl_5$ reacts with hydrocarbons (I) containing a *tert.*-H atom (β-methylpentane, methyl-*cyclo*hexane) after a short period, whereas H in primary or *sec.* union in normal and quaternary hydrocarbons (II) (*n*-heptane, ββ-dimethylbutane, *cyclo*-pentane or -hexane) is attacked only at a higher temp. The presence of 0·1% of (I) in (II) can thus be detected. The incidence of the reaction is frequently greatly delayed, but the difficulty is overcome by addition of a contact substance formed from $SbCl_5$ and the attackable hydrocarbon. Reaction with substances of group (II) is induced by the presence of those of group (I), and quant. separation of the members of the different groups cannot be effected simply by use of the theoretical amount of $SbCl_5$; this is achieved by repeated application of the theoretical amount of $SbCl_5$ with intermediate purification of the unattacked hydrocarbon fractions. H. W.

Photochemical chlorination of methane. C. PADOVANI and F. MAGALDI (Giorn. Chim. Ind. Appl., 1933, **15**, 1—7).—The influence of Hg arc radiation, particularly rich in the line at 2530 Å., on the reaction between CH_4 and Cl_2 has been studied. With a CH_4 : Cl ratio of 2 : 1 the Cl consumption increases with increase of the duration of irradiation to an approx. const. val. of 79% at 9 sec.; for a 7 : 1 mixture the const. val. is about 94%, whilst with a greater proportion of CH_4 the percentage increases steadily with time. The ratio of MeCl to other products is about 0·2 for the Cl-rich mixtures, but rises steadily to nearly 1·8 for 15 : 1 mixtures; if the reaction proceeds in a large vessel, this ratio is extremely small. H. F. G.

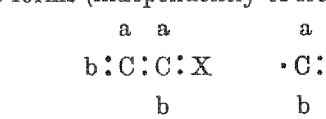
Vapour-pressure measurements with *iso*-butane. W. HUCKEL and W. RASSMANN (J. pr. Chem., 1933, [ii], **136**, 30—40).—The *iso*butane prepared from $Bu^{\beta}I$ and Zn–Cu is shown by fractional distillation and v.-p. measurements to be impure, but concordant vals. of v.p. are obtained from two differently prepared fractions. These differ slightly from those for the gas from $Bu^{\beta}I$ and Al–Hg, and also from the vals. of Huckel and Ackermann (this vol., 372), but markedly from those of Burrell and Robertson (A., 1916, i, 6). It is concluded that their *iso*butane was contaminated with a more volatile substance, and it is suggested that Huckel and Ackermann's *iso*butane was slightly contaminated with *n*-butane on account of the mode of prep. H. A. P.

Catalytic vapour-phase oxidation of tetra-alkylmethanes. W. L. FAITH, S. SWANN, jun., and D. B. KEYES (Ind. Eng. Chem., 1933, **25**, 224).—Oxidation of γγ-dimethyl- and γγ-diethyl-*n*-pentanes with air and Cu, V_2O_5, and CeO_2 (cf. A., 1932, 28) under a variety of conditions gave only CO_2, CO, H_2O, traces of aldehydes of low mol. wt., and unsaturated hydrocarbons, their behaviour in this respect resembling that of *n*-hydrocarbons. H. A. P.

Highly-polymerised compounds. LXXVI. Viscosity of solutions of thread molecules with branched chains. H. STAUDINGER and W. KERN (Ber., 1933, **66**, [*B*], 373—378).—The sp. viscosity in CCl_4, C_6H_6, dioxan, or EtOAc of the following substances has been measured at 20°, 40°, and 60°: pentatriacontane, *σ-ethylpentatriacontane* (I), b.p. 260—265°/0·5 mm., m.p. 20—21° or m.p. 27—28° after long preservation; *σ-ethylpentatriacontan-α-ol*, m.p. 38—41°, obtained from stearone and a large excess of MgEtI and reduced by red P and HI to (I); *σ-phenylpentatriacontane*, m.p. 61—62°; *σ-phenylpentatriacontan-σ-ol*, m.p. 50—51°; *Me*$_2$, m.p. 30—34°, and *Et*$_2$, m.p. 39—42°, *dicetylmalonate*; *Me dicetylacetate*, m.p. 47—49°. It is found that mols. with branched chain have the tendency when dissolved to assume the most extended form. The viscosity of dil. solution of compounds with the same length of chain is independent of the structure of the mol. H. W.

Attempted explanation of unexpected reactions of geometrical isomerides of ethylenic compounds. A. BERTHOUD (Bull. Soc. neuchateloise Sci. nat., 1931, **56**, 413—424).—The occurrence of *trans*-addition to ethylenic compounds is partly explained by the assumption that prior dissociation

of the mols. of the addendum occurs and that the subsequent stages of the reaction involve the intermediate formation of a free radical, *e.g.*, $CHPh{:}CHPh + Br \longrightarrow \cdots CHPh{\cdot}CHBrPh$ (I); $(I) + Br_2 \longrightarrow CHBrPh{\cdot}CHBrPh + Br$ etc. The presence of an incomplete octet in the free radical allows the existence of two forms (independently of free rotation):



one of which gives rise to the *cis*- and the other to the *trans*-isomeride. This theory is equally applicable to acetylenic compounds and to the dehalogenation of halogenoethanes, and is extended to conjugated compounds; it does not, however, explain the difference in behaviour of some geometrical isomerides, *e.g.*, maleic and fumaric acids, in additive reactions. H. A. P.

Number of structurally isomeric hydrocarbons of the ethylene series. H. R. HENZE and C. M. BLAIR (J. Amer. Chem. Soc., 1933, **55**, 680—686).—Theoretical. A relationship is established between the no. of structural isomerides and the alkyl groups attached to the C:C linking. Formulæ are advanced for calculating the no. of isomerides of each of the structural types from their C content, but their use involves the knowledge of the total no. of alkyl groups (*i.e.*, structurally isomeric mono-substituted paraffins) of $N-2$ and all smaller C contents. H. B.

Pyrolysis of α-unsaturated hydrocarbons. C. D. HURD and H. T. BOLLMAN (J. Amer. Chem. Soc., 1933, **55**, 699—702).—Pyrolysis of diallyl (425—650°), o-methyl-Δ^{α}-pentene (600—675°), allyl-*cyclo*hexane (500—650°) (dibromide, b.p. 129—131°/11 mm.), and δ-phenyl-Δ^{α}-butene (500—700°) at the temp. quoted gives C_3H_6 as the predominating product; allene is not formed. Saturated gaseous hydrocarbons, C_2H_4, H_2, and liquid products are also formed. The primary change in the pyrolysis of hydrocarbons is probably not a simple fission into two compounds (even though these may be isolated). H. B.

Preparation of βδ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene. H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1933, **52**, 234—238).—When the alcohol from mesityl oxide and MgMeI is heated, a mixture of H_2O and hydrocarbon distils at about 80°; the latter is finally dehydrated by repeated distillation from o-$C_6H_4(CO)_2O$ and then from Na in N_2, thus giving βδ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene, b.p. 93·1—93·2± 0·1°, f.p. −114°, which is readily oxidised in air and is reduced to βδ-dimethylpentane, b.p. 78·9—80°. Other data (lit. and revised) are given. H. B.

αζ-Dimethyl-$\Delta^{\alpha\gamma\epsilon}$-hexatriene. URION (Compt. rend., 1933, **196**, 353—354).—$\Delta^{\beta\zeta}$-Octadiene-δε-diol by catalytic decomp. with reduced Cu gives $\Delta^{\beta\delta\zeta}$-*octatriene*, fractionated into two stereoisomeric *forms*, (I) (*trans-cis-trans*-), b.p. 137—143°/764 mm. [slightly contaminated with (II); liquid Br_6-compound], and (II), m.p. 52·5°, b.p. 147—148°/764 mm. (Br_6-derivative, m.p. 122°), which rapidly oxidises to an aldehydic resin in air. J. W. B.

Effect of high temperatures and pressures on unsaturated hydrocarbons. II. Hexadecene. G. HUGEL and KOHN (Ann. Office Nat. Combust. liq., 1932, **7**, 239—277; Chem. Zentr., 1932, ii, 3076).—At > 400° polymerisation and cracking, particularly of polymerides, occur. The decomp. takes place only in the vapour phase, and hence depends on the pressure below the crit. temp. (for $C_{16}H_{32}$, 458°). Δ^{α}- and Δ^{β}-Octene undergo polymerisation and fission with formation of hexadecane or octane and diolefines. At 500° and high pressures C_6H_{14} and C_7H_{16} are unaffected. Mineral oils are decomposed in the vapour phase at 400—450°, and also in the liquid phase above 450°. A. A. E.

Crystalline rubber hydrocarbon. E. W. WASHBURN (Physical Rev., 1931, [ii], **38**, 1790—1791).—Rubber crystals, m.p. −35° to 0°, have been obtained. L. S. T.

Number of stereoisomeric and non-stereoisomeric alkinenes. D. D. COFFMAN (J. Amer. Chem. Soc., 1933, **55**, 695—698).—Theoretical. The no. of stereoisomeric and non-stereoisomeric acetylenes, CH·CR, is deduced from the no. of stereoisomeric and non-stereoisomeric mono-substituted paraffins. Formulæ are advanced for calculating the no. of stereoisomeric and non-stereoisomeric acetylenes CR:CR′, but their use involves a knowledge of the no. of stereoisomeric and non-stereoisomeric mono-substituted paraffins of $N-3$ and all smaller C contents. H. B.

Acetylene polymerides and derivatives. IV. Addition of hydrogen bromide to vinylacetylene: bromoprene [β-bromo-$\Delta^{\alpha\gamma}$-butadiene] and βδ-dibromo-Δ^{β}-butene. V. New synthetic rubbers. III. Polymerisation of bromoprene. W. H. CAROTHERS, A. M. COLLINS, and J. E. KIRBY (J. Amer. Chem. Soc., 1933, **55**, 786—788, 789—795). —IV. The primary product from vinylacetylene, conc. HBr, and CuBr is considered to be δ-bromo-$\Delta^{\alpha\beta}$-butadiene (not isolable), which then rearranges to *β-bromo-$\Delta^{\alpha\gamma}$-butadiene* (*bromoprene*) (I), b.p. 42—43°/165 mm.; some *βδ-dibromo-Δ^{β}-butene*, b.p. 168—169° (with loss of HBr)/760 mm., from (I) and HBr, is also formed. Maleic anhydride and (I) give *4-bromo-Δ^{4}-tetrahydrophthalic acid*, m.p. 186·5—187°, whilst α-naphthaquinone and (I) afford (probably) *2-bromo-1 : 4 : 11 : 12-tetrahydroanthraquinone*, m.p. (block) 138° (turns blue at 115°) (cf. A., 1932, 1232), which is oxidised by air in dil. EtOH–NaOH to 2-bromoanthraquinone.

V. The polymerisation of (I) is closely analogous to, but occurs more rapidly than, that of chloroprene (B., 1932, 156). Spontaneous polymerisation in presence of a little air gives (after 8—10 days) μ-polybromoprene (II), which is tough, resilient, and elastic, and when kept becomes harder and less resilient owing to atm. oxidation (preventible by application of anti-oxidants to the surface). Exposure of (I) to light from a Cooper-Hewitt lamp at 25° affords plastic α-polybromoprene (pptd. from the mixture by EtOH), which when heated passes into (II). (I) heated at 80°/5 days in presence of a little thiodiphenylamine yields β-polybromoprene, b.p. 104—110°/11 mm., whilst slow polymerisation of (I)

in presence of *e.g.* β-$C_{10}H_7$·NHPh affords the granular ω-polybromoprene. (I) is readily dispersed in H_2O; the resulting emulsion polymerises rapidly to form a stable latex (cf. *loc. cit.*). H. B.

Reaction of atomic hydrogen with chloroform. H. FROMHERZ and H. SCHNELLER (Z. physikal. Chem., 1933, **B**, **20**, 158—160).—HCl, MeCl, and an apparently polymerised solid containing Cl are formed, with luminescence and considerable heat evolution. R. C.

Formation of hexafluoroethane and tetrafluoroethylene from carbon tetrafluoride. O. RUFF and O. BRETSCHNEIDER (Z. anorg. Chem., 1933, **210**, 173—183).—The products formed by a C arc burning in CF_4 contain C_2F_6 and C_2F_4, separated after converting the latter into *dibromotetrafluoroethane*, m.p. −111·5°, b.p. 47·4°, which, when treated with Zn and AcOH, yields C_2F_4 m.p. −142·5°, b.p. −76·3°. Chemically, C_2F_6 is inert, and C_2F_4 resembles C_2H_4. V.p., *d*, and heats of vaporisation are recorded. F. L. U.

Change of molecular structure during chemical reaction. II. Rearrangement of butyl bromides. W. HÜCKEL and P. ACKERMANN (J. pr. Chem., 1933, [ii], **136**, 15—29).—The formation of *sec.*-BuBr (in addition to *tert.*-BuBr; cf. A., 1911, i, 250) when $Bu^{\beta}Br$ is heated at 210—230° is proved by treatment of the product with AgOAc, which gives the corresponding acetates and butenes (the latter preponderating in glacial AcOH at the b.p.), hydrogenation of the latter to butanes, and determination of the v.p.–temp. curve, which is found to lie between those of *n*- and *iso*-butanes. *sec.*-BuBr is found to be unchanged under the same conditions. Redeterminations of the v.p.–temp. curves of *n*- and *iso*-butanes give results at variance with those of Burrell and Robertson (A., 1916, i, 6) in the case of the latter. The degree of homogeneity of the butenes is determined by measuring the v.p. of the total hydrocarbon and of the residue after the bulk has been distilled. Catalytic dehydration of $Bu^{\beta}OH$ (*phenylurethane*, m.p. 86°) over graphite at 400° gives pure *iso*butene (*nitrosochloride*, m.p. 98°; *nitrosopiperidide*, m.p. 137—138°); *sec.*-BuOH (*phenylurethane*, m.p. 64·5°) gives *trans*- and a little *cis*-*n*-Δ^{β}- containing approx. 10% of *n*-Δ^{α}-butene (composition from b.p./1 atm.), but free from *iso*butene, as pure *n*-butane is formed on hydrogenation. *sec.*-BuBr gives with AgOAc in AcOH a mixture of *n*-Δ^{β}- and -Δ^{α}-butenes containing more Δ^{β}-butene than the above; $Bu^{\beta}Br$ gives a mixture converted by H_2 into pure *iso*butane, whence the impurities are regarded as polymerides. H. A. P.

Rotatory powers of the chlorides produced by heating certain chloroformates in solvents. (MISS) M. B. HARFORD, J. KENYON, and H. PHILLIPS (J.C.S., 1933, 179—181).—Decomp. of *l*-β-octyl chloroformate (I) (A., 1932, 611) and *l*-Et phenylchloroformoxyacetate (II) (A., 1931, 1291) when heated in various solvents affords *l*-rotatory chlorides, CO_2, and HCl [also octylene from (I)]. The chlorides from (I) have approx. the same rotation, but those from (II) vary, which supports the view that the cationic β-octyl radical affords an unsaturated compound rather than inverts to a *d*-chloride, whereas with (II) the opposite reaction is the more facile. J. L. D.

Identification of alcohols in dilute aqueous solution. H. HENSTOCK (J.C.S., 1933, 216).—A method of identifying alcohols in low concns. (> 1·5%) by their *p*-nitrobenzoates is described. J. L. D.

Determination of lower alcohols in dilute aqueous solutions. A. VANSCHEIDT and O. EREMEEVA (J. Gen. Chem. Russ., 1932, **2**, 800—805).—1 c.c. of saturated aq. $NaNO_2$ and 2 c.c. of H_3PO_4 are added to 5—10 c.c. of solution, containing 10—60 mg. of EtOH or MeOH, and a stream of CO_2-free air is passed through the solution at 35°. The mixture of air, alkyl nitrite, and oxides of N is passed through a heated Cu spiral, and successively through absorption tubes containing a solution of $Ag_2Cr_2O_7$ and $K_2Cr_2O_7$ in conc. H_2SO_4 at 135—140°, and 50% KOH. The gain in wt. of the KOH tube represents CO_2 originating from oxidation of alkyl nitrite, and the alcohol content is hence calc. The presence of small quantities of MeCHO does not interfere; Et_2O, if present, should first be removed by aeration. R. T.

Action of calcium hypochlorite on alcohols aldehydes, and ketones. I. F. SUKNEVITSCH and A. A. TSCHILINGARIAN (J. Gen. Chem. Russ., 1932, **2**, 783—789).—EtOH and aq. $Ca(OCl)_2$ containing 10% of available Cl give on distillation $CHCl_3$ and EtOCl; the latter is transformed into CH_2Cl·OEt by passing C_2H_4 into the receiver, whilst if it is passed through the reaction mixture, practically no $CHCl_3$ is formed. HOCl and Et_2O also give EtOCl, subsequently converted into MeCHO with evolution of heat and disappearance of the yellow colour. No $CHCl_3$ is formed from $Ca(OCl)_2$ and CMe_3·OH, only the corresponding hypochlorite. $Pr^{\beta}CHO$, $Bu^{\beta}CHO$, and heptaldehyde do not give $CHCl_3$, but are oxidised to the corresponding acids, and no yellow colour, due to the formation of a hypochlorite, is observed. $Pr^{\alpha}OH$, $Bu^{\alpha}OH$, and $Bu^{\beta}OH$, which have no *tert.*-C next to OH, yield $CHCl_3$ and the corresponding hypochlorite, subsequently giving an aldehyde and the ester of the corresponding acid with the alcohol employed. The first step in the reaction between $Ca(OCl)_2$ and EtOH is the formation of EtOCl, which then gives MeCHO, and the enolic form of the latter is chlorinated to CCl_3·CHO, which decomposes with alkali into $CHCl_3$ and a formate. A second reaction is the addition of EtOCl to the enol of MeCHO, giving CH_2Cl·CH(OH)·OEt, which splits off EtOH with alkali and the enol formed reacts again in the same way, finally giving CCl_3·CHO. The reaction with $COMe_2$ is explained similarly, as is also the inability of paracetaldehyde, MeOH, and CMe_3·OH to yield $CHCl_3$. G. A. R. K.

Tertiary aliphatic carbinols containing an adjacent tertiary hydrogen, the related chlorides, and dehydration products. F. C. WHITMORE and W. L. EVERS (J. Amer. Chem. Soc., 1933, **55**, 812—816).—The following carbinols are prepared from $COMePr^{\beta}$ and the appropriate Mg alkyl bromide: βγ-dimethylpentan-γ-ol, b.p. 38—39°/7 mm. (*chloride*, b.p. 133—138°), dehydrated by heating with a little

I to βγ-dimethyl-Δ^{β}- and -Δ^{γ}-pentenes; *βγ-dimethylhexan-γ-ol*, b.p. 42—43°/6 mm. (*chloride*, b.p. 41—43°/12 mm.), dehydrated to βγ-dimethyl-Δ^{β}- and -Δ^{γ}-hexenes; *βγ-dimethylheptan-γ-ol*, b.p. 56—57°/5 mm., 42°/2 mm. (*chloride*, b.p. 54°/8 mm.), dehydrated to βγ-dimethyl-Δ^{β}-, b.p. 136·2—136·8°/743 mm., and -Δ^{γ}-, b.p. 138·4—138·8°/740·5 mm., -heptenes; *βγ-dimethyloctan-γ-ol*, b.p. 69—70°/5 mm. (*chloride*, b.p. 53—55°/3 mm.), dehydrated to βγ-dimethyl-Δ^{β}-, b.p. 158·4—158·8°/733 mm., and -Δ^{γ}-, b.p. 161·2—161·4°/739 mm., -octenes. The Δ^{β}- and Δ^{γ}-olefines (structures determined by ozonolysis) are formed in the ratio 2 : 1. H. B.

Additive properties of secondary αα′-diacetylenic alcohols and their alcoholic properties. C. K. Liang (Bull. Soc. chim., 1933, [ii], **53**, 33—41, 41—47).—MgEtBr and excess of an acetylenic hydrocarbon give a Grignard reagent, which with HCO_2Et (0·5 mol.) yields compounds (*A*) of the type $(CR{:}C)_2CH{\cdot}OH$. Thus are prepared: $\Delta^{\delta\eta}$-*undecadi-inen-ζ-ol*, b.p. 138—139°/19 mm.; $\Delta^{\epsilon\theta}$-*tridecadi-inen-η-ol*, b.p. 155—156°/15 mm.; $\Delta^{\iota\lambda}$-*pentadecadi-inen-θ-ol* (I), b.p. 150—151°/5 mm.; $\Delta^{\eta\kappa}$-*heptadecadi-inen-ι-ol*, b.p. 192—193°/8 mm.; $\Delta^{\kappa\nu}$-*tricosadi-inen-μ-ol*, m.p. 24°; αε-*diphenyl-* (II), m.p. 69—70°, *-di-*p-*tolyl-* (III), m.p. 95—96°, and *-di-*2 : 4-*dimethylphenyl-* (IV) -$\Delta^{\alpha\delta}$-*pentadi-inen-γ-ol*, m.p. 93—94°. The aromatic, but not the aliphatic, compounds show a large exaltation of *n*. Unless an excess of acetylenic hydrocarbon is used in these preps., the resultant Grignard reagent contains MgEtBr, which with HCO_2Et leads to $CHEt_2{\cdot}OH$ and mixed Et monoacetylenic alcohols. In this way are obtained: Δ^{δ}-*octinen-γ-ol*, b.p. 80—82°/25 mm., Δ^{δ}-*decinen-γ-ol*, b.p. 100—102°/15 mm., and Δ^{δ}-*undecinen-γ-ol*, b.p. 96—97°/4 mm., also obtained from EtCHO and the Mg or Na derivatives of the acetylenic hydrocarbons. Compounds (*A*) are decomposed by H_2SO_4–AcOH. (II) is oxidised by 6% $KMnO_4$ to BzOH only, but with O_3 gives also tartronic acid. (I), (II), and (IV) with hot 20% $HgCl_2$–EtOH add only 1 mol. of $HgCl_2$; the *compounds* from (I) and (IV) are destroyed by hydrolysis, but the *compound* from (II) with hot 15% HCl gives αε-*diphenyl-*Δ^{α}-*pentinen-γ-ol-ε-one*, m.p. 96—97°, oxidised to BzOH by $KMnO_4$. With hot 12% KOH–EtOH (II) and (III) give much resin and αε-*diphenyl-*, m.p. 131°, and αε-*di-*2 : 4-*dimethylphenyl-pentan-γ-ol-*βδ-*dione*, m.p. 180°, respectively, giving on oxidation the expected aromatic acid. (III) in EtOAc with aq. colloidal Pd and H_2 is reduced at each acetylenic linking successively, affording αε-*-di-*p-*tolylpentan-γ-ol*, m.p. 96°, *-di-*p-*tolyl-*Δ^{α}-*penten-*Δ^{δ}-*inen-γ-ol*, m.p. 94° (probably the *trans* form, since it is unchanged by illumination), and (?) cis-αε-*di-*p-*tolyl-*Δ^{α}-*penten-γ-ol*, an oil, b.p. 180—182°/4 mm., changed by illumination into the (?) trans *form*, m.p. 93°.

Compounds, $(CR{:}C)_2CH{\cdot}OH$, show one reactive OH group with $ZnEt_2$. The following derivatives were prepared by the usual methods: *ζ-bromo-*$\Delta^{\delta\eta}$-*undecadi-inene*, b.p. 126—127°/21 mm.; *θ-chloro-*$\Delta^{\iota\lambda}$-*pentadecadi-inene* (by $SOCl_2$ in C_5H_5N), b.p. 130—133°/5 mm.; *ι-ethoxy-*, b.p. 165—166°/6 mm., and *ι-acetoxy-*$\Delta^{\eta\kappa}$-*heptadecadi-inene*, b.p. 188—189°/8 mm.; and αε-*di-*p-*tolyl-*$\Delta^{\alpha\delta}$-*pentadi-inen-γ-ol diphenylurethane*, m.p. 154°. The acetylenic linkings are oxidised by $KMnO_4$, HNO_3, etc., but with cold CrO_3–AcOH $\Delta^{\eta\kappa}$-*heptadecadi-inen-ι-one*, b.p. 155—158°/5 mm. [*semicarbazone*, m.p. 305° (decomp.)], and αε-*diphenyl-*$\Delta^{\alpha\delta}$-*pentadi-inen-γ-one*, m.p. 64—65°, are obtained in 75—90% yield. MgEtBr and $\Delta^{\iota\lambda}$-pentadecadi-inen-θ-ol in hot Et_2O give the Grignard reagent, which with PhCHO gives a little $CH_2Ph{\cdot}OH$ and $\Delta^{\iota\lambda}$-pentadi-inen-θ-one [*semicarbazone*, m.p. 290° (decomp.)], but by further reaction only resins and more $CH_2Ph{\cdot}OH$. R. S. C.

Identification and biochemical oxidation of α-glucoheptulitol. (Mme.) Y. Khouvine and G. Nitzberg (Compt. rend., 1933, **196**, 218—220).—The individuality of α-glucoheptulitol (I), obtained by reduction of α-glucoheptulose (II) (Bertrand and Nitzberg, A., 1928, 620), is established by fractionation and *X*-ray analysis. Cultures of sorbose bacteria in yeast extract oxidise 80% of (I) in 1·5 months to (II), and not to β-glucoheptulose, anticipated if (I) were identical with β-glucoheptitol. A. C.

Explosion of ethereal extracts. N. Krasovski (Ukrain. Chem. J., 1932, **7**, [Sci.], 98—104).—The causes of explosion of Et_2O extracts during their distillation are discussed. R. T.

Apparatus for the micro-determination of ethoxyl and methoxyl groups, and of glycerol. R. Guillemet (Bull. Soc. chim., 1932, [iv], **51**, 1547—1551).—Micro-determination of OEt groups by Pregl's technique gives low vals. owing to retention of EtI by moist P. Condensation of the liberated I in a dry U-tube or, better, absorption by moist KI crystals (in a special apparatus) allows accurate determination of OEt and OMe groups. Aq. glycerol can be evaporated and determined by the same technique within ±1%. R. S. C.

Mechanism of polymerisation. H. Hibbert and S. Z. Perry (Canad. J. Res., 1933, **8**, 102).—$(CH_2)_2O$ polymerises in presence of aq. alkali to polyethylene glycol ethers, $H{\cdot}[O{\cdot}CH_2{\cdot}CH_2]_n{\cdot}OH$, the compounds where n=1—9 having been isolated in addition to cryst. higher polyethylene glycols. With MeOH in place of H_2O the terminal groups are ·OMe and ·OH, and with amines (NH_2R) they are probably ·NHR and ·OH. "Polymerisation" in this case therefore occurs by addition of the unstable ring to the OH group. H. A. P.

Oxides of isoprene and butadiene. R. Pummerer and W. Reindel [with, in part, K. Traulsen] (Ber., 1933, **66**, [*B*], 335—339).—Isoprene is converted by BzO_2H (prep. described) in EtCl into β-*methylbutadiene* αβ-*oxide* (I), b.p. 81°/735 mm., in which the presence of a double linking is established by reaction with ICl. (I) is violently isomerised by mineral acids, particularly H_2SO_4, to tiglaldehyde (II) (p-*nitrophenylhydrazone*, m.p. 181°; semicarbazone, m.p. 219°), accompanied by a non-distillable polymeride of (I) or (II). Hydrogenation of (I) (Pd–C) gives a non-homogeneous, saturated product with an intense odour of amyl alcohol. Under similar conditions, butadiene affords Δ^{γ}-*butene* αβ-*oxide*, b.p. 66·5°/735 mm. H. W.

Unsaponifiable matter from the oils of elasmobranch fish. IX. Structure of batyl and selachyl alcohols. W. H. DAVIES, I. M. HEILBRON, and W. E. JONES (J.C.S., 1933, 165—167; cf. following abstract).—Oxidation of batyl alcohol by Criegee's method (A., 1931, 461) affords CH_2O and *glycollaldehyde octadecyl ether*, m.p. 51° (2 : 4-*dinitrophenylhydrazone*, m.p. 73°) [also formed by treating octadecyl allyl ether (A., 1931, 62) with O_3–O_2 in AcOH during 3·5 hr.], which with CrO_3 in hot AcOH during 0·5 hr. affords *glycollic acid octadecyl ether*, m.p. 62—63° (*Et* ester, m.p. 41—42°; *methylamide*, m.p. 83—84°). Contrary to Toyama (A., 1924, i, 604), batyl alcohol is optically active, having $[\alpha]_{5461}^{20}$ +2·6° in $CHCl_3$ (acetate, $[\alpha]_{D}^{20}$ −8·5° in $CHCl_3$). As batyl alcohol is obtained by hydrogenation of selachyl alcohol, the latter is represented as α-oleyl glyceryl ether. J. L. D.

Evidence from surface films on the constitution of batyl and chimyl alcohols. N. K. ADAM (J.C.S., 1933, 164—165).—Batyl alcohol and synthetic α-octadecyl glyceryl ether form identical unimol. films, on H_2O, which supports the view (A., 1930, 852) that they are identical. Chimyl alcohol gives similar films, but the transition point between the condensed and expanded films is about 15° lower because the C chain is shorter by 2 C atoms. J. L. D.

Sulphonated oils. XIV. Sulphonated oil made from sperm oil. Preparation of salts of pure cetyl hydrogen sulphate and their properties. XV. Properties of aqueous solutions of pure salts of cetyl hydrogen sulphate. K. NISHIZAWA (J. Soc. Chem. Ind. Japan, 1931, **35**, 548—550B, 550—551B).—XIV. [With T. TOMITSUKA.] Crystallographic data for the *Na*, *K*, NH_4, *Mg*, and *Ca* salts of cetyl H sulphate are detailed (with illustrations).

XV. The K, Mg, and Ca salts are very sparingly sol. in H_2O, but their solutions possess an appreciably lower surface tension to air or kerosene than H_2O. The lowering of the surface tension by the more sol. Na and NH_4 salts is of the same order as that obtained by Na ricinoleate or Na sulphoricinoleate. Data for relative η of the solutions are also plotted. E. L.

Synthetic glycerides. IV. Esters of aromatic and aliphatic acids. D. T. JACKSON and C. G. KING (J. Amer. Chem. Soc., 1933, **55**, 678—680).—The β-palmitate, m.p. 71·5°, -stearate, m.p. 78·5—79·5°, -laurate, m.p. 47°, and -*p*-nitrobenzoate (I), m.p. 187·5°, of glycerol αγ-$(CPh_3)_2$ ether (II) are prepared from (II) and the requisite acid chloride in C_6H_6–quinoline; removal of the CPh_3 groups from (I) by HBr–$CHCl_3$ gives glyceryl β-*p*-nitrobenzoate, but in the other cases the α-monoglyceride results. The βγ-dipalmitate, m.p 40·5—41·5°, -distearate, m.p. 46—48°, and -dibenzoate (III), m.p. 92—94°, of glycerol α-CPh_3 ether are similarly prepared; removal of CPh_3 from (III) affords glyceryl αβ-dibenzoate, whilst the others give the αγ-diglycerides. H. B.

Lecithins. Y. YOKOYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, **8**, 490—491).—Photomicrographs of three α- and three β-lecithin derivatives (two from human brain and four from soya bean), cryst., are reproduced. R. S. C.

Synthesis of lecithins and kephalins. I. Synthesis of dipalmityl-β-kephalin and -β-lecithin. I. KABASHIMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, **8**, 492—495).—The double salt of Ba β-glycerophosphate and $Ba(NO_3)_2$ with K_2SO_4 gives $BaSO_4$ and the K_2 salt; the latter with palmityl chloride and KOH, or, better, $Ba(OH)_2$, gives *dipalmityl-β-glycerophosphoric acid*, isolated as *Ag* salt (I). $CH_2Br{\cdot}CH_2Br$ and *o*-$C_6H_4(CO)_2NK$ at 150° give N-β-*bromoethylphthalimide*, m.p. 82°, whence β-*bromoethylamine picrate*, m.p. (anhyd.) 130—131°, (+0·5H_2O) 99°, is obtained. This with (I) in $COMe_2$–C_6H_6 at 85—90° affords *dipalmityl-β-kephalin*, cryst., quantitatively hydrolysed to β-*glycerophosphoric acid* (II). $CH_2Br{\cdot}CH_2Br$ and NMe_3 at 125—130° give "β-*bromocholine bromide*" [*trimethyl-β-bromoethylammonium bromide*], the *picrate*, m.p. 158—159°, of which with (I) affords *dipalmityl-β-lecithin*, sinters at 81°, darkens at about 170°, and decomp. at about 190°, which is quantitatively hydrolysed to (II). The solubilities of the products and their complex salts are those of natural β-kephalins and -lecithins. R. S. C.

Enzymic scission of lysochitin and lecithin. Isomeride of the lecithins. A. CONTARDI and A. ERCOLI (Gazzetta, 1933, **63**, 37—46).—When lecithinase-*B* free from -*C* (obtained from rice husks after long keeping) is added to aq. solutions of lysochitin a *substance*, m.p. 183° (decomp.), separates, which contains N and P in the proportions corresponding with a palmitostearolecithin. The synthesis of the *stearate* and *palmitate* of lysochitin is described. These substances have no hæmolytic action. E. E. J. M.

Thermal decomposition of ethyl mercaptan and ethyl sulphide. N. R. TRENNER and H. A. TAYLOR (J. Chem. Physics, 1933, **1**, 77—88; cf. A., 1931, 175).—Products of the thermal decomp. of EtSH and Et_2S at 380—410° are H_2S, C_2H_4, and polysulphides. An intermediate product, b.p. 48—49·5°, with mercaptan properties, has been isolated in both cases. This product undergoes unimol. decomp. with energy of activation of about 40 kg.-cal. F. L. U.

Derivatives of selenium diethyl. T. SMEDSLUND (Finska Kem. Medd., 1932, **41**, 13—26).—Se di-β-chloroethyl dichloride (I) and H_2O (or dil. alkali) give *Se di-β-chloroethyl oxide* (II), m.p. 88°, and then *Se di-β-hydroxyethyl oxide* (III), m.p. 121° (decomp.). *Se di-β-bromoethyl dibromide* (IV) similarly treated gives *Se di-β-bromoethyl oxide* (V), m.p. 61°, and (III). (II) and (V) decompose on keeping. *Se di-β-hydroxyethyl dichloride* (VI), m.p. 85—86°, is obtained by boiling an aq. solution of (I), and the *dibromide* (VII), m.p. 94—95° (decomp.), by boiling an aq. solution of (IV), or from (III) and conc. HBr. (I) and (IV) heated to 130—160° give Se and ethylene chloride or bromide. (VII) at 170° gives $CH_2Br{\cdot}CH_2{\cdot}OH$. Se di-β-bromoethyl (VIII) and di-β-chloroethyl with aq. $COMe_2$ give *Se di-β-hydroxyethyl*, b.p. 143°/2 mm. (corresponding *phenylcarbimide*, m.p. 130°), which adds Cl and Br in $CHCl_3$ giving (VI) and (VII). *Se di-β-methoxyethyl*, b.p. 94°/7 mm. (*dichloride*, m.p. 71—72°; *dibromide*, m.p. 60—61°), is obtained from (VIII) and NH_3 in EtOH. R. P. B.

Constitution and structure of fatty acids. E. L. LEDERER (Fettchem. Umschau, 1933, **40**, 2—6).—A review. E. L.

Preparation and decomposition of mixed acid anhydrides. A. BARONI (Gazzetta, 1933, **63**, 23—37).—Interaction in Et_2O of an acid chloride with the Na salt of a different acid gives acetomono- (I), -di-, and -tri-chloroacetic and mono- (II) and *s*-di-chloroacetic anhydrides, b.p. 80—83°/16 mm., 79—80°/16 mm., 88—89°/20 mm., 117°/16 mm., and 100—102°/15 mm., respectively. (I) and (II) are also obtained by heating $CH_2Cl{\cdot}CO_2H$ with Ac_2O. Butyric, trichlorobutyric, and benzoic acids when heated with Ac_2O give acetobutyric, b.p. 165°, *acetotrichlorobutyric*, b.p. 110—111°/20 mm., and acetobenzoic and *s*-butyric, b.p. 191°, *trichlorobutyric*, b.p. 138—140°, and benzoic anhydrides. Decomp. of a mixed anhydride with acid or with EtOH gives mainly the acyl derivative corresponding with the stronger acid. E. E. J. M.

Preparation of pure formic acid. A. A. PRIANISCHNIKOV and Z. F. SCHACHOVA (J. Gen. Chem. Russ., 1932, **2**, 821—825).—The vals. given by the Internat. Bureau of Standards for the m.p., b.p., and *d* of pure HCO_2H are confirmed. R. T.

Determination of acetic acid. M. MUGDAN and J. WIMMER (Angew. Chem., 1933, **46**, 117—118).—AcOH is determined by oxidation with KOH and CuO at 200—240° to $H_2C_2O_4$, which is then titrated with $KMnO_4$. Ca, if present, must be removed with K_2CO_3 and SO_3'' must be oxidised with H_2O_2. HCO_2H and mineral acids do not interfere. A. G.

Preparation of ethyl β-iodopropionate. J. W. BAKER (J.C.S., 1933, 216).—$CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ with NaI in boiling EtOH during 24 hr. affords $CH_2I{\cdot}CH_2{\cdot}CO_2Et$ in 81% yield. J. L. D.

Dimorphism of aliphatic compounds. III. Ethyl margarate. IV. Ethyl esters [of fatty acids]. J. W. C. PHILLIPS and S. A. MUMFORD (Rec. trav. chim., 1933, **52**, 175—180, 181—194).—III. The α-form (I), f.p. 25·25°, of Et margarate forms unbroken series of solid solutions (showing neither max. nor min.) with α-modifications of Et penta- and nona-decoates, palmitate, and stearate. The f.p. (17·2°) of the β-form (II), *i.e.*, the temp. at which the exothermic transition (I)⟶(II) occurs, and the m.p. (20·6°) of (II), *i.e.*, the temp. at which the transition (II)⟶(I) takes place, are both lowered by addition of higher or lower homologues, as is the rate of the transition (I)⟶(II). The f.-p. curves of (I) with the above α-homologues show two arrests; the data suggest that the transition (I)⟶(II) is complex. Et penta- and nona-decoates exhibit enantiotropic dimorphism similar to that of Et margarate, whilst tetra- and octa-decyl alcohols show the same dimorphism as does cetyl alcohol (A., 1931, 1003). Data are also given for tetradecyl, cetyl, and octadecyl acetates; each of these exists in two monotropic forms.

IV. The alternation of dimorphic type previously shown (A., 1932, 451) for the Et esters of high fatty acids occurs only above Et myristate. Both odd- and even-membered esters below this exist in monotropic modifications; the m.p. of the stable β-forms alternate, whilst the f.p. of the metastable α-forms lie on a smooth curve, the f.p. increasing with rise in C content. Examination of 10 binary systems of Et esters (decoate—nonadecoate) (including even–even, even–odd, and odd–odd) shows that in all the cases studied, the α-forms give unbroken series of solid solutions showing neither max. nor min. An equation is derived connecting the f.p. of the binary mixture and its α-components. Et undecoate, tridecoate, and nonoate probably exist in γ-modifications which resemble the third (C_1) modification of the higher esters (C_{17}—C_{21}); the change γ⟶β is effected by rubbing. H. B.

Unsaturated acids and their derivatives. IX. Configuration of tetrabromostearic acid, m.p. 60°. T. MARUYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, **8**, 486—489; cf. A., 1932, 832).—The following prefixes (the historical order of discovery) are adopted for the tetrabromostearic acids: α-, m.p. 114°; β-, liquid; γ-, m.p. 60° (I); δ-, m.p. 58°. (I) (modified prep. from soya-bean oil) with Zn and H_2SO_4 gives $\Delta^{\theta\lambda}$-*octadecadienoic acid* [reconverted into (I) and other isomerides by Br], the constitution of which is proved by oxidation of the *Me* ester to azelaic (II), *n*-hexoic, and a little malonic acid (partly oxidised further to $H_2C_2O_4$). (I) and KOH–EtOH at different temp. give: (*a*) at 28° a liquid acid, $C_{18}H_{30}O_2Br_2$, either 0λ- or ιλ-*dibromo*-$\Delta^{\theta\mu}$-*octadecadienoic acid*, since it gives, when oxidised, (II) and valeric (III), but not oxalic, acid; (*b*) at 80° an acid, $C_{18}H_{29}O_2Br$, either θ- or ι-*bromo*-$\Delta^{\theta\kappa\mu}$-*octadecatrienoic acid*, since oxidation affords (II), (III), and $H_2C_2O_4$; (*c*) at 150°, the *acid*, $Me{\cdot}[CH_2]_3{\cdot}[CH{:}CH]_2{\cdot}C{:}C{\cdot}[CH_2]_7{\cdot}CO_2H$, oxidised to (II), (III), and $H_2C_2O_4$. On the principle that HBr is eliminated from *cis* positions it follows that (I) is θιλμ-tetrabromostearic acid and that the θι- and λμ-Br atoms are in the *trans* and *cis* positions, respectively; no choice can be made between the two steric formulæ thus possible for (I). In the parent γ-linoleic acid the configurations at the θ- and λ-ethylenic linkings are probably *trans* and *cis*, respectively. R. S. C.

Isomerism in the β-elæostearic acid series. E. EIGENBERGER (J. pr. Chem., 1933, [ii], **136**, 75—116).—Hydrolysis of freshly-prepared β-elæostearin (I) with EtOH–KOH (containing a little H_2O only) gives *K* β-*elæostearate* (II); the acid obtained (in solution) under carefully defined conditions can be reconverted into (II), but the free acid, m.p. 71—71·5°, isolated is a mixture. Crystallisation of (II) from 50% EtOH gives *K* β_1-*elæostearate* (III) [convertible into a *Ag* salt which with EtOH–KOH regenerates (III)], which when crystallised from EtOH rearranges into (II); a *K* β_1-acid salt, $C_{18}H_{29}O_2K$,$C_{18}H_{30}O_2$, is described. Samples of (I) which have been allowed to autoxidise in the dark contain $COMe_2$-sol. and -insol. material; hydrolysis of the insol. part with EtOH–KOH causes evolution of O_2 and gives *K* β_2-*elæostearate* (IV), also formed by autoxidation of (II) or (III); the β_2-acid is produced when the above acid mixture is heated above the m.p. When the acid from (III) is heated at 250° in CO_2, the resulting product sublimed, the sublimate extracted with

light petroleum, and the extract evaporated in CO_2, cryst. material is first obtained; the filtrate contains β_3-*elæostearic acid*, an oil [amorphous K salt, also formed when (III) is heated to 210°/vac.], which changes into the β_2-acid on keeping. Numerous other interconversions are studied. A corresponding series of Na salts is prepared. (IV) has the max. solubility and min. sp. conductivity in 94·6% (wt.) EtOH at 20° and 25°, respectively; (II) has the max. conductivity and (III) has min. solubility. H. B.

Polymerisation of methyl esters of higher unsaturated fatty acids. XI. Structure of the dimerides of the methyl ester of linoleic acid. K. Kino (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1933, **20**, 103—108).—Ozonolysis of dimeric Me linoleate (I) (obtained by heating in H_2 at 290—300°) affords Me H azelaate and an aldehyde oxidised to an acid $(Me[CH_2]_4\cdot CH\cdot CH\cdot CH_2\cdot CO_2H)_2$. If hydrolysed prior to ozonolysis, subsequent esterification of the acid product gives Me_2 azelaate. Hence (I) has the structure $(Me[CH_2]_4\cdot CH\cdot CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Me)_2$. J. W. B.

Oxidation of hydroxy-acids and sugars by periodic acid. P. Fleury and J. Lange (Compt. rend., 1932, **195**, 1395—1397).—MeOH, EtOH, pentaerythritol, glycollic, malic, and citric acids are not oxidised by cold HIO_4, but compounds containing α-diol groupings are oxidised in 1—2 hr. (cf. Malaprade, A., 1928, 269), $CH_2\cdot OH$ groups being converted into CH_2O (I), $CH\cdot OH$ into HCO_2H (II) or into glyoxylic acid (III) when adjacent to $\cdot CO_2H$ in the original mol. Tartaric acid (1 mol.) is oxidised to (III) (2 mols.); gluconic acid to (I) (1 mol.), (II) (3 mols.), and (III) (1 mol.); saccharic acid to (II) (2 mols.) and (III) (2 mols.), glucose to (I) (1 mol.) and (II) (5 mols.). Dihydroxyacetone is abnormal, affording (I) and glycollic acid. Similarly, fructose gives (I), (II) (3 mols.), and glycollic acid. A. C.

Alkoxy-acids and their esters. S. Sabetay (Bull. Soc. chim., 1932, [iv], **51**, 1619—1620).—Concerning priority (cf. Rothstein, A., 1932, 832; Sabetay, A., 1928, 1130 *et seq.*). R. S. C.

Emetics derived from lactic acid. Volmar and Betz (Compt. rend., 1933, **196**, 355—357).—Max. fixation of Sb_2O_3 by *N*-lactic acid at 100° in the presence of increasing concn. of *N*-NaOH under otherwise standard conditions occurs with equimol. concn. of lactic acid and its Na salt, and under such conditions the time curve for the fixation of Sb exactly resembles that of an ordinary esterification. Using these optimum conditions is obtained cryst. *Na antimonyl lactate*, $Sb(OH)(\cdot O\cdot CHMe\cdot CO_2Na)_2$, m. p. 230° (decomp.), completely hydrolysed by H_2O. J. W. B.

Hydroxy- and bromo-esters derived from the hydrogenation of ω-acetyl esters. E. J. Lease and S. M. McElvain (J. Amer. Chem. Soc., 1933, **55**, 806—808).—The rate of reduction (H_2, PtO_2, EtOH) of $Ac\cdot[CH_2]_n\cdot CO_2Et$ ($n = 1$—5) to $OH\cdot CHMe\cdot[CH_2]_n\cdot CO_2Et$ (converted by PBr_3 in C_6H_6 into $CHBrMe\cdot[CH_2]_n\cdot CO_2Et$) generally decreases with rise in the val. of n. The following are new: *Et δ-acetylvalerate*, b.p. 107—108°/9 mm.; *Et ε-acetylhexoate*, b.p. 121—122°/9 mm.; *Et δ-hydroxy-*, b.p. 94—95°/2 mm., and *δ-bromo-*, b.p. 69—71°/2 mm., *-hexoates*; *Et ε-hydroxy-*, b.p. 103—104°/2 mm., and *ε-bromo-*, b.p. 85—87°/2 mm., *-heptoates*; *Et ζ-hydroxy-*, b.p. 111—113°/2 mm., and *ζ-bromo-*, b.p. 95—96°/2 mm., *-octoates*; *Et γ-bromovalerate*, b.p. 52—54°/2 mm. Rapid distillation of *Et γ-hydroxyvalerate*, b.p. 85—86°/2 mm., does not give γ-valerolactone. H. B.

Carbon suboxide. C. D. Hurd and F. D. Pilgrim (J. Amer. Chem. Soc., 1933, **55**, 757—759).—C_3O_2, conveniently prepared in 35—49% yield by passing diacetyltartaric anhydride through a Pyrex-glass tube at 625—650°, reacts with 2 mols. of $NH_2\cdot OH$ (at −15°) and $NHPh\cdot OH$ (in EtOAc at 0°) to give malonhydroxamic acid and its NN'-Ph_2 derivative, m.p. 128°, respectively. H. B.

Properties of *d*-xylonolactone. V. Hasenfratz (Compt. rend., 1933, **196**, 350—353).—The action of H_2S on *Pb* d-*xylonate* ($+5H_2O$), m.p. 59°, $[\alpha]_D^{18}$ −5·9° in H_2O, affords cryst. *d*-xylono-γ-lactone, m.p. 99—103°, $[\alpha]_D^{15}$ +85·5° to +24·2° (39 days), which, like *l*-arabo- and *l*-ribono-lactones (A., 1927, 229), affords a mixture of pyromucic and *iso*pyromucic acids by thermal decomp., and with Ac_2O–$ZnCl_2$ yields a Ac_3 derivative, m.p. 99°, $[\alpha]_D^{18}$ +62·4° in EtOH, but does not give cryst. Me and Et esters. J. W. B.

Complexes of hydroferro- and hydroferricyanic acids with aldehydes and ketones. P. Duprat (Bull. Inst. Pin, 1933, **37**, 17—24, 36—37).—In extension of Baeyer and Villiger's work (A., 1902, i, 355) the formation of cryst. additive complexes between aldehydes and ketones (A) and $H_4Fe(CN)_6$ (B) (obtained pure and cryst. by decomp. of its Et_2O complex over H_2SO_4 in a vac.), either in the pure liquid, in ligroin, or, sometimes, aq. solution, is investigated. Thus are obtained *complexes* with MeCHO, $CCl_3\cdot CHO$, *n*-heptaldehyde, PhCHO, anisaldehyde, $CHPh{:}CH\cdot CHO$, $CH_2Ph\cdot CHO$, citral, furfuraldehyde, all of type AB. $COEt_2$ and menthone give *complexes* A_2B; in O-free solvents camphor gives the *complex* A_2B, fenchone gives the complexes $A_2B+3{\cdot}4H_2O$ and anhyd., and AB+EtOH and solvent-free; camphenilone affords the *complex* A_2B+2H_2O and $+0{\cdot}5H_2O$; whereas no additive compound could be isolated with CH_2O, $CH_2{:}CH\cdot CHO$, CH_2PhAc, $CO(CH_2Ph)_2$, benzylidene- and furfurylidene-camphor, products of indefinite composition being obtained with $COMe_2$ and COMeEt. These complexes are only slowly hydrolysed by H_2O. The earlier results using $H_3Fe(CN)_6$ (*loc. cit.*) are confirmed, most of the above giving cryst. complexes; thus fenchone gives A_2B+2H_2O; camphor, $A_2B+0{\cdot}5H_2O$; menthone, A_2B+H_2O, and PhCHO affords $AB+4{\cdot}5H_2O$. J. W. B.

Action of phosphoryl chloride on aldehydes. M. Backès (Compt. rend., 1933, **196**, 277—279).—Aldehydes, when treated with $POCl_3$, form aldols if the C atom adjacent to the CHO group carries a H atom. If the H atom is absent, chlorination occurs. Thus, β-hydroxy-α-methylvaleraldehyde (I) (semicarbazone, a gum; 2 : 4-*dinitrophenylhydrazone*, m.p. 161°) and its dimeride (semicarbazone, a gum) are formed from EtCHO, β-hydroxy-ααγ-trimethylvaler-

aldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 177°) and its dimeride, cryst., b.p. 160°/4 mm., from $CHMe_2$·CHO, β-*hydroxy*-α-n-*amylnonaldehyde*, b.p. 103—106°/0·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 124·5°), and its *dimeride*, b.p. 185°/0·5 mm., from *n*-heptaldehyde. (I) and $POCl_3$ give α-methyl-Δ^{α}-pentenaldehyde, also obtained from $Pr^{\alpha}CHO$.

R. S. C.

General method for the preparation of aldehydes by degradation of acids. G. Darzens and A. Lévy (Compt. rend., 1933, **196**, 348—350).—α-Alkoxy-acids are converted by distillation under atm. pressure in the presence of a little reduced Cu into aldehydes; R·CH(OR′)·CO_2H ⟶ R·CHO + R′·OH + CO. Thus α-*methoxy*-n-*heptoic*, b.p. 122°/15 mm., α-*methoxy*-n-*dodecoic*, m.p. 52°, b.p. 145°/4 mm., and α-*methoxystearic acid*, m.p. 62·5°, b.p. 190°/5 mm., afford respectively *n*-hex-, undec-, and *n*-heptadec-aldehyde in 70%, 75%, and 100% yield.

J. W. B.

Synthesis of αα-dimethylated aliphatic aldehydes of high mol. wt. G. Darzens and A. Levy (Compt. rend., 1933, **196**, 184—187).—If R of α-glycol Me ethers is large, boiling in HCO_2H causes migration with formation of an aldehyde, CMe_2R·CHO. If R is small, the ketone $CHMe_2$·COR, or a mixture of it and the aldehyde, is obtained. The following examples of these reactions are given: α-bromostearic acid ⟶ *Me* α-*methoxystearate*, b.p. 184—185°, m.p. 17·5° and 34°, ⟶ γ-*methoxy*-β-*methylnonadecan*-β-*ol*, m.p. 0° and 18°, ⟶ αα-*dimethylstearaldehyde*, b.p. 165—177°, m.p. 14·5°; *Me* α-*methoxylaurate*, b.p. 124°/2 mm., ⟶ γ-*methoxy*-β-*methyltridecan*-β-*ol*, b.p. 134°/3 mm., ⟶ αα-dimethyldodecaldehyde; *Me* α-*bromo*-, b.p. 116°/2 mm., ⟶ *Me* α-*methoxy-hexoate*, b.p. 126°/15 mm., ⟶ γ-*methoxy*-β-*methylundecan*-β-*ol*, b.p. 112°/?, ⟶ a mixture of 30% of αα-dimethyldecaldehyde and 70% of Pr^{β} octyl ketone; *Me* α-*methoxyheptoate*, b.p. 90°/12 mm., ⟶ γ-*methoxy*-β-*methyloctan*-β-*ol*, b.p. 86°/11 mm., ⟶ Pr^{β} amyl ketone.

A. C.

Action of hydrogen cyanide on methylglyoxal. C. V. Smythe (Biochem. Z., 1933, **257**, 371—384).—When CN′ is added to a solution of AcCHO a double compound is formed which is readily oxidised by O_2 giving AcOH, CO_2, and a small amount of HCO_2H. In the absence of O_2 or other oxidising agents, a mol. of free AcCHO may be used as oxidising agent, $AcCO_2H$ (0·5 mol. per mol. AcCHO disappearing) and a product containing at least 6 C atoms being formed. The velocities of the aerobic and anaerobic reactions are of the same order, and in presence of both O_2 and free AcCHO both reactions proceed simultaneously. With excess of CN′ the reaction with O_2 proceeds almost quantitatively.

P. W. C.

Rapid pyrogenation of keten. J. A. Muller and (Miss) E. Peytral (Compt. rend., 1933, **196**, 279—280).—Keten, when in contact with Pt at 1150° for 0·002—0·003 sec., decomposes to C_2H_4 (19·6—22·8%), C_2H_2 (1·9—4·3%), CO (60·9—66·1%), CH_4 (8·0—10·6%), H_2 (2·0—3·3%), and C. The amount of C formed increases with the time of contact. Primary decomp. into CO and CH_2 is postulated.

R. S. C.

Metallic compounds of the enolic forms of monocarbonyl compounds. XV. Preparation of keten diethylacetal. H. Scheibler (Ber., 1933, **66**, [*B*], 428).—In reply to Snell and McElvain (this vol., 259), an improved prep. of the compound is described. Analysis is best effected by determination of OEt according to Vieböck and Schwappach.

Alleged specific test for acetone. R. J. W. Le Fevre and J. Pearson (J.S.C.I., 1932, **51**, 433—434T).—The test of Raw (A., 1932, 1235) is not sp. for $COMe_2$ but gives positive results (indigotin formation) with ketones R·COMe, where the group R does not materially diminish the incipient polarisation of the CO group on which the reaction evidently depends.

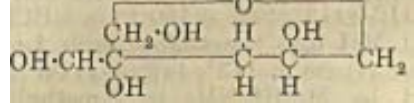
Preparation of the ketol $C_6H_{10}O_3$ and of methylglyoxal. M. Henze and R. Müller (Z. physiol. Chem., 1933, **214**, 281—284; cf. this vol., 88).—Details of the prep. of AcCHO (I) from $COMe_2$ (cf. Riley *et al.*, A., 1932, 833) and of γ-hydroxyhexane-βε-dione from (I) and COMe·CH_2·CO_2Et are given.

J. H. B.

Stereochemistry of aliphatic ketoximes. S. Furukawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 71—86).—The *oximes* of Me palmityl, m.p. 73—74°, and Me lauryl, m.p. 56—57°, ketones could each be obtained in only one form and by the Beckmann change (H_2SO_4 in AcOH) and subsequent hydrolysis of the acid amide afford pentadecylamine and palmitic acid, and undecylamine and lauric acid, respectively. *Et palmityl ketoxime* is separated by fractional crystallisation into two stereoisomeric *forms* (I), m.p. 58—59° [converted into a mixture containing (II) by irradiation] and (II), m.p. 44—45°, from which similarly different proportions of pentadecylamine and palmitic acid are obtained. Similar differences in the proportion of the products were obtained in the case of the stereoisomeric *forms*, m.p. 52·5—53·5° (*Bz* derivative, m.p. 32·5—33°) (converted into the high-m.p. form by HCl in dry Et_2O) and m.p. 64—65° (*Bz* derivative, m.p. 37·5°), of *Et stearyl*, and with the two *forms*, m.p. 43·5—44·5°, and m.p. 26·5—27·5°, of *Pr palmityl ketoxime*. In these cases both low- and high-m.p. forms are unchanged after fusion at 100°. In agreement with these results hydrolysis of the amide obtained by the Beckmann change from ginnonoxime (A., 1932, 1138) gives *n*-decoic acid and *n*-nonadecylamine in addition to the products previously recorded. *Dipalmityl ketoxime*, m.p. 50—60°, similarly gives *palmitpentadecylamide*, m.p. 92—93°.

J. W. B.

***iso*Saccharinose.** P. Schorigin and N. N. Makarova-Semlianskaja (Ber., 1933, **66**, [*B*], 387—389).—Reduction of *iso*saccharine by Na–Hg in faintly

(I.) 

acid solution leads to non-cryst. iso*saccharinose* (I) (p-*nitrophenylhydrazone*, m.p. 168—169°; Ac_3 derivatives, m.p. 98° and 85—86°, respectively).

H. W.

3 : 5-Benzylidene- and 5 : 6-benzylidene-1 : 2-*iso*propylideneglucose. P. A. LEVENE and A. L. RAYMOND (Ber., 1933, **66**, [*B*], 384—386).—Contrary to Brigl, 3 : 5-benzylidene-1 : 2-*iso*propylideneglucose (I) (Brigl and Grüner, A., 1932, 1115) is not identical with the 5 : 6-benzylidene-1 : 2-*iso*propylideneglucose (II) of Levene and Meyer (A., 1923, i, 92). The Bz derivatives of (I) and (II) have m.p. 124°, $[\alpha]_D$ +3·5°, and m.p. 111·5—112°, $[\alpha]_D^{20}$ −43·6° in $CHCl_3$, respectively, whilst the p-$C_6H_4Me{\cdot}SO_2$ compounds have m.p. 121—121·5° and $[\alpha]_D^{20}$ +13·5° in $CHCl_3$ and (non-cryst.) $[\alpha]_D^{20}$ −16·5° in $CHCl_3$, respectively. The supposition that (I) is unstable and passes into (II) under the influence of high temp. is supported by the observation that Brigl's compound is obtained in diminished yield when his directions are followed but a higher temp. is used, and that the process of Levene and Meyer, if continued for only a short time, leads to (I). H. W.

Attempted preparation of esters of sugars and chloroacetic acid. K. BRASS and E. KURZ (Ber., 1933, **66**, [*B*], 442—446).—Attempts to prepare cellulose trimonochloroacetate leads to esters of the greatly degraded carbohydrate. β-*d*-Glucose is transformed by $CH_2Cl{\cdot}CO_2H$ and $(CH_2Cl{\cdot}CO)_2O$ in presence of $ZnCl_2$ or conc. H_2SO_4 into esterified and condensed products, whereby partial isomerisation occurs. Fructose appears to yield a $(CH_2Cl{\cdot}CO)_3$ derivative and to be anhydrised. β-Glucose penta-acetate (I) when heated for 20 min. at 130° with $CH_2Cl{\cdot}CO_2H$ and $(CH_2Cl{\cdot}CO)_2O$ affords α-*glucopyranose* 2 : 3 : 4 : 6-*tetra-acetate* 1-*chloroacetate*, m.p. 129—130°, $[\alpha]_D^{13}$ +100·74° in $C_2H_2Cl_4$, converted by HBr–AcOH at 5—17° into acetobromoglucose (II), m.p. 87·2—88°, $[\alpha]_D^{25}$ +199·84° in $CHCl_3$; when the temp. is restricted to 120°, (I) gives β-*glucopyranose* 2 : 3 : 4 : 6-*tetra-acetate* 1-*chloroacetate* (II), m.p. 134—134·5°, $[\alpha]_D^{13}$ −1·39° in $C_2H_2Cl_4$, also transformed into (II). (III) is partly converted into (I) by treatment with $CH_2Cl{\cdot}CO_2H$ and $(CH_2Cl{\cdot}CO)_2O$ at 120°. (I), $(CH_2Cl{\cdot}CO)_2O$, and conc. H_2SO_4 at 65° yield α-*glucopyranose* 2 : 3 : 4-*triacetate* 1 : 6-*dimonochloroacetate*, m.p. 93·5—94°, $[\alpha]_D^{13}$ +95·46° in $C_2H_2Cl_4$. Cellobiose octa-acetate is transformed by $CH_2Cl{\cdot}CO_2H$ and $(CH_2Cl{\cdot}CO)_2O$ at 120° into *cellobiose hepta-acetate* 1-*chloroacetate*, m.p. 218—219°, $[\alpha]_D^{13}$ +46·55° in $C_2H_2Cl_4$, whence acetobromocellobiose, m.p. 170—171·5°, $[\alpha]_D^{25}$ +94·70° in $CHCl_2$. H. W.

Carbohydrates. XV. Benzoyl and benzylidene derivatives of fructose. P. BRIGL and R. SCHINLE (Ber., 1933, **66**, [*B*], 325—330; cf. this vol., 148).—Fructose is converted by BzCl (4 mols.) and C_5H_5N in $CHCl_3$ at −10° and finally at room temp. into β-*fructose* 1 : 3 : 4 : 5-*tetrabenzoate*, m.p. 174—175°, $[\alpha]_D^{20}$ −164·9° in $CHCl_3$, which rapidly reduces warm Fehling's solution, is transformed by Ac_2O and NaOAc into β-*fructose* 1 : 3 : 4 : 5-*tetrabenzoate* 2-*acetate*, m.p. 112—113°, $[\alpha]_D^{20}$ −160·7° in $CHCl_3$, and by Ag_2O and MeI into β-*methylfructoside* 1 : 3 : 4 : 5 : -*tetrabenzoate* (I), m.p. 113°, $[\alpha]_D^{20}$ −171·3° in $CHCl_3$, hydrolysed by MeOH–NH_3 to β-methylfructoside, m.p. 119°, $[\alpha]_D^{20}$ −171·8°. An isomeric *tetrabenzoate* (II), m.p. 123—124°, $[\alpha]_D^{20}$ −6·10° to −13·7° in $CHCl_3$, is best obtained by complete benzoylation of fructose and subsequent treatment of the product with HBr–AcOH followed by Ag_2CO_3 in MeOH; the yield is poor. Fructose and BzCl (5 mols.) in $CHCl_3$ afford keto*fructose* 1 : 3 : 4 : 5 : 6-*pentabenzoate*, m.p. 124—125°, $[\alpha]_D^{20}$ +40·9° in $CHCl_3$, which slowly reduces boiling Fehling's solution. The open structure is established by its transformation by HCl and EtSH into 2 : 3-*diethylthiolfructose* 1 : 3 : 4 : 5 : 6-*pentabenzoate*, m.p. 128—129°, $[\alpha]_D^{20}$ +51·5° in $CHCl_3$; (I) and (II) do not react with HCl and EtSH.

Treatment of fructose with PhCHO and $ZnCl_2$ at room temp. affords *dibenzylidenefructose*, m.p. 160°, $[\alpha]_D^{20}$ −22·9° in $CHCl_3$ (*Ac*, m.p. 145—146°, $[\alpha]_D^{20}$ −37·5° in $CHCl_3$, and *Bz*, m.p. 147°, $[\alpha]_D^{20}$ −18·05° in $CHCl_3$, derivatives). H. W.

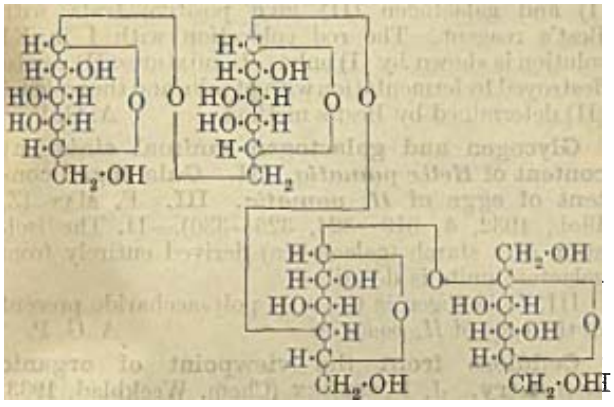
***am*-Hexose which occurs in the organism.** Y. KOTAKE and M. NISHAGAKI (Proc. Imp. Acad. Tokyo, 1932, **8**, 507—510).—The liquid in the chamber of the eye, the cerebro-spinal fluid, and various other organs contain *vitamose* (I). The concn. of (I) in the extract from ox testicles (chiefly by pptn. by $CdSO_4$) is described. Solutions of (I) yield a *hexosazone*, m.p. 205°, and *di*-2 : 4-*dinitrophenylhydrazone*, decomp. about 240° (rapid heating) (photomicrographs), give Trommer's reaction in the cold, Folin and Denis' reaction in very dil. solution, Selivanov's reaction rapidly when boiled, reduce $KMnO_4$, HIO_3, and HIO, are decomposed by O_2 (to give a little hexose), and are readily fermented by much yeast, but do not give pentose reactions. (I) is considered to be an *am*-hexose. R. S. C.

Synthetic hexose phosphates. II. K. JOSEPHSON and S. PROFFE.—See this vol., 428.

New structural type of polysaccharides. H. H. SCHLUBACH, H. KNOOP, and M. LIU (Naturwiss., 1933, **21**, 62—63).—Methylirisin, containing 3 OMe groups to each hexose unit, yields on acid hydrolysis tetra- and di-methylfructose in about equal amount; irisin is, therefore, made up of two differently arranged fructose units. R. K. C.

Constitution of stachyose. M. ONUKI (Proc. Imp. Acad. Tokyo, 1932, **8**, 496—499).—Stachyose (I), $C_{24}H_{42}O_{21}$, +1·5H_2O (lost at 115° in vac.) (cf. lit.) [Ac_{14} (p-$NO_2{\cdot}C_6H_4{\cdot}CO)_{14}$, and ($CPh_3{\cdot}$)$_4$ derivatives], has 14 free OH groups, of which 4 are primary. The Me_{14} *ether* with 0·5% HCl–MeOH (1 mol.) gives 1 : 3 : 4 : 6-tetramethyl-*d*-fructose, 2 : 3 : 4 : 6-tetramethyl-*d*-galactose (II), and a fraction, b.p. 108—112°/0·02 mm., which, when methylated and hydrolysed with 7% HCl, affords 2 : 3 : 4 : 6-tetramethyl-*d*-glucose and (II). With 20% AcOH (I) yields fructose and manninotriose; the triose is oxidised by Br to manninotrionic acid, affording the *Me* ester, b.p. 220°/0·02 mm., which with HCl (2 mols.) at 90° gives 2 : 3 : 5 : 6-tetramethyl-*d*-gluconic acid, (II), and 2 : 3 : 4-trimethyl-*d*-galactose (III), b.p. 132°/0·02 mm., m.p. 85°, $[\alpha]_D^{21}$ +154·07°⟶ +122·02° in 30 hr. in H_2O. The structure of (III) is proved by the following reactions: it reduces Fehling's solution, but does not give an osazone or anilide; when methylated, hydrolysed, and treated with NH_2Ph, it gives 2 : 3 : 4 : 6-tetramethylgalactopyranoseanilide; with Br it affords trimethylgalactonic acid (phenylhydrazide, m.p. 170—171°), the lactone

of which has the mutarotation curve of a δ-lactone; with CPh_3Cl it gives 6-triphenylmethyl-2 : 3 : 4-trimethylgalactose. (I) is, therefore,



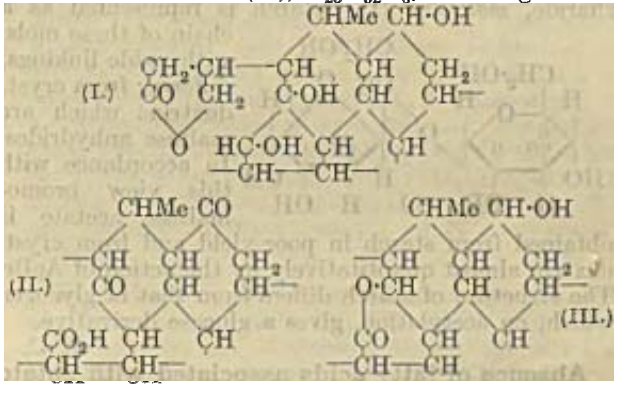
(III), obtained from uronic acid, has been crystallised (cf. A., 1931, 465). R. S. C.

Synthesis of phenolic glucosides. B. Helferich and E. Schmitz-Hillebrecht [with E. Günther, F. Strauss, O. Peters, and S. Petersen] (Ber., 1933, **66**, [*B*], 378—383).—Acetates of reducing sugars are converted fairly rapidly and at a moderate temp. by phenols into phenolic glucosides and AcOH in the presence of acid catalysts. α- and β-Forms are simultaneously produced, but their amounts are frequently so dissimilar that little difficulty is experienced in their separation. The steric direction is influenced by the nature of the sugar and phenol, but the selection of the α- or β-acetate as initial material has little or no influence. The conditions of condensation, in particular the nature and amount of catalyst, control the direction. Active catalysts are acids, acid salts, or salts which tend to complex formation and give acidic complexes with OH-compounds. Anhyd. $ZnCl_2$ and p-$C_6H_4Me{\cdot}SO_3H$ are particularly useful. The following examples are cited: phenol-α-*d*-glucoside tetra-acetate, m.p. 114—115° (corr.), $[\alpha]_D^{20}$ +168° in $CHCl_3$, from β-*d*-glucose-penta-acetate (I), PhOH, and $ZnCl_2$; *phenol*-β-*d*-*glucoside tetra-acetate*, from (I), PhOH, and p-$C_6H_4Me{\cdot}SO_3H$ at 100°; α-naphthol-β-*d*-glucoside tetra-acetate, m.p. 178—179° (corr.), $[\alpha]_D^{9}$ −72° in $CHCl_3$; 2-β-naphthol-β-*d*-glucoside tetra-acetate, m.p. 135—136° (corr.), $[\alpha]_D^{21}$ −19° in $CHCl_3$; methyl-arbutin tetra-acetate, m.p. 103—104° (corr.), $[\alpha]_D^{22}$ −16° in $CHCl_3$; guaiacol-β-*d*-glucoside tetra-acetate, m.p. 155—156°, $[\alpha]_D^{9}$ −29° in $CHCl_3$; phenol-α-*d*-galactoside tetra-acetate; phenol-β-*d*-galactoside tetra-acetate, m.p. 123—124° (corr.), $[\alpha]^{20}$ −26·4° in $CHCl_3$; *o*-cresol-β-*d*-galactoside tetra-acetate, m.p. 113—114° (corr.), $[\alpha]_D^{8}$ −4° in $CHCl_3$; phenol-β-*d*-xyloside triacetate, m.p. 147·5—148·5° (corr.), $[\alpha]_D^{18}$ −50° in $CHCl_3$; *phenol*-β-d-*fructoside tetra-acetate*, m.p. 128—130·5°, $[\alpha]_J^{20}$ −146° in $CHCl_3$; *phenol*-β-d-*fructoside*, m.p. 172·5—173·5° (corr.), $[\alpha]_D^{19}$ −210° in H_2O; phenol-α-cellobioside hepta-acetate, m.p. 228° (corr.), $[\alpha]_D$ +83° in $CHCl_3$; *phenol*-β-*gentiobioside hepta-acetate*, m.p. 194—195° after softening at about 186°, $[\alpha]_D^{18}$ −29° in $CHCl_3$, whence *phenol*-β-*gentiobioside*, m.p. 190—193° after softening at about 185°; $[\alpha]_D^{18}$ −67° in H_2O. H. W.

C C

Emulsin. X. B. Helferich, H. Appel, and R. Gootz (Z. physiol. Chem., 1933, **215**, 277—284).—The following glucosides were prepared: *phenol*-β-l-*arabinoside*, m.p. 176—179°, $[\alpha]_D^{17}$ +243° in H_2O; -β-d-*arabinoside*, m.p. 177—179° (corr.), $[\alpha]_D^{18}$ −244° in H_2O; -α-d-*arabinoside*, m.p. 152·5—154·5° (corr.), $[\alpha]_D^{18}$ −5·5° in H_2O; -α-l-*rhamnoside* (I), m.p. 75—77° (corr.), $[\alpha]_D$ −106° in H_2O [*triacetate*, m.p. 130—131° (corr.), $[\alpha]_D^{18}$ −80° in $CHCl_3$]; -β-l-*rhamnoside*, m.p. 159—161° (corr.), $[\alpha]_D^{18}$ +87·5° in H_2O [*triacetate*, m.p. 147—148° (corr.), $[\alpha]^{18}$ +52·5° in $CHCl_3$]. Only (I) is hydrolysed appreciably by emulsin. F. O. H.

Digitalis glucosides. VI. Oxidation of anhydrodihydrodigitoxigenin. Problem of gitoxigenin. W. A. Jacobs and R. C. Elderfield (J. Biol. Chem., 1933, **99**, 693—699).—After hydrolysis (NaOH in aq. C_5H_5N) anhydrodihydrodigitoxigenin (Windaus and Stein, A., 1929, 71) is oxidised by 5% $KMnO_4$ to *hydroxydihydrodigitoxigenin* (I), m.p. 193—196°, which differs from dihydrogitoxigenin and is further oxidised by CrO_3 to a monobasic *diketo-lactonic acid* (II), $C_{23}H_{32}O_6$, sintering above

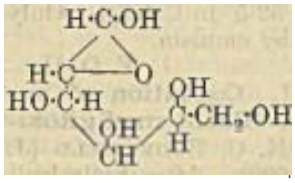


192°, m.p. 196—200°, different from the isomeric acid obtained in the oxidation of dihydrogitoxigenin (A., 1930, 1413). Reduction of (II) with H_2–PtO_2 in EtOAc affords a neutral *hydroxydilactone* (III), $C_{23}H_{34}O_5$, m.p. 145°, resolidifying and remelting at 232—234°. The position of the second OH group in gitoxigenin is still in doubt. It cannot be that previously assigned (*loc. cit.* and *ibid.*, 749, 1187) nor can it be a primary alcohol group on C_1, since certain reactions differ from those of dihydrostrophanthidol, which contains such a OH group (A., 1930, 1413), and which is dehydrated by HCl (*d* 1·19) at 0° to *monoanhydrodihydrostrophanthidol*, m.p. 175—176°. J. W. B.

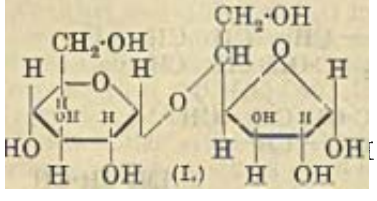
[Solanine.] IX. [*Solanum*] *tuberosum* solanine (*t*-solanine). G. Oddo and G. Caronna (Gazzetta, 1932, **62**, 1108—1118; cf. A., 1929, 299).—The Ac derivative of *t*-solanine, considered by Zemplén and Gerecs (A., 1929, 51) to be a trianhydro-Ac_{13} compound, is a *polyacetylsolanine acetate*. With KOH–MeOH or MeONa it yields *t*-solanine and MeOAc, and with HCl–EtOH *t*-solanidine, more probably $C_{25}H_{39}ON$ (A., 1912, i, 798) than $C_{26}H_{41}ON$ (Zemplén, *loc. cit.*). Acetylation of *t*-solanine under conditions unfavourable to salt-formation produces *acetyl*-t-*solanine*, m.p. 120°, which with HBr–AcOH

gives the following products (I) rhamnose tetra-acetate; (II) *anhydrobromonona-acetyldihydrosolanidineglucosogalactoside*, m.p. 130°, whence glucose, and, with KOH–EtOH or NaOMe, galactose and *anhydrosolanidineglucoside*, m.p. 167°, also obtained, m.p. 178°, from (III), which is *anhydropenta-acetylsolanidineglucoside hydrobromide*, m.p. 115° (decomp.). E. W. W.

Plant synthesis of carbohydrates and polysaccharides. H. HIBBERT (Canad. J. Res., 1933, 8, 103—104).—The formation of polysaccharides from monosaccharide in the plant may occur by inter- or intra-mol. addition of an OH group to the ethylene-oxide ring of the equilibrium form of glucose and fructose (annexed formula) or its anhydride (cf. this vol., 373). H. A. P.



Structure of starch. R. SUTRA (Compt. rend., 1932, **195**, 1282—1284).—The α- and β-maltose octa-acetates obtained by acetylating starch (this vol., 261) are regarded as derivatives of the disaccharide, *maltososе* (I). Starch is represented as a chain of these mols. with oxide linkings, differing from cryst. dextrins which are maltose anhydrides. In accordance with this view bromomaltose acetate is obtained from starch in poor yield and from cryst. dextrin almost quantitatively by the action of AcBr. The structure of starch differs from that of glycogen which, on acetylation, gives a glucose derivative. A. C.



Absence of fatty acids associated with potato starch. L. LEHRMAN and E. KABAT (J. Amer. Chem. Soc., 1933, **55**, 850).—Potato starch does not contain fatty acids associated with it, since extraction with light petroleum gives only 0·02% of extractive and hydrolysis affords approx. 0·02% of "fat by hydrolysis." H. B.

Inulin. III. Depolymerisation of inulin. E. BERNER (Ber., 1933, **66**, [*B*], 397—400).—Mainly a reply to Pringsheim and Weiss (this vol., 149). The author's method of determining minute amounts of ash in inulin and the adsorptive power of inulin for EtOH are described in detail. H. W.

Thermal decomposition of inulin. E. BERNER (Kongl. Norske Vidensk. Selskab, 1933, **5**, 167—170; cf. A., 1930, 1025).—When inulin is heated with glycerol (I) at 140° it gives, not simpler fructosans (cf. A., 1928, 276), but their glycerol ethers. The process is favoured by a large excess of (I) and prolongation of the reaction time. There is thus obtained glycerol α(?)-monofructoside, isolated as a somewhat impure hexa-acetate, b.p. 230°/high vac., converted by Me_2SO_4 and NaOH into the *Me*$_6$ *ether*, b.p. 125°/0·02 mm., $[\alpha]$ +20·8° in $CHCl_3$. The product obtained by Schlubach and Elsner (A., 1932, 1022) by use of $(\cdot CH_2\cdot OH)_2$ (II) cannot be obtained free from (II), and is probably similar in constitution. H. A. P.

Microscopical detection of glycogen and galactogen and their separation. F. MAY and F. KORDOWICH (Z. Biol., 1932, **93**, 233—238).—Glycogen (I) and galactogen (II) give positive tests with Best's reagent. The red coloration with I in KI solution is shown by (I) only. In mixtures, (I) can be destroyed by fermentation with ptyalin and the residual (II) determined by Best's method. A. G. P.

Glycogen and galactogen (animal sinistrin) content of *Helix pomatia*. II. Galactogen content of eggs of *H. pomatia*. III. F. MAY (Z. Biol., 1932, **4**, 319—324, 325—330).—II. The isolation of a starch (galactogen) derived entirely from galactose units is described.

III. Galactogen is the only polysaccharide present in the eggs of *H. pomatia*. A. G. P.

Cellulose from the viewpoint of organic chemistry. J. BÖESEKEN (Chem. Weekblad, 1933, **30**, 20—24).—A review. Cellulose is a poly-β-glucose consisting of long chains of pyranose groups linked by O at the first and fourth C atoms. The no. of such groups in the mol. is about 100. The chains form parallel bundles, with the first C atom of one glucose group adjacent to the fourth C atom of the neighbouring glucose group. H. F. G.

Cellulose. XLVII. Relation between cellulose and cellulose-dextrins. II. Crystallisation of cellulose nitrate. K. HESS, C. TROGUS, and K. DZIENGEL (Annalen, 1933, **501**, 49—84).—Limit-dextrin 2 (I), obtained by hydrolysis (MeOH–NaOH at 20°) of its acetate (A., 1932, 47) and subsequent pptn. from a solution in 2*N*-NaOH, shows the same Röntgen diagram as does hydrocellulose. Pptn. of limit-dextrin nitrate (II) [methods of prep. from (I) and HNO_3–H_2SO_4 and HNO_3–AcOH described] and of fibrous cellulose nitrate (III) from 1—2% solutions in $COMe_2$ with H_2O, gives products which show three (not sharp) interference rings; slow pptn. from solutions in $COMe_2$ by light petroleum at 30° affords products showing sharp and identical Röntgen diagrams. These results also indicate that a second modification of (III) exists. The formation of additive compounds of (II) and $COMe_2$, 4-methyl*cyclo*hexanone, and *cyclo*hexanone is demonstrated by the methods previously described (*ibid.*, 568, 802); one form only is isolated in each case, and this is identical with the corresponding ketone–cellulose nitrate I compound (in the first two cases) [in the last case, one form only is isolated from (II) or (III) (cf. *loc. cit.*)]. The total double refraction of (III) and its additive compounds is negative; that of the compound of (II) with *cyclo*hexanone is positive (the other two are negative). Some variation is found in the difference between the *n* of the solvent and solution for (II) and various specimens of (III) in $COMe_2$, and (II) shows a higher sp. rotation (in $COMe_2$, *cyclo*hexanone, and 4-methyl*cyclo*hexanone) than any of the samples of (III) examined. Stabilised (II) is also more sol. in MeOH–$COMe_2$ than stabilised (III). Some of the possible causes of these slight differences in physical properties are discussed. The same foreign substance (isolation described) appears to be formed during the prep. of (II) as with (III) (*ibid.*, 222). H. B.

Partial fission of animal cellulose. L. Zechmeister and G. Tóth (Z. physiol. Chem., 1933, **215**, 267—276).—Acid hydrolysis of tunicin from *Phallusia mammilaris* (A., 1893, i, 380, 497), followed by treatment with various concns. of EtOH, yields a dextrin fraction and fractions containing one or more of cellobiose, -triose (I), -tetraose (II), and -hexaose (III). Comparison of the properties of (I), (II), and (III) and of their acetates with the corresponding derivatives from vegetable cellulose (A., 1931, 716) indicates that the structures of the two celluloses have a common basis. F. O. H.

Cellulose methylene ether. F. C. Wood (J.S.C.I., 1933, **52**, 33—34T; cf. A., 1931, 1401).—Schenk's work on the action of AcOH–Ac_2O–Pr_2 formal mixtures on cellulose (A., 1932, 1117) is criticised. His analytical figures do not correspond with the supposed compound $(C_6H_9O_5)_2CH_2$. No significance can be attached to the val. 7—8% CH_2O in the products, other than that this represents an equilibrium val. which is also obtained by the action of a H_2SO_4–paraformaldehyde mixture on cellulose. The analysis of methylenated cellulose is conducted by a modified Beltzer method.

Compounds of high mol. wt. II. Butyl ethers of cellulose. A. Nowakowski (Rocz. Chem., 1933, **13**, 49—56).—Alkaline suspensions of cellulose react with Bu$^{\alpha}$Cl to yield *ethers*, m.p. 171—226°, containing 2·1—2·7 Bu groups per 6 C atoms, possessing a high degree of plasticity, and sol. in C_6H_6, but not in MeOH. R. T.

Determination of tetramethylammonium. J. J. Bikerman (Z. anal. Chem., 1932, **90**, 335—337).—NMe_4 compounds can be determined by heating with 50% aq. NaOH in a Ni retort, finally to dark redness, and absorbing the NMe_3 produced in standard H_2SO_4.

Quaternary ammonium salts from dimethylhalogenoalkylamines. II. Polymerisation of dimethyl-γ-halogenopropylamines. C. F. Gibbs, E. R. Littmann, and C. S. Marvel (J. Amer. Chem. Soc., 1933, **55**, 753—757).—Dimethyl-γ-phenoxypropylamine (I), b.p. 130—132°/20 mm. (*chloroplatinate*, m.p. 147°), from γ-phenoxypropyl bromide and EtOH–$NHMe_2$, is converted by Knorr and Roth's method (A., 1906, i, 457) into dimethyl-γ-chloropropylamine (II). The polymeride (III) formed when (II) is heated at 100° (bath) for 36 hr. is basic and contains some non-ionic Cl. These facts are not explicable by Knorr and Roth's structure (*loc. cit.*), but are accounted for by the suggested structure $\{Cl(CH_2)_3\cdot NMe_2[\cdot(CH_2)_3\cdot NMe_2]_{n-2}\cdot(CH_2)_3\cdot NMe_2\}Cl_{n-1}$, for (III); the ratio of non-ionic to ionic Cl indicates that n—12—13 (M about 1500), whilst titration with acid gives M=about 4000. (I) and conc. HBr give *dimethyl-γ-bromopropylamine*, b.p. 51°/15 mm., 34—35°/6 mm. (*hydrobromide*; *chloroplatinate*, decomp. 125—130°), which when kept (alone; in EtOH or Et_2O) or heated at 100° (bath), passes into a *polymeride* (IV), m.p. 225—240° (decomp.). (IV) is slightly basic and contains varying amounts of Br (according to method of prep.), some non-ionic Br, and some unsaturated material (Br–H_2O; $KMnO_4$) (probably formed by loss of HBr from the γ-bromopropyl group), indicating that it is a mixture of two types of polymerides, viz., as (III) and $\{CH_2{:}CH\cdot CH_2\cdot NMe_2[\cdot(CH_2)_3\cdot NMe_2]_n\cdot(CH_2)_3\cdot NMe_2\}Br_{n+1}$. H. B.

Local anæsthetics derived from dialkylaminopropanediols. II. Esters of piperidinopropanediol. E. W. Scott and T. H. Rider (J. Amer. Chem. Soc., 1933, **55**, 804—805).—γ-Piperidinopropane-αβ-diol diphenylcarbamate hydrochloride is a better local anæsthetic than the *di-α-naphthylcarbamate hydrochloride*, m.p. 202—203°, the *di-p-tolylcarbamate hydrochloride*, m.p. 223—225°, and the dibenzoate and di-*p*-aminobenzoate hydrochlorides. H. B.

Formation of nitrate, ammonia, and fatty acids from α-amino-acids and nitrate from ammonium carbonate by oxidation with potassium permanganate. B. Sjollema and J. W. Dienske (Rec. trav. chim., 1933, **52**, 229—233).—Oxidation of various NH_2-acids with $KMnO_4$ as previously described (A., 1931, 943) gives varying amounts of nitrate (calc. as HNO_3) (10—52%), NH_3 (11—39%), and fatty acids. AcOH (72 mol.-%) is obtained from alanine, $Pr^{\beta}CO_2H$ (46%) from valine, AcOH (12%) and *iso*valeric acid (37%) from leucine, α-methylbutyric acid (43%) from *iso*leucine, and $H_2C_2O_4$ (8·6%) from serine. Except in the last case oxidation occurs at Cα and CO_2 is eliminated; the α-CO-acid is probably an intermediate. Similar oxidation of NH_4 lactate gives HNO_3=4% of the original N; HNO_3 is not produced from $(NH_4)_2CO_3$ alone, but in presence of glucose (and related substances) (1—3 mg. per mg. of N) about 1% of N is oxidised to HNO_3. H. B.

Equilibria in the formol titration. M Levy (J. Biol. Chem., 1933, **99**, 767—779).—Theoretical considerations and titrations indicate that only NH_2-acid anions react significantly with CH_2O and that two types of new anions are formed, due to the reaction with one or two mols. of CH_2O. Contrary to Harris (A., 1925, i, 450), the theory of Sorensen (A., 1908, i, 115) is upheld. The importance of variations in the dielectric const. of the solvent produced by addition of CH_2O is refuted (A., 1929, 648). F. O. H.

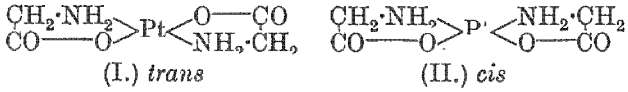
Oxidative deamination of amino-acids by methylglyoxal. B. Kisch (Biochem. Z., 1933, **257**, 334—336).—Glycine is very readily and serine a little less readily deaminised by AcCHO, the optimum p_H being 11 (similar to that using resorcinol or hydroxyquinol as catalyst). Glycyl-glycine and -tyrosine are only slightly deaminised and alanine scarcely at all. The deamination of glycine is an oxidative process and depends on the rate of aeration, almost disappearing on excluding O_2. P. W. C.

Preparation of glycine. I. V. Kulikov and E. A. Slastenina (J. Gen. Chem. Russ., 1932, **2**, 777—782).—A 55% yield of pure glycine is obtained from $CH_2Cl\cdot CO_2H$ and NH_3 (A., 1928, 49), the product being purified by extraction with MeOH and washing with H_2O (cf. A., 1931, 1042). G. A. R. K.

Geometrically isomeric platinodiglycines. A. A. Grunberg and B. W. Ptizyn (J. pr. Chem., 1933, [ii], **136**, 143—158).—Interaction of K_2PtCl_4

and $NH_2{\cdot}CH_2{\cdot}CO_2H$ in H_2O gives a ppt. of $[PtB_2]$ (I) (B=$NH_2{\cdot}CH_2{\cdot}CO_2$·] (cf. A., 1912, i, 243), whilst a more sol. *isomeride* (II) and the yellow salt $K[PtCl_2B]$ remain in solution. Both (I) and (II) are non-ionised. The latter is shown to be the *cis*-compound by the $CS(NH_2)_2$ method, but (I) gives misleading results, as it is insol. in the cold, and at the b.p. gives $[Pt\{CS(NH_2)_2\}_4]Cl_2$. The *trans* structure of (I) is, however, definitely proved by the formation of the cryst. *compound* $[PtCl_2B_2]$ (III) with boiling dil. or conc. HCl; this is a dibasic acid, and is readily converted by $CS(NH_2)_2$ into the *compound* $[PtB_2\{CS(NH_2)_2\}_2]Cl_2$. In H_2O (III) gives AgCl only slowly in the cold, but more rapidly on warming with $AgNO_3$. Its Na salt in dil. aq. solution at the b.p. regenerates (I). With cold dil. NH_3 (III) gives a yellow solution which becomes colourless on warming and on subsequent cooling deposits the *compound* *trans*-$[Pt(NH_3)_2B_2]$ (IV), which with HCl gives *trans*-$[Pt(NH_3)_2B_2]Cl_2$ (*chloroplatinite*), converted by $CS(NH_2)_2$ into *trans*-$[Pt(NH_3)_2\{CS(NH_2)_2\}_2]Cl_2$. Prolonged heating of (IV) with conc. HCl gives *trans*-$[Pt(NH_3)_2Cl_2]$.

The action of conc. HCl on (II) gives a little (III) (impurity) and a yellow solution which contains the corresponding *cis*-dichloride, for it gives the *salt* *cis*-$[Pt(NH_3)_2B_2]Cl_2$ with warm NH_3 [this is shown to have the *cis*-configuration by its behaviour towards $CS(NH_2)_2$] and a colourless salt with $(\cdot CH_2{\cdot}NH_2)_2$ (isolated as the *salt* $[Pt\ en\ B_2]PtCl_4$). The solution of (III) in HCl gives $[Pt\ en_2]Cl_2$ with $(CH_2{\cdot}NH_2)_2$ under the same conditions. The formulæ :



(I.) *trans* (II.) *cis*

are therefore assigned to the stereoisomeric platinodiglycines. H. A. P.

Constitution of monosodium *d*-glutamate. Chao-Lun Tseng and E. Ju-Hwa Chu (Sci. Quart., Pekin, 1932, **3**, 1—5).—Na *d*-glutamate is probably $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2Na$, since at 150—160° (2·5 hr.) it gives Na *l*-pyrrolidonecarboxylate. Ch. Abs.

Diamino-acid, canavanin. II. M. Kitagawa and H. Yamada (J. Biochem. Japan, 1932, **16**, 339—349).—Canavanin (A., 1930, 121, 384), $C_5H_{12}O_3N_4$, m.p. 182—183° (decomp.) [flavianate, $C_5H_{12}O_3N_4,(C_{10}H_6O_8N_2S)_2$, m.p. 210—215° (decomp.); picrate, m.p. 163—164° (decomp.); Cu salt, $(C_5H_{11}O_3N_4)_2Cu$, m.p. 205—207° (decomp.); *Me ester dihydrochloride*, m.p. 166—167° (decomp.); *Bz*$_3$ derivative, m.p. 86° (decomp.); *sulphate*, m.p. 172° (decomp.)], is not a ureide, but probably a guanidine derivative. Hydrolysis by canavanase (optimum p_H 7·7) yields carbamide and *canalin*, $C_4H_{10}O_3N_2$, m.p. 214° [*dipicrate*, m.p. 192—193° (decomp.); *dihydrochloride*, m.p. 166° (decomp.); *Bz*$_2$ derivative, m.p. 99° (decomp.); *Cu* salt, $C_8H_{18}O_6N_4Cu$]. F. O. H.

Use of cysteine cuprous mercaptide in the determination of cystine. H. B. Vickery and A. White (J. Biol. Chem., 1933, **99**, 701—715).—After hydrolysis of the protein [containing > 20 mg. of cystine (I)] with $8N$-H_2SO_4 in presence of Sn, cysteine Cu^I mercaptide is pptd. by adding an aq. suspension of Cu_2O to the diluted hydrolysate; $10N$-NaOH is then added at 10° until p_H 4—5 (Congo-red) is reached, the ppt. removed, washed, and Cu pptd. by H_2S in very dil. HCl suspension. The filtrate and washings from the CuS are conc. in vac., sulphate is removed by cold saturated $Ba(OH)_2$, and the combined filtrate and washing again conc. The (I) content of the protein is then found by determination of org. S by Denis' method (A., 1911, ii, 66). The results agree with those obtained by the Folin–Marenzi, Sullivan, or Okuda methods. The average recovery of (I) added to casein (*a*) after hydrolysis, (*b*) before hydrolysis, and (*c*) to the hydrolysate freed from cysteine (II), was 92·2, 92·8, and 94·6%, respectively. From pure (II), by dissolving out from excess Cu_2O with $8N$-H_2SO_4, *cysteine* Cu^I *mercaptide* (III) [corresponding with 98% of the (II)] was isolated, the N, S, Cu, and H_2O content corresponding with $C_3H_6O_2NSCu,CuSO_4,2H_2O$, whereas after neutralisation the fundamental compound in the ppt. appears to be the Cu^I salt of (III), $C_3H_5O_2NSCu_2$. From the ppt. only 80% of the original (I) [after aeration of the (II)] could be recovered, some decomp. (NH_3 and probably $AcCO_2H$) occurring. By this method 0·41% of (I) was found in horse hæmoglobin, corresponding closely with 1 mol. of (I) per mol. of mol. wt. 66,400. J. W. B.

White mercury fulminate. A. Dansi (Annali Chim. Appl., 1933, **23**, 29—33).—This may be obtained by treating 25 g. of EtOH (95%) at 50° with a solution of 2·5 g. of Hg and 0·05—0·7 g. of Cu in 25 g. of HNO_3 (*d* 1·4), the product being purer (98·4—99·5%) than in absence of Cu. The effect of Cu is not due to intermediate formation of Cu fulminate. Ni, Zn, Co, or Cd in place of Cu yields a grey fulminate. T. H. P.

Semicarbazone formation and incomplete dissociation of a salt of the ammonium type. P. D. Bartlett (J. Amer. Chem. Soc., 1933, 55, 741—749; cf. A., 1932, 916).—The relationship between the rate of reaction of furfuraldehyde and semicarbazide (I) (under the catalytic influence of AcOH) (cf. *loc. cit.*) and the concn. of AcOH is linear only below 0·05*M*. The velocity coeff. falls rapidly above this concn. A similar relationship is found for (I) and $AcCO_2H$. The results are explicable by the incomplete dissociation of semicarbazide acetate (II) in aq. solution. The dissociation const. of (II) into mols. is approx. 0·12 at 0° and 25°. The effects of the incomplete dissociation of (II) on semicarbazone formation and the mechanism of the reaction are discussed. H. B.

Biuret reaction. III. Biuret reaction of amino-acid amides. M. M. Rising and P. S. Yang (J. Biol. Chem., 1933, **99**, 755—765).—The biuret reaction of α-NH_2-acid amides occurs in the absence of alkali-producing internal salts [Cu (amino-acid amide)$_2$],xH$_2$O. Thus by addition of aq. $Cu(OAc)_2$ either with or without KOH to the appropriate NH_2-acid amide (prep., A., 1931, 1150) are obtained: *Cu* dl-*leucinamide* (I), m.p. 248—250° (decomp.) (cf. Bergell and Brugsch, A., 1910, i, 546); *Cu* l-*asparag-*

ine, decomp., 302—304°; *Cu glycinamide*, decomp., 205—207°; and *Cu* d-*alaninamide*, decomp. 227—231°. In agreement with the structures containing bound internal ions assigned, these derivatives are non-conductors in aq. solution, but electrolysis of (I) in presence of KOH causes migration of a coloured anion. The structures of these derivatives support the theory (A., 1931, 77) that four basic N atoms are involved in the biuret reaction. The min. no. of acid H atoms is two (in strongly basic compounds), but with more weakly basic mols. containing acid groups, four acid H atoms take part, alkali salt formation with two of these being a fundamental preliminary. J. W. B.

Nitroalkylguanidines. Dearrangement and preparation by nitration. T. L. Davis and R. C. Elderfield (J. Amer. Chem. Soc., 1933, **55**, 731—740).—*N*-methyl-, *N*-butyl-, and *NN*-dimethylguanidine (as sulphates) are converted by KNO_3 and conc. H_2SO_4 into the corresponding *N'*-NO_2-derivatives. *NN'*-Diethyl- and *NN'N''*-trimethylguanidine (I) could not be nitrated, indicating that nitration occurs only when the alkylguanidines contain a free NH_2-group. The nitrates of *N*-methyl-, *N*-*n*-butyl-, *N*-*n*-heptyl-, and *NN*-dimethyl-guanidine with conc. H_2SO_4 also give the *N'*-nitro-*N*-alkylguanidines; *NN'*-dimethylguanidine and (I) are similarly recovered unchanged. The formation of these last NO_2-derivatives is considered not to involve dehydration. Nitroguanidine (II) is not produced from guanidine nitrate, H_3PO_4, and P_2O_5 after 30 hr. at room temp. or 30 min. at 65°; after 48 hr. at room temp., 82% of (II) results (probably owing to the intermediate production of HNO_3 or nitrophosphoric acid). *N'*-Nitro-*N*-alkylguanidines decompose in hot aq. solution to $NH_2{\cdot}NO_2$ and alkylcyanamides (III); (III) then undergoes hydrolysis (to the carbamide) or polymerisation (to trialkyl*iso*melamine). Decomp. in presence of an aq. alkylamine at p_H about 6·13 at 175° gives 40—50% of *NN'*-dialkylguanidine, also formed (in 40% yield) with the trialkyl*iso*melamine (40%) when the reaction is carried out at the b.p./about 1·6 atm. in CO_2. The basicity of guanidine and its derivatives is considered to be a property of the mol. and not of a particular N atom. *N'-Nitro*-N-*n*-*heptylguanidine*, m.p. 115°, and NN'-*di*-n-*heptyl*- and -*di*-n-*butyl-guanidine picrates*, m.p. 278° (decomp.), and 122·5°, respectively, appear to be new. Tribenzyl*iso*melamine has m.p. 146—147°, re-solidifying with m.p. 157—158° (decomp.). H. B.

Glucononitrile. A. Wohl and O. Wollenberg (Annalen, 1933, **500**, 281—286).—Glucononitrile (I), m.p. 146—148°, is obtained in 54—55% yield from glucoso, $NH_2{\cdot}OH$,AcOH (convenient method of prep. described) and Ac_2O–AcOH at 100° (bath). Arabinose is formed when a 10% aq. solution of (I) is heated at 85° in CO_2. H. B.

Rapid determination of cyanogen and mercury in mercury oxycyanide. A. Angeletti (Annali Chim. Appl., 1933, **23**, 38—41).—When a complex cyanide is boiled with yellow HgO, all the CN yields $Hg(CN)_2$,HgO, and treatment of the latter with KI proceeds: $Hg(CN)_2,HgO+8KI+H_2O=2K_2HgI_4+2KCN+2KOH$, the Hg being wholly present in the sol. complex compound. The CN may then be determined by distilling the acidified solution, according to Bellucci and Ricca's procedure (A., 1924, ii, 791) and the Hg by Cattelain's modification (A., 1930, 1148) of Vanino and Treubert's process. T. H. P.

Absorption spectrum and photochemical decomposition of diazomethane. F. W. Kirkbride and R. G. W. Norrish.—See this vol., 359.

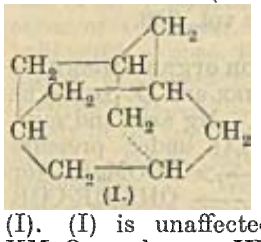
Action of carbon monoxide on organo-magnesium compounds. F. G. Fischer and O. Stoffers (Annalen, 1933, **500**, 253—270).—Mg aryl and *tert.*-alkyl bromides heated with CO under pressure react thus: $2MgRBr+2CO \longrightarrow >CR{\cdot}OMgBr$ (or $R{\cdot}CO{\cdot}MgBr$) $\longrightarrow$ ($:CR{\cdot}OMgBr$) $\longrightarrow$ $OH{\cdot}CHR{\cdot}COR$ [which may undergo autoxidation to $(\cdot COR)_2$]. Thus, MgPhBr at 75—85° gives 90% of benzoin and a little benzil; *p*-$C_6H_4Me{\cdot}MgBr$ at 150°/100 atm. affords *p*-toluin and *p*-tolil; α-$C_{10}H_7{\cdot}MgBr$ at 160°/180 atm. yields 63% of α-naphthil; $MgBu^{\gamma}Br$ furnishes hexamethylacetoin. Elimination of HBr occurs when CEt_3Br is treated with Mg. $CPh_3{\cdot}MgCl$ and CPh_3 do not react with CO at 160°/140 atm. With Mg alkyl and aralkyl halides, $CH_2R{\cdot}MgHal$, reaction occurs thus: $CH_2R{\cdot}MgX+CO \longrightarrow CH_2R{\cdot}C{\cdot}OMgX$ (or $CH_2R{\cdot}CO{\cdot}MgX$) $\longrightarrow$ $(CH_2R)_2C(MgX){\cdot}OMgX$ $CHR{:}CH{\cdot}CH_2R$. Thus, MgEtBr at 110° gives 25% of Δ^{β}-pentene; MgBuCl at 125° affords 65% of Δ^{δ}-nonene; Mg *iso*amyl bromide at 100° yields 70% of of β6-*dimethyl*-Δ^{δ}-*nonene*, b.p. 57—63°/13 mm.; $CH_2Ph{\cdot}MgCl$ at 120° furnishes PhMe, $(\cdot CH_2Ph)_2$, $CH_2Ph{\cdot}OH$, and 60% of αγ-diphenylpropene. In these cases, small amounts of higher-boiling by-products (unsaturated alcohols) are also formed. Mg *cyclo*hexyl bromide undergoes both types of reaction; with CO at 135°, 25% of *cyclo*hexylmethylene*cyclo*hexane and 45% of dodecahydro-benzoin and -benzil, m.p. 38°, are produced. Mg β-decahydronaphthyl bromide affords an unsaturated hydrocarbon, b.p. 145°/3 mm., m.p. 93—98°, and compounds, m.p. 128—130° and 151°. Reaction is not observed between CO and Mg pyrryl bromide at 100°/90 atm., *p*-$NMe_2{\cdot}C_6H_4{\cdot}MgBr$ (145°/90 atm.), $(:C{\cdot}MgBr)_2$ (145°/90 atm.), ZnPhBr (in PhMe at 130°/100 atm.), or $AlEt_3$ (250°/150 atm.). The reactions are catalysed by NaOEt or, better, $Mg(OEt)_2$ or $RO{\cdot}MgX$. Solutions of MgEtI+$OEt{\cdot}MgI$ in Et_2O have higher conductivities than MgEtI. H. B.

Germanium tetraiodide and its action on hexamethylenetetramine and caffeine. T. Karantassis and L. Capatos (Bull. Soc. chim., 1933, [iv], **53**, 115—116).—On mixing GeI_4 and $(CH_2)_6N_4$ in $CHCl_3$ a white cryst. *ppt.* with a slight yellowish tinge, $GeI_4,4(CH_2)_6N_4$, is obtained. Caffeine gives a green microcryst. *powder*, $GeI_4,4C_8H_{10}O_2N_4$. It decomposes slowly on exposure to air, liberating I and giving a yellow powder with a white efflorescence. M. S. B.

Carbon rings with a large number of carbon atoms. L. Ruzicka (Bull. Soc. chim. Belg., 1932, **41**, 565—587).—An account of the properties and

structure of natural and synthetic C ring compounds containing up to 34 C atoms. O. J. W.

Adamantane, a new hydrocarbon extracted from petroleum. S. LANDA and V. MACHACEK (Coll. Czech. Chem. Comm., 1933, **5**, 1—5).—The naphtha, b.p. 150—250°, of petroleum from Hodonin and Gbely contains about 30% of material which is volatile in steam (100°) and has a terpene-like odour.


(I.)

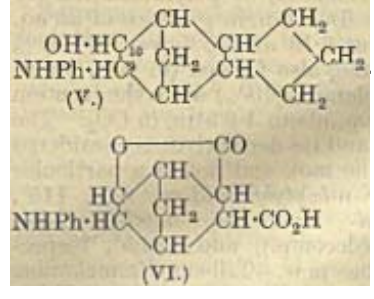
Cooling of the aromatic fraction, b.p. 190—195°, to −80° gives crystals of *adamantane*, $C_{10}H_{16}$, m.p. (sealed tube) 268°, mol. heat of combustion 1451·7 g.-cal. at const. vol. (crystallographic data given), to which is assigned structure (I). (I) is unaffected by *X*-rays, CrO_3, alkaline $KMnO_4$, and conc. HNO_3, and is responsible for the above terpene-like odour. H. B.

Molecular rearrangements in the *cyclo*hexane series; passage into the *cyclo*pentane series. M. TIFFENEAU (Compt. rend., 1932, **195**, 1284—1286; cf. Levy and Sfiras, A., 1932, 395).—2-Iodo-1-methyl-*cyclo*hexanol is dehalogenated by $AgNO_3$ with the formation of 90% of 2-methyl*cyclo*hexanone (I) and 10% of *cyclo*pentyl Me ketone (A., 1932, 744). 2-Methyl-Δ^1-*cyclo*hexene oxide, b.p. 137—139°, isomerises at 220—230°/atm. pressure into equal parts of (I) and, probably, 1-*methyl*cyclo*pentane*-1-*aldehyde* (*semicarbazone*, m.p. 160—161°) by rupture of the oxide ring at the Me-C atom followed by a shortening to the 5-ring. 4-Methyl-Δ^1-*cyclo*hexene oxide similarly isomerises to a mixture of 3-methyl*cyclo*pentane-1-aldehyde and 4-methyl*cyclo*hexanone. A. C.

Graduated additive powers of unsaturated ring systems. II. K. ALDER and G. STEIN [with W. FRIEDRICHSEN] (Annalen, 1933, **501**, 1—48).—Contrary to the previous statement (A., 1931, 489), di*cyclo*hexadiene (di*cyclo*octene) (and related compounds) and *cyclo*hexene form adducts with PhN_3; reaction is, however, very slow. Two types of adducts (dihydro-1 : 2 : 3-triazoles) are obtained: (*a*) from di*cyclo*heptenes and di*cyclo*octenes; (*b*) from monocyclic olefines. Thermal decomp. occurs thus: (*a*) $\cdot C(-N)\cdot C\cdot NPh > N$ (I) $\longrightarrow N_2 + \cdot C(\cdot C) > NPh$ (II) (often accompanied by an anil); (*b*) $\cdot CH(-N)\cdot CH\cdot NPh > N$ (III) $\longrightarrow N_2 + \cdot CH_2 \cdot C{:}NPh$, which occurs at a much lower temp. than (*a*). Hydrolytic fission of these types by dil. acid occurs thus: (*a*) (I) $\longrightarrow$ $\cdot C(OH)\cdot C\cdot NHPh$ [also formed from (II) and dil. acid]; (*b*) (III) $\longrightarrow N_2 + NH_2Ph + \cdot CH_2 \cdot CO$ (*e.g.*, the adduct from PhN_3 and *cyclo*pentene affords *cyclo*pentanone).

Me propenyl ketone and PhN_3 give (after 12—14 days at room temp.) an *adduct* (IV), $C_{11}H_{13}ON_3$, m.p. 106—107° (decomp.), which when heated to 140° affords N_2, the anil of CH_2Ac_2, and a small amount of a substance, b.p. about 240°/16 mm. (IV) and dil. H_2SO_4 give CH_2Ac_2. Styryl Me ketone and PhN_3 afford (after 12 weeks) an *adduct*, $C_{16}H_{15}ON_3$, m.p. 111°, whilst isoprene furnishes (after several months) an *adduct*, $C_{11}H_{13}N_3$, m.p. 72°. The *diacetate*, m.p. 155°, of dioximinodi*cyclo*pentadiene (Thiele, A., 1900, i, 298) and PhN_3 in EtOAc give an *adduct*, $C_{20}H_{19}O_4N_5$, m.p. 214°. Similarly, 3 : 6-*endo*methylene-Δ^1- and 3 : 6-endoxo-3 : 6-dimethyl-Δ^4-tetrahydrophthalic anhydrides, γ-fenchene, and dimeric $\Delta^{1:3}$-*cyclo*hexadiene afford 1 : 1-*adducts*, m.p. 154°, 210° (decomp.), 177°, and 154—155°, respectively. Di*cyclo*heptene derivatives containing the *endo*-CMe_2 group (as in bornylene and *apo*bornylene) do not form adducts with PhN_3. The *adduct*, $C_{16}H_{15}O_3N_3$, m.p. 232°, from PhN_3 and 3 : 6-*endo*ethylene-Δ^1-tetrahydrophthalic anhydride is converted by successive treatment with dil. KOH and 50% AcOH into an *anilino-lactone*, $C_{16}H_{17}O_4N$, m.p. 227°. Me di*cyclo*pentadiene-3 : 7-dicarboxylate and PhN_3 in EtOAc give an *adduct*, $C_{20}H_{21}O_4N_3$, m.p. 145° (decomp.), and a *compound*, $C_{20}H_{21}O_4N$, m.p. 163°. Successive treatment of the *adduct*, $C_{18}H_{17}O_3N_3$, decomp. 208°, from 3 : 6-*endoiso*propylidenemethylene-Δ^4-tetrahydrophthalic anhydride and PhN_3 with dil. NaOH and dil. AcOH affords an amino-lactone, m.p. 223°, whilst the *adduct*, $C_{23}H_{22}O_4N_6$, m.p. 203—204°, from PhN_3 (2 mols.) and Me 3 : 6-*endo*methylene-3 : 6-dihydrophthalate (1 mol.) is converted by dil. AcOH into a *compound*, $C_{23}H_{24}O_5N_4$, m.p. 179°. The adduct from 3 : 6-endoxo-Δ^4-tetrahydrophthalic anhydride and PhN_3 is similarly converted into an *amino-lactone*, $C_{14}H_{13}O_2N$, m.p. 180° (with charring); treatment with conc. HCl gives a *chloro-base*, $C_{14}H_{14}O_5NCl$, m.p. 234°.

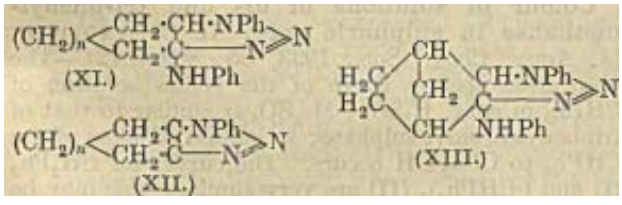
Reduction (H_2, colloidal Pd, EtOH) of the adduct (A., 1931, 473) from α-di*cyclo*pentadiene and PhN_3 gives a *dihydro*-derivative, m.p. 129—130°, decomposed by dil. H_2SO_4 to the *anilino-alcohol* (V), m.p. 134° [*picrate*, m.p. 187—188° (decomp.); Ac_2 derivative, m.p. 151°], and thermally to the corresponding 9 : 10-*phenylimino*-derivative, m.p. 62° [converted by dil. H_2SO_4 into (V)], and a smaller amount of the anil of an aldehyde (*semicarbazone*, $C_{11}H_{17}ON_3$, m.p. 159—160°) The adduct (*ibid.*, 489) from PhN_3 and 3 : 6-*endo*methylene-Δ^4-tetrahydrophthalic anhydride with dil. NaOH and dil. AcOH gives the *lactonic acid* (VI), m.p. 236° [(mono) *Me* ester (VII) (CH_2N_2), m.p. 204° (*Ac* derivative, m.p. 159°)]. Thermal decomp. of the adduct, m.p. 138—139°, from PhN_3 and Me 3 : 6-*endo*methylene-Δ^4-tetrahydrophthalate affords *Me* 4 : 5-*phenylimino*-3 : 6-*endomethylenehexahydrophthalate*, m.p. 86°, hydrolysed (dil. HCl or H_2SO_4) to (VII). The adduct (*loc. cit.*) from PhN_3 and santene is converted by dil. H_2SO_4 into 2-*anilino*-1 : 2-*dimethyl*-3 : 6-endo*methylene*-cyclo*hexanol*, b.p. 192°/16 mm. (*hydrochloride*, m.p. 195—196°; *picrate*, m.p. 163°), by dil. HCl into the -cyclo*hexyl chloride*, m.p. 64° (*picrate*, m.p. 121°), and by


(V.)

(VI.)

picric acid in C_6H_6 into a *picrate*, $C_{21}H_{22}O_7N_4$, m.p. 117°.

The *adduct* (VIII), m.p. 53°, from PhN_3 and *cyclo*pentene is hydrolysed (dil. H_2SO_4) to *cyclo*pentanone, whilst thermal decomp. gives *cyclo*pentanoneanil (IX), b.p. 129—131°/19 mm. The adduct, m.p. 222° (decomp.), from *cyclo*pentene and *p*-$C_6H_4Br{\cdot}N_3$ undergoes thermal decomp. to *cyclo*pentanone-*p*-bromoanil (X), b.p. 173°/20 mm. The *adduct*, m.p. 76—77°, from PhN_3 and *cyclo*heptene is, however, hydrolysed (dil. H_2SO_4) to hexahydrobenzaldehyde; thermal decomp. gives *cyclo*heptanoneanil, b.p. 155°/16 mm. The *adduct* from PhN_3 and *cyclo*octene has m.p. 87°. (VIII) or (IX) and PhN_3 at 100° afford the *dihydrotriazole* (XI, $n=1$), m.p. 192° (decomp.), converted by $H_2C_2O_4,2H_2O$ in EtOAc into 2-*anilino*cyclo*pentanone*, m.p. 64° [*semicarbazone*, m.p. 216°; *Ac* derivative, m.p. 83°; *hydrochloride*, m.p. 146° (decomp.)], which is oxidised ($KMnO_4$–$COMe_2$) to *glutaranilic acid*, m.p. 128°. (IX) and *p*-$C_6H_4Br{\cdot}N_3$ similarly afford a *compound*, $C_{17}H_{17}N_4Br$, m.p. 208° (decomp.), whilst an *isomeride*, m.p. 182° (decomp.),



is obtained from (X) and PhN_3. *cyclo*Hexanoneanil (or *cyclo*hexene) and PhN_3 at 100° give the *dihydrotriazole* (XI, $n=2$), m.p. 187° (decomp.), converted by $H_2C_2O_4$ (as above) into the *triazole* (XII, $n=2$), m.p. 117—118°. *cyclo*Heptanoneanil similarly affords the *dihydrotriazole* (XI, $n=3$), m.p. 194° (decomp.), convertible into the *triazole* (XII, $n=3$), b.p. 270°/16 mm., m.p. 118° (also formed during the initial condensation), whilst *cyclo*octanoneanil and PhN_3 at 100° give the *triazole* (XII, $n=4$), b.p. 240°/20 mm., m.p. 83°. Norcamphoranil, b.p. 157°/20 mm., similarly affords the *triazole* (XIII), m.p. 238°, convertible by $H_2C_2O_4$ in EtOAc into 2-*anilino*-3 : 6-*endomethylene*cyclo*hexanone*, m.p. 98° (*semicarbazone*, m.p. 190°). 2 : 5-*endo*Ethylene*cyclo*hexanoneanil, b.p. 168—171°/20 mm., and PhN_3 at 100° give a *compound*, $C_{20}H_{22}N_4$, m.p. 259°. Camphoranil and 6 : 6-dimethyl-2 5-*endo*ethylene*cyclo*hexanoneanil, b.p. 170—172°/20 mm., m.p. 83°, do not react with PhN_3 at 150°. H. B.

New type of reaction between unsaturated hydrocarbons and sulphuric acid. I. *cyclo*-Hexene and sulphuric acid. S. Nametkin and L. Abakumuvskaja (Ber., 1933, **66**, [*B*], 358—360).—Gradual addition of *cyclo*hexene to H_2SO_4 (*d* 1·84) at 2—5° results in the separation of an oily layer from which are obtained (i) a saturated *hydrocarbon* $C_{12}H_{22}$, b.p. 216—219°/739 mm., which could not be normally dehydrogenated, the only isolable product being a little $C_{10}H_8$; (ii) a saturated *hydrocarbon* $C_{18}H_{32}$, b.p. 145—147°/1·5—2 mm.; (iii) an unsaturated *hydrocarbon* $C_{24}H_{40}$, b.p. 200—203°/1·5—2 mm., apparently containing one double linking. Dilution of the acid layer (see above) with H_2O causes the separation of a highly unsaturated, unstable liquid. H. W.

Structure of the benzene nucleus. B. L. Vanzetti (Rend. Sem. Fac. Sci. Cagliari, 1931, **1**, 77—79; Chem. Zentr., 1932, ii, 3075).

Korner's benzene formula and modern theory. E. Macciotta (Rend. Sem. Fac. Sci. Cagliari, 1931, **1**, 114—117; Chem. Zentr., 1932, ii, 3075).

Electronic theory and substitution in benzene. E. Macciotta (Rend. Sem. Fac. Sci. Cagliari, 1931, **1**, 110—113; Chem. Zentr., 1932, ii, 3075).—The C_6H_6 ring is regarded as a closed negative ring of C atoms neutralising one another and all negative towards the outer zone of positive H. Positive substituents give stable compounds and induce a polarity leading to *m*-substitution, whilst negative substituents cause a weakening at the point of attack, leading to *o*- and *p*-substitution. A. A. E.

Mechanism of the Friedel–Crafts reaction. E. Wertyporoch and T. Firla (Annalen, 1933, **500**, 287—295; cf. A., 1931, 1150).—Partly an account of work previously reviewed (this vol., 127). The following is new. The amounts of PhEt, $C_6H_4Et_2$, and C_6Et_6 (I) formed from varying quantities of EtCl(Br), C_6H_6, and $AlCl_3(Br_3)$ are determined; production of (I) is favoured by $AlCl_3$. (I) is obtained in about 42% yield from C_6H_6 (0·25 mol.), EtCl (1·5 mol.), and $AlCl_3$ (0·1 mol.); increase in the amount of $AlCl_3$ causes less (I) and more $C_6H_2Et_4$ to be formed. C_6H_6 (1 c.c.), $Pr^{\beta}Cl$ (10 c.c.), and $AlCl_3$ (1·3 g.) afford 0·2 g. of a *tetraisopropylbenzene*, m.p. 117—118°, whilst $C_6H_4Pr_2$ (2 c.c.), PrCl (50 c.c.), and $AlCl_3$ (0·74 g.) give 0·3 g. of *hexapropylbenzene*, m.p. 101°. PrCl is converted by large amounts of $AlCl_3$ into HCl, $Pr^{\beta}Cl$, and condensation products, b.p. 120—127° (*M* 405) and 160—170° (*M* 470). H. B.

Decomposition of iodobenzene dichloride. VII. Action of solutions of iodobenzene dichloride in several liquids on Zerevitinov's reagent. VIII. Analogies between the action of equimolecular solutions of chlorine, iodine, iodine chloride, and iodine trichloride, with the same reagent. E. V. Zappi and H. Degiorgi (Bull. Soc. chim., 1932, [iv], **51**, 1605—1611; cf. A., 1932, 1120).—$PhICl_2$ (I) in C_6H_6, $CHCl_3$, or C_5H_5N with MgMeI in amyl ether gives 20·5, 21·1, or 50·9% yields, respectively, of C_2H_6, the order of increasing yield being that of increasing ε and dipole moment. Cl_2 in C_6H_6 or $CHCl_3$ gives 20·7 or 17·0% yields of C_2H_6, respectively, I in C_5H_5N 49·2, ICl in $CHCl_3$ or C_5H_5N 20·8 or 46·2, and ICl_3 (0·5 mol.) in $CHCl_3$ or C_5H_5N 20·9 or 46·5%, respectively. (I) is polar, since it lowers the ε of C_6H_6 and $CHCl_3$. These results lead to the belief that (I) is ionised in solution to $PhICl^+$ and Cl^-, and that the reaction proceeds thus: $2Cl^- + 2MgMeI \longrightarrow 2MgClI + C_2H_6$. This explains why the yield of C_2H_6 never exceeds 50%. R. S. C.

Coupling action of the Grignard reagent. IV. Benzylidene chloride and benzotrichloride. R. C. Fuson and W. E. Ross (J. Amer. Chem. Soc., 1933, **55**, 720—723; cf. A., 1927, 46).—$CHPhCl_2$ and 2*M*-MgMeI in Et_2O give α-stilbene dichloride (I); $CHPhCl_2 + 2MgMeI \rightarrow (I) + C_2H_6 + 2MgClI$. $CHPhCl_2$

and MgPhBr give (I), Ph_2, and $CHPh_3$, but no $(\cdot CHPh_2)_2$ (cf. Reychler, A., 1906, i, 821). $CPhCl_3$ and 0·2*M*-MgMeCl afford tolane tetrachloride (II); with 2*M*-MgMeCl, a mixture (22% yield) of *cis*- (1 pt.) and *trans*- (5 pts.) -$\alpha\alpha'$-dichlorostilbenes results. The same mixture is obtained from (II) and 2*M*-MgMeCl, indicating that (II) is first produced in the above reaction. H. B.

Physical constants of *o*- and *m*-nitrotoluene. (Mme.) Hennaut-Roland (Bull. Soc. chim. Belg., 1933, **42**, 80—84).—New determinations are made of the crit. solution temp. in *iso*pentane, n^{15} (various H and He lines), and of d_4, η, 0, and γ at various temp. of *o*- and *m*-nitrotoluenes. H. A. P.

Nitro-compounds obtained by direct nitration of toluene in preparation of T.N.T. P. De Beule (Bull. Soc. chim. Belg., 1933, **42**, 27—79).—The various stages in the nitration of PhMe to the $(NO_2)_3$ stage are critically re-examined, and a table shows the behaviour of every intermediate product on further nitration. Contrary to previous lit., *m*-nitrotoluene gives, amongst other isomerides, 3 : 5-dinitrotoluene on direct nitration, and this is further nitrated with difficulty to 2 : 3 : 5- and 2 : 4 : 5-trinitrotoluenes. A colorimetric method for the detection and determination of 3 : 5-$C_6H_3Me(NO_2)_2$ is described. New m.p. are given for highly purified specimens of *o*-, *m*-, and *p*-mono-, 2 : 4-, 2 : 6-, 2 : 3-, 2 : 5-, 3 : 4-, and 3 : 5-di-, and 2 : 4 : 6-, 2 : 4 : 5-, 2 : 3 : 4-, and 2 : 3 : 6-tri-nitrotoluenes. H. A. P.

Photo-sensitive nitro-compounds. I. N. N. Voroschcov and K. A. Gribov. **II. *pp'*-Dinitrophenyl disulphide; 1-nitronaphthalene-2-sulphonic acid.** N. N. Voroschcov and V. V. Koslov (J. Gen. Chem. Russ., 1932, **2**, 929—938, 939—962).—I. Several nitronaphthalenesulphonic acids are photosensitive and darken on exposure to light, especially in the form of wool dyeings. Of the isomeric 1-nitronaphthalene acids, the 1 : 8 is the most sensitive, the 1 : 7 and the 1 : 6 are about equally sensitive, but the latter assumes a darker shade; the 1 : 5 acid is merely bleached on exposure. Their salts and the corresponding sulphinic acids and sulphonamides behave in the same way, showing that the nature of the S-containing group is unimportant. 1 : 6-Dinitronaphthalene-4 : 8-disulphonic acid is very sensitive, whilst the parent C acid is not; 1-$C_{10}H_7\cdot NO_2$ itself is slightly sensitive. The darkening is attributed to the reduction of the NO_2 group; it is assisted by the addition of aromatic amines and can then be utilised for photographic reproduction.

1-*Nitronaphthalene-7-sulphinic acid*, obtained by reduction of $NO_2\cdot C_{10}H_6\cdot SO_2Cl$ with Na_2SO_3, blackens without melting at 150—155°. The 1 : 6-*acid* was similarly prepared and does not melt. 1 : 7-$NO_2\cdot C_6H_4\cdot SO_2NH_2$ has m.p. 227—228° and the 1 : 6 compound m.p. 187·5—188°. The 1 : 7-*anilide* has m.p. 176—177°, the 1 : 6-*anilide* m.p. 173—174°.

II. The oxidation of crude *pp'*-dinitrophenyl disulphide (I), prepared from *p*-$C_6H_4Cl\cdot NO_2$ and Na_2S, with HNO_3 leads to *p*-$NO_2\cdot C_6H_4\cdot SO_3H$ with *pp'*-dinitrophenylsulphone, m.p. 255°, not 282° (A., 1908, i, 631), and H_2SO_4. The two latter products are due to the presence in (I) of an *isomeride*, m.p. 134°, probably $(C_6H_4\cdot NO_2)_2S{:}S$; pure (I), m.p. 182°, gives no sulphone on oxidation.

α-Naphthylamine-2-sulphonic acid was diazotised and treated with Cu-bronze, Cu_2O, or $CuSO_3,Cu_2SO_3$ under a variety of conditions, giving 1-*nitronaphthalene-2-sulphonic acid* (*monohydrate*, m.p. 104·7°; *chloride*, m.p. 120·5°; amide, m.p. 214·3°) in yields up to 40%, with 2 : 4-dinitronaphthol and 2-$C_{10}H_7\cdot SO_3H$.

The photo-sensitivity of the three nitrobenzenesulphonic acids decreases in the order $o>p>m$, but all are much less sensitive than 1 : 8-$NO_2\cdot C_{10}H_6\cdot SO_3H$; *oo'*-dinitrodiphenyl disulphide is as sensitive as the corresponding acid and therefore the juxtaposition of S, not SO_3H, and NO_2 is the determining factor. (I) is not photo-sensitive; (II) is as sensitive as the 1 : 8-acid, especially its salts with aromatic amines. G. A. R. K.

Aryl chlorosulphinates and aryl sulphites. M. Battegay and L. Denivelle (Compt. rend., 1932, **195**, 1291—1292; cf. A., 1931, 473).—A claim for priority against Carre and Libermann (this vol., 48). A. C.

Colour of solutions of di- and tri-phenylmethanes in sulphuric acid. L. C. Anderson (J. Amer. Chem. Soc., 1933, **55**, 809—812).—The absorption spectra curve of the yellow solution of $CHPh_3$ in conc. $H_2SO_4+Me_2SO_4$ is similar to that of triphenylcarbinyl sulphate; oxidation of some of the $CHPh_3$ to $CPh_3\cdot OH$ occurs. The curves for CH_2Ph_2 (I) and $(\cdot CHPh_2)_2$ (II) are very similar; this may be due to oxidation of (I) to a derivative of (II) or fission of (II) to a derivative of (I). H. B.

Velocity of liberation of hydrocarbons by the action of indene on aliphatic organo-magnesium compounds. Method of measuring the attraction between alkyl radicals and the magnesyl group. D. Ivanov and I. Abdoulov.—See this vol., 356.

Hydrogenation of naphthalene. A. M. Popov (Ukrain. Chem. J., 1932, **7**, [Tech.], 41—56).—$C_{10}H_8$ undergoes hydrogenation in presence of Ni and other catalysts at 180—200°/200 atm. (max.). The $C_{10}H_8$ should previously be purified by treatment with $<1\%$ of Na. R. T.

1-Methyl- and 1 : 7-dimethyl-4-*iso*propylnaphthalene. W. S. Rapson and W. F. Short (J.C.S., 1933, 128—130).—(2-*Cymylmethyl*)*methylmalonic acid*, m.p. 170°, passes at 180° into β-2-*cymyl*-iso*butyric acid* (I), b.p. 190—195°/14 mm., the *Me* ester, b.p. 142—148°/8 mm., of which is reduced to γ-2-cymyl*iso*butyl alcohol, converted through the bromide and cyanide into γ-2-*cymyl*-β-*methylbutyric acid*, b.p. 182—188°/9 mm., the acid *chloride*, b.p. 150—151°/8 mm., of which readily cyclises with $AlCl_3$ to 1-*keto*-3 : 5-*dimethyl*-8-iso*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (II), b.p. 150—155°/8 mm. With Na and EtOH at 110°, (II) affords a mixture dehydrogenated by S at 180—230° to 1 : 7-*dimethyl*-4-iso*propylnaphthalene*, m.p. 60° (*picrate*, m.p. 92°). Hydrolysis followed by decarboxylation of Et 2-cymylmethylmalonate affords β-2-*cymylpropionic acid*, m.p. 85°, converted (as above) into 1-methyl-4-*iso*propylnaphthalene (A., 1922, i, 1001). J. L. D.

Preparation and properties of octachloronaphthalene. I. V. Schvemberger and V. Gordon (J. Gen. Chem. Russ., 1932, **2**, 921—928).—Octachloronaphthalene (I) is best obtained by chlorination of $C_{10}H_8$ in presence of Fe with or without I; it can also be obtained by prolonged heating of Na α-naphthylamine-3 : 6 : 8-trisulphonate with PCl_5 at 200—225°. It has m.p. 197·5—198°, b.p. 440—442°/754 mm., 258—260°/2·5 mm., is attacked by alcoholic but not by aq. alkalis, and oxidised by HNO_3 to hexachloronaphthaquinone, m.p. 222·5°, and tetrachlorophthalic acid, m.p. 254·3—254·7° (corr.). Further chlorination of (I) leads to decachlorohydrindene, m.p. 138°. G. A. R. K.

Synthesis of chrysene and certain derivatives. G. R. Ramage and R. Robinson (Nature, 1933, **131**, 205).—Dehydration of ββ′-diphenyladipic acid with hot 85% H_2SO_4 gives *cis*- and *trans*-diketohexahydrochrysene. Reduction of the *cis*-compound (Clemmensen) yields a hexahydrochrysene, reduced by Se to chrysene. The prep. of a norketohydroxyœstrin is foreshadowed. L. S. T.

Constitution of β-carotene; 2 : 6-dimethylnaphthalene from the polyene chain. R. Kuhn and A. Winterstein (Ber., 1933, **66**, [*B*], 429—432).—Thermal decomp. of β-carotene (I) at 170—190°/1 mm. leads to 2 : 6-dimethylnaphthalene (II). For other reasons and since (II) is also obtained from *trans*-crocetin Me_2 ester which does not contain a ring, the possibility that (I) contains two dissimilar rings is not adopted, and (II) is regarded as derived from 12 C atoms of the polyene chain. H. W.

Colour and structure of amides. (Mme.) Ramart-Lucas and (Mlle.) Wohl (Compt. rend., 1933, **196**, 120—122).—Ultra-violet absorption curves show that the amides NHAcAr (Ar=Ph, *o*- and *p*-tolyl) have all the same constitution. The curve for NHAcR (R=Ph, *p*-tolyl) differs from that of NAcRMe; the former exists in solution as an equilibrium mixture of the ·CO·NHR and ·C(OH):NR forms (cf. Hantzsch, A., 1931, 608). H. B.

2 : 4 : 6-Trichloroaniline. F. D. Chattaway and H. Irving (J.C.S., 1933, 142—143).—NH_2Ph,HCl in anhyd. $CHCl_3$ with Cl_2 gives 2 : 4 : 6-trichloroaniline (I) (*picrate*, m.p. 81·5—82·5°; *phthalanil*, m.p. 175—176°; *dichloroacetyl* derivative, m.p. 184—184·5°; Ac_2 derivative, m.p. 81—82°) (yield 80%). The alleged mol. compound of (I) with AcCl is probably the Ac_2 derivative. A. A. L.

Phenylmethylethylbetaines and the geometrical stereoisomerism of organic quinquevalent nitrogen compounds. (Mme.) M. Guaisnet-Pilaud (Compt. rend., 1932, **195**, 1286—1289).—The quaternary iodide from $NPhMe_2$ and $CH_2I{\cdot}CO_2Et$ gives a single betaine hydrate if treated with excess of Ag_2O (A., 1930, 1563). Under the same conditions ($NPhMeEt{\cdot}CH_2{\cdot}CO_2Et$)I affords a mixture of a *betaine monohydrate* (I), m.p. 175·5°, and *dihydrate* (II), m.p. 79—79·5°, fractionated by EtOH. Both give the same *chloroplatinate* (+$2H_2O$), m.p. 134°, with dehydration (anhyd. *form*, decomp. 155°). (I) is changed to (II) by exposure to moist air, but they differ chemically in that (I) affords a *H oxalate*, m.p. 124·5°, whilst (II) gives an *oxalate*, m.p. 166°, and a *H oxalate* (+H_2O), m.p. 69·5°. A. C.

Reduction of Schiff bases. III. Condensations of *sec.*-aromatic amines with formaldehyde in acid solution; nuclear or *N*-methylations by formaldehyde. E. C. Wagner (J. Amer. Chem. Soc., 1933, **55**, 724—731).—When methyl-, ethyl-, *n*-propyl-, *n*-butyl-, and *iso*amylanilines are treated with aq. 35% CH_2O (1 equiv.) in dil. HCl below or at 20° and the solutions treated (within 5 min.) by Zn dust (usually at < 25°), *N*-methylation occurs; the corresponding *tert.*-bases are isolated in 55—88% yield. When the initial condensation is allowed to proceed until solids separate, *hydrochlorides* of the (probable) composition $[p\text{-}NR{\cdot}C_6H_4{\cdot}CH_2(HCl)]_n$ result (probably by rearrangement of the unit $NPhR{\cdot}CH_2$). These are reduced by Zn dust and dil. H_2SO_4 at 70—85° to *N*-alkyl-*p*-toluidines in 54—80% yield. The *hydrochlorides* of *N*-*n*-propyl-, b.p. 237·3—238·8°, -*n*-butyl-, and -iso*amyl*-, b.p. 267—268°, -*p*-toluidines have m.p. 155°, 148—149°, and 146°, respectively. The hydrochloride of $NPhMePr^{\alpha}$ has m.p. 120—122° (lit. 106°). 4 : 4′-Tetra-alkyldiaminodiphenylmethanes are often produced as by-products in the condensations. H. B.

Synthesis of organic bases with triple linking. C. Mannich and F. T. Chang (Ber., 1933, **66**, [*B*], 418—420).—Synthesis is effected in dioxan at 100° according to the scheme $CPh{:}CH+CH_2O+NHR_2 = CPh{\cdot}C{\cdot}CH_2{\cdot}NR_2+H_2O$. The following compounds are described: *γ-diethylamino-α-phenyl-*Δ^{α}*-propinene*, b.p. 137°/18 mm. (*hydrochloride*, m.p. 136—137°), hydrogenated to γ-diethylamino-α-phenylpropane (hygroscopic *hydrochloride*, m.p. 119—120°); *γ-dimethylamino-α-phenyl-*Δ^{α}*-propinene*, b.p. 128°/18 mm. (*hydrochloride*, m.p. 156°; *methiodide*, decomp. 240°), which with Br in $CHCl_3$ affords a non-cryst. *dibromide* (*sulphate*, m.p. 126°), but does not yield a tetrabromide; it is hydrogenated to γ-dimethylamino-α-phenyl-Δ^{α}-propene (*hydrochloride*, m.p. 147°; hydrobromide, m.p. 148°, adding Br_2 to form *αβ-dibromo-γ-dimethylaminopropane hydrobromide*, m.p. 137°) or further to γ-dimethylamino-α-phenylpropane (methiodide, m.p. 176°); with H_2SO_4–H_2O (3 : 1 vol.) it yields ω-dimethylaminopropiophenone (hydrochloride, m.p. 160°); *γ-diethylamino-α-*p*-nitrophenyl-*Δ^{α}*-propinene* (*hydrochloride*, m.p. 215°), hydrogenated to γ-diethylamino-α-*p*-aminophenylpropane (p-*nitrobenzoyl* derivative, m.p. 129°) and reduced by Sn and HCl to γ-diethylamino-α-*p*-aminophenyl-Δ^{α}-propinene (*Bz* compound, m.p. 108°); *γ-piperidino-α-phenyl-*Δ^{α}*-propinene*, b.p. 175—180°/18 mm. (*hydrochloride*, m.p. 216°); *γ-diethylamino-α-*p*-anisyl-*Δ^{α}*-propinene*, b.p. 169—172°/15 mm. (*hydrochloride*, m.p. 168°); *γ-piperidino-α-*p*-anisyl-*Δ^{α}*-propinene* (*hydrochloride*, m.p. 196°); *γ-dimethylamino-α-*o*-aminophenyl-*Δ^{α}*-propinene*, b.p. about 166°/1 mm. (p-*nitrobenzoyl* derivative, m.p. 102°). H. W.

Nitroamines. V. E. Macciotta (Rend. Sem. Fac. Sci. Cagliari, 1931, **1**, 84—87; Chem. Zentr., 1932, ii, 3083).—*o*- and *p*-$C_6H_4(NH_2)_2$ with HNO_3 do not yield the nitroamines; *o*-$C_6H_4(NH_2)_2$ gives

6-*nitro*-1 : 2 : 3-*benzotriazole*, m.p. 210°, whilst the *p*-compound gives a black substance resembling aniline-black. A. A. E.

Stereochemistry of 2 : 2′-disubstituted diphenyls. III. Optical resolution of o-(2-dimethylaminophenyl)phenyltrimethylammonium iodide. (Miss) F. R. Shaw and E. E. Turner (J.C.S., 1933, 135—140; cf. A., 1932, 1125).—Improved preps. are described for 2 : 2′-dinitro-, -diamino-, and -bisdimethylamino-diphenyl, m.p. 72—73° (*hydriodide*, m.p. 256—257°; *chloroplatinate*). The last-named gives dl-o-(2-*dimethylaminophenyl*)-*phenyltrimethylammonium iodide*, m.p. 190—192° (decomp., bath initially at 180°), which gives d-o-(2-*dimethylaminophenyl*)*trimethylammonium* d-*camphor*-10-*sulphonate*, m.p. 189—190°, $[\alpha]^{20}_{6791}$ +60·6° [*iodide*, m.p. 190—192° (decomp.), $[\alpha]^{20}_{6791}$ +50·5°]. The optical isomerides are similarly obtained. Rates of racemisation in H_2O at 99·5° are recorded. The iodides are not racemised by HCl at room temp. A. A. L.

Diphenyl series. III. Nitration of 2 : 4′-derivatives. IV. Nitro-compounds of 2 : 4′-dihalogenodiphenyl derivatives. C. Finzi and A. Mangini (Gazzetta, 1932, **62**, 1184—1192, 1193—1203; cf. A., 1932, 1025).—III. HNO_3 (*d* 1·46) nitrates 2 : 4′-diacetamidodiphenyl to the 3′-NO_2-derivative (I), m.p. 216°, the constitution of which is determined by hydrolysis to 3′-*nitro*-2 : 4′-*diaminodiphenyl* (II), m.p. 144° (from which 3-nitrodiphenyl is obtained, and, by partial diazotisation, 3-nitro-4-aminodiphenyl), and by reduction of (II) to 2 : 3′ : 4′-*triaminodiphenyl*, which as an *o*-diamine condenses with phenanthraquinone to 2-o-*aminophenylphenanthraphenazine*, m.p. 235°. Nitration of (I) with $EtNO_3$ does not give the 4 : 3′-$(NO_2)_2$-compound (cf. *loc. cit.*), but 5 : 3′-*dinitro*-2 : 4′-*diacetamidodiphenyl*, m.p. 205—206°, hydrolysed to 5 : 3′-*dinitro*-2 : 4′-*diaminodiphenyl* (III), m.p. 242—243°, the structure of which is determined by conversion into 3 : 3′-dinitrodiphenyl, and [the *tetra-amine* obtained from (III) having given only an impure *phenanthraphenazine*, and not having combined with benzil] by the formation of 2-*iodo*-3 : 5′-*dinitro*-4′-*piperidyldiphenyl*, m.p. 125°, from the I_2-derivative (see below).

IV. The following are prepared from the NH_2-compounds: 2 : 4′-*dichloro*-, m.p. 122°, 2 : 4′-*dibromo*-, m.p. 137—137·5°, and 2 : 4′-*di-iodo*-, m.p. 134°, -4-*nitrodiphenyl*; 2 : 4′-*dichloro*-, m.p. 91°, 2 : 4′-*dibromo*-, m.p. 90°, and 2 : 4′-*di-iodo*-, m.p. 112°, -3′-*nitrodiphenyl*; 2 : 4′-*di-iodo*-4 : 3′-*dinitrodiphenyl*, m.p. 156°; 2-*iodo*-3 : 4′-*dinitro*-4-*acetamidodiphenyl*, m.p. 237—238°; 2 : 4′-*dichloro*-, m.p. 172°, 2 : 4′-*di-iodo*-, m.p. 206°, -5 : 3′-*dinitrodiphenyl*; 4′-*acetamido*-2-*cyanodiphenyl*, m.p. 172° (whence 4′-*aminodiphenyl*-2-*carboxylic acid*, m.p. 215—216°); 4′-*amino*-2-*cyanodiphenyl*, m.p. 117°.

Diphenyl-2 : 4′-dicarboxylic acid with $EtNO_3$–H_2SO_4 yields *mono*- and *di-nitro*-derivatives, m.p. 262° and 293°, respectively. 2 : 4′-Dihydroxydiphenyl (*Me*$_2$ *ether*, m.p. 70°), which with $EtNO_3$ gives an ill-defined product, is nitrated by HNO_3–AcOH to a $(NO_2)_2$-compound, m.p. 187°. E. W. W.

Reducing action of ferrous oxalate on azoxy-compounds. I. Gasopoulos (Praktika, 1931, **6**, 495—497; Chem. Zentr., 1932, ii, 3083).—Azoxybenzene is readily reduced to azobenzene by FeC_2O_4 in 72% yield. 3 : 3′-Diamino-4 : 4′-dimethyl-, m.p. 202—203°, 4 : 4′-dimethoxy-, m.p. 161—162°, and 4 : 4′-diethoxy-azobenzene, m.p. 161°, were similarly prepared. A. A. E.

Stereoisomerism of azoxybenzenes. IV. Dipole moments and configuration. K. A. Gehrckens and E. Muller (Annalen, 1933, **500**, 296—306; cf. A., 1932, 734).—The dipole moments of "*n*"- and *iso*-azoxybenzenes indicate that these are *trans*- and *cis*-forms, respectively. The following vals. (all $\times 10^{-18}$ e.s.u.) are recorded: "*n*"-, 1·70, and *iso*-, 4·67, -azoxybenzene; "*n*"-, 1·73, and *iso*-, 4·36, -*o*-azoxytoluene; "*n*"- 1·73, and *iso*-, 5·06, -*p*-azoxytoluene; "*n*"-, 2·41, and *iso*-, 6·17, -*o*-azoxyanisoles. The vals. for the *p*-bromoazoxybenzenes, m.p. 73° and 94°, are 2·60 and 0·90, respectively, indicating that both of these are *trans*-forms. H. B.

Dinaphthyl bases. II. Reduction of 1 : 1′-azoxy- and 1 : 1′-azo-naphthalenes. Isolation of 1 : 1′-hydrazonaphthalene. W. M. Cumming and G. Howie (J.C.S., 1933, 133—135; cf. A., 1932, 376).—Neutral reduction of *s*-1 : 1′-azoxynaphthalene, or alkaline reduction of *s*- and *as*-azoxy- (I) and azonaphthalenes (II), m.p. 188° (sublimes 170°) (improved prep.), gives 1 : 1′-*hydrazonaphthalene*, m.p. 153° [decomp. giving (II) and α-naphthylamine], which undergoes the benzidine conversion in acid, neutral, and alkaline solution. The substance previously described as hydrazonaphthalene (J.C.S., 1923, **123**, 2464) is dinaphthyline. Preps. of naphthidine, dinaphthyline, and dinaphthyleneimine from the above substances are described. A. A. L.

Fluorenone. II. A. C. Sircar and K. C. Bhattacharyya (J. Indian Chem. Soc., 1932, 9, 522—526).—The tinctorial properties (on wool and cotton) of the *bisazo-compounds* obtained by coupling diazotised 2 : 7-diaminofluorenone with PhOH, *m*-$C_6H_4(OH)_2$, salicylic acid, β-$C_{10}H_7$·OH, 2-hydroxy-3-naphthoic, α-naphthylamine-4-sulphonic, α-naphthol-4-sulphonic, *R*-, *G*-, Cleve's, Laurent's, *H*-, Schaffer's, and chromotropic acids, and $NPhMe_2$ are described. J. W. B.

[Diazo-compounds.] IV. Catalytic effect of alizarin on the decomposition of diazo-compounds. V. Stabilisation of diazotates. G. Oddo and R. Indovina (Gazzetta, 1932, **62**, 1119—1138, 1138—1144; cf. A., 1891, 553; 1895, i, 514; 1897, i, 341).—IV. The velocity of decomp. of diazonium salts from NH_2Ph, *o*-, *m*-, and *p*-toluidine, 1 : 2 : 4-, 1 : 3 : 4-, and 1 : 4 : 5-xylidine, and 1 : 2 : 5 : 4-ψ-cumidine in presence of NaOH in varying concn. is increased on addition of alizarin. Comparative velocities of decomp. are tabulated.

V. Solutions of diazonium salts treated with a small quantity of NaOH give, after partial decomp., a solution of a Na salt, stable at room temp. and on exposure to light. Addition of more NaOH renders the salt less stable, and of HCl regenerates the diazonium salt. E. W. W.

Diazonium dichloroiodides. A. ALGERINO (Gazzetta, 1932, **62**, 1145—1150).—The following, of type ArN_2ICl_2, are prepared from the amine diazotised in HCl and treated with ICl_3: benzene-, *o*-, *m*-, and *p*-toluene-, *o*-*nitrobenzene*-, m.p. 125° (decomp.), and *m*- and *p*-nitrobenzene-diazonium dichloroiodides. Action of NH_3 on the last three yields the corresponding azoimides. E. W. W.

Oxidising action of isomeric diazonium hydroxides. Z. E. JOLLES [with E. BUSONI] (Gazzetta, 1932, **62**, 1150—1160; cf. A., 1932, 155).—PhN_2OH oxidises various reducing agents; alkaline $FeSO_4$ is oxidised by *p*-nitro- and *p*-bromo-benzene-, *p*-toluene-, phenetole-, and α- and β-naphthalene-diazonium hydroxides. From PhN_2OH the products are C_6H_6, Ph_2, and PhN_3; the other diazonium compounds give corresponding products. E. W. W.

Action of thionyl chloride on phenol. P. CARRE and D. LIBERMANN (Compt. rend., 1933, **196**, 275—277).—PhOH and $SOCl_2$, best in the mol. proportions 3 : 2, give first HCl and then SO_2 (about 1 mol.); Et_2O then ppts. *tr*-p-*hydroxyphenylsulphonium chloride* (I), solid, hygroscopic, which with BzCl in C_5H_5N gives the Bz_3 derivative (chloroplatinate, m.p. 165—168°), but with BzCl in aq. NaOH, *tri*-p-*benzoyloxyphenylsulphonium hydroxide*, m.p. (anhyd.) 128°, (+H_2O) 35°. The primary reaction product, when boiled with H_2O, gives H_2SO_4 by oxidation of the SO_2 liberated, and, when distilled in vac., yields di-*p*-hydroxyphenyl sulphide and a mixture of *o*- and *p*-$C_6H_4Cl{\cdot}OH$. The following reaction mechanism is considered proved: $PhOH+SOCl_2 \longrightarrow HCl+HO{\cdot}C_6H_4{\cdot}SOCl$ (II); (II) $\longrightarrow HCl+O{:}C_6H_4{:}SO$ (III); (III) $+SOCl_2+2PhOH \longrightarrow 2HCl+SO_2+O{:}C_6H_4{:}S(C_6H_4{\cdot}OH)_2$ (IV); (IV)+HCl $\longrightarrow$ (I). Condensation takes place mainly in the *p*-, but also in the *o*-position. When PhOH (1 mol.), $SOCl_2$ (1 mol.), and C_5H_5N (1 mol.) react in dry Et_2O, and the product, after removal of the base, is distilled in vac., much Ph_2S and some Ph chlorosulphite (chlorosulphinate) are formed. The last-named compound decomposes when distilled in vac., if a trace of C_5H_5N is present (cf. A., 1931, 473; this vol., 48). R. S. C.

Intramolecular rearrangement of phenyl ethers with aluminium chloride. R. A. SMITH (J. Amer. Chem. Soc., 1933, **55**, 849).—A 65% yield of a mixture of 4- and 6-*iso*propyl-*m*-cresols is obtained from *m*-tolyl Pr^{β} ether (1 mol.) and $AlCl_3$ (1 mol.). H. B.

Betti condensation. Effect of substituents on stability and optical rotation of the resulting amines. F. E. RAY and W. A. MOOMAW (J. Amer. Chem. Soc., 1933, **55**, 749—752).—β-$C_{10}H_7{\cdot}OH$ (1 mol.), *m*-$C_6H_4Cl{\cdot}CHO$ (2 mols.), and NH_3 in EtOH (cf. Betti, A., 1901, i, 81, 611) give the m-*chlorobenzylidene* derivative, m.p. 109°, of dl-m-*chlorophenyl*-2-*hydroxy*-α-*naphthylmethylamine* (I), m.p. 124—125° (*hydrochloride*, decomp. 220—230°), resolved by *l*-malic acid into *d*-, m.p. 126° (not sharp), $[\alpha]_D^{25}$ +79·5° in Et_2O, and *l*-, m.p. 122°, $[\alpha]^{25}$ −55·5° in Et_2O, forms. dl-o-*Chlorophenyl*- (II), m.p. 129—130° (*hydrochloride*, decomp. 185—190°; o-*chlorobenzylidene* derivative, m.p. 173°) (resolved similarly into *d*-, $[\alpha]_D^{25}$ +89·8° in Et_2O, and *l*-, $[\alpha]_D^{25}$ −83·7° in Et_2O, forms), and dl-p-*chlorophenyl*- (III), m.p. 120° (*hydrochloride*, decomp. 190—195°; p-*chlorobenzylidene* derivative, m.p. 150°), -2-*hydroxy*-α-*naphthylmethylamines* are similarly prepared. (III) could not be resolved (probably owing to its instability). The stability (towards alkali) is (III)<(II)<(I)< phenyl-2-hydroxy-α-naphthylmethylamine (IV), whilst the order of optical activity is (II)>(I)>(IV)>(III)(?). The above condensation with $NO_2{\cdot}C_6H_4{\cdot}CHO$ gives chiefly nitrohydrobenzamides. H. B.

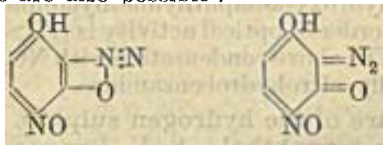
Structure of the hydrogen sulphite compound of nitroso-β-naphthol. S. V. BOGDANOV (J. Gen. Chem. Russ., 1932, **2**, 770—776; cf. A., 1932, 842).—On boiling the H sulphite compound of nitroso-β-naphthol (I) with NH_2OH in presence of AcOH (not HCl), the *dioxime* of 1 : 2-*diketo*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-4-*sulphonic acid* (II) is formed; it readily loses the SO_3H group with alkalis, yielding 1 : 2-naphthaquinonedioxime (III) at low temp. and its anhydride (IV) at high temp. Boiling (II) with HCl gives NH_4 2-nitroso-α-naphthol-4-sulphonate (V); this supports the suggestion (*loc. cit.*) that (II) is probably the intermediate compound in the formation of (V) from (I) and NH_2OH in HCl; some (III) and (IV) are also produced. G. A. R. K.

Pyrocatechol compounds of alkaline earths. R. SCHOLDER and M. WOLF (Z. anorg. Chem., 1933, **210**, 184—194).—The following *compounds* are described (A=·O·C_6H_4·O·): $Ca(AH)_2,3{\cdot}5H_2O$; $Sr(AH)_2,4{\cdot}5H_2O$; $Ba(AH)_2,6H_2O$; $Sr(AH)_2,2AH_2,5H_2O$; $Ba(AH)_2,2AH_2,5H_2O$; CaA,H_2O; $SrA,3{\cdot}5H_2O$; $BaA,0{\cdot}5H_2O$; $[CaA_3]K_2,2H_2O$; $[CaA_3]K_4,6H_2O$; $[CaA_3]Na_4,8H_2O$; $[Ca_2A_5]K_6,10H_2O$; $[Ca_2A_5]Na_6,24H_2O$; $8CaA,7K_2A,28H_2O$; $[Ca_2A_7]Na_{9\cdot5}H_{0\cdot5},xH_2O$. Their constitution is discussed. F. L. U.

Oxidation in presence of absorbent charcoal. A. GANDINI (Gazzetta, 1933, **63**, 9—12).—Quinol in Et_2O solution in contact with Norit is oxidised by O_2 at atm. pressure first to quinhydrone and then to benzoquinone. Thymoquinol reacts similarly, but pyrocatechol does not. Buchu-camphor gives γ-acetyl-α-*iso*propyl-*n*-butyric acid (A., 1923, i, 474). Under similar conditions but without C negative results are obtained. E. E. J. M.

2-Aminoresorcinol and its derivatives. M. V. LICHOSCHERSTOV and V. E. SHABOTINSKAJA (J. Gen. Chem. Russ., 1932, **2**, 761—769).—Reduction of 2-nitroresorcinol with Sn and HCl affords the double *salt* of 2-*aminoresorcinol* (I) with $SnCl_2$, $C_6H_3(OH)_2NH_2,HCl,SnCl_2$, m.p. 240° (decomp.), whilst $SnCl_2,H_2O$ in HCl gives the *hydrochloride* of (I), m.p. 240—243° (decomp.), from which (I) can be liberated with Na_2CO_3 in presence of $NaHSO_3$, m.p. 159—160° (Ac_3 derivative, m.p. 164—165°). (I) with Br in AcOH gives 4 : 6-*dibromo*-2-*aminoresorcinol* (II), m.p. 214—216°, and can be coupled with diazo-compounds. When diazotised in aq. solution in presence of excess of HCl with $NaNO_2$ or with amyl nitrite in EtOH, (I) gives principally a colourless 4-*nitro*-2-*diazoresorcinol* (III) together with a dark brown *isomeride* (IV), which is the sole product on

diazotisation in AcOH. (III) on warming with conc. H halides gives colourless explosive salts, of true diazonium structure, readily hydrolysed back to (III) and giving an intense colour with alkalis. The following structures are suggested for (III) and (IV), although the quinone-oxime structures tautomeric with these are also possible :

(IV.)  (III.)

(II) gives on diazotisation a reddish-brown *diazo-compound*, probably an inner anhydride. Both (III) and (IV) are reduced by $SnCl_2$ to 4-*amino*-1 : 3-*dihydroxy*-2-*phenylhydrazine hydrochloride*, giving hydrazones with aldehydes. G. A. R. K.

***cis–trans*-Isomerism of *iso*eugenol.** C. Junge (Riechstoffind., 1932, **7**, 112; Chem. Zentr., 1932, ii, 2818—2819).—Acetylation of technical *iso*eugenol affords the trans-*acetate*, m.p. 79° (whence trans-iso-*eugenol*, m.p. 34°, stable in absence of air). Fractional distillation of the *iso*eugenol from the non-cryst. technical acetate, followed by benzoylation, gives cis-iso*eugenol benzoate*, m.p. 68° (whence cis-iso-*eugenol*, b.p. 115°/5 mm., n^{20} 1·57002). With $FeCl_3$ *cis-iso*eugenol (*phenylurethane*, m.p. 118°) gives an olive-green and *trans-iso*eugenol (*phenylurethane*, m.p. 152°) a yellowish-green colour. A. A. E.

Naphthols. II. Chlorination of 1 : 5-dihydroxynaphthalene. A. S. Wheeler and W. J. Mattox (J. Amer. Chem. Soc., 1933, **55**, 686—690).—1 : 5-$C_{10}H_6(OAc)_2$ and Cl_2 in CCl_4 containing I at room temp. give the *monoacetate* (I), decomp. 158—160° (after turning green), of 4 : 8-*dichloro*-1 : 5-*dihydroxynaphthalene*, m.p. 194° (*diacetate*, m.p. 143°; *dibenzoate*, m.p. 179°; *monobenzoate*, m.p. 157—158°); at 80°, 4 : 4 : 8-*trichloro*-5-*acetoxy*-3 : 4-*dihydro*-α-*naphthol* (II), m.p. 174°, also obtained by further chlorination of (I), results. (I) and (II) are oxidised (CrO_3, AcOH) to 8-*chloro*-5-*acetoxy*-1 : 4-*naphthaquinone* (III), m.p. 143° [2-*anilino*-, m.p. 172°, 2-o-*aminoanilino*-, m.p. 271° (decomp.), 2-p-*hydroxyanilino*-, m.p. 226° (decomp.), and 2-p-*toluidino*-, m.p. 169°, derivatives], chlorinated in AcOH to the 2 : 8-Cl_2-derivative, m.p. 158—159°. 8-*Chloro*-5-*hydroxy*-1 : 4-*naphthaquinone*, m.p. 112°, from (III) and EtOH–HCl, is reduced ($SnCl_2$) to 8-*chloro*-1 : 4 : 5-*trihydroxynaphthalene*, m.p. 115—120° (decomp.) (*triacetate*, m.p. 147°; *tribenzoate*, m.p. 210°), whilst (III) is reduced (Zn, dil. H_2SO_4) to 8-*chloro*-1 : 4-*dihydroxy*-5-*acetoxynaphthalene*, m.p. 173° (decomp.) (*dibenzoate*, m.p. 216°). H. B.

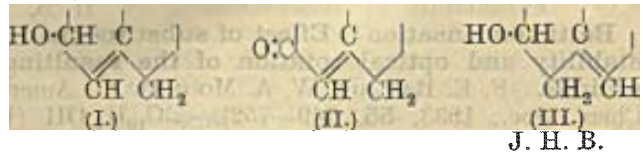
9 : 10-Dihydroxy-9 : 10-di-α-naphthyl-9 : 10-dihydrophenanthrene and 2 : 2′-di-α-naphthoyldiphenyl. T. W. Jezierski [with W. Maruszewska] (Rocz. Chem., 1933, **13**, 44—48).—9 : 10-*Dihydroxy*-9 : 10-*di*-α-*naphthyl*-9 : 10-*dihydrophenanthrene*, m.p. 263—264°, prepared from phenanthrene and α-$C_{10}H_7$·MgI, yields 2 : 2′-*di*-α-*naphthoyldiphenyl*, m.p. 204·5—205°, on oxidation with CrO_3 in boiling AcOH. R. T.

Production of arylmercapto-compounds (hydroxythiophenols). Imperial Chem. Industries and K. W. Palmer.—See B., 1933, 183.

Dehydrogenations in the coniferyl series. I. Dehydrodieugenol and dehydrodi*iso*eugenol. H. Erdtman (Biochem. Z., 1933, **258**, 172—180; cf. A., 1908, i, 783).—Dehydrodieugenol (I) (*di*-p-*nitrobenzoate*, m.p. 172—173°), best prepared by oxidation of eugenol with $FeCl_3$, yields tetrahydrodehydrodieugenol, identical with the dehydrodicœrulignol of Fichter and Christen (A., 1925, i, 813), on catalytic hydrogenation with PtO_2. It also yields a *Me*$_2$ *ether*, b.p. 240—242°/6 mm., which, on oxidation with $KMnO_4$, gives diveratric acid and on treatment with O_3 an *ozonide* which gives CH_2O on decomp. with H_2O. The p-*nitrobenzoates* of eugenol and (?-)cresol have m.p. 78—80° and 117—119°, respectively. Dehydrodi*iso*eugenol (II) (p-*nitrobenzoate*, m.p. 157—158°) prepared from *iso*eugenol by oxidation with $FeCl_3$ yields a *Me ether*, m.p. 126°, which gives veratric acid on oxidation. iso*Eugenol* p-*nitrobenzoate* has m.p. 123—124°. These results and theoretical considerations show that (I) is 3 : 3′-diallyl-5 : 5′-dimethoxy-6 : 6′-dihydroxydiphenyl, whilst in (II), which contains no CO group, 2 mols. of *iso*eugenol are linked through the O of the OH of one mol. and the propenyl group of the other. W. McC.

Constitution of cholesterol. IX. Bromo-derivatives of cholesterol. F. Pirrone (Gazzetta, 1932, **62**, 1101—1108).—By crystallisation from $COMe_2$, the bromination product of cholesterol (cf. A., 1932, 54) yields products for which the following constitutions are suggested : 6 : 7-*dibromocholesterol* (I), m.p. 106—107°, 7 : 7′-*dibromo*-6 : 6′-*dihydrodicholesterol*, m.p. 112—114°, and 7′-*bromo*-6 : 7 : 6′ : 7′-*tetrahydrodicholesterol*, m.p. 74—76°. (I) is reduced to cholesterol, with HCN gives a *dicyanocholesterol*, m.p. 102—103°, and with $AgNO_3$ a hydroxycholesterol, m.p. 100—105°, and a *product*, m.p. 234—235°. E. W. W.

Relation of cholestenone to cholesterol. Cholestenone, the ketone of *allo*cholesterol. K. Bonstedt (Z. physiol. Chem., 1933, **214**, 173—176).—Oxidation of *allo*cholesterol (I) with CrO_3 in AcOH gives cholestenone (II) and oxycholestenone. Since (II) is thus related to (I) which is αβ-unsaturated, cholesterol (III) probably has the double linking in the βγ-position.



(I.) (II.) (III.)

J. H. B.

[**Preparation of**] **ergosterol from ergot.** A. V. Trufanov (Khim. Farm. Prom., 1932, 132—133).—The ground ergot (2 kg.) is refluxed with abs. EtOH (3 litres for 6 hr., 2·5 for 3 hr.) and then Et_2O (3 litres for 6 hr.). The Et_2O is removed, and the fat dissolved in the combined EtOH, conc., and saponified (4—6 hr., 100 g. KOH). After concn. to 300 c.c. the mixture is kept cool for 24 hr., diluted with H_2O, extracted with Et_2O (washed with H_2O, acidified with

HCl, dried, and distilled). The residue is recryst. from light petroleum (once) and EtOH (twice).
CH. ABS.

Constitution of ergosterol. C. K. CHUANG (Annalen, 1933, **500**, 270—280).—Alternative structures (Rosenheim–King–Wieland–Dane formulation) are suggested for ergosterol from data already published. Ergostane (Reindel and Walter, A., 1928, 295) is oxidised (CrO_3–AcOH at 80°) to *nor*allo*cholanic acid*, $C_{23}H_{38}O_2$, m.p. 170° (*Me* ester, m.p. 79·5°), which is also obtained by similar oxidation of the carbinol from Me *allo*cholanate (Windaus *et al.*, A., 1926, 723) and MgPhBr. H. B.

Phystosterols. II. Sterols of rice oil. C. ANTONIANI (Atti R. Accad. Lincei, 1932, [vi], **16**, 510—514).—Rice husk yields a sterol, $C_{27}H_{46}O$, m.p. 143° (corr.), $[\alpha]_D$ −42·8°, forming an *acetate*, m.p. 135·5° (corr.), $[\alpha]_D$ −41·7° [*dibromide*, m.p. 133° (corr.)], and a *dihydro*-derivative, m.p. 145·5°, $[\alpha]_D$ +20·9°. The phytosterols *B*, *C*, and *D* of Nabenhauer and Anderson (B., 1927, 48) are mixtures of the sterol with its dihydro-compound (cf. Weinhagen, A., 1918, i, 56). T. H. P.

Action of dehydrating agents on β-phenylethyl alcohol. L. PALFRAY, S. SABETAY, and (MLLE.) D. SONTAG (Compt. rend., 1932, **195**, 1392—1394; cf. A., 1929, 440).—Mixtures of β-phenylethyl alcohol with various dehydrating agents were distilled at 250° or refluxed. $H_2C_2O_4$ gives *β-phenylethyl oxalate*, m.p. 51—51·5°, b.p. 221—223°/2—3 mm., Ac_2O the acetate. *o*-$C_6H_4(CO)_2O$ gives styrene, which is also obtained in varying amounts by using calcined alum, anhyd. $CuSO_4$, dry NaOH, K_2CO_3, BaO, and CaO+$Ca(OH)_2$, and is, in some cases, accompanied by unidentified liquids. $SOCl_2$ gives β-phenylethyl chloride and mercaptan, and Br the bromide. Conc. aq. NaOH or KOH, and Na_2CO_3 are without action. $NaHSO_4$ affords β-phenylethyl ether (72%), b.p. 180·5°/15 mm. (cf. A., 1929, 695). A. C.

Velocity of rearrangement of phenylvinylcarbinol esters. J. MEISENHEIMER, W. SCHMIDT, and G. SCHAFER (Annalen, 1933, **501**, 131—150).—The rearrangement of α-phenylallyl (I) into cinnamyl (II) *p*-nitrobenzoate at the b.p. of xylene (in absence of solvent) is influenced by numerous factors. Some of these are: the specimen of (I) used, the nature of the vessel (Pt, quartz, glass) in which the change is carried out, the presence of air, and the decomp. products formed [*p*-NO_2·C_6H_4·CO_2H (III) can be isolated] during the heating. The change is accelerated by addition of 0·847 mol.-% of (III). Rearrangement occurs to the extent of 7% after 15 hr. in Et_2O at 137° [and is independent of the concn. (0·05-1*M*)], and 6% after 24 hr. in C_5H_{12}; addition of (III) has little effect. The conversion of *α-phenylallyl* 3 : 4 : 5-*tribromobenzoate* (IV), m.p. 75·6° (corr.), into *cinnamyl* 3 : 4 : 5-*tribromobenzoate* (V), m.p. 103·5° (corr.), at about 137° (in absence of solvent) in high vac. is catalysed by 3 : 4 : 5-$C_6H_2Br_3$·CO_2H. The velocity of rearrangement in various solvents is (qualitatively) proportional to the dielectric const. of the solvent. The f.-p. diagram of (IV) and (V) shows that these exist in different modifications; the f.-p. diagram of (I) and (II) is given. *α-Phenylallyl*, m.p. 124° (from $COMe_2$) and 115° (from C_6H_6), and *cinnamyl*, m.p. 143·2° (corr.), *anthraquinone-2-carboxylates* are described. H. B.

Mechanism of reduction by sodium amalgam and alcohol. I. Reduction of aromatic ketones to hydrols. W. E. BACHMANN (J. Amer. Chem. Soc., 1933, **55**, 770—774).—$COPh_2$, 4-methyl-, 4 : 4′-dimethyl-, 4-phenyl-, and 4 : 4′-diphenyl-benzophenones, and fluorenone are reduced by 2% Na–Hg (which has practically no action on EtOH) and a little EtOH in Et_2O–C_6H_6 to the corresponding hydrols in almost quant. yield. Reduction occurs thus: (i) $2COPh_2 + 2Na \longrightarrow 2CPh_2{\cdot}ONa \rightleftharpoons (CPh_2{\cdot}ONa)_2$; (ii) $2CPh_2{\cdot}ONa + 2EtOH \longrightarrow COPh_2 + CHPh_2{\cdot}OH + 2NaOEt$; the regenerated $COPh_2$ is then reduced in the same manner. Reduction can also be accomplished in two stages, viz., (i) by Na–Hg in Et_2O–C_6H_6, (ii) subsequent addition of EtOH. Reduction of $COPh_2$ by Li–Hg and K–Hg occurs similarly. H. B.

Heteropolarity. XIX. Phenoxy-, phenylthiol-, and phenylseleno-groups as auxochromes in triphenylcarbenium salts. W. DILTHEY [with F. HARENBERG] (J. pr. Chem., 1933, [ii], **136**, 49—74).—Comparison of the absorption max. and colours of solutions of mono-, di-, and tri-*p*-methoxy-, -phenoxy-, -methylthiol- (Brand, *et al.*, A., 1925, i, 397), -phenylthiol-, and -phenylseleno-triphenylcarbenium perchlorates in AcOH–$HClO_4$ and conc. H_2SO_4 shows that the bathochromic effect of the substituents is SePh>SPh, SMe>OPh, OMe; the third substituent exerts a hypsochromic effect in all cases. Anisyloxy is slightly more bathochromic than OPh and introduction of a third anisyloxy-group has, surprisingly, a bathochromic effect. The *p*-OMe·C_6H_4·S group is only very slightly more bathochromic than SPh. The stability of the perchlorates (in AcOH–$HClO_4$) towards hydrolysis by 75% EtOH decreases in the order OPh, SPh, SePh; the phenylselenotriphenylcarbenium perchlorates could not be isolated. The introduction of OPh into the 4- and 4 : 4′-positions of $COPh_2$ has approx. the same effect on the colour as OMe; the SPh group has, however, a pronounced bathochromic effect. A reply is made to Burawoy (this vol., 62).

p-OEt·C_6H_4·OPh, $COCl_2$, and $AlCl_3$ in CS_2 give 4 : 4′-*di*-p-*ethoxyphenoxybenzophenone*, m.p. 167°. 4 : 4′-*Dianisyloxybenzophenone*, m.p. 198—199°, prepared similarly from *p*-OMe·C_6H_4·OPh (I) or from *p*-OMe·C_6H_4·ONa and 4 : 4′-dibromobenzophenone (II), is demethylated ($AlCl_3$–C_6H_6) to 4 : 4′-*di*-p-*hydroxyphenoxybenzophenone*, m.p. 214° (*Ac*$_2$ derivative, m.p. 177—178°). (I), BzCl, and $AlCl_3$ in CS_2 afford 4-*anisyloxybenzophenone*, m.p. 104—105°, demethylated ($AlCl_3$) to 4-p-*hydroxyphenoxybenzophenone*, m.p. 109°. NaOPh, (II), and Cu-bronze at 210° give 4 : 4′-*diphenoxybenzophenone* (III), m.p. 147°; 4 : 4′-*diphenylthiol*- (IV), m.p. 139°, 4 : 4′-*di*-p-*ethoxyphenylthiol*-, m.p. 170—171°, and 4 : 4′-*dianisylthiol*-, m.p. 121—122°, *-benzophenones* are similarly prepared using NaSPh, *p*-OEt·C_6H_4·SNa, and *p*-OMe·C_6H_4·SNa, respectively. 4 : 4′-Dihydroxybenzophenone and *p*-$C_6H_4Br{\cdot}NO_2$ give (Ullmann method) 4 : 4′-*di*-p-*nitrophenoxybenzophenone*, m.p. 150—151°. MgPhBr

and (III) give impure 4 : 4′-diphenoxytriphenylcarbinol (*perchlorate*, decomp. 130—132°), whilst 4 : 4′ : 4″-triphenoxytriphenylcarbinol (*perchlorate*, m.p. 236—238°) is prepared from (III) and Mg *p*-phenoxyphenyl bromide. 4-Phenylthiolbenzophenone and MgPhBr give the corresponding carbinol (unstable perchlorate) and a little *4-phenylthioltriphenylmethane*, m.p. 118—119°, whilst MgPhBr and (IV) afford 4 : 4′-diphenylthioltriphenylcarbinol [*perchlorate*, m.p. about 190° (decomp.)]. Mg *p*-phenylthiolphenyl bromide and (IV) yield 4 : 4′ : 4″-triphenylthioltriphenylcarbinol [*perchlorate*, m.p. 145° (slow decomp. from 140°)], reduced (Zn dust, AcOH) to 4 : 4′ : 4″-*triphenylthioltriphenylmethane*, m.p. 105—106°. H. B.

Presence of conjugated double linkings in abietic acid. B. Arbusov (J. Gen. Chem. Russ., 1932, **2**, 806—813).—Abietic acid (I) and maleic anhydride combine when heated in C_6H_6 to a *compound* $C_{24}H_{32}O_5$ (II) (cf. A., 1932, 1254), m.p. 226·5—227°, $[\alpha]_D$ −28·93 in MeOH, giving with alkalis the corresponding tribasic *acid*, which when heated reverts to (II) without melting. (II) affords a 60% yield of retene when heated with Se to 300—320°; this cannot be due to the dehydrogenation of (I), formed by the fission of (II) into its components, since (II) does not decompose below 390°, when it gives off succinic anhydride. It is suggested that the formation of retene from (II) is analogous to the elimination of Me on C_{12} and would be expected if the double linkings in (I) occupy the positions 7 : 8 and 13 : 14 or 6 : 7 and 5 : 13; some other combinations are possible, but positions 5 : 6 and 7 : 8, and 5 : 13 and 14 : 8 appear to be excluded. (II) is oxidised by $KMnO_4$ to a *compound* $C_{24}H_{34}O_7$, m.p. 191—192°, probably a δ-lactone. (II) is also formed from some primary resin acids from *P. insignis* and *P. Pithyusa* and from abietic acid prepared by vac. distillation of colophony, although some samples (*e.g.*, from French colophony) did not react. G. A. R. K.

Acid benzoates of zinc and cadmium. P. Pfeiffer and Y. Nakatsuka (J. pr. Chem., 1933, [ii], **136**, 241—248).—The following *salts* are prepared: $H_2[Zn(OBz)_4]$, $+2H_2O$, giving $Zn(OBz)_2$, $+$ Et_2O and $+H_2O$; $H_2[Cd(OBz)_4]$, $+2H_2O$, giving $Cd(OBz)_2$, $+H_2O$,Et_2O, $+H_2O$,EtOH, and $+1·5H_2O$ ($1H_2O$ lost at 160°); $Ca[Cd(OBz)]_4$], and $Ba[Cd(OBz_4)]$, $+3H_2O$ (lost at 160°). The prep. of $Cd(OBz)_2$, $+H_2O$ is modified. Attempts to prepare acid salts led to *Cd(O·CO·C$_6$H$_4$Cl*-m and -p)$_2$,$2H_2O$, *Cd salicylate*, $+3H_2O$ (lost on heating), and *Cd(O·CO·C$_6$H$_4$-OH*-p)$_2$, $+7·5(?8)H_2O$ and $+4H_2O$. R. S. C.

Mechanism of the Perkin reaction. D. A. Brodski (J. Gen. Chem. Russ., 1932, **2**, 814—820).—Ac_2O reacts with Na, Na_2CO_3, and K_2CO_3 forming the corresponding acetates; Kalnin's suggestion (A., 1929, 63), that in Perkin's reaction acetates can be replaced by indifferent org. or inorg. compounds, which assist in the enolisation of the Ac_2O, is criticised. C_5H_5N and piperidine acetates can be employed in place of NaOAc, and piperidine *p*-nitrophenylacetate condenses with PhCHO in the absence of Ac_2O. Contrary to Kalnin's observation (*loc. cit.*), the yield of cinnamic acid is not affected by the presence of an excess of NaOAc, whilst the diminution of the yield on the addition of AcOH shows that benzylidene diacetate cannot be an intermediate product in the reaction (A., 1898, i, 109). $CH_2Cl·CO_2Na$ and Ac_2O do not yield $(CH_2Cl·CO)_2O$; the formation of α-chlorocinnamic acid from these and PhCHO cannot, therefore, be due to this cause as suggested by Michael (A., 1901, i, 358). G. A. R. K.

γ-Hydroxy-α-phenylbutyric acid and its lactone. P. Carré and D. Libermann (Compt. rend., 1933, **196**, 117—118).—The Na derivative of $CH_2Ph·CN$ reacts with $CH_2Cl·CH_2·OH$ in Et_2O to give 40—45% of *γ-hydroxy-α-phenylbutyronitrile*, b.p. 188—190°/10 mm. (*phenylurethane*, m.p. 89°), hydrolysed by 20% $Ba(OH)_2$ to *γ-hydroxy-α-phenylbutyric acid* (I), m.p. 99—100°. (I) could not be etherified or benzoylated, nor could a phenylurethane be obtained, owing to the ready formation of the *lactone*, b.p. 203—205°/30 mm., which is also obtained when an aq. solution of (I) is heated to 50—60°. H. B.

Preparation of 3 : 4-dimethoxycinnamic acid. A. Oliverio (Rend. Sem. Fac. Sci. Cagliari, 1931, **1**, 117—118; Chem. Zentr., 1932, ii, 3087).—Veratraldehyde and malonic acid in 87% EtOH–NH_3 afford 88%, and in AcOH 92%, of 3 : 4-dimethoxycinnamic acid, m.p. 181°. A. A. E.

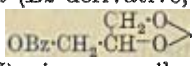
Stereochemistry of diphenyls. XXVII. Comparison of the racemisation of 6 : 6′-difluoro- and 6 : 6′-dimethoxy-diphenic acids. W. M. Stanley, E. McMahon, and R. Adams. **XXVIII. Preparation and properties of 2 : 2′-difluoro-6 : 6′-dinitro-5 : 5′-dimethyldiphenyl-3 : 3-dicarboxylic acid.** E. C. Kleiderer and R. Adams (J. Amer. Chem. Soc., 1933, **55**, 706—716, 716—719).—XXVII. 6 : 6′-Dimethoxydiphenic acid, m.p. 293—294° (lit. 288—290°) [brucine salt, m.p. 198—199° (corr.) (lit. 268°); *amide*, m.p. 273—274°], is resolved by quinine (cf. Kenner and Turner, A., 1928, 1244) into *a*-, m.p. 291—292°, $[\alpha]^{20}$ +108·5° in $COMe_2$ [diquinine salt, m.p. 98—100° (corr.) (lit. about 60°); *Me* ester, m.p. 98—99°; *amide*, m.p. 230—231° (corr.)], and *l*-forms (I), m.p. 291—292°, $[\alpha]_l^{20}$ −114·9° in $COMe_2$ [diquinine salt, m.p. 178—179° (corr.) (lit. 172—173°); *Me* ester (II), m.p. 101—102°; *amide* (III), m.p. 230—231° (corr.)]. (I) and (II) racemise at about the same rate [which is faster than that of (III)]. 2-Iodo-3-aminobenzoic acid [by reduction ($SnCl_2$, conc. HCl, and a little EtOH) of the 3-NO_2-acid] is diazotised in 48% HF and the resulting solution kept at 30±2° for 2 days, whereby 2-*iodo*-3-*fluorobenzoic acid*, m.p. 152—153° (corr.) [*Me* (IV), b.p. 127—128°/4 mm., and *Et* (V), b.p. 148—150°/6 mm., esters], results. (IV) and Cu powder at 180—240° give the *Me* ester, m.p. 116—117°, of 6 : 6′-*difluorodiphenic acid*, m.p. 308—311° (corr.) (after previous shrinking and softening) [*Et* ester, m.p. 105—107°, prepared from (V)]; the acid is resolved by quinine into d-, m.p. 305—306° (corr.), $[\alpha]^{20}$ +16·8° in 95% EtOH [*quinine* salt, m.p. 163—165° (corr.)], and l-*forms*, m.p. 305—306° (corr.), $[\alpha]^{20}$ −22·5° in 95% EtOH [*quinine* salt, m.p. 221—222° (corr.)]. These active acids racemise readily in 0·1*N*-NaOH at 100° (bath), less readily in boiling

EtOH, AcOH, and Ac_2O, and slowly in 0·1*N*-NaOH at 20° and EtOH–conc. HCl; the rates are much faster than those of (I).

XXVIII. 5-Bromo-4-fluoro-5-nitro-*m*-xylene and dil. HNO_3 at 150° give *5-bromo-4-fluoro-6-nitro-m-toluic acid*, m.p. 249—251° (corr.) [*Me* (VI), m.p. 88—89° (corr.), and *Et*, m.p. 65—66° (corr.), esters], the constitution of which is inferred from the similar production of 6-nitro-*m*-toluic acid from 4-nitro-*m*-xylene. (VI) and Cu-bronze at 220—225° give the *Me* ester, m.p. 191—193° (corr.), of 2 : 2′-*difluoro*-6 : 6′-*dinitro*-5 : 5′-*dimethyldiphenyl*-3 : 3′-*dicarboxylic acid*, m.p. (block) 301—304°, m.p. (tube) 318—320° (corr.; decomp.), resolved by strychnine into d-, m.p. 297—301° (corr.; decomp.), $[\alpha]_D^{20}$ +15° in MeOH [*strychnine* salt, m.p. 190—193° (corr.; decomp.)], and l-*forms*, m.p. 298—300° (corr.; decomp.), $[\alpha]_D$ −17° in MeOH [*strychnine* salt, m.p. 224—228° (corr.; decomp.)], which are not racemised appreciably in boiling EtOH, AcOH, *cyclo*hexanone, or 0·1*N*-NaOH, in agreement with the relatively large size of the 6 : 6′-NO_2-groups. H. B.

Depside esters of dihydric phenols, and polydepsides. T. Currie and A. Russell (J.C.S., 1933, 140—142; cf. A., 1932, 1030).—Na vanilloxide in $COMe_2$ with 3 : 3′ : 4′-trimethoxy-*p*-dibenzoyl chloride gives 3 : 3′ : 3″ : 4″-*tetramethoxy*-pp-*tribenzaldehyde*, m.p. 159° (nomenclature, *loc. cit.*). The following are similarly obtained: 3 : 3′ : 3″ : 3‴ : 4‴-*pentamethoxy*-ppp-*tetra*-, m.p. 249°, 3 : 4″-*dimethoxy*-pp-*tri*-, m.p. 152°, and *tris*-(3 : 3′ : 3″ : 4″-*tetramethoxy*-pp-*tribenzoyl*)-2 : 3 : 4-*trihydroxy-benzaldehyde*, m.p. 263° (decomp.), *quinol bis*-(3 : 3′ : 4′-*trimethoxy*-p-*dibenzoyl*), m.p. 229°, -(3′ : 4′-*dimethoxy*-p-*dibenzoyl*), m.p. 230°, and -(3 : 4″-*dimethoxy*-pp-*tribenzoyl*) *ethers*, m.p. 278—279°, *resorcinol bis*-(3′ : 4′-*dimethoxy*-p-*dibenzoyl*), m.p. 194°, and -(4′-*methoxy*-p-*dibenzoyl*) *ethers*, m.p. 154°, and *pyrocatechol bis*-(3′ : 4′-*dimethoxy*-p-*dibenzoyl*) *ether*, m.p. 175°. The above aldehydes with $KMnO_4$ by an improved method give 3 : 3′ : 3″ : 4″-*tetramethoxy*-pp-*tri*-, m.p. 251—252° [*chloride*, m.p. 171° (decomp.)], 3 : 3′ : 3″ : 3‴ : 4‴-*pentamethoxy*-ppp-*tetra*-, m.p. 327°, and 3 : 4″-*dimethoxy*-pp-*tri*-*benzoic acid*, m.p. 233° (*chloride*, m.p. 155°). A. A. L.

Formation of an intermediate in the action of phosphorus pentachloride on aldehydes. S. C. J. Olivier and A. P. Weber (Rec. trav. chim., 1933, **52**, 169—174).—2 : 6-$C_6H_3Cl_2$·CHO (I) (1 mol.) and PCl_5 (1 mol.) give at first *di*-α : 2 : 6-*trichlorobenzyl ether* (II), m.p. 180—185° [yield 5—6 g. from 10 g. of (I)], converted (almost quant.) by PCl_5 (1 mol.) at 170° into 2 : 6-*dichlorobenzylidene chloride* (III), b.p. about 155° (bath)/12 mm. (II) is not obtained when mixtures of (I) and (III) are heated, whilst (III) results in almost quant. yield from equimol. amounts of (I) and PCl_5 in ½ hr. at 160°. (II), which is considered to be an intermediate in the reaction between (I) and PCl_5, gives (I) and (III) when it is fused and then kept at 100° for 2 min. H. B.

Photochemical reactions of *o*-nitrobenzylidene acetals. VII. (αβ-*o*-**Nitrobenzylideneglycerol.**) I. Tanasescu and E. Macovski (Bull. Soc. chim., 1932, [iv], **51**, 1556—1565; cf. this vol., 275).—Hibbert's technique applied to the condensation of *o*-NO_2·C_6H_4·CHO (I) and glycerol gives only αβ-*o*-nitrobenzylideneglycerol (II), b.p. 224—226°/15 mm., and a small distillation residue, also obtained when pure (II) is distilled. The constitution of (II) is proved by methylation (MeI–Ag_2O) to the α′-*Me ether*, b.p. 203—208°/11 mm., hydrolysed by dil. HCl to glycerol α-Me ether and re-formed therefrom by (I) in 20% H_2SO_4 at 120°. (II) with BzCl gives α-*benzoyl*-α′β-*o*-*nitrobenzylideneglycerol*, two isomeric forms, m.p. 125—126° (III) and an oil (IV), respectively. Illumination of (III) in C_6H_6 usually gives an isomeride, m.p. 120—121° after softening at 115—116°, considered to be probably α-*benzoyl*-α′-*o*-*nitrosobenzoylglycerol* (*Bz* derivative, an oil), possibly in equilibrium with  . Illumination of (IV) gives an oily isomeride, sometimes obtained also from (III) probably by way of (IV). R. S. C.

Homologues of cinnamaldehyde. II. α-Phenyl- and α-benzyl-cinnamaldehyde. P. Schorigin, V. Issagulianz, and I. Matschinskaja (Ber., 1933, **66**, [*B*], 389—393; cf. A., 1931, 485).—PhCHO and CH_2Ph·CHO in EtOH–H_2O in presence of NaOH afford (*a*) α-phenylcinnamaldehyde (I), m.p. 94—95° (phototropic *semicarbazone*, m.p. 188·5—189·5°); (*b*) a very sparingly sol. compound, m.p. 187—199°, probably *polymeric* αβγ-*triphenylglutardialdehyde*, which does not give the typical aldehyde reactions, yields PhCHO, possibly CH_2Ph·CHO, and (I) when heated in vac., and gives PhCHO under the action of NaOH; (*c*) αβγ-*triphenylvalerolactone*, m.p. 151—162° (*Na* and *Ag* δ-*hydroxy*-αβγ-*triphenylvalerate*). Similarly, PhCHO and CH_2Ph·CH_2·CHO give α-*benzylcinnamaldehyde*, m.p. 53—54°, with odour of CHPh.CH·CHO and jasmine [non-phototropic *semicarbazone* (?) CHPh:C(CH_2Ph)·CH(OH)·NH·NH·CO·NH_2, m.p. 187—188°]. H. W.

Phototropic and thermotropic anils from 5-bromosalicylaldehyde. C. M. Brewster and L. H. Millam (J. Amer. Chem. Soc., 1933, **55**, 763—766).—The following are prepared from 5-bromosalicylaldehyde (convenient prep. given) and the requisite amines usually in EtOH and occasionally by direct fusion only: 5-*bromosalicylidene*-o-, m.p. 86·5° (using EtOH) and 165° (no solvent), and -p-, m.p. 163·5°, -*toluidines*; -α-*naphthylamine* (I), m.p. 109·5°; -p-*phenetidine*, m.p. 156°; -o-, m.p. 110°, and -p-, m.p. 156°, -*anisidines*; -p-*aminoazobenzene* (II) yellowish-brown and red forms, m.p. 212°; -2-*amino*-5-*azotoluene*, m.p. 212°; -o-, m.p. 192·5°, and -p-, m.p. 239°, -*aminophenols*; -p-*xylidine*, m.p. 67°; -m-4-*xylidine*, m.p. 131·5°; -p-*aminobenzoic acid*, m.p. 282°; -m- (III), m.p. 169°, and -p-, m.p. 207°, -*nitroanilines*; -o-, m.p. 88°, -m-, m.p. 127·5°, and -p-, m.p. 158°, -*chloroanilines*; -o- (IV), m.p. 78°, and -p- (V), m.p. 178°, -*bromoanilines*; -2 : 4-, m.p. 148°, and 2 : 5-, m.p. 139°, -*dichloroanilines*; *di*-5-*bromosalicylidene*-p-*phenylenediamine*, m.p. 277°, -m-*toluylenediamine*, m.p. 188°, -*dianisidine* (VI), m.p. 279°, -o-*tolidine*, m.p. 242°, and -*benzidine*, m.p. 345°. *Salicylidene*-p-*toluidine* (VII), m.p. 95°, and the above

anils [except (II), (III), (IV), and (VI)] are thermotropic, whilst (I), (V), and (VII) are phototropic. All m.p. are corr. H. B.

Differentiation of *O*- and *N*-methyl groups. P. PFEIFFER and E. OCHIAI (J. pr. Chem., 1933, [ii], **136**, 125—128).—Piperonal (1 mol.) and $AlBr_3$ (3 mols.) in C_6H_6 at 100° (bath) give 49% of 3 : 4-$(OH)_2C_6H_3$·CHO and 8·5% of anthracene (formed from C_6H_6, the intermediately formed CH_2Br_2, and $AlBr_3$ with subsequent atm. oxidation of the dihydroanthracene). $NPhMe_2$ is unaffected by $AlBr_3$ in C_6H_6, whilst *p*-NMe_2·C_6H_4·CHO affords *p*-dimethylaminotriphenylmethane. Since OMe-compounds are demethylated by $AlBr_3$ in C_6H_6 (A., 1928, 420), it is easy to differentiate between *O*- and *N*-Me groups. H. B.

Structure of lignin. F. BRAUNS and H. HIBBERT (Pulp and Paper Canada, 1933, **34**, 187—188).—A synopsis of recent work on the empirical formula of spruce lignin, indicating $C_{47}H_{52}O_{16}$. This is supported by analytical data on "MeOH lignin" and "glycol lignin," and their Me derivatives. H. A. H.

Asymmetric syntheses. II. Action of optically active nitrates on cyclic ketones. R. L. SHRINER and E. A. PARKER (J. Amer. Chem. Soc., 1933, **55**, 766—770; cf. this vol., 159).—*d*-β-Octyl nitrate, prepared by a modification of Chapman and Smith's method (J.C.S., 1867, **20**, 581), 4-methyl-*cyclo*hexanone, and KOEt in EtOH–Et_2O give the d-*K* salt (I), $[\alpha]_D^{25}$ +9·02°, of 2-nitro-4-methyl*cyclo*hexanone; *l*-β-octyl nitrate (II) similarly affords the l-*K* salt (III), $[\alpha]_D^{25}$ −4°, whilst *dl*-β-octyl nitrate yields the inactive *K* salt. The rapid racemisation of (I) and (III) indicates that the new asymmetric centre is at C_2. *cyclo*Hexanone and (II) similarly give an impure salt, $[\alpha]_D^{25}$ −6·72°. H. B.

Hydrogenation, under pressure, of 5-phenyl-3-methyl-Δ²-*cyclo*hexenone and of 5-phenyl-3-*p*-tolyl-Δ²-*cyclo*hexenone. A. D. PETROV and L. I. ANZUS [with A. O. SAVELJEV and E. W. IKONEN] (Ber., 1933, **66**, [*B*], 420—423).—5-Phenyl-3-methyl-Δ²-*cyclo*hexenone is converted by H_2 at 225—245° into 3-cyclo*hexylmethyl*cyclo*hexane*, b.p. 243—243·5°/atm. press. *p*-Tolyl styryl ketone and COMe·CH_2·CO_2Et in presence of NaOEt afford 6-*carbethoxy*-5-*phenyl*-3-p-*tolyl*-Δ²-cyclo*hexenone*, m.p. 133—134°, hydrolysed to 5-*phenyl*-3-p-*tolyl*-Δ²-cyclo*hexenone* (I), m.p. 106°. (I) is hydrogenated with some difficulty at 220—240°, yielding mainly 1-cyclo*hexyl*-3-p-*methyl*cyclo*hexylbenzene*, b.p. 194—198°/8 mm., with a little completely hydrogenated *substance*, $C_{19}H_{34}$, and cracked products. H. W.

Derivatives of diphenyl. C. F. H. ALLEN and W. L. BALL (Canad. J. Res., 1932, **7**, 643—645).—*p*-Phenylphenacyl bromide and KOAc in hot 60% EtOH give the acetate (I), m.p. 111°, hydrolysed by EtOH containing a little H_2SO_4 (not by other methods) to p-*phenylphenacylcarbinol*, m.p. 123—128° [*phenylurethane*, m.p. 186—187°; 2 : 4-*dinitrophenylhydrazone*, m.p. 222—223° (decomp.)]. *p*-Phenylacetophenone, PhCHO, and KOH in hot EtOH give *benzylidene*-p-*phenylacetophenone*, m.p. 156°, the *dibromide* (II), m.p. 189°, of which is hydrolysed to p-*phenylbenzoylbenzoylmethane*, *p*-C_6H_5·C_6H_4·CO·CH_2Bz, m.p. 112° [*Cu* derivative, m.p. 290° (decomp.)]; this with NH_2OH in AcOH gives 5-*phenyl*-3-p-*diphenylyl*iso*oxazole*, m.p. 182—183°, the constitution of which is proved by exclusion, since (II) with NH_2OH gives 3-*phenyl*-5-p-*diphenylyl*iso*oxazole*, m.p. 195°. R. S. C.

Molecular re-arrangements of α-glycols. VIII. Reduction of αβ-dinaphthyl ketone (an attempt to compare the electro-negativities of α- and β-naphthyl radicals). IX. Conclusion (the pinacolin rearrangement as a method of establishing relative electro-negativities of organic radicals). M. MIGITA (Bull. Chem. Soc. Japan, 1933, **8**, 22—27, 27—35; cf. this vol., 271).—VIII. Reduction of αβ-dinaphthyl ketone (I) and α-*naphthyl* p-*diphenylyl ketone* (II) with Zn dust and AcOH is anomalous, probably owing to steric factors. At 25° αβ-*dinaphthylcarbinol*, m.p. 112—113°, and α-*naphthyl*-p-*diphenylylcarbinol*, m.p. 131°, but, when boiled, αβ-*dinaphthylmethane*, m.p. 96°, and α-*naphthyl*-p-*diphenylylmethane*, m.p. 146°, are formed. (I) is unchanged in EtOH by sunlight, and with Mg and MgI_2 in Et_2O–C_6H_6 gives a red solution (probably containing ketyl), from which only resins were obtained. (II), m.p. 140—141°, is prepared from α-$C_{10}H_7$·CN and the Grignard reagent from *p*-bromodiphenyl (m.p. 90—91°; modified prep.).

IX. A discussion of results and theories already published. R. S. C.

Grignard reaction in synthesis of ketones. I. Deoxybenzoins. S. S. JENKINS (J. Amer. Chem. Soc., 1933, **55**, 703—706).—Prolonged interaction of NH_2Bz and CH_2Ph·MgCl (3—4 equivs.) gives a 77% yield of deoxybenzoin; *m*-C_6H_4Cl·CO·NH_2 similarly affords m-*chlorophenyl benzyl ketone* (72%), m.p. 62° (all m.p. are corr.) (anti-*oxime*, m.p. 120°, rearranged by PCl_5 in Et_2O to *phenylacet*-m-*chloroanilide*, m.p. 95°), whilst *p*-anisamide (I) yields anisyl benzyl ketone (74%), m.p. 77° (*anti*-oxime, m.p. 118·5°, rearranged to phenylacet-*p*-anisidide). Mg *o*-chlorobenzyl bromide and (I) give *anisyl* o-*chlorobenzyl ketone* (55%), m.p. 97·5° (cf. Buck and Ide, A., 1931, 732) (*anti*-oxime, m.p. 99°, rearranged to *o*-chlorophenylacet-*p*-anisidide, m.p. 166°), whilst Mg *p*-chlorobenzyl bromide and (I) furnish *anisyl* p-*chlorobenzyl ketone* (66%), m.p. 137·5° (anti-*oxime*, m.p. 138·5°, rearranged to p-*chlorophenylacet*-p-*anisidide*, m.p. 184°). The above anilides are also prepared from the requisite acids (or chlorides) and anilines. H. B.

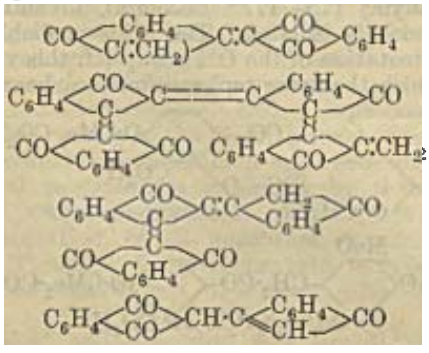
Thermal interconversion of mixed benzoins. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1933, **55**, 855).—When benzanisoin is heated at 125—130° for 3 hr., some anisbenzoin is produced. H. B.

Spontaneous resolution of 4-methoxy-*ms*-methyldeoxybenzoin, CHPhMe·CO·C_6H_4·OMe. (MME.) BRUZAU (Compt. rend., 1933, **196**, 122—124).—4-Methoxy-*ms*-methyldeoxybenzoin [anisyl α-phenylethyl ketone], prepared by Ney's method (A., 1882, 1197), from *p*-OMe·C_6H_4·MgBr and CHPhMe·CO·NH_2, or from PhOMe, CHPhMe·COCl, and $AlCl_3$ in CS_2, when cryst. from EtOH gives

material of m.p. 58—60°, 78—80° (prisms), or 54—80°. The prisms are optically active forms of the ketone and are separable by hand. p-*Tolyl* α-*phenylethyl ketone*, m.p. 46—47°, and Ph α-phenylethyl ketone do not show similar properties. H. B.

Reaction between αβ-unsaturated ketones and organic magnesium compounds. Unsaturated mesitylenic ketones. E. P. KOHLER and C. E. BARNES (J. Amer. Chem. Soc., 1933, **55**, 690—695).—2 : 4 : 6-Trimethylphenyl αβ-dibromo-β-phenylethyl ketone, m.p. 126—127°, is treated with MeOH–NaOMe, the reaction mixture acidified (HCl), and the solution boiled, whereby *benzoyl*-2 : 4 : 6-*trimethylbenzoylmethane* (I), m.p. 79°, is obtained. MgPhBr and (I) give 2 : 4 : 6-*trimethylphenyl* β-*hydroxy*-ββ-*diphenylethyl ketone*, m.p. 75°, which is dehydrated by warm dil. HCl to 2 : 4 : 6-trimethylphenyl β-phenylstyryl ketone (II), m.p. 104°. Contrary to the previous statement (A., 1907, i, 1050), MgPhBr and (II) afford 2 : 4 : 6-*trimethylphenyl* βββ-*triphenylethyl ketone*, m.p. 194—195°, also obtained from CPh_3Cl and the enolate $C_6H_2Me_3\cdot C(:CH_2)\cdot OMgBr$ (from acetomesitylene and MgEtBr). MgMeI and (II) in Et_2O–C_6H_6 (not in Et_2O) yield 2 : 4 : 6-*trimethylphenyl* ββ-*diphenylpropyl ketone*, m.p. 87°, synthesised from MgPhBr and 2 : 4 : 6-*trimethylphenyl* β-*methylstyryl ketone* (III), m.p. 84°, which is prepared [as (II)] from (I) and MgMeI. MgEtBr and (II) give 2 : 4 : 6-*trimethylphenyl* ββ-*diphenylbutyl ketone*, m.p. 106°, whilst MgMeI and (III) afford 2 : 4 : 6-*trimethylphenyl* β-*phenyl*isobutyl *ketone*, m.p. 184—185°. H. B.

Derivatives of di-indone. III. Action of di-indone on aldehydes in alcoholic [alkali]. M. V. IONESCU and H. SLUSANSCHI (Bull. Soc. chim., 1932, [iv], **51**, 1551—1556; cf. this vol., 162).—Di-indone does not react with MeCHO in EtOH–NaOH or EtOH–NaOEt, but with CH_2O gives, in both cases, a *substance*, $C_{19}H_{10}O_3$, probably *methylenedi-indone* (I), m.p. 218°. It dissolves slowly in cold, rapidly in hot, NaOH or EtOH–NH_3 to give pink and orange-red solutions, respectively. With boiling AcOH it gives a purplish-black *substance*, $C_{37}H_{18}O_5$, m.p. 280° (decomp.), probably *methyleneanhydrobisdi-indone* (II), unchanged by NH_3, but decomposed by alcoholic alkali to a deep blue solution. With boiling EtOH–NaOEt (I) affords a bright yellow, cryst. *substance*, $C_{27}H_{14}O_4$, m.p. 335°, possibly *anhydrotri-indandione*



(I.)

(III.)

(IV.)

(III) (giving slowly a pale yellow solution in alcoholic alkali), and an amorphous, pale yellow *substance*, $C_{18}H_{10}O_3$, possibly an isomeride (IV) of di-indone (giving a greenish-blue solution in alkali). (I) is unchanged by NaOEt and does not condense with indandione in presence of NaOEt. It bears no relation to the alkaline condensation products from bisdi-indone. R. S. C.

Migration of acyl groups in polyhydric phenols. F. MAUTHNER (J. pr. Chem., 1933, [ii], **136**, 205—212).—1-Acetylpyrogallol Me_2 ether with $AlCl_3$ in $PhNO_2$ gives 2-hydroxy-3 : 4-dimethoxyacetophenone. Acetylresorcinol Me ether (from resorcinol Me ether and AcCl at 100°; b.p. 125—126°/11 mm.) gives similarly pæonol, m.p. 50° (p-*nitrophenylhydrazone*, m.p. 238—239°), volatile in steam, and *iso*pæonol, involatile in steam. Acetylorcinol Me ether yields only acetylevernone, and 2-*methoxydiacetylquinol*, m.p. 95—96°, gives 2 : 5-*dihydroxy*-4-*methoxyacetophenone*, m.p. 165—166° [p-*nitrophenylhydrazone*, m.p. 255—256° (decomp.)], yielding with Me_2SO_4 in NaOH–H_2O–EtOH 2 : 4 : 5-trimethoxy- and 2-*hydroxy*-4 : 5-*dimethoxy-acetophenone*, m.p. 111—112°. Acetylguaiacol is scarcely changed at room temp., and 3 : 5-*diacetoxybenzoic acid*, m.p. 156—157°, is stable to $AlCl_3$ at 70°. R. S. C.

Synthesis of 2 : 3 : 5-trihydroxyacetophenone. F. MAUTHNER (J. pr. Chem., 1933, [ii], **136**, 213—216).—The Ac_3 derivative of hydroxyquinol (I) with $AlCl_3$ in $PhNO_2$ at room temp. gives a small amount of a *substance*, m.p. 182—183°, and 2 : 3 : 5-*trihydroxyacetophenone*, m.p. 206—207° [p-*nitrophenylhydrazone*, m.p. 241—242° (decomp.); Ac_3 derivative, m.p. 106—107°], giving on methylation the known Me_3 ether, and also obtained in poor yield from (I) by the Hoesch synthesis. R. S. C.

Manufacture of condensation products from polyhydric alcohols and cyclic ketones. I. G. FARBENIND. A.-G.—See B., 1933, 182.

Anodic oxidation of benzene. R. M. ARCHIBALD.—See this vol., 358.

Constitution and reactivity. V. Nitration and bromination of aminoanthraquinones. VI. Replacement of the sulphonic acid group in chloroanthraquinonesulphonic acids by chlorine. K. LAUER (J. pr. Chem., 1933, [ii], **136**, 1—4, 5—8).—V. Nitration of 1- and 2-aminoanthraquinones with 1·05 equiv. of $NaNO_3$ in abs. H_2SO_4 at 5° gives mixtures of 2- and 4-, and 1- and 3-NO_2-derivatives, respectively, unaccompanied by $(NO_2)_2$-compounds. Substituents in the 1-NH_2 group increase the proportion of 4-NO_2-compound in the order of increasing acidity, viz., $CH_2{:}<\cdot CO_2Alk<Ac<Bz<\cdot CO_2\cdot CH_2Cl<CO\cdot CO_2H<\cdot SO_2\cdot NC_7H_7$. Parallel results are obtained by bromination with 1·05 equiv. Br in $PhNO_2$ at 30°. Vals. of the differences of the heats of activation, $q_{1:2}$—$q_{1:4}$, and $q_{2:3}$—$q_{2:1}$ (cf. this vol., 69) for the bromination and nitration of the aminoanthraquinones and their *N*-substituted derivatives are given.

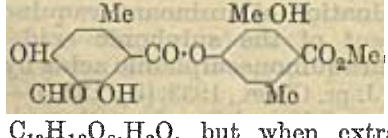
VI. A kinetic study of the replacement of SO_3H by Cl in the chloroanthraquinonesulphonic acids using the method previously employed for the anthraquinonedisulphonic acids (*loc. cit.*) indicates that replacement of the first SO_3H group by Cl reverses

the reactivity of the remaining one. Thus whilst in the disulphonic acids the reactivity of the first SO_3H in different isomeric pairs is in the order 1 : 5>1 : 8; 1 : 7>1 : 6; 2 : 6>2 : 7, in the chlorosulphonic acids this order is reversed. Vals. of $K\times10^3$ at 94°, 104°, and 114°, and of q and $\alpha\times10^{-10}$ are given. H. A. P.

Amination by ammonolysis [of 2-chloroanthraquinone]. III. Effect of inorganic salts. P. H. Groggins and A. J. Stirton (Ind. Eng. Chem., 1933, **25**, 169—175; cf. this vol., 277).—In the prep. of 2-amino- from 2-chloro-anthraquinone by ammonolysis the side reactions of hydrolysis to 2-hydroxyanthraquinone and *sec.*-amine formation are not markedly affected by NH_4 salts, but are strongly inhibited by small amounts of oxidising agents, particularly $KClO_3$. $KClO_3$ needs narrowly defined conditions for max. action, but equally good results are obtained over a wider range of conditions by the combined action of $KClO_3$ and NH_4NO_3. Addition of Cu salts to this binary mixture enables the amination to be carried out at 160° instead of 190—200°, but does not result in any marked improvement in purity or yield of product. Excess of oxidising agent and undue prolongation of the reaction are to be avoided, as they lead to the production of 1 : 2-diamino- and 2-amino-1-hydroxy-anthraquinones. Reducing agents, *e.g.*, sulphites and N_2H_4, diminish the yield and purity of 2-aminoanthraquinone. Using a large excess of NH_3 and small additions of $KClO_3$ and NH_4NO_3, 2-aminoanthraquinone can be prepared on a semi-technical scale in a yield of 97% of theory of material of 97·5% purity. This affords a cheaper route than that from the -2-sulphonic acid. H. A. P.

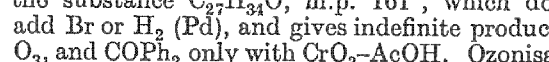
Manufacture of chlorocyanoanthraquinones. I. G. Farbenind. A.-G.—See B., 1933, 183.

Lichen acids. IV. Atranorin. F. H. Curd, A. Robertson, and R. J. Stephenson (J.C.S., 1933, 130—133; cf. A., 1932, 850).—Atranorin, regarded as (I), extracted by an improved process has the

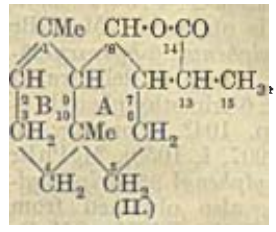
(I.) 

formula $C_{19}H_{18}O_8,H_2O$, but when extracted with $CHCl_3$ it contains Cl. The latter product gives an O-*Me*$_3$ *ether* (II), m.p. 123°, an O-*Me*$_2$ *ether*, m.p. 136°, and a *substance* containing Cl, m.p. 106—107° (*semicarbazone*, m.p. 208°). (II) is hydrolysed to Me *iso*rhizonate. Me orsellinate in Et_2O with $ZnCl_2$ and HCN gives Me hæmotommate and iso*hæmotommate*, m.p. 130°. A. A. L.

Bitter substances. IV. Bitter substances of elecampane. K. F. W. Hansen (J. pr. Chem., 1933, [ii], **136**, 176—192).—Tetrahydroalantolactone (I) is converted by NaOEt in EtOH at 170—180° into an *isomeride*, m.p. 60—61°; the formation of other hydrocarbons in addition to eudalene by complete reduction to hydrocarbon and subsequent dehydrogenation does not therefore disprove the formula previously assigned (cf. A., 1931, 734; Ruzicka and Pieth, *ibid.*, 1301). The action of MgPhBr on (I) is accompanied by loss of H_2O from the carbinol to give the substance $C_{27}H_{34}O$, m.p. 161°, which does not add Br or H_2 (Pd), and gives indefinite products with O_3, and $COPh_2$ only with CrO_3–AcOH. Ozonisation of the crude mixture of dihydro-alanto- (II) and *-iso*-alanto-lactones (III), decomp. of the ozonide, and oxidation of the product with $KMnO_4$ in $COMe_2$ (cf. A., 1931, 1301) gives a *ketolactonic acid* (IV), m.p

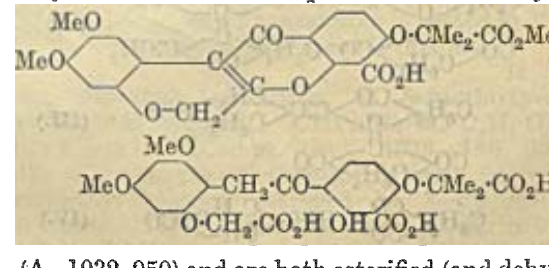
(IV.) 

190—191° [*Me* ester, b.p. 190—210°/1 mm. (CH_2N_2); this did not give a cryst. semicarbazone]. The annexed formula is therefore assigned to (II). The



product of isomerisation of (III) by addition and removal of HCl (cf. A., 1931,1065) also gave (IV) on similar treatment. The adducts from CH_2N_2 and alanto- and *iso*alanto-lactones (cf. A., 1931, 734) give with H_2–PtO_2 different resinous products (*picrates*, m.p. 158—159° and -168°, respectively), and hence presumably are not hydrogenated in ring B. Similarly, on elimination of N_2 by heating in CO_2 at their m.p. they give *substances*, $C_{16}H_{22}O_2$, m.p. 119—120°, and amorphous, which give yellow colorations with $C(NO_2)_4$ but do not take up H_2, and on oxidation give only succinic and not the expected *cyclo*propanecarboxylic acid. Treatment of *iso*alantolactone with KCN in aq. EtOH at the b.p. and alkaline hydrolysis of the resulting nitrile gives *dihydroisoalantolactonecarboxylic acid*, m.p. 174°, which readily gives 30% of theory of CO with warm H_2SO_4; this, however, is no criterion of the *tert.* nature of the CO_2H group, as (I) does the same. The CO_2H group is actually primary, and therefore attached at C_{15}, as is shown by the ease of hydrolysis of its Me ester. An impure carboxylic acid similarly prepared from an "80—90%" alantolactone also gave no evidence of the presence of a *tert.* CO_2H group. The second double linking in both alanto- and *iso*alanto-lactones is therefore at C_{13-15} [formula (II)]. H. A. P.

Tephrosin. III. Acidic derivatives of tephrosin. E. P. Clark (J. Amer. Chem. Soc., 1933, **55**, 759—762).—Oxidation of tephrosin by the method previously described (A., 1931, 491) gives an isomeric *tephrosindicarboxylic acid* (+$3H_2O$), m.p. 127—128°, m.p. (anhyd.) 175—177° (decomp.), in addition to that previously isolated. The acids probably differ in the orientation of the OH group (cf. this vol., 69): they furnish the same tephrosinmonocarboxylic acid



(A., 1932, 950) and are both esterified (and dehydrated) by MeOH–HCl to the *Me* ester (I), m.p. 220—221°,

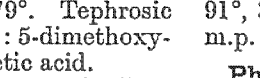
which is hydrolysed (10% EtOH–KOH) to the *tricarboxylic acid* (II), m.p. 178—179°. Tephrosic acid (A., 1932, 950) is probably 4 : 5-dimethoxy-2-2′ : 4′-dihydroxyphenacylphenoxyacetic acid. H. B.

Grayanotoxin, the poisonous constituent of the leaves of *Leucothoe grayana*, Max. I. M. YAMASHITA (Sci. Rep. Tohoku, 1932, **21**, 537—544).—The following facts, some of them contrary to the statements of Kubo (A., 1912, ii, 281), concerning the sternutatory substance, grayanotoxin, are reported: m.p. 238—238·5°, $[\alpha]_D^{15\cdot5}$ −3·15° in AcOH; it is $C_{23}H_{40}O_7$ or $C_{22}H_{36}O_7$, gives a Ac_3, m.p. 211·5—212·5°, and a Bz_3 derivative, m.p. 201—201·5°, contains an Ac group, but no CO, CO_2H, or phenolic OH group, and is saturated (Br, H_2–Pt black); it is not a glucoside or saponin. Its isolation is modified. R. S. C.

Rottlerin. A. HOFFMANN and L. FARI (Arch. Pharm., 1933, **271**, 97—101).—Analyses of hexa-acetylrottlerin, m.p. 212°, *tetrahydrorottlerin*, m.p. 200—201°, from rottlerin (H_2, Pd–C), and *hexa-acetyltetrahydrorottlerin*, m.p. 183—185°, indicate that rottlerin has the formula $C_{31}H_{30}O_8$ and not the usually accepted $C_{33}H_{30}O_9$ and that it contains two double linkings. S. C.

Menthone series. X. Complete optical resolution of *dl*-neomenthol by means of *l*-menthol. J. READ and W. J. GRUBB. **XI. Diagnosis and characterisation of the stereoisomeric menthols.** J. READ, W. J. GRUBB, and D. MALCOLM (J.C.S., 1933, 167—170, 170—173).—X. By successive application to *dl*-neomenthol of *l*- and *d*-menthoxyacetyl chloride, *l*- and *d*-neomenthol, $[\alpha]_D \mp 8{\cdot}65°$, have been obtained, purified through l-*neomenthyl* p-*nitrobenzoate*, m.p. 95°, $[\alpha]_D^{13}$ −17·9°, the pure *l*-neomenthol having $[\alpha]_D^{14}$ −8·82°. l-*Neomenthyl* 3 : 5-*dinitrobenzoate*, m.p. 153°, $[\alpha]_D^{13}$ −23·9°; d- (I), m.p. 116° (decomp.), $[\alpha]_D$ +8·9°, and l-*camphor*-10-*sulphonate*, m.p. 92° (decomp.), $[\alpha]_D$ −50·3°, and l-, m.p. 64°, $[\alpha]_D$ −81·1°, and d-*menthoxyacetate*, m.p. 28·5°, $[\alpha]_D$ +32·0°, of *l*-neomenthol have been prepared. (Of these only (I) shows anomalous rotatory dispersion.) Separation of *dl*-neo- and *dl-iso*- from *dl*-menthol is described and the crystallographic examination of *dl*-neomenthol (dl-*neomenthyl* p-*nitrobenzoate*, m.p. 78·5°; 3 : 5-*dinitrobenzoate*, m.p. 130°; and β-*naphthoate*, m.p. 98°) is given.

XI. The m.p. and optical rotatory powers of the following *l*-menthyl, *l*-neomenthyl, and *d-iso*menthyl derivatives are summarised: *d*- and *l*-camphor-10-sulphonate, *d*- and *l*-menthoxyacetate, *p*-nitrobenzoate, 3 : 5-dinitrobenzoate, and β-naphthoate. The use of these esters in the diagnosis and separation of the stereoisomeric menthols is reviewed, and certain numerical relationships exhibited by their optical rotatory powers are discussed. A method is given for the purification of *dl-iso*menthol (p-*nitrobenzoate*, m.p. 64·5°, and 3 : 5-dinitrobenzoate, m.p. 130°), and pure *d-iso*menthol, m.p. 82·5°, $[\alpha]_D$ +25·9° (p-*nitrobenzoate*, m.p. 54°, $[\alpha]_D^{15}$ +24·9°; d-, m.p. 30—31°, $[\alpha]_D$ +35·4°, and l-*camphor*-10-*sulphonate*, m.p. 33—34°, $[\alpha]_D^{15}$ −20·7°), has been obtained from *l*-piperitone. l-*Menthyl* l-α-*bromocamphor*-π-*sulphonate*, m.p. 96—97°, $[\alpha]_D$ −109·2°; dl-*menthyl* p-*nitrobenzoate*, m.p. 91°, 3 : 5-*dinitrobenzoate*, m.p. 121°, and β-*naphthoate*, m.p. 70°, are described. F. R. S.

Phenylcamphor and its derivatives. II. 4-*p*-Nitrophenylcamphor and 4-*p*-aminophenylcamphor. S. NAMETKIN and A. KITSCHKIN (J. pr. Chem., 1933, [ii], **136**, 137—142).—4-Phenylcamphor is converted by HNO_3 (*d* 1·5) at −12° to −6° into the p-NO_2-derivative, m.p. 150—151°, which is identified by oxidation by $KMnO_4$ to *p*-nitrobenzoic acid with intermediate formation of a *dilactone*, probably  , m.p. 155—157°. Reduction of the NO_2-compound gives 4-p-*aminophenylcamphor*, m.p. 144—144·5° (*Bz* derivative, m.p. 208—209°), a colourless base which forms red salts, and as an indicator gives the same end-point as phenolphthalein. Slow decomp. of the corresponding diazonium salt in presence of $CuSO_4$ gives 4-p-*hydroxyphenylcamphor*, m.p. 122—124°. H. A. P.

Stability of the oxide linking in tetrahydrofuran derivatives. R. PAUL (Compt. rend., 1932, **195**, 1289—1291; cf. A., 1932, 166).—2-Tetrahydrofurfuryl alcohol (I) is converted by HBr at 110° into a mixture of αε-dibromopentan-β-ol and αβε-tribromopentane (II) which is completely converted into (II) by PBr_5. Ring fission of (I) is effected by autoclaving with Ac_2O–$ZnCl_2$ at 200°, affording αβε-pentanetriol triacetate (55%). Treatment of the reaction product of tetrahydrofurfuryl bromide and Mg with H_2O gives tetrahydrosylvane, b.p. 80°/761 mm., d_{15}^{21} 0·853, n_D^{21} 1·40595. When the Mg compound is heated at 110—115° ring fission between O and the *sec.*-C atom occurs, and treatment with H_2O gives Δ^{δ}-*pentenol*, b.p. 139°/760 mm., in 50% yield (*allophanate*, m.p. 148°). A. C.

Preparation of furan from furoic acid. H. GILMAN and M. B. LOUSINIAN (Rec. trav. chim., 1933, **52**, 156—159).—Furoic acid heated with a little CuO or $CuSO_4$ (anhyd. or $+5H_2O$) in crude tar bases (b.p. >250°) at 170—220° gives 85% of furan. H. B.

Orientation in the furan nucleus. IV. Equivalence of the α-positions and of the β-positions in furan. H. GILMAN, R. R. BURTNER, and R. J. VANDERWAL (Rec. trav. chim., 1933, **52**, 151—155).—The *chloride*, b.p. 109—112°/4 mm., m.p. 69—70°, from Et(2) H furan-2 : 5-dicarboxylate (I) is reduced (H_2, Pd–$BaSO_4$, xylene) and then hydrolysed (6*N*-HCl), thus giving 5-aldehydo-2-furoic acid, m.p. 200° (decomp.), decarboxylated (quinoline and Cu-bronze at 210—220°) to furfuraldehyde. Furoic acid prepared by oxidation of this is identical with that obtained by successive decarboxylation and hydrolysis of (I), thus showing the equivalence of the 2- and 5-positions. The *chloride*, b.p. 149—151°/18 mm., from Et H 2 : 5-dimethylfuran-3 : 4-dicarboxylate (II) is similarly reduced to 3-aldehydo-2 : 5-dimethyl-4-furoic acid, m.p. 176°, which on successive decarboxylation and oxidation gives the same 2 : 5-dimethyl-3-furoic acid as is obtained by successive decarboxylation and hydrolysis of (II), thus showing the equivalence of the

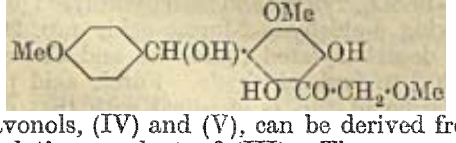
3- and 4-positions. Furan is considered to be a dynamic equilibrium mixture of several forms. H. B.

Orientation in the furan nucleus. H. GILMAN and R. R. BURTNER (J. Amer. Chem. Soc., 1933, **55**, 859—860).—3-Methylfuran gives a 2-chloromercuri-derivative, m.p. 142°, and with fuming HNO_3 affords 2-nitro-3-methylfuran. H. B.

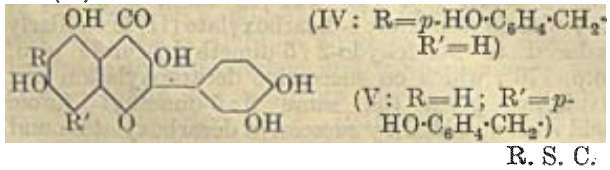
[Existence of isomeric 2 : 4-dinitrophenylhydrazones.] E. SIMON (Ber., 1933, **66**, [*B*], 320).—In reply to Bredereck (this vol., 154), it is pointed out that the existence of two forms of the 2 : 4-dinitrophenylhydrazones of furfuraldehyde and 2-methylfurfuraldehyde has been observed by the author (A., 1932, 763). H. W.

Halogen-substitution products of furfuraldehyde. H. SCHEIBLER, J. JESCHKE, and W. BEISER (J. pr. Chem., 1933, [ii], **136**, 232—240).—Furfurylidene diacetate (I) and Br in $CHCl_3$ give oily (?) open-chain compounds and a 10% yield of 5-*bromofurfuraldehyde*, m.p. 85°, b.p. 112°/16 mm. [*oxime*, m.p. 101°; *semicarbazone*, m.p. 215° (decomp.); *phenylhydrazone*, m.p. 80—85°], giving *s*-bromopyromucic acid by the Cannizzaro reaction. The prep. of tetraiodofuran is modified. The *triacetomercuri*-derivative of (I) with HCl, best in AcOH–EtOH, gives the *trichloromercuri*-derivative, and with I in Et_2O 5-*iodofurfuraldehyde*, m.p. 110°, and (?) *di-iodofurfuraldehyde*, sinters from 130°. R. S. C.

Constitution of fukugetin and garcinin. M. MURAKAMI (Proc. Imp. Acad. Tokyo, 1932, **8**, 500—502).—Fukugetin (I) and garcinin (II), both $C_{22}H_{16}O_8,2H_2O$, are obtained in 0·9 and 0·45% yield, respectively, from the bark of *Garcinia spicata* by extraction with MeOH, and therefore occur free and not as glucosides. (II) and (I) with Me_2SO_4 give cryst. Me_5 ethers, decomp. 141—142° (lit. oils), +1 and $1·5H_2O$, respectively; both ethers contain three OH groups (Zerevitinov) and, when oxidised, give some anisic acid; with boiling KOH–EtOH they give veratric acid (20% yield), anisic acid (poor yield), and a *phenol* (III), $C_{15}H_8O(OH)_3(OMe)_3$, giving with Me_2SO_4 a non-phenolic *compound*, $C_{15}H_8O(OH)(OMe)_5$, m.p. 161—163°, which is oxidised by $KMnO_4$ to anisic acid. (III) must contain the nucleus of phloroglucinol [which, with protocatechuic acid, is obtained from (I) and (II) by KOH–fusion], and the anisyl residue must be attached to the nucleus by a CH_2 group, since it is obtained as a secondary oxidation product on alkali-treatment; the last OH must be in a side-chain. (III) is, therefore,



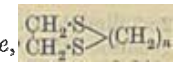
Two flavonols, (IV) and (V), can be derived from the demethylation product of (III). These may be (I) and (II).



R. S. C.

Carbohydrates and polysaccharides. XLIII. Cyclic acetal and ketal formation from α-phenylglycerol as further examples of the "ring partition principle." (MISS) M. E. PLATT and H. HIBBERT (Canad. J. Res., 1932, **7**, 629—642).—α-Phenylglycerol (I) condenses with $COMe_2$ (II) to give the two possible 5-membered ring-compounds only, and with *p*-NO_2·C_6H_4·CHO (III) to give the 6-membered ring (two stereoisomeric forms) and a mixture of 5-membered ring-compounds. Cinnamyl alcohol with BzO_2H in $CHCl_3$ at 0° gives (I), b.p. 184—186°/5 mm., m.p. 98—99° (lit. an oil), and with MeI and Ag_2O in Et_2O affords *cinnamyl Me ether*, b.p. 94—96°/8 mm., oxidised by $KMnO_4$ in aq. $COMe_2$ to *α-phenylglycerol γ-Me ether* (IV), m.p. 54°, b.p. 159°/8 mm. α-Phenylallyl alcohol with MeI and Ag_2O in Et_2O gives the *Me ether*, b.p. 77·5—78·5°/14—15 mm., oxidised by $KMnO_4$ to *α-phenylglycerol α-Me ether* (V), m.p. 68°. (I), (II), and anhyd. $CuSO_4$ at 60° give a mixture of *isopropylidene* derivatives, separable into fractions (*a*), b.p. 151—154°/11 mm., and (*b*), b.p. 154—157°/11 mm. Fraction (*a*), when methylated, gives a nearly pure ether, b.p. 115—117°/5—6 mm., which is hydrolysed to (V) by MeOH containing a drop of conc. HCl. Fraction (*b*) yields similarly an impure ether, b.p. 111—114°/5—6 mm., yielding some (IV) when hydrolysed. (V) and (II) in presence of anhyd. $CuSO_4$ give *βγ-isopropylidene-α-phenylglycerol α-Me ether*, b.p. 117—120°/7 mm., proved to be homogeneous by reconversion into pure (V) by hydrolysis. (IV) gives similarly *αβ-isopropylidene-α-phenylglycerol γ-Me ether*, b.p. 115—117°/7—8 mm., hydrolysed to pure (IV). (V) and (III) in presence of a drop of 40% H_2SO_4 give two stereoisomeric *forms* of *βγ-p-nitrobenzylidene-α-phenylglycerol α-Me ether*, m.p. 79—80° and 57—58°, respectively. (IV) gives similarly *αβ-p-nitrobenzylidene-α-phenylglycerol γ-Me ether*, an oil (cannot be distilled). (I) and (III) give a cryst. and an oily compound; the former, m.p. about 120—122° (*Bz* derivative, m.p. 141—143°), is a mixture of stereoisomeric *αγ-p-nitrobenzylidene-α-phenylglycerols* (VI), since it yields, when methylated, a mixture, m.p. 90—97°, of *β-Me ethers* (separable into *forms*, m.p. 96° and 113—115°, respectively), which is rather slowly hydrolysed by EtOH–HCl to *α-phenylglycerol β-Me ether*, b.p. 153—156°/5—6 mm., m.p. 44°. The last-named ether with (III) gives a mixture of *p*-nitrobenzylidene derivatives, m.p. 91—97°. The oily portion of (VI) gives an oily mixture of Me ethers which, when hydrolysed, gives a small amount of (IV); it yields oily acyl derivatives and with CPh_3Cl in dry C_5H_5N an oil, which gives an oil when methylated. R. S. C.

Cyclic and polymeric compounds from reactions of ethylene mercaptan with polymethylene halides. N. B. TUCKER and E. E. REID (J. Amer. Chem. Soc., 1933, **55**, 775—781).—CH_2Cl_2 (1 mol.) and $(·CH_2·SH)_2$ (I) (1 mol.) in EtOH–NaOEt give 26% of 1 : 3-dithiolan, m.p. —51°, and 0·2% of the cyclic *tetrasulphide*, $(CH_2)_2$  $(CH_2)_2$ (II, *n*—1), m.p. 121°. (I) and *s*-$C_2H_4Br_2$ similarly give 46% of 1 : 4-dithian (III), whilst trimethylene

dibromide affords the cyclic *disulphide*,  (IV, n—3), m.p. 47°, and 1% of the *tetrasulphide* (II, n=3), m.p. 122°. Tetra- and penta-methylene dibromides give traces of the *tetrasulphides* (II, n—4 and 5, respectively), m.p. 73° and 89°, respectively, whilst hexamethylene dibromide affords a trace of the *disulphide* (IV, n=6), m.p. 65°. In all the above experiments large amounts of polymeric material (mixtures which are partly separable by extraction with various solvents) of the probable composition $[\cdot(CH_2)_2\cdot S\cdot(CH_2)_n\cdot S\cdot]_x$ are produced. The polymeric material formed during the prep. of (I) is separated into fractions, m.p. 30—40° to 118—121°, some of which contain ·S·S· groupings. All the polymerides give (III) when heated with s-$C_2H_4Br_2$; (III) is also produced from most of the polymerides by heating in a current of dry HCl and from $(\cdot CH_2\cdot SBu)_2$ and s-$C_2H_4Br_2$. H. B.

Theory of the ease of ring formation of cyclic imines. H. Freundlich and G. Salomon (Ber., 1933, **66**, [*B*], 355—357).—Ruzicka's theory of the ease of formation of C rings (A., 1926, 727) is directly applicable to the production of cyclic imines from halogenoalkylamines (Freundlich and Kroepelin, A., 1926, 1010). Ph, attached to the same C atom as halogen, enormously enhances the ease of ring formation. H. W.

Action of ultra-violet light on pyridine. II. Reactions of photopyridine with naphthylamine- and aminonaphthol-sulphonic acids and with alkalis. H. Freytag (J. pr. Chem., 1933, [ii], **136**, 193—201; cf. A., 1932, 1149).—Photopyridine on filter-paper gives with acid solutions of naphthylamine- and aminonaphthol-sulphonic acids in concn. > 1 : 10,000 immediate colorations, which have a brown ground colour with α- and a red with β-$C_{10}H_7\cdot NH_2$ derivatives. The colours are weakened by alkali, but can usually be restored by acids. The compounds formed show characteristic fluorescence in filtered ultra-violet light. Alcoholic solutions of the acids give colorations only as the EtOH evaporates. Alkali prevents formation of the colour. β-Naphthylamine-7-sulphonic acid does not give a colour under any conditions. Photopyridine gives with NaOH, KOH, or $Ca(OH)_2$, but not with Na_2CO_3, Na_2HPO_4, aq. NH_3, or Na borate, a transient purple colour, removed by acid, and fluorescing purplish-violet in ultra-violet light. R. S. C.

Photochemical oxidation of α-picoline. H. John and G. Behmel (Ber., 1933, **66**, [*B*], 426—427).—Irradiation of a solution of α-picoline in C_6H_6 in presence of anthraquinone (I) yields 5·3% of picolinic acid and about 10% of dark resin, sol. in *N*-NaOH, sparingly sol. in 2*N*-HCl, which does not give a ppt. with picric acid in EtOH. 97·5% of (I) is recovered. H. W.

N-Alkylated 1 : 5-aminoketones and their conversion into piperidine derivatives. C. Mannich and K. T. Lesse (Arch. Pharm., 1933, **271**, 92—97).—β-Dimethylamino-αα-dimethylpropaldehyde (I) (cf. A., 1932, 503) and $COMe_2$ condense in presence of NaOEt giving *α-dimethylamino-ββ-dimethyl-Δ$^\gamma$-hexen-ε-one*, b.p. 100—105°/11 mm. [*hydrochloride*, m.p. 147°; *methiodide*, m.p. 172°; *oxime*, m.p. 69°; *oxime hydrochloride*, m.p. 177° (decomp.); *semicarbazone*, m.p. 134°; *semicarbazone hydrochloride*, m.p. 165°], hydrogenated (Pd–C) to *α-dimethylamino-ββ-dimethylhexan-ε-one*, b.p. 92°/13 mm. [*hydrochloride* (II), m.p. 100—101°; *chloroaurate*, m.p. 118·5°; *methiodide*, m.p. 133°; *oxime*, m.p. 58·5° (*hydrochloride*); *semicarbazone*, m.p. 128° (*hydrochloride*, m.p. 163°)]. *α-Dimethylamino-ββ-dimethylhexan-ε-ol*, b.p. 98°/12 mm. (*chloroaurate*, m.p. 116°; *p-nitrobenzoate hydrochloride*, m.p. 162°), is obtained by reducing (II) with Na–Hg in AcOH, and when treated with $SOCl_2$ affords 1 : 1 : 2 : 5 : 5-*pentamethylpiperidinium chloride*, m.p. 260° (*picrate*, m.p. 201°), which when heated decomposes into MeCl and 1 : 2 : 5 : 5-*tetramethylpiperidine*, b.p. 147—148° (*hydrochloride*, m.p. 221°). The following were prepared from (I) and COPhMe: *α-dimethylamino-ε-phenyl-ββ-dimethyl-Δ$^\gamma$-penten-ε-one*, b.p. 159—161°/0·8 mm. [*hydrochloride*, m.p. 162—163°; *oxime hydrochloride*, m.p. 178° (decomp.); *semicarbazone hydrochloride*, m.p. 195°], with a *compound*, $C_{23}H_{20}O_2N$, m.p. 102—103°, from (I) with 2 mols. COPhMe; *α-dimethylamino-ε-phenyl-ββ-dimethylpentan-ε-one*, b.p. 165—170°/10 mm. [*hydrochloride*, m.p. 149—150°; *semicarbazone hydrochloride*, m.p. 176° (decomp.)]; *α-dimethylamino-ε-phenyl-ββ-dimethylpentan-ε-ol*, m.p. 41°, b.p. 168—170°/15 mm. (*benzoate hydrochloride*, m.p. 91—92°); *ε-chloro-α-dimethylamino-ε-phenyl-ββ-dimethylpentane hydrochloride*, m.p. 150°; 2-*phenyl*-1 : 1 : 5 : 5-*tetramethylpiperidinium chloride*, m.p. above 250° (*chloroaurate*, m.p. 118°); 2-*phenyl*-1 : 5 : 5-*trimethylpiperidine*, b.p. 145—147°/12 mm. [*hydrochloride*, m.p. 148° (decomp.)]. *α-N-Piperidino-ββ-dimethyl-Δ$^\gamma$-hexen-ε-one*, b.p. 140—142°/12 mm. (*nitrate*, m.p. 105°), is obtained in a similar manner from β-piperidino-αα-dimethylpropaldehyde and $COMe_2$. S. C.

Piperidine derivatives. XII. Local anæsthetics derived from reduction products of 3-acetylpyridine. F. M. Strong and S. M. McElvain (J. Amer. Chem. Soc., 1933, **55**, 816—822).—Et nicotinoacetate (*hydrochloride*, m.p. 156—157·5°), from Et nicotinate, EtOAc, and NaOEt, is hydrolysed (10% HCl) to 3-acetylpyridine, b.p. 90—92°/5 mm., m.p. 13—14° (*hydrochloride*, m.p. 176—177·5°), which is reduced (H_2, PtO_2, H_2O) to 3-*α-hydroxyethylpyridine* (I), b.p. 123—125°/5 mm. [*hydrochloride*, m.p. 92—93°; *benzoate hydrochloride*, m.p. 175—176°; *p-nitrobenzoate hydrochloride*, m.p. 199—200°, reduced (Fe, dil. HCl) to the *p-aminobenzoate*, b.p. 227—230°/4 mm., m.p. 100—101°]. Reduction (H_2, PtO_2, dil. HCl) of (I) affords 3-ethylpiperidine (II) and two diastereoisomeric 3-*α-hydroxyethylpiperidines*, m.p. 58—61° and 103—104° (III) (*hydrochloride*, m.p. 152—153°). Successive treatment of (III) with the appropriate aralkyl or alkyl halide (in dioxan) and BzCl gives 1-*benzyl-*, m.p. 199—200°, 1-*β-phenylethyl-*, m.p. 196—198°, 1-*γ-phenylpropyl-*, m.p. 158—159°, 1-*ε-phenylamyl-*, m.p. 141—142°, and 1-*n-hexyl-*, m.p. 142—144°, -*α*-3-*piperidylethyl benzoate hydrochlorides*. γ-Chloropropyl benzoate and (II) give *γ-3-ethylpiperidinopropyl benzoate hydrochloride*, m.p. 164—165°. Pharmacological data for most of the above ester hydrochlorides are given. H. B.

Condensation of piperidinoacetonitrile with resorcinol and phloroglucinol. M. YAMASHITA (Sci. Rep. Tôhuku, 1932, **21**, 545—548).—Piperidinoacetonitrile with $ZnCl_2$, HCl, and resorcinol or phloroglucinol in AcOH gives the *hydrochlorides*, decomp. 243—245° and 244—245°, respectively, of *piperidinomethyl* 2 : 4-*dihydroxy-* and 2 : 4 : 6-*trihydroxy-phenyl ketone*. The free bases or their picrates could not be obtained. R. S. C.

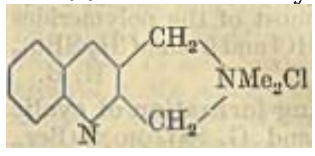
Indole group. I. Synthesis of 3-phenyloxindole. M. BAKUNIN and D. PECCERILLO (Gazzetta, 1933, **63**, 3—8).—α-Phenyl-*o*-nitrocinnamic acid when boiled for 12 hr. with a conc. solution of 10 times its wt. of $Ba(OH)_2$ gives 3-phenyldioxindole (A., 1912, i, 50), which with gaseous HCl gives a *substance* $C_{14}H_{10}O_2NEt$, m.p. 166°. The mechanism of the reaction is discussed. E. E. J. M.

Constitution of bisdiethylanilineisatin and of the green colouring matter obtained by oxidation. C. CANDEA (Gazzetta, 1933, **63**, 75—80).—Condensation of isatin with $NPhEt_2$ in presence of $ZnCl_2$ gives *bisdiethylanilinoisatin* [(4-*diethyl*-3 3-*bisaminophenyl*)*oxindole*], $(NH<\begin{matrix}C_6H_4\\CO\end{matrix}>C(C_6H_4\cdot NEt_2)_2$, which is colourless and gives on oxidation with PbO_2 a green colouring matter, probably $NH_2\cdot C_6H_3\cdot C(C_6H_4\cdot NEt_2)_2OH$ (A., 1886, 154). E. E. J. M.

Synthesis of 8-ethoxyquinoline-5-sulphonic acid. N. N. ORLOV and G. M. BOGDANOV (J. Appl. Chem., Russia, 1932, **5**, 803—808).—Quinoline-8-sulphonic acid, obtained (yield 90%) from C_9H_7N and fuming (18%) H_2SO_4 at 180°, is treated with solid NaOH, and 8-hydroxyquinoline (yield 64%) distilled in steam. On esterification with EtBr it yields 8-ethoxyquinoline, b.p. 220° (yield 68%), which is sulphonated with fuming H_2SO_4, the mixture being cooled. CH. ABS.

Quinoline derivatives. XLI. Derivatives of β-2-phenyl-4-quinolylaminoacetic acid. H. JOHN and G. BEHMEL (J. pr. Chem., 1933, [ii], **136**, 121—124; cf. this vol., 165).—The *acid chloride hydrochloride* (impure), m.p. 272°, *diethylamide*, m.p. 149°, β-*hydroxyethylamide*, m.p. 210°, and β-*chloroethyl* ester, m.p. 104°, are prepared. H. B.

Synthesis of quinoline derivatives with basic side-chains. C. MANNICH and B. REICHERT (Arch. Pharm., 1933, **271**, 116—127).—Me β-dimethylaminoethyl ketone, PhCHO, and NaOEt give α-*dimethylamino*-ε-*phenyl*-Δ^5-*penten*-γ-*one* (*hydrochloride*, m.p. 158°), also obtained from $NHMe_2$, paraformaldehyde, and benzylideneacetone, but in presence of HBr, α-*dimethylamino*-β-*benzylidenebutan*-γ-*one* (*hydrochloride*, m.p. 148°) is obtained, whereas *o*-$NO_2\cdot C_6H_4\cdot CHO$ with either catalyst furnishes α-*dimethylamino*-β-(*o*-*nitrobenzylidene*)*butan*-γ-*one* (I), m.p. 134° (decomp.) [*hydrochloride*, m.p. 158°, $+H_2O$, m.p. 122·5°; *phenylhydrazone hydrochloride*, $+H_2O$, m.p. 217° (decomp.); *semicarbazone*, m.p. 165° (decomp.).] The latter is reduced by $SnCl_2$ to 2-*methyl*-3-*dimethylaminomethylquinoline*, m.p. 56° [*dihydrobromide*, m.p. 250° (decomp.)], the *methiodide*, m.p. 233° (decomp.), of which is reduced to NMe_3 and 2 : 3-dimethylquinoline with Na–Hg, whilst hydrogenation (Pd–C) produces the *isooxime* of α-*dimethylamino*-β-(*o*-*hydroxylaminobenzylidene*)*butan*-γ-*one*, m.p. 102·5°, $+3H_2O$, m.p. 69° [*hydrochloride*, m.p. 214°; *methiodide*, m.p. 223° (decomp.)], which is extraordinarily resistant to acids or alkalis, but is converted by acylating agents into esters of 2-*hydroxymethyl*-3-*dimethylaminomethylquinoline*, m.p. 73° [*hydrochloride* (II), m.p. 219° (decomp.); *methiodide* m.p. 202° (decomp.); O-*benzoate* N-*hydrochloride*, m.p. 188°; O-*acetate* N-*hydrochloride*, m.p. 191°]. 2-*Chloromethyl*-3-*dimethylaminomethylquinoline dihydrochloride*, m.p. 197° (decomp.), obtained from (II) and $SOCl_2$, immediately undergoes intramol. alkylation on treatment with dil. KOH with the formation of the *chloride* of the tricyclic *base* (annexed formula),



m.p. 126°. 2-*Dimethylaminomethyl*-6-(*o*-*nitrobenzylidene*)*cyclohexanone hydrobromide*, m.p. 182°, is reduced by $SnCl_2$ to 1 : 2 : 3 : 4-*tetrahydro*-4-*methyleneacridine*, m.p. 167° (*hydrochloride*, m.p. 230°), from which 4-methylacridine is obtained by distillation with Zn. The above compounds have no particular pharmacological action. S. C.

Preparation of anti-malarials. J. N. RAY, G. S. AHLUWALIA, and B. D. KOCHHAR (J. pr. Chem., 1933, [ii], **136**, 117—119).—1-*Hydroxy*-β-*naphthyl o-nitrostyryl ketone*, m.p. 218°, from 2-acetyl-α-naphthol, *o*-$NO_2\cdot C_6H_4\cdot CHO$, and EtOH–NaOH, is reduced ($SnCl_2$–conc. HCl in EtOH–EtOAc) to 2-1′-*hydroxy*-β-*naphthylquinoline*, m.p. 150°. The following are similarly prepared: 1-*hydroxy*-β-*naphthyl* 2-*nitro*-4 : 5-*methylenedioxystyryl*, m.p. 205°, and 2-*nitro*-4 : 5-*dimethoxystyryl*, m.p. 245°, *ketones*; 1-*methoxy*-β-*naphthyl o-nitrostyryl*, m.p. 127°, and 2-*nitro*-4 : 5-*dimethoxystyryl*, m.p. 202°, *ketones*; 2-1′-*methoxy*-, m.p. 105°, 6 : 7-*methylenedioxy*-2-1′-*hydroxy*-, m.p. 235°, and 6 : 7-*dimethoxy*-2-1′-*methoxy*-, m.p. 170°, -β-*naphthylquinolines*. H. B.

Occurrence of phenanthridine in coal tar. J. SIELISCH and R. SANDKE (Ber., 1933, **66**, [*B*], 433—434).—The presence of phenanthridine (I) in the mixture of bases from anthracene oil is established. The amended data are recorded: (I) m.p. 106°, b.p. 349°/760 mm. ($HgCl_2$ compound, m.p. 195—207° after softening at 190°; methiodide, m.p. 204·5°.) H. W.

Activation of complex salts in aqueous solution. III. P. PFEIFFER and Y. NAKATSUKA (Ber., 1933, **66**, [*B*], 415—418; cf. A., 1932, 578).—The following *salts* have been prepared: [Ni phen$_3$]Br_2,$7H_2O$: [Ni phen$_3$]$(NO_3)_2$,$9H_2O$; [Ni phen$_3$]SO_4,$9H_2O$; [Ni phen$_3$]$(O\cdot SO_2\cdot C_{10}H_{15}O)_2$,$7H_2O$ (phen=phenanthroline). In H_2O they are activated in the opposite sense by NH_4 camphorsulphonate and NH_4 α-bromo-π-camphorsulphonate, respectively. *l*-Nicotine also causes activation. Attempts to separate an optically active [Ni phen$_3$] salt from the solution by KBr, HBr, or $NaNO_3$ were fruitless. With tridipyridyl compounds the optical effect is < with phenanthroline salts. Activation of Co and Mn phenanthroline salts is recorded. H. W.

Mechanism of the condensation between amines, formaldehyde, and ketones. K. Bodendorf and G. Koralewski (Arch. Pharm., 1933, **271**, 101—116).—A study of the reactions between $NHMe_2$ or piperidine with CH_2O and a series of ketones shows that neither dimethylaminomethyl alcohol (*picrate*, m.p. 91°; *hydrochloride*) nor piperidinomethyl alcohol (*hydrochloride*, m.p. 105—110°) is an intermediate product in the prep. of γ-ketotrialkylamines. γ-Ketobutanol and 2-hydroxymethyl*cyclo*hexanone react immediately with *sec.* amines, but not with amine salts, to form the corresponding ketoamines, whereas 1-*phenyl*-2 : 3-*dimethyl*-4-*hydroxymethyl*-5-*pyrazolone*, m.p. 159—160° (*Bz* derivative, m.p. 126°), and γ-phenyl-β-propen-α-ol (I) fail to react, although 1-phenyl-2 : 3-dimethyl-5-pyrazolone reacts normally with CH_2O and $NHMe_2$. The latter reacts with Ph vinyl ketone giving ω-dimethylaminopropiophenone, whilst (I) reacts abnormally with piperidine forming a *substance*, m.p. 74° (*picrate*, m.p. 178—179°), and not the expected ω-piperidino-α-phenylallylene. Benzoylacetone and Et acetoacetate react with CH_2O and $NHMe_2$ to give the corresponding bismethylene derivatives. The mechanism of the condensation is explained by assuming the formation of a loose 4-membered, semi-acetal ring complex between CH_2O and the enol modification of the ketone, which then reacts with the *sec.* amine, the ring opening in the process. S. C.

Molecular compound from pyramidone and diallylbarbituric acid. P. Pfeiffer and E. Ochiai (J. pr. Chem., 1933, [ii], **136**, 129—132).—The *compound* $C_{13}H_{17}ON_3,C_{10}H_{12}O_3N_2$, m.p. 131° (softens at 92·5°), is prepared by interaction of pyramidone with diallylbarbituric acid in $COMe_2$. By the thermal method of Rheinboldt (cf. A., 1926, i, 25) it is shown to be a definite compound, but to be decomposed on fusion with separation of one of its constituents. H. A. P.

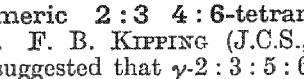
Crystalline organic thio-salts of As, Mo, Sn, Te, W, and Ge. L. Debucquet and L. Velluz (Bull. Soc. chim., 1932, [iv], **51**, 1565—1571).—The following *compounds* have been prepared by the prolonged action of H_2S on the solution obtained by boiling the metal oxide with piperidine or piperazine hydrate: $MoS_3,C_4H_{10}N_2,H_2S$, $MoS_3,2C_5H_{11}N,H_2S$, $2WS_3,2C_4H_{10}N_2,H_2S$, $WS_3,2C_4H_{10}N_2,H_2S$, $As_2S_3,C_4H_{10}N_2,H_2S$, $As_2S_5,3C_4H_{10}N_2,3H_2S$, $As_2S_3,2C_5H_{11}N,H_2S$, $SnS_2,C_4H_{10}N_2,H_2S$, $TeS_2,C_4H_{10}N_2,H_2S$, $GeS_2,C_4H_{10}N_2,H_2S$. E. S. H.

Stereoisomeric 2 : 3 4 : 6-tetramethylpiperazines. IV. F. B. Kipping (J.C.S., 1933, 143—144).—It is suggested that γ-2 : 3 : 5 : 6-tetramethylpiperazine has the constitution previously assigned (cf. A., 1931, 851; 1932, 754), since it has not been resolved; α-2 : 3 : 5 : 6-tetramethylpiperazine has also resisted resolution. The following have been prepared: d-*camphor*-10-*sulphonate*, m.p. 248—251°, 258—260°, $[\alpha]_{5461}$ +14·9°, and d-α-*bromocamphor*-π-*sulphonate*, m.p. 256—257°, $[\alpha]_{5461}$ +62·5°, of γ-2 : 3 : 5 : 6-tetramethylpiperazine; *di*-d-*camphor*-10-*sulphonate*, m.p. 261°, $[\alpha]_{5461}$ +20·0°, and *d*-tartrate, m.p. 164—165°, $[\alpha]_{5461}$ +20·3°, of γ-2 : 3 : 4 : 5 : 6-pentamethylpiperazine; γ-2 : 3 : 4 : 5 : 6-*pentamethylpiperazine*-d-*methylenecamphor*, m.p. 123°, $[\alpha]_{5461}$ +509° (which gives with Br the *dihydrobromide*, m.p. 268—270°, of the base), and its *d*-camphor-10-sulphonate, m.p. 263—264°, $[\alpha]_{5461}$ +266° and *d*-α-bromocamphor-π-sulphonate, m.p. 257°, $[\alpha]_{5461}$ 278°; *d*-camphor-10-sulphonate, m.p. 213—215° (decomp.) $[\alpha]_{5461}$ +15·2°, and d-α-*bromocamphor*-π-*sulphonate*, m.p. 207° $[\alpha]_{5461}$ +68·5°, of 1-nitroso-γ-2 : 3 : 4 : 5 : 6-pentamethylpiperazine; *d*-camphor-10-sulphonate, m.p. 208—211°, $[\alpha]_{5461}$ +28·4°, *d*-α-bromocamphor-π-sulphonate, m.p. 204—205°, $[\alpha]_{5161}$ +63·6°, *d*-α-chlorocamphor-π-sulphonate, m.p. 215—216°, [α] +49·5°, and *d*-tartrate, m.p. 174—175°, $[\alpha]_{5461}$ +9·7°, of *p*-toluenesulphonyl-γ-2 : 3 : 4 : 5 : 6-pentamethylpiperazine; *mono*-, m.p. 113—114°, $[\alpha]_{5461}$ +17·4°, and *di*-d-*camphor*-10-*sulphonate*, m.p. > 320°, $[\alpha]_{5461}$ +23·8°, *mono*-, m.p. 230—231°, $[\alpha]_{5461}$ +73·0°, and *di*-d-α-*bromocamphor*-π-*sulphonate*, m.p. >320°, $[\alpha]_{5461}$ +89·7°, of α-2 : 3 : 5 : 6-tetramethylpiperazine; and α-2 : 3 : 5 : 6-*tetramethylpiperazinedi*-d-*methylenecamphor*, m.p. 320°, +822°. F. R. S.

Action of bromine on 2-nitrofluorene. L. Guglialmelli and M. R. Franco (Anal. Farm. Bioquim., 1932, **3**, 1—23; Chem. Zentr., 1932, ii, 2820).—9-Bromo-2-nitrofluorene is accompanied, when the quantity of solvent (AcOH) is restricted, by 2-bromo-7-nitro- and (?) 5-bromo-2-nitro- (m.p. 100—110°) -fluorene. The mobility of the Br atom in 9-bromo-2-nitrofluorene was demonstrated by condensation with amines. 2-*Nitro*-9-*piperidino*-, m.p. 311°, and -9-*phenylmethylamino*-, m.p. 147°, -*fluorene*, and *piperazine* derivatives, $C_{17}H_{17}O_2N_3$, m.p. 225—230°, and $C_{30}H_{24}O_4N_4$, m.p. 230°, are described. A. A. E.

Reaction of 2 : 4-dichloroquinazoline with sodium azide. R. Stolle and F. Hanusch (J. pr. Chem., 1933, [ii], **136**, 120).—2-Chloro-4-ethoxyquinazoline and NaN_3 in EtOH give 4-*ethoxy*-1 : 2-*tetrazolo*-1 : 2-*dihydroquinazoline*, m.p. 165°, hydrolysed by 2*N*-NaOH to the same OH-derivative as is obtained from azidotetrazolodihydroquinazoline (I) (this vol., 404) and NaOEt. (I) is, therefore, 4-azido-1 : 2-tetrazolo-1 : 2-dihydroquinazoline. H. B.

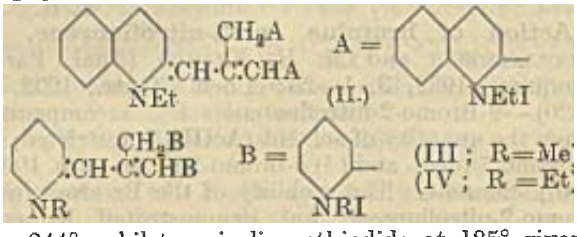
Constitution of bases obtained from protein. IV. F. Wrede, E. Bruch, and G. Feuerriegel (Z. physiol. Chem., 1933, **214**, 63—70; cf. A., 1932, 624).—Electrolytic reduction in 20% H_2SO_4 of prolyl-leucine anhydride gave 5-*iso*butyl-1′ : 2′-pyrrolidino-1 : 2-piperazine,



b.p. 110 /15 mm. (*chloroaurate*, m.p. 197°), identical with the base $C_{11}H_{22}N_2$ from protein. *dl*-Valine and bromo*iso*hexoyl bromide give a mixture of racemic *bromoisohexoylvalines*, m.p. 185°, which in 25% aq. NH_3 affords racemic leucylvaline (I), m.p. 272—274°. The Et ester hydrochloride of (I) with NH_3 in MeOH gives *leucylvaline anhydride* (II), m.p. 277°. Electrolytic reduction of (II) yields 2-iso*propyl*-5-iso*butylpiperazine* (*chloroaurate*, blackens at 245° without melting). Similarly, racemic *bromoisovaleroylphenylalanine*, m.p. 147° (obtained from bromo*iso*hexoylvaline and

phenylalanine), gives racemic *valylphenylalanine*, m.p. 235° (decomp.), which was converted into the *anhydride* (III), m.p. 247—248°. Reduction of (III) gave 2-*benzyl*-5-*isopropylpiperazine* [*chloroaurate*, sinters at about 230° (decomp.)]. By corresponding stages the Pr derivative was obtained: *bromovaleryl bromide*, b.p. 186° (decomp.), racemic *bromovalerylphenylalanine*, m.p. 116°, racemic *norvalylphenylalanine*, m.p. 241°, *anhydride*, m.p. 238°, 2-*benzyl*-5-*propylpiperazine* (*chloroaurate*, black mass at 240°).

Cyanine dyes. V. Lepidyl-, quinaldyl-, and picolyl-carbocyanines. T. Ogata (Proc. Imp. Acad. Tokyo, 1932, **8**, 503—506; cf. this vol., 285).—Lepidine ethiodide (0·002 mol.) and $CH(OEt)_3$ (I) (0·004 mol.) in AcOH or $EtCO_2H$ (0·3 c.c.) at 165° give a 67% yield of neocyanine ethiodide, the yield being poorer in other solvents and 0 in non-acidic solution. (I), quinaldine ethiodide, and succinic acid at 170° give similarly the *dye* (II), m.p. 244·5° (decomp.), in 4% yield. (I), α-picoline methiodide, and anhyd. $H_2C_2O_4$ at 175—178° give a 4% yield of the *dye* (III),



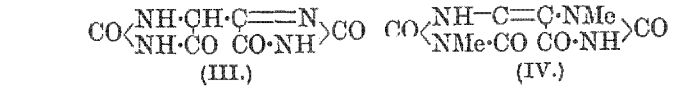
m.p. 244°, whilst α-picoline ethiodide at 185° gives the *dye* (IV), m.p. 227°, in 23% yield. The dyes are photographic sensitisers, the sensitivity max. for (II) and (III) being 740 and 640 mμ, respectively.

R. S. C.

Condensation of aldehydes with hydrazones. A. Giacalone (Gazzetta, 1933, **63**, 20—22).—PhCHO condenses with 1 mol. of its *p*-tolylhydrazone in presence of $ZnCl_2$, giving a *compound* $C_{42}H_{36}N_4$, m.p. 245°, which does not react with Ac_2O. Alternative formulæ are suggested.

E. E. J. M.

Condensation of hydantoins with parabanic acids. H. Biltz, F. Lachmann, and (in part) R. Lemberg (J. pr. Chem., 1933, [ii], **136**, 217—231).—Parabanic acid (I) and hydantoin (II) at 160° give 1 : 5-*dehydro*-5 : 5′-*dihydantyl*, m.p. 222° [*Na* (+$4H_2O$), m.p. about 140° (decomp.), *K*, and *NH*$_4$, m.p. 240° (decomp.), salts], probably (III), since it is oxidised by HNO_3, CrO_3, or H_2O_2–AcOH to (I) (1 mol. only) and reduced by HI–PH_4I to (II) (1 mol. only). CH_2N_2 gives the 3 : 1′ : 3′-*Me*$_3$ derivative, m.p. 175—176°, stable to acids, Ac_2O, and Zeisel HI, slowly hydrolysed by alkali to NH_3 and NH_2Me, and oxidised by HNO_3 to dimethylparabanic acid. (III) with boiling Ac_2O gives the 2(?2′) : 1′ : 3′-*Ac*$_3$ derivative, m.p. 95—96°, which with boiling EtOH gives the (?)1′ : 3′-*Ac*$_2$ derivative, m.p. 152°, hydrolysed by EtOH–HCl to (III). 1-Methylhydantoin and 1-

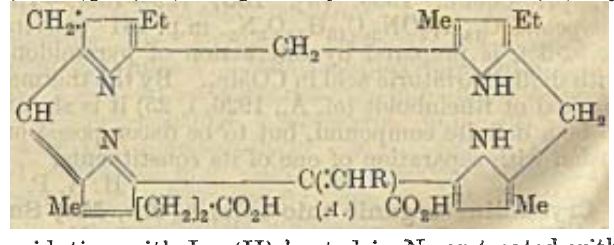


methylparabanic acid at 220° gives 1(?3) : 3′-*dimethyl*-5 : 5 *dihydantylidene* (IV), m.p. 273° [*Ac* derivative (V), m.p. 213°, hydrolysed by EtOH–HCl; *Et*$_2$ derivative, m.p. 126—127°], giving with CH_2N_2, 1 : 3 : 1′ : 3′-*tetramethyl*-5 : 5′-*dihydantylidene*, m.p. 217—218° (OMe test negative), also obtained from (V) and CH_2N_2, oxidised by H_2O_2 or Br–H_2O to dimethylparabanic acid (2 mols.), and giving with Cl_2–MeOH 5 : 5′-*dimethoxy*-1 : 3 : 1′ : 3′-*tetramethyl*-5 : 5′-*dihydantylidene*, m.p. 182°. Other Me derivatives of (I) and (II) do not condense. The prep. of 3-methylhydantoin is modified.

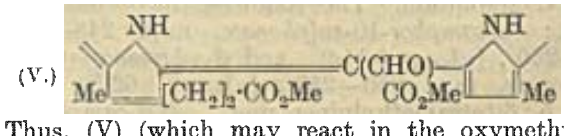
R. S. C.

Chlorophyll. XXX. Pyrrorhodin and derivatives. H. Fischer and P. Pratesi. **XXXI. Chlorin e_4, chloroporphyrin e_5, and *iso*phæoporphyrin a_5.** H. Fischer, J. Heckmaier, and E. Plotz (Annalen, 1933, **500**, 203—215, 215—252).—XXX. Pyrrorhodin (A., 1928, 1383) (*Fe* and *Cu* salts; *oxime*) [now prepared by dehydration of pyrroporphyrin (I) with oleum] and Br in Et_2O–AcOH give β-bromopyrrorhodin, which with MeOH–KOH in C_5H_5N affords pyrroverdin. Bromopyrroporphyrin XV is dehydrated by oleum to *bromopyrrorhodin* XV, decomp. >250° (*Fe* and *Cu* salts) (which reacts difficultly or not at all with NH_2OH), and is converted by MeOH–KOH at 130—135° into (I). Acetylpyrroporphyrin (*oxime*) is similarly dehydrated (to the not isolated verdin) only with difficulty.

XXXI. Successive treatment of chlorin *e* (*A*, R=CO_2H) with HI–AcOH in N_2 at 50° and NaOAc gives chloroporphyrin e_6 (II) and a little chloroporphyrin e_5 (III) [*Cu* salt; impure *Ac* derivative; (mono)*Me* ester (*Bz* derivative), esterified (Me_2SO_4) to (V) (below)]; (III) is probably formed from (II) by

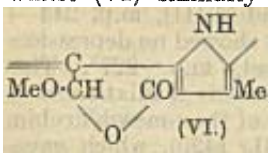


oxidation with I. (II) heated in N_2 or treated with HCO_2H gives chloroporphyrin e_4 (IV). Chlorin *e*, which is isomeric with (II), is decarboxylated by boiling with C_5H_5N to *chlorin* e_4 (*A*, R=H), m.p. 250°, decomp. 270—280° [*Me*$_2$ ester, m.p. 166° (crystallographic data by Steinmetz)], which is isomeric with, and convertible (HI–AcOH) into, (IV). The Me_2 ester of (IV) is converted by I in AcOH into the above Me ester of (III), whilst (III) is reduced by HI–AcOH at 50° to (IV). These results suggest that (III) is γ-hydroxymethylrhodoporphyrin rather than γ-formylrhodoporphyrin (A., 1931, 744); the question is undecided but the latter formulation is favoured by spectroscopic data, analytical data, and the following results. (III) affords two different Me_2 esters when treated with CH_2N_2 and MeOH–HCl, which can be formulated as (V) and (VI), respectively.



Thus, (V) (which may react in the oxymethylene form) is reduced (HI–AcOH) to rhodoporphyrin,

whilst (VI) similarly gives (IV). The *hæmin* (*Cu* salt) of (V) affords rhodoporphyrin when freed from Fe by HBr–AcOH [but gives (III) using conc. H_2SO_4] and reacts with NH_2OH (shown spectroscopically), whilst the *hæmin* (*Cu* salt) of (VI) gives (HBr–AcOH) (III) and does not react with NH_2OH. (V), unlike (VI), yields rhodoporphyrin Me_2 ester when heated to 270°.

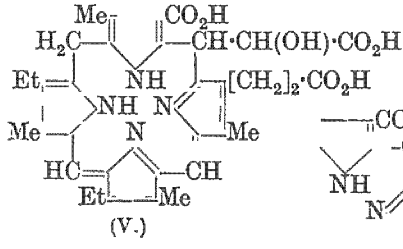


(VI.)

The constitution of phæoporphyrin a_6 (VII) is discussed (cf. A., 1931, 1431; 1932, 757). Reduction (HI–AcOH at 65°) of native phæophorbide gives (probably) the unstable *iso*phæoporphyrin a_5 (VIII), which passes readily into phæoporphyrin a_5 (IX) and with NH_2OH affords the oxime of (IX); (VIII) cannot therefore be identical with the protophæoporphyrin a_5 of Stoll and Wiedemann (A., 1932, 1265). (IX) reacts with NH_2OH at a much faster rate than (VII). Benzoylation or addition of HCN to phæoporphyrin a_6 Me Et ester Et ether (X) could not be accomplished; the Me_2 ester Et ether and MeOH–conc. HCl give (probably) *iso*phæoporphyrin a_7 (spectrum). The change undergone by several chlorophyll porphyrins on treatment with alkali can easily be confused with the phase test. Treatment of phæoporphyrin a_5 Me_2 ester in C_5H_5N with 30% MeOH–KOH causes the ester to pass into the alkali, giving a greenish-yellow solution (which gradually turns brownish-red), from which the unchanged ester can be recovered; (X), phæoporphyrin a_5 Me ester (XI), and phylloerythrin ester show a similar colour reaction. (XI) and benzoquinone in EtOH–C_5H_5N give phæoporphyrin a_7 as the main product. The following substances (all of which give a negative phase test) are allomerised by EtOH–benzoquinone in N_2 [subsequent reduction (HI–AcOH) gives small amounts of (VII) (cf. A., 1932, 756)]: methylchlorophyllide *a*, the phyllin from methylchlorophyllide *a*+*b*, phæophytin *a*+*b* and its phyllin, phæophorbide *a* and *a*+*b*, and the phyllins of native phæophorbide *a* and of methylphæphorbide *a*. Allomerisation of methylchlorophyllide *a*+*b* with O_2 in EtOH gives (after reduction) phæoporphyrin a_7, whilst reduction of the product formed by the action of O_2 on allomerised (EtOH–benzoquinone in N_2) ethylchlorophyllide affords (X). Methylchlorophyllide and MeOH–benzoquinone in absence of air give (after reduction) *phæoporphyrin* a_6 *Me*$_2$ ester *Me ether*, m.p. 259°. The *Cu* salt of phæoporphyrin a_6 Me Et ester Me ether has m.p. 192° (not sharp). H. B.

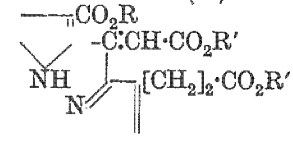
Chlorophyll series. IX. Transformations establishing the nature of the nucleus. J. B. Conant and C. F. Bailey. **X. Esters of chlorin *e*.** J. B. Conant and K. F. Armstrong. **XI. Position of the [carbo]methoxyl group.** J. B. Conant and E. M. Dietz (J. Amer. Chem. Soc., 1933, 55, 795—800, 829—839, 839—849).—IX. Chlorin *f* is a dihydroporphyrin, since it is dehydrogenated by alkaline $K_3Fe(CN)_6$ or by O_2 and 10% NaOH containing MgO and ZnO to iso*rhodoporphyrin* (I), $C_{32}H_{34}O_4N_4$ [*Me*$_2$ ester (II), m.p. (block) 264° (softens at 261°)], which is identical with the porphyrin previously obtained (A., 1931, 369) as a by-product during the pyrolysis of phæopurpurin 7, and with the *ψ*-verdoporphyrin of Fischer *et al.* (A., 1931, 1431). It follows, therefore, that the nucleus of the phæophorbides and chlorophyll *a* is a dihydroporphyrin ring. Reduction of (I) with HI–AcOH and oxidation (air) of the resulting leuco-compound gives rhodo porphyrin, also formed [with pyrroporphyrin (III)] from (II), 25% MeOH–KOH, C_5H_5N, MgO, and ZnO at 185—190°. (I) and boiling anthracene afford (III) and an unidentified porphyrin. Chlorin *e* is considered to be a dihydro*iso*rhodoporphyrin with a lactic [glycollic ?] acid residue on one of the bridge C atoms [see Part X], since it is oxidised by $K_3Mo(CN)_8$ to CO_2 and chlorin *k* (IV) (cf. A., 1931, 1075). Reduction of (IV) with HI–AcOH and oxidation of the resulting leuco-compound gives chloroporphyrin e_4 and another porphyrin (or mixture). Rhodin *g* is oxidised [$K_3Mo(CN)_8$] to *rhodin* n, $C_{33}H_{32}O_5N_4$, which contains a CO group, since its (mono)*Me* ester, sinters at 140—150°, gives a *semicarbazone*.

X. The Me_3 esters prepared by esterification (CH_2N_2; Me_2SO_4; MeOH–HCl) of chlorin *e* (V) are identical, since they give the same *Cu* salt, m.p. 218—220°; the *Zn* salts from the esters prepared as quoted have m.p. 237—238°, 243—245°, and 236—237°, respectively, but depression does not occur with any two. The *Cu* salt of chlorin *e* Et_3 ester has m.p. 154—155°. Hydrolysis of chlorin *e* Me_3 ester (VI) (*A*, R=R′=R″=Me) with cold MeOH–KOH–C_5H_5N in N_2 regenerates (V), whilst partial hydrolysis (similar conditions) gives *chlorin* e α-*Me* ester (*A*, R=R″=H, R′=Me), which is esterified by CH_2N_2 to (VI) and by diazoethane to the α-*Me Et*$_2$ ester, m.p. 152° [*Cu* salt, m.p. (block) 166·5—167°], is converted by heating with Ph_2 at 215° in N_2 into (by loss of 1 mol. of



(V.)

(A.)

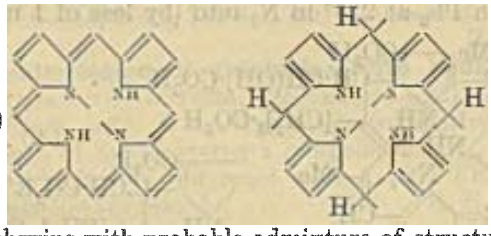


CO_2) the *Me* ester of pyrochlorin *e* carboxylic acid [*Me*$_2$ ester, m.p. (block) 206—208°], and when oxidised [$K_3Mo(CN)_8$] does not give CO_2, but affords a *chlorin*, $C_{35}H_{36}O_6N_4$ (*Me* ester, m.p. 260—262°). Partial methylation (CH_2N_2 in Et_2O–C_5H_5N) of (V) affords *chlorin* e β-*Me* ester (VII) (*A*, R=Me, R′=R″=H), which is esterified by CH_2N_2 to (VI) and by diazoethane to the β-*Me Et*$_2$ ester, m.p. 155—157° (*Cu* salt, m.p. 187—189°). (VII) when heated with Ph_2 at 245—265° in N_2 gives chloroporphyrin e_4 Me ester and an unidentified porphyrin Me ester, whilst oxidation [$K_3Mo(CN)_8$] affords CO_2 and a product which appears to form an insol. complex with the reagent. Hydrolysis of (VI) with cold 12% HCl yields *chlorin* e *Me*$_2$ ester (*A*, R=R′=Me, R″=H), sinters >230° (block), which is not oxidised by $K_3Mo(CN)_8$ and gives only a little CO_2 when heated with Ph_2. The group >C:CH·CO_2R′ in *A* is probably interconverted into >CH·CH(OH)·CO_2R′ in solution.

XI. Pure methylphæophorbide *a* (VIII), $C_{36}H_{38}O_5N_4$

(details of prep. given), does not give phæopurpurin 7 when oxidised [$K_3Mo(CN)_8$]; that previously isolated (A., 1931, 1075) arises from an impurity in (VIII). Oxidative hydrolysis of (VIII) with O_2 and dil. MeOH–KOH in cold aq. C_5H_5N gives *chlorin* g (mono)*Me* ester (IX), $C_{35}H_{38}O_7N_4$, which is stable in solution and converted by CH_2N_2 and diazoethane into dimethyl- and diethyl-phæopurpurin 7 (X), respectively. Pyrolysis of (IX) in boiling Ph_2 and N_2 affords mainly *iso*rhodoporphyrin, whilst (X) and C_5H_5N–Na_2CO_3 give iso*rhodoporphyrin* Et_2 ester, m.p. 240—241°. These results show that the CO_2Me group in (IX) is part of the bridge grouping, and thus confirm the position of the Me group in chlorophyll *a* assigned by Fischer *et al.* (A., 1931, 1432). Phæopurpurin 7 (prep. from various sources described) and boiling Ph_2 give CO, CO_2, and chlorin *f* Me ester; it contains a CO_2Me group attached to a pyrrole ring, and its precursor appears to be a second form of chlorophyll *a* (designated a_2; structure suggested). Chlorophyll *a* (a_1) is best represented by the alternative formula previously suggested (A., 1931, 1075). Stoll and Wiedemann's formulæ (A., 1932, 1265) for chlorophylls *a* and *b* are unlikely; contrary to these authors, hydrolysis of phæophorbide *a* gives chlorin *e* even in presence of a reducing agent. Contrary to Fischer *et al.* (*ibid.*, 1263), the conversion of phæopurpurin 7 into 18 has not been observed. H. B.

Constitution of the porphyrins. E. Clar and F. Haurowitz (Ber., 1933, **66**, [*B*], 331—334).—The absorption spectra of tetramethylhæmatoporphyrin in MeOH and of mesoporphyrin in HCl–EtOH and NH_3–EtOH indicate the constitution (I) for the

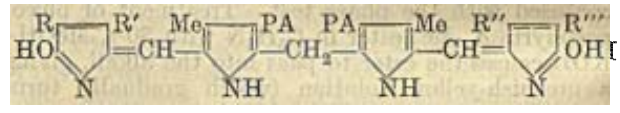


(I.) (II.)

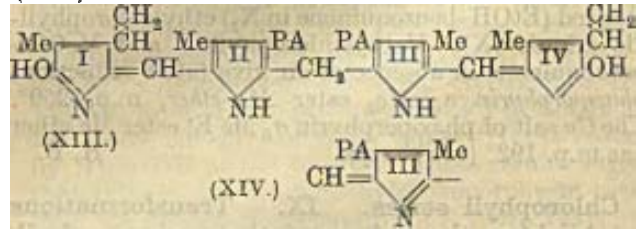
porphyrins with probable admixture of structure (II) in small proportion. H. W.

Constitution of bile pigment. X. Constitution of bilirubin. Syntheses of neo- and *iso*-neo-xanthobilirubic acid. W. Siedel and H. Fischer (Z. physiol. Chem., 1933, **214**, 145—172; cf. this vol., 76).—With Br in AcOH, 2-*aldehydo*-4-*methyl*-3-*ethylpyrrole*-5-*carboxylic acid* (I), decomp. 199° (obtained by hydrolysis of the Et ester), yields 5-*bromo*-2-*aldehydo*-4-*methyl*-3-*ethylpyrrole* (II), m.p. 115° (*aldazine*, m.p. 200°), and 5 : 5′-*dibromo*-4 : 4′-*dimethyl*-3 : 3′-*diethylpyrromethene* (III), m.p. 184° (*Cu* salt). (II) combines with opsopyrrolecarboxylic acid in presence of HBr to form the *hydrobromide* (IV), not melted at 300°, of 5-*bromo*-4 : 3′-*dimethyl*-3-*ethyl*-4′-β-*carboxyethylpyrromethene* (*picrate*, m.p. 199°). Heated to 180° with NaOMe, (IV) gives xanthobilirubic acid, under reflux *neoxanthobilirubic acid Me ether* (V), m.p. 160° (*Me* ester, m.p. 70°). Hydrogenation of (V) with HI–AcOH gives neobilirubic acid (VI), the benzylidene derivative (VII), m.p. 276°, of which showed no depression with the analytical compound, m.p. 248°. With 10% NaOMe at 150°, neoxanthobilirubic acid (VIII), m.p. 244—246°, was obtained directly. It showed no depression with the analytical compound, m.p. 227°. The suspicion that the analytical acid is a mixture was confirmed by a resorcinol fusion of the *s*-mesobilirubin of Fischer and Adler (A., 1931, 1420), which gave iso*neoxanthobilirubic acid* (IX), m.p. 242°, which when mixed with (VIII) gave the m.p. of the analytical acid. (IX) was converted into iso*neobilirubic acid* [*benzylidene* compound, m.p. 273°, gave no depression with the analytical product, but m.p. 246—247° with (VII)]. Neoxanthobilirubic acid forms a *Me* ester, m.p. 174°, (IX) a *Me* ester (X), m.p. 205°. The analytical ester, m.p. 190—191°, recryst. from MeOH–EtOH gave a final product of m.p. 203°, identical with (X). Thus all products obtained from analytical neoxanthobilirubic acid must be mixtures of three isomerides (two symmetrical and one unsymmetrical). Similarly, analytical "xanthobilirubic acid" contains two isomerides, *xanthobilirubic acid*, m.p. 287° (*Me* ester, m.p. 212°), and iso*xanthobilirubic acid*, m.p. 289° (*Me* ester, m.p. 189°).

The known mesobilirubins have the following constitution:



For mesobilirubin-XIIIα (XI) R=R‴=Me, R′=R″=Et; for -IIIα R′=R″=Me, R=R‴=Et; for -IXα R=R″=Me, R′=R‴=Et (α denotes ring opening at the α-methine bridge); PA=·CH_2·CH_2·CO_2H. (XI) is obtained by the various methods given and is identical with Fischer and Adler's product. Treatment of the Me ether of neoxanthobilirubic acid with CH_2O and HCl gives the *Me*$_2$ *ether hydrochloride* of (XI), m.p. 295° [free *base* (XII), m.p. 193°, *Me*$_2$ ester of diether, m.p. 144°]. The Gmelin reaction of (XI) remains at the green phase, which is ascribed to the lack of a quinonoid form. Hydrolysis of (XII) with $AlCl_3$ in *cyclo*hexane affords (XI). Bilirubin (XIII) and uteroverdin (XIV) are formulated:



(XIII.)

(XIV.)

Ring closure to a furan ring by loss of H_2 between the OH and vinyl groups of ring IV is not excluded.

Reactions of 2 : 4-dichloroquinazoline and 2 : 3-dichloroquinoxaline with sodium azide. R. Stollé and F. Hanusch (J. pr. Chem., 1933, **136**, 9—14).—Interaction of 4-chloro-1 : 2-dihydro-1 : 2-tetrazolophthalazine (A., 1932, 1266) with N_2H_4 at 130° gives the 4-*hydrazino*-compound, m.p. 287° (*CHPh.* derivative, m.p. 300°), converted by HN_3 into the 4-azido-compound (*loc. cit.*). With 2 : 4-

dichloroquinazoline NaN_3 gives 4(or 1)-*azidodihydro*-1 : 2(or 3 : 4)-*tetrazoloquinazoline*, m.p. 145° (decomp.), which, when heated with NaOEt in EtOH, gives the 4(or 1)-*OH*-compound, m.p. 243° (decomp.). Similarly, from 2 : 3-dichloroquinoxaline, 3-*azido*-, m.p. 265° (decomp.), and 3-*hydroxy*-1 : 2-*dihydro*-1 : 2-*tetrazoloquinoxaline*, m.p. 288° (decomp.), are formed. *NN'*-Diphenyloximinochloride is converted by anhyd. N_2H_4 in light petroleum into the *dihydrazide*, $NH_2{\cdot}NH{\cdot}C(:NPh){\cdot}C(:NPh){\cdot}NH{\cdot}NH_2$, m.p. 156° (decomp.) [$(CMe_2:)_2$-derivative, m.p. 203°), which with NaN_3 gives 1 : 1'-diphenyl-5 : 5'-ditetrazolyl.

H. A. P.

Derivatives of 2 : 3-pyridinethioindoxyl [3-hydroxy-4 : 5-pyridothiophen]. A. E. Tschitschibabin and N. N. Voroschcov, jun. (Ber., 1933, **66**, [*B*], 364—372).—2-Pyridylthiolacetic acid (I), m.p. 127—133° (slight decomp.) [hydrochloride, m.p. 168—170° (decomp.)], is transformed by Ac_2O at 100—145° into the "3-hydroxy-4 : 5-pyridylthiophen" (II), m.p. 180·5—181·5°, of Koenigs and Geisler (A., 1925, i, 166), which on account of the ready hydrolysis by H_2O to (I) and for other reasons (see below) cannot have the constitution ascribed to it. 3 : 5-Dibromo-2-aminopyridine is converted by diazotisation in conc. HCl into 3 : 5-dibromo-2-hydroxy- and 2-chloro-3 : 5-dibromo-pyridine (III), m.p. 43—44°. (III), $SH{\cdot}CH_2{\cdot}CO_2H$, and NaOAc at 180—190° afford 3 : 5-*dibromo*-2-*pyridylthiolacetic acid*, m.p. 145—148°, transformed by Ac_2O at 100—130° into a *compound* $C_7H_3ONBr_2S$, decomp. 222—224°, closely analogous to (II) but not re-converted into the initial material (in this case the production of a "pyridylthiophen" is impossible). 3-*Pyridylthiolacetic acid*, m.p. 170—173°, obtained by diazotisation of 3-aminopyridine followed by coupling with $SH{\cdot}CH_2{\cdot}CO_2H$ in presence of K_2CO_3 and NaOAc, is unchanged by Ac_2O under the conditions described above. 2-Thiolpyridine-3-carboxylic acid, from the 2-chloro-acid and KHS, is transformed by $CH_2Cl{\cdot}CO_2H$ and Na_2CO_3 in boiling H_2O into 3-*carboxy*-2-*pyridylthiolacetic acid* (IV), m.p. about 220°, whilst Me 2-chloropyridine-3-carboxylate and $SH{\cdot}CH_2{\cdot}CO_2H$ at 110° yield 3-*carbomethoxy*-2-*pyridylthiolacetic acid* (V), m.p. 82—83°. (IV) and (V) are converted by CH_2N_2 in MeOH into *Me* 3-*carbomethoxy*-2-*pyridylthiolacetate* (VI), m.p. 100—100·5°. Treatment of (VI) with NaOMe in MeOH affords *Me* 3-*hydroxy*-4 : 5-*pyridylthiophen*-2-*carboxylate*, m.p. 160—161°, transformed by CH_2N_2 into *Me* 3-*methoxy*-4 : 5-*pyridylthiophen*-2-*carboxylate*, m.p. 98—99°. Treatment of (IV) or (VI) with boiling HCl doubtless yields 3-hydroxy-4 : 5-pyridothiophen, since the solutions in KOH are oxidised by $K_3Fe(CN)_6$ or air to an insol. violet dye which gives a colourless vat with alkaline $Na_2S_2O_4$.

2-Chloropyridine-3-carboxylic acid and $SH{\cdot}CH_2{\cdot}CO_2H$ yield small amounts of two *compounds*, m.p. 257° and 145—148°, respectively. 2-Chloro-3-nitropyridine and KSH in EtOH yield 3 : 3'-*dinitro*-2 : 2'-*dipyridyl disulphide*, m.p. 202—205°. 2-Methylthiolpyridine methiodide appears to be formed by the action of MeI on (I).

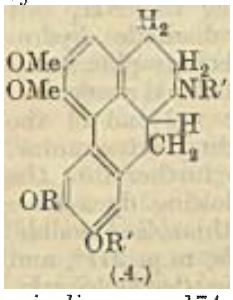
H. W.

Tricarbocyanines. (Miss) N. I. Fisher and (Miss) F. M. Hamer (J.C.S., 1933, 189—193).—Tricarbocyanines, in which the 2 heterocyclic nuclei are joined by a 7-C unsaturated chain, may be prepared by adding an EtOH solution of a heterocyclic NH_4 salt containing a reactive Me group to one of 2 : 4-dinitrophenylpyridinium chloride (which has been previously heated with alkali so as to liberate glutaconaldehyde) or preferably by heating the NH_4 salt solution with glutaconaldehyde dianilide hydrochloride and alkali. These are photographic sensitisers and the max. of the sharply defined absorption band lies 190—205 mμ nearer the red end of the spectrum than that of the corresponding carbocyanine, making it possible to photograph further into the infra-red than formerly. The following dyes have been prepared: from 1-methylbenzthiazole ethiodide, 2 : 2'-*diethylthiotricarbocyanine iodide*, m.p. 211°, and from the methochloride, 2 : 2'-*dimethylthiotricarbocyanine chloride*, m.p. 154°; from 1-methyl-α-naphthathiazole ethiodide, 2 : 2'-*diethyl*-5 : 6 : 5' : 6'-*dibenzthiotricarbocyanine iodide*, m.p. 191°, and from the methochloride, 2 : 2'-*dimethyl*-5 : 6 : 5' : 6'-*dibenzthiotricarbocyanine chloride*, m.p. 166°; from 2-methyl-β-naphthathiazole ethiodide, 2 : 2'-*diethyl*-3 : 4 : 3' : 4'-*dibenzthiotricarbocyanine iodide*, m.p. 183°, and from the methochloride, 2 : 2'-*dimethyl*-3 : 4 : 3' : 4'-*dibenzthiotricarbocyanine chloride*, m.p. 181°; from 2-methylthiazoline ethiodide, 3 : 3'-*diethyl*-, m.p. 192°, and from the methiodide, 3 : 3'-*dimethyl*-*thiazolinotricarbocyanine iodide*, m.p. 213°; from 1-methylbenzselenazole ethiodide, 2 : 2'-*diethyl*-, m.p. 225°, and from the methiodide, 2 : 2'-*dimethyl*-*selenotricarbocyanine iodide*, m.p. 198°; from *p*-toluquinaldine ethiodide, 6 : 6'-*dimethyl*-1 : 1'-*diethyl*-2 : 2'-*tricarbocyanine iodide*, m.p. 248°; from quinaldine ethiodide (in small yield) 1 : 1'-*diethyl*-2 : 2'-*tricarbocyanine iodide*, m.p. 219°; and from 2 : 3 : 3-trimethylindolenine methiodide, Ac_2O, and NaOAc, 1 : 3 : 3 : 1' : 3' : 3'-*hexamethylindotricarbocyanine iodide*, m.p. 207°. (All m.p. are also decomp. points.)

F. R. S.

Constitution of laurotetanine. G. Barger, T. Eisenbrand, L. Eisenbrand, and E. Schlittler (Ber., 1933, **66**, [*B*], 450—461).—Vanillin Et ether, m.p. 64—65°, from vanillin and Et_2SO_4, is transformed by hippuric acid, NaOAc, and Ac_2O at 100° into the *azlactone* of 3-*methoxy*-4-*ethoxybenzylidenehippuric acid*, m.p. 162—163°, converted by boiling 10% NaOH into 3-*methoxy*-4-*ethoxyphenylpyruvic acid* (I), m.p. 190—191° (decomp.). Oxidation of (I) with $NaOH$–H_2O_2 affords 3-*methoxy*-4-*ethoxyphenylacetic acid*, m.p. 183—185° (decomp.), whence 6-*nitro*-3-*methoxy*-4-*ethoxyphenylacetic acid* (II), m.p. 169—170°. *iso*Vanillin Et ether, m.p. 52—53°, similarly yields successively the *azlactone* of 4-*methoxy*-3-*ethoxybenzylidenehippuric acid*, m.p. 180—181°, 4-*methoxy*-3-*ethoxyphenylpyruvic acid*, m.p. 155°, 4-*methoxy*-3-*ethoxyphenylacetic acid*, m.p. 72° ($+1H_2O$), m.p. 67—68°, and 6-*nitro*-4-*methoxy*-3-*ethoxyphenylacetic acid*, m.p. 185—186°. 6-*Nitro*-3-*methoxy*-4-*ethoxyphenylacet*-β-3' : 4'-*dimethoxyphenylethylamide*, m.p. 152—153°, obtained under defined conditions from the chloride of (II) and homoveratrylamine (prep. described), is transformed by P_2O_5 in boiling PhMe into 6 : 7-*dimethoxy*-1-6'-*nitro*-3'-*methoxy*-4'-*ethoxybenzyl*-3 : 4-*dihydro*isoquinoline, m.p. 139—140°. The

corresponding *ethiodide*, m.p. 203—204° (decomp.), is reduced by Zn dust and HCl to 6 : 7-*dimethoxy*-1-6′-*amino*-3′-*methoxy*-4′-*ethoxybenzyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline dihydrochloride*, m.p. about 185° (decomp.) after becoming pink at 173°, transformed by successive treatment with $NaNO_2$ in $2N$-H_2SO_4–MeOH and Zn dust and HCl into



(A.)

2 : 5 : 6-*trimethoxy*-3-*ethoxy*-N-*ethylnoraporphine* (III) (cf. *A*, R=R″=Et, R′=Me), isolated as the *hydriodide*, decomp. 210°. In similar sequence are prepared: 6-*nitro*-4-*methoxy*-3-*ethoxyphenylacet*-β-3′ : 4′-*dimethoxyphenylethylamide*, m.p. 160°, 6 : 7-*dimethoxy*-1-6′-*nitro*-4′-*methoxy*-3′-*ethoxybenzyl*-3 : 4-*dihydroiso*-*quinoline*, m.p. 174—175°, and its *ethiodide*, m.p. 207° (decomp.), 6 : 7-*dimethoxy*-1-6′-*amino*-4′-*methoxy*-3′-*ethoxybenzyl*-N-*ethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline dihydrochloride* (+H_2O), m.p. 178° (decomp.), and 3 : 5 : 6-*trimethoxy*-2-*ethoxy*-N-*ethylnoraporphine* (IV), (*A* : R=Me, R′=R″=Et), isolated as the *hydriodide*, decomp. 205—210°. Ethylation of laurotetanine affords non-cryst. *ON*-diethyl-laurotetanine (V), isolated as the hydriodide, m.p. 210° (decomp.). The Hofmann degradation of (IV) leads to 3 : 5 : 6-*trimethoxy*-2-*ethoxy*-8-*vinylphenanthrene*, m.p. 142° after softening at 141° [oxidised by $KMnO_4$ to a compound, m.p. (indef.) 213°], identical with that derived similarly from (V), whereas (III) affords 2 : 5 : 6-*trimethoxy*-3-*ethoxy*-8-*vinylphenanthrene*, m.p. 141° after softening at 139°, oxidised to 2 : 5 : 6-*trimethoxy*-3-*ethoxyphenanthrene*-8-*carboxylic acid*, m.p. 209°. Laurotetanine has therefore the constitution *A* (R=Me, R′=H, R″=Et). $ClCO_2Et$ and (V) give an optically inactive *compound* $C_{26}H_{33}O_6N$, m.p. 129—130°, identical with that derived from (IV). Similarly, (V) and (IV) are transformed by BzCl into the optically inactive *substance* $C_{30}H_{33}O_5N$, m.p. 138° after softening at 136°, thus confirming the above structure.

H. W.

Alkylation of hydrocupreine. K. H. Slotta and R. Behnisch (Ber., 1933, **66**, [*B*], 360—364).—Higher alkyl ethers are prepared by treatment of hydrocupreine (I) with the requisite alkyl *p*-toluenesulphonate in boiling EtOH in presence of KOH. Use of higher temp. or pressure or of a large excess of ester diminishes the yield owing to formation of quaternary salts. The ethers are isolated as the monosulphates from which the amorphous base is readily obtained pure, although its m.p. is frequently some degrees lower than that of the cryst. compound. The following *-hydrocupreines* are described: n-*propyl*-, m.p. (amorph.) 136°, (cryst.) 142° (*sulphate*, m.p. 251°; *hydrochloride*, m.p. 247°); n-*butyl*-, m.p. (amorph.) 147° (*sulphate*, m.p. 244°); iso*amyl*-, m.p. (amorph.) 152° (*sulphate*, m.p. 238°); n-*hexyl*-, m.p. (amorph.) 145° (*dihydrochloride*, m.p. 184°). (I) and $C_6H_4Me{\cdot}SO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$, when reaction is interrupted as soon as the mixture becomes gelatinous, afford β-chloroethylhydrocupreine, m.p. (amorph.) 154°, (cryst.) 156° (*sulphate*, m.p. 218°), whereas prolongation of the change appears to lead to the β-hydroxyethyl compound. iso*Amyl*, b.p. 156°/0·06 mm., and n-*hexyl*, b.p. 145—150° (bath)/0·05 mm., p-*toluenesulphonates* are described. H. W.

Structure of strychnine and brucine. III. Decomposition of strychnine and strychnidine methochlorides by hydrogen in the presence of palladium. O. Achmatowicz (Rocz. Chem., 1933, **13**, 25—36).—Strychnine methochloride with H_2 (Pd) gives chano-Nb-*methylhydrostrychnine* (I), $C_{22}H_{26}O_2N_2$, m.p. 145°, the dihydro-derivative of (I) (II), m.p. 201°, and *dihydrostrychnine methochloride* (III), +$2H_2O$, m.p. 250°. (III) does not react with H_2 or with KOMe; dihydrostrychnine cannot be obtained from it by thermal decomp. KOH and (III) yield *dihydromethylstrychnine*, m.p. 274—276°. Electro-reduction of (I) or (II) yields *dihydro*-chano-Nb-*methylhydrostrychnidine* (IV), $C_{22}H_{30}ON_2$, m.p. 176° (*methiodide* and *methochloride*, uncrystallisable). Catalytic reduction of strychnidine methochloride yields chiefly (IV), together with dihydrostrychnidine and salts of *strychnidine*-X (V), m.p. 233—235° (*methiodide*, m.p. 290°), a new isomeride of strychnidine. The *methochloride* of (V), m.p. 292°, yields *methoxy*-, m.p. 143—145°, and *hydroxymethoxy-methyldihydrostrychnidine*-X, m.p. 304—305°, when heated with NaOMe in MeOH solution. R. T.

Solanine. IX. [*Solanum*] ***tuberosum* solanine.** G. Oddo and G. Caronna.—See this vol., 379.

Synthesis of glucoalkaloids. M. Polonovski, M. Polonovski, and A. Lemettre (J. Pharm. Chim., 1933, [viii], **17**, 145—154).—By passing dry HCl into a solution of β-tetra-acetylglucosidyl bromide and the alkaloid in dry $COMe_2$ and subsequent hydrolysis are obtained the *glucosides* of quinine, m.p. 138°, $[\alpha]^{19}$ −120° in H_2O (sulphate, m.p. 110°; picrate, m.p. 128°; chloroaurate, m.p. 109°); atropine, m.p. 97—98°, $[\alpha]^{19}$ −4·24° in EtOH (hydrobromide, m.p. 126°; picrate, m.p. 162°); hyoscyamine, m.p. 86°, $[\alpha]_D^{19}$ −11·7° in EtOH (hydrobromide, m.p. 115—116°; picrate, m.p. 122°), and of genatropine as its tartrate, m.p. 111°, $[\alpha]_D^{19}$ +6·60° (picrate, m.p. 117—118°) (none of the salts was analysed). Conversion of the OH group into a glucoside has no effect on the physiological action of these alkaloids, nor on their bactericidal action on *Staphylococci*. J. W. B.

Nitration and bromination of heterocyclic arsenic compounds. G. A. Razuvaiev and M. M. Koton (J. Gen. Chem. Russ., 1932, **2**, 889—892).—Diphenylylene chloroarsine (I) in AcOH is oxidised by HNO_3 to the *nitrate* of the corresponding arsinic acid, m.p. 156—157°, giving an intense blue colour with $NHPh_2$ and H_2SO_4, but in presence of conc. H_2SO_4 a yellow *dinitro-acid* (probably the *mm′*), m.p. >320°, is formed by simultaneous nitration and oxidation. Similarly, chlorophenoxarsine (II) gives, respectively, the *nitrate* of phenoxarsinic acid, m.p. 170°, and the *dinitro-acid*, decomp. above 275° without melting. On bromination (I) and (II) behave like the acyclic arsines, adding Br_2, the As^V derivative being immediately hydrolysed to the arsinic acid. 10-Acetyl-9 : 10-dihydrophenarsazine (III) on nitration gives a mixture of NO_2-, brown, m.p. 225°, and $(NO_2)_2$-derivatives, yellow, both of which are As^{III} derivatives; they are accompanied by phenarsazinic acid.

Bromination of (III) leads to fission of the heterocyclic ring. G. A. R. K.

Reaction of iodine monochloride with organic mercury compounds. F. C. Whitmore and M. A. Thorpe (J. Amer. Chem. Soc., 1933, **55**, 782—786).—Hg dianisyl and ICl in CCl_4 (or H_2O) give 95% of p-C_6H_4I·OMe, also formed similarly from p-OMe·C_6H_4·HgCl. β-$C_{10}H_7$·HgCl affords (in 95% EtOH) 95% of 2-$C_{10}H_7I$ and p-C_6H_4Me·HgCl yields (best in aq. NaCl) 92% of p-C_6H_4MeI. $HgPh_2$ gives (in CCl_4 or H_2O) 78% of PhI, whilst CH_2Ph·CH_2·HgCl furnishes about 30% of CH_2Ph·CH_2I (I) and 35% of CH_2Ph·CH_2Cl (II). (II) is produced from (I) and ICl, but not from (I) and $HgCl_2$. H. B.

Abnormal reactions of organometallic compounds. Cinnamyl chloride and magnesium. Grignard reagent from halogenated tertiary amines. S. A. Harris (Iowa State Coll. J. Sci., 1932, **6**, 425—428).—The Grignard reagent from cinnamyl chloride in Et_2O and Mg behaves as if its structure is CHPh(MgCl)·CH:CH_2. Dicinnamyl and liquid hydrocarbons, one of which is CHPh:CH·CH_2·CHPh·CH:CH_2, are also formed.

3-Bromo- and 3 : 5-dibromo-pyridine do not form Grignard reagents in the cold; at higher temp. tars are formed, and during the reaction Michler's ketone gives a colour reaction. 2-Iodopyridine reacts with Mg to give a green solution and an insol. tar; the solution gives no colour reaction with Michler's ketone, but if the ketone is added immediately to the solution and tar a positive reaction is obtained. o-C_6H_4I·NMe_2 and o-C_6H_4Br·NMe_2 give high yields of Grignard reagents in presence of I. Ch. Abs.

Organic selenium compounds. II. New type of aromatic selenium halide. D. G. Foster (J. Amer. Chem. Soc., 1933, **55**, 822—829).—SePhEt (from PhSe·MgBr and EtBr) (cf. A., 1928, 655) and Br give $SePhEtBr_2$ (I), m.p. 86° (cf. Edwards *et al.*, A., 1928, 1147), also prepared from Br and the reaction product from SePhBr, EtBr, Mg, and a little Mg–Cu couple in Et_2O, which decomposes slowly at room temp. and fairly rapidly in boiling Et_2O to SePhBr and EtBr. A by-product in the prep. of (I) is *Se Ph tribromide* (II), m.p. 105—106°, also obtained from SePhBr and Br in Et_2O–CS_2, and from $PhSeO_2H$, conc. HBr, and aq. NH_4Br. (II) and Cl_2 in Et_2O give *Se Ph trichloride* (III), m.p. 133—134° (decomp.), also formed from SePhBr and Cl_2 in Et_2O, by saturation of a saturated aq. solution of $PhSeO_2H$ with HCl, and by thermal decomp. of $SePhEtCl_2$ and subsequent treatment (of the SePhCl) with Cl_2. $SePhI_3$ could not be prepared, probably owing to its instability. (II) and (III) are not hydrolysed by H_2O [(III) changes into an oil], but with aq. NaOH give $PhSeO_2H$. The methods of prep. and reactions of (II) and (III) indicate that they are salts of the hypothetical $PhSe(OH)_3$ (which has basic properties). H. B.

Phenylmethylselenetine mercuri-iodide. M. P. Balfe and H. Phillips (J.C.S., 1933, 127—128).—*dl*-Phenylmethylselenetine bromide and K mercuritri-iodide give *dl*-phenylmethylselenetine mercuritri-iodide, m.p. 90°, and a mol. *compound* (I), m.p. 140°, of selenetine mercuri-tri-iodide (1 mol.) and -tetra-iodide (3 mols.) (cf. Pope and Neville, J.C.S., 1902, **81**, 1552). *d*-Phenylmethylselenetine *d*-bromocamphorsulphonate, m.p. 174°, $[\alpha]_{893}$ +61·2°, obtained from the *dl*-salt, affords with $PtCl_4$ the chloroplatinate (+EtOH), m.p. 95°, $[\alpha]_{5893}$ +11·8°, and with K mercuritri-iodide or HgI_2 and KI, optically inactive (I), m.p. 135°. The racemisation is to be attributed to the instability of the selenetine ion. F. R. S.

Organic compounds of selenium. III. Action of selenium oxychloride on esters of salicylic acid. R. E. Nelson, R. A. Schroeder, and W. R. Bunting (J. Amer. Chem. Soc., 1933, **55**, 801—803).—$SeOCl_2$ (1 mol.) and o-OH·C_6H_4·CO_2R (2 mols.) give 4 : 4′-dihydroxy-3 : 3′-dicarbalk(aryl)oxydiphenyl selenide dichlorides, which are reduced (Zn dust in $CHCl_3$) to the selenides (which add 2Br and 2I), and hydrolysed by aq. $NaHCO_3$ to the dihydroxides. The following are described: 4 : 4′-*dihydroxy*-3 : 3′-*dicarbomethoxydiphenyl selenide*, m.p. 158° (*dichloride*, m.p. 176°; *dibromide*, m.p. 143°; *di-iodide*, m.p. 150°; *dihydroxide*, m.p. 137°); -3 : 3′-*dicarbethoxydiphenyl selenide*, m.p. 88° (*dichloride*, m.p. 165°; *dibromide*, m.p. 147°; *di-iodide*, m.p. 140°; *dihydroxide*, m.p. 107°); -3 : 3′-*dicarbopropoxydiphenyl selenide*, unstable viscous oil (*dichloride*, m.p. 130°; *dibromide*, m.p. 110°; *di-iodide*, m.p. 78°; *dihydroxide*, m.p. 63°); -3 : 3′-*dicarboisopropoxydiphenyl selenide*, m.p. 81° (*dichloride*, m.p. 173°; *dibromide*, m.p. 159°; *di-iodide*, m.p. 96°; *dihydroxide*, m.p. 83°); -3 : 3′-*dicarbobutoxydiphenyl selenide*, unstable viscous oil (*dichloride*, m.p. 133°; *dibromide*, m.p. 95°; *di-iodide*, m.p. 65°; *dihydroxide*, m.p. 57°); -3 : 3′-dicarboamyloxydiphenyl selenide, an unstable viscous oil (*dichloride*, m.p. 138°; *dibromide*, m.p. 121°; di-iodide, a viscous oil; *dihydroxide*, m.p. 97°); -3 : 3′-*dicarbophenoxydiphenyl selenide*, m.p. 138° (*dichloride*, m.p. 185°; *dibromide*, m.p. 160°; *di-iodide*, m.p. 120°; *dihydroxide*, m.p. 122°). H. B.

Optical activity and coagulation of the degradation products of caseinogen. II. B. Jirgensons (Biochem. Z., 1933, **257**, 427—436).—The optical activity and coagulation of the peptones obtained by degradation of caseinogen on heating for 3 hr. at 130—140° in glycerol are investigated. In acid solution, coagulation is effected most readily with SO_4'' and CNS′, in feebly alkaline solution by Cl′ and Br′. Optimal coagulation at p_H 4·3 is obtained by MeOH, EtOH, and Pr$^{\alpha}$OH, respectively, in concns. of 5·8, 3·6, and 2·1 mols. per litre, at p_H 6·9 in concns. of 3·5, 3·0, and 2·6, and at p_H 7·4 in concns. of 2·2, 2·8, and 3·4 mols. per litre. P. W. C.

Highly-sensitive specific colour reaction of tyrosine on *p*-substituted phenols. Tyrosine content of various proteins, particularly of collagen and gelatin. O. Gerngross, K. Voss, and H. Herfeld (Ber., 1933, **66**, [*B*], 435—442).—When 1 c.c. of 1% tyrosine is boiled with 1 drop of 1% 2-nitroso-α-naphthol in EtOH and 1—2 drops of HNO_3 (*d* 1·4) are added to the hot solution a dark purple colour is developed which is distinct in dilution 1 : 10^6. The colour is gradually bleached on exposure to light, and Beer's law is not followed, so that quant. measurement is based on the limit of visibility with increasing dilution. Reaction is not given by any

known natural NH_2-acid except tyrosine. Positive results are given by *N*-benzoyltyrosine, tyrosol, tyramine, *p*-$C_6H_4Me{\cdot}OH$, *p*-$C_6H_4Et{\cdot}OH$, 1 : 3 : 4- and 1 : 2 : 4-xylenol, *p*-$C_6H_4Cl{\cdot}OH$, *p*-chloro- and *p*-bromo-*m*-cresol, chloroxylenol, *p*-$OH{\cdot}C_6H_4{\cdot}SO_3Na$, *p*-$OH{\cdot}C_6H_4{\cdot}NHAc$, *m*-$OH{\cdot}C_6H_4{\cdot}OBz$, *m*-$OH{\cdot}C_6H_4{\cdot}OMe$, phenolphthalein, β-$C_{10}H_7{\cdot}OH$ and "folliculin," whilst negative results are recorded for *ON*-dibenzoyl- and *o*-nitro-tyrosine, 3 : 4-dihydroxyphenylalanine, adrenaline, thyroxine, PhOH, *o*-, *m*-, and *p*-$C_6H_4(OH)_2$, *o*- and *m*-$C_6H_4Me{\cdot}OH$, 1 : 3 : 5-, 1 : 4 : 5- and 1 : 2 : 3-xylenol, *iso*pseudocumenol, *p*-$OH{\cdot}C_6H_4{\cdot}NO_2$, trichlorophenol, *p*-$C_6H_4Me{\cdot}SH$, *p*-$OH{\cdot}C_6H_4{\cdot}CHO$, *p*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, *p*-$OH{\cdot}C_6H_4{\cdot}NH_2$, *p*-$OH{\cdot}C_6H_4Bz$, resacetophenone, *p*-methyl*cyclo*hexanol, decahydro-β-naphthol, α-$C_{10}H_7{\cdot}OH$, vanillin, *o*-vanillin, coniferin, fisetin, tannin, eugenol, thymol, terpineol, and *p*-benzoquinone. Examination of gelatins and collagens discloses the presence of tyrosine except in such as have been treated with HNO_2 or ClO_2. Whether it is present as an actual component of the protein or only as an accompanient is regarded as an open question. H. W.

Apparatus for the study of the destruction of organic matter. E. Kahane (Bull. Soc. chim., 1933, [iv], **53**, 95—97).—An all-glass apparatus is described for the oxidation of org. matter by $HClO_4$–HNO_3 and collection of volatile products. The acid mixture is preferable to $HClO_4$ alone. R. S. C.

Determination of organic nitrogen in the presence of nitrates by Kjeldahl's method. R. Cambier and L. Leroux (Compt. rend., 1932, **195**, 1280—1282).—The NO_3' is removed as HNO_3 by vac. distillation of the solution with H_2SO_4 at 30—40°, and finally at 100°. The residual liquid gives accurate vals. for org. N by ordinary Kjeldahl procedure. A. C.

Determination of halogens in organic substances by the ammonia–sodium method. Determination of fluorine in organic compounds. F. Govaert (Compt. rend., 1932, **195**, 1278—1280).—Trifluorotoluene, $CF_3{\cdot}CO_2Et$, and PhF, with non-reactive F, are accurately analysed for F by this method (cf. this vol., 80). A. C.

Determination of fluorine in organic compounds by a lamp method. G. Cadenbach (Angew. Chem., 1933, **46**, 130).—The substance is volatilised in a stream of H_2 through a strongly heated Ag tube and burnt under a Ag funnel. HF is detected by $Ca(OAc)_2$ or $La(OAc)_3$ and determined by 0·2*N*-KOH. S. C.

Iodometric determination of mercury in organic compounds. J. Opienska-Blauth (Przemysł Chem., 1933, **17**, 14—18).—Rupp's iodometric method (A., 1901, ii, 348) gives results which are, according to the compound under analysis, either high, owing to combination of I with the org. part of the mol., or low, as a result of partial hydrolysis of the complex. In the case of Hg salicylate satisfactory results are given only by very pure samples. R. T.

Micro-determination of alcohol in alcohol–air mixtures. M. Nicloux (Compt. rend. Soc. Biol., 1931, **107**, 527—529; Chem. Zentr., 1932, ii, 2083—2084).—The EtOH is retained by bubbling the air through H_2O, and determined by distillation in a Schloesing–Aubin apparatus. A. A. E.

Determination of thymol. C. V. Bordeianu (Z. anal. Chem., 1933, **91**, 421—425).—Errors of 10—70% are involved in the usual iodometric determination of thymol. By mercurating thymol to the dimercuriacetate with excess of $Hg(OAc)_2$ in 50% aq. AcOH, diluting with H_2O, and determining $Hg^{\cdot\cdot}$ in the filtrate with NH_4CNS, a mean accuracy of 0·6% can be attained. F. L. U.

Micro-determination of picrolonic acid by means of acridine. H. Schiedewitz (Z. physiol. Chem., 1933, **214**, 177—178).—The picrolonate is dissolved in 20 c.c. of hot H_2O with addition of 1 c.c. of dil. HCl and treated with 15 c.c. of 0·3% acridine in aq. HCl. The acridine salt is separated by filtration and weighed. J. H. B.

Tannin spot-tests. J. H. Hoch (J. Amer. Pharm. Assoc., 1933, **22**, 121—124).—The sensitivity of the reaction of tannin with 33 reagents has been examined. The reactions of a group of 8, being the most sensitive, with aq. dilutions of 7 drugs indicate that the sensitivity of the reaction is not affected by either the time (5—30 min.) or temp. of maceration or the filtration of the extract. E. H. S.

Reactions and determination of ephedrine. J. A. Sánchez (Semana méd., 1932, II, 1183—1185).—NaOH and I in KI afford CHI_3. Evaporation with NaOH and $KMnO_4$, then heating with EtOH and H_2SO_4, gives an odour of BzOEt. Distillation with $KMnO_4$ gives PhCHO. Bouchardat's, Wavelet's, Walser's, Sánchez' (molybdic), and Bertrand's (silicotungstic) reagents, and Br–H_2O, react. Distillation with NaOH or CaO and Zn gives PhCHO and NHMeEt. $NaNO_2$ and HCl give white nitrosoephedrine. Nitration, reduction with Zn, and treatment with $NaNO_2$ gives a diazo-compound which in alkaline solution gives with PhOH yellow, resorcinol dark orange, β-naphthol red, phloroglucinol dark orange, thymol intense red. For the determination, 10 c.c. (0·1% solution) are heated with NaOH solution (3 c.c.) and 0·1*N*-I (30 c.c.) for 30 min. to 60°; the solution is then cooled and titrated with $Na_2S_2O_3$ (1 c.c. I=0·0020625 g. ephedrine, ±0·5%). Ch. Abs.

Separation of alkaloids by means of buffer mixtures. S. Elgazin (Khim. Farm. Prom., 1932, 128—131).—A solution of harmine and harmaline (1 kg. of hydrochlorides in 10 kg. H_2O at 80—85°) is filtered through animal C and treated with NaOAc (3 kg.), which ppts. 80% of the harmine; the operation is repeated on the mother-liquor. For the separation of strychnine from brucine 1 pt. is dissolved in 10 pts. of 10% NH_4Cl and treated with 10% aq. NH_3 at 80—85° until all the strychnine is pptd., brucine being pptd. from the cooled mother-liquor with NaOH. Ch. Abs.

Micro-chemical reaction of scopolamine. Z. F. Klan (Časopis Ceskoslov. Lék., 1932, **12**, 91—94; Chem. Zentr., 1932, ii, 2085).—$AuCl_3$ forms cryst. reaction products. A. A. E.

Biochemistry.

Components of the atmosphere and synthetic gases in relation to animal life. J. W. HERSHEY (Nature, 1933, **131**, 238—239).—A discussion of results previously obtained (*ibid.*, 1928, **122**, 684). L. S. T.

Solubility and tendency to dissociate in ammonium sulphate solutions of carbon monoxide-hæmoglobin. S. P. L. SØRENSEN and M. SØRENSEN (Biochem. Z., 1933, **258**, 16—47; cf. A., 1931, 245).—Methods for preparing highly purified, stable CO-hæmoglobin (I) (unchanged after 18 months) from horse-blood, for analysing (I), and for determining the p_H of its solutions are described. Each g. of the hydrate of (I) contains 0·353 g. of H_2O. The effect of the concn. of $(NH_4)_2SO_4$ added to solutions of (I) on the equilibrium (II) between dissolved and pptd. (I) is in accordance with the equation given by Green (A., 1932, 73). The curve showing the effect of $[H^+]$ (p_H 4·39—7·64) on (II) exhibits two min., one at p_H 6·6 and another at 5·4. The latter probably corresponds with a sparingly sol. sulphate containing 12—$13H_2SO_4$ per mol. of (I). Min. at these points are also found on the curve showing the ionisation in acid and alkaline solutions of (I). The tendency of (I) to dissociate in solution is indicated by the effect of the concn. of (I) on (II). This tendency is very slight when the concn. is high, but increases considerably with dilution. (I) cannot be fractionated by freezing or by crystallisation. W. McC.

Hæmoglobin content of normal serum. P. MULLER (Klin. Woch., 1932, **11**, 1352—1353; Chem. Zentr., 1932, ii, 2482).—Normal serum always contains hæmoglobin (7—20 mg. per 100 c.c.), the amount depending on the coagulation velocity etc. The yellow colour of non-icteric serum is largely dependent on this hæmoglobin content. A. A. E.

Constitution of hæmocyanin and hæmoerythrin by means of their ultra-violet absorption spectra. J. ROCHE and P. DUBOULOZ (Compt. rend., 1933, **196**, 646—648).—Application of Laporta's method (Bol. Soc. Ital. Biol. sper., 1932, **7**, 630) to hæmoerythrin (I) affords an Fe-free protein and a cryst. *hæmoferrin* (II), rich in Fe and an ultra-violet absorption spectrum (band at 2950 Å.) closely similar to that of hæmocuprin (III), similarly obtained from hæmocyanin (IV) (Schmitz, A., 1931, 497, 753; Laporta, *loc. cit.*; the specimens prepared by these two methods also give almost identical spectra and are probably identical). Hence (I) and (IV) probably consist of a protein combined with the metal complexes (II) or (III), which possess very similar constitutions. The ultra-violet absorption spectra of oxyhæmocyanin (absorption between 3800 and 3000 Å.; band at 3450 Å.) and oxyhæmoerythrin are also very similar, reduction causing considerable diminution in intensity and disappearance of the 3450 Å. band in the former case. J. W. B.

Mol. wts. of the blood-pigments of the invertebrates. T. SVEDBERG (Nature, 1933, **131**, 325; cf. A., 1932, 1151).—Five forms of the erythrocruorin type of respiratory protein differing with regard to sedimentation const. have been found in the blood of invertebrates and two in the blood-corpuscles. Each of the five forms is characteristic of one of the following groups: oligochæte worms, polychæte worms (I), gastropods (II), crustaceans (III), and insects (IV), whilst the two forms of the second type occur in the erythrocytes of the capitellide and glyceride worms. Only one sedimentation const. has been observed for the chlorocruorin type of respiratory protein, whilst the hæmocyanin type has six consts. representing the groups (II), cephalopods (two consts.), xiphosurans, and (III) (three consts.). Several species within a group have the same sedimentation const., and hence, probably, the same mol. wt., to within 2%. Among (I) six species of six different families have a sedimentation const. of $57·5\times10^{-13}$ corresponding with a mol. wt. of 285×10^4; among (II) eleven species of seven different families have a const. of $99·5\times10^{-13}$ (mol. wt. 5×10^6), whilst in (III) five species of three families have a const. of $23·0\times10^{-13}$. The lowest const. for a respiratory pigment in blood is that of the erythrocruorin of (IV); it is approx. one half that of the hæmoglobin of vertebrates and corresponds with a comparatively low mol. wt. The respiratory proteins of invertebrates possessing red corpuscles give low sedimentation consts. The constancy of the mol. wts. of the respiratory blood-proteins within various animal groups is discussed in relation to variation of the chemical composition of the blood-pigment. L. S. T.

Globins. II. Hæmatins, globins, and the specificity of hæmatin pigments. J. ROCHE (Bull. Soc. Chim. biol., 1933, **15**, 110—129).—The spectroscopic characteristics of artificial compounds of various hæmatins with the globins (I) of muscle- (II) and blood-pigments (III) and the relative affinity of muscle-hæmoglobin for O_2 and CO indicate that the globin is responsible for the differences in the oxy- and carboxy-hæmoglobins of various animals. The protohæmatins of (II) and (III) are identical, whilst the "span" relationship (A., 1924, i, 1362) applies equally to both. The protein of chlorocruorin is not identical with the (I) of (II) or (III), but can combine with hæmatins. The hæmatin of helicorubin yields the same product as protohæmatin when combined with (I). A hæmoglobin is formed by the combination of (I) with cytochrome *c* (A., 1925, i, 1112). The functions of the hæmatins and globins are discussed. F. O. H.

Determination of protein in blood-serum by oxidation. P. BOULANGER and H. WAREMBOURG (Compt. rend. Soc. Biol., 1931, **106**, 958—960; Chem. Zentr., 1932, ii, 3446).—Oxidation with $KMnO_4$ and with $CrO_3+H_2SO_4$ (iodometric) gives concordant vals. A. A. E.

Analysis of whole blood. IV. Glutathione. S. R. BENEDICT and G. GOTTSCHALL (J. Biol. Chem., 1933, **99**, 729—740).—The blood is deproteinised with tungstomolybdic acid (A., 1929, 1189) and the filtrate treated with aq. NaOAc and aq. $NaHSO_3$ followed by arsenophosphotungstic acid (A., 1922, ii, 405). A blue colour slowly develops and, 10—30 min. after

mixing, comparison is made with standards similarly prepared. Methionine does not interfere. F. O. H.

Occurrence of acetylcholine in ox-blood. I. VOGELFANGER (Z. physiol. Chem., 1933, **214**, 109—110).—When the reaction was prevented from becoming alkaline during evaporation of the EtOH extract acetylcholine was isolated from ox-blood. J. H. B.

Volumetric micro-determination of uric acid in urine and blood. S. RUSZNYÁK and E. HATZ (Biochem. Z., 1933, **257**, 420—426).—The method, which depends on the titration until colourless with 0·01—0·005*M*-$K_3Fe(CN)_6$ of the blue solution obtained by the usual Folin–Wu reagents, is described and a table indicates its accuracy. P. W. C.

Relation between sodium chloride and residual nitrogen. E. KERPEL-FRONIUS (Z. ges. exp. Med., 1932, **85**, 235—247).—Excess excretion of N compounds reduces the urinary concn. of Cl; when oliguria supervenes there is Cl′ retention and hyperchloræmia (I). During experimental exsiccosis in animals there may occur a sudden fall in the concentrating power of the kidney. In infants suffering from dehydration the (I) is not renal in origin, but is due to H_2O loss without corresponding reduction in Cl′. In (I) the blood has an increased osmotic pressure. The increase in non-protein-N of the blood in (I) is not a compensatory osmotic process, but is dependent on dehydration. Tissue alterations of osmotic pressure run parallel with those of the blood. NUTR. ABS.

Colorimetric determination of free cholesterol in blood-serum. A. GRIGAUT (Compt. rend. Soc. Biol., 1933, **112**, 34—36).—A modification of the author's method for determination of cholesterol (I) permits its use for determination of esterified (I), free (I) being determined by difference. NUTR. ABS.

Direct determination of free cholesterol in the blood without precipitation. O. KANNER (Compt. rend. Soc. Biol., 1931, **108**, 383—384; Chem. Zentr., 1932, ii, 2998).—Blood (2 c.c.) is diluted (to 15 c.c.) with 60% EtOH containing 0·5% NaOH and vigorously shaken 12 times with light petroleum. The petroleum layer is washed with 15 c.c. H_2O, and cholesterol in the residue on evaporation is determined colorimetrically (Liebermann). A. A. E.

Plasma-protein, cholesterol, and [corpuscle] sedimentation rate in various kinds of animals. B. SWEDIN (Biochem. Z., 1933, **257**, 411—419).—The readily Et_2O-sol. cholesterol, the protein, and the sedimentation rate for ox, horse, dog, goat, hedgehog, and rabbit are determined. The cholesterol vals. showed fair agreement for all the animals except rabbit, but no relationship could be detected between the sedimentation rate and the amount of plasma-protein. P. W. C.

Influence of intravenous injection of diastase on the blood-sugar of normal and depancreatised animals. G. MANSFELD (Biochem. Z., 1933, **257**, 333).—An erroneous statement attributed to the author by Wilson and Strieck (A., 1932, 1054) is disclaimed. P. W. C.

Action of hydrocyanic acid on the optical properties of blood-sugar. J. THOMAS and E. J. BIGWOOD (Bull. Soc. Chim. biol., 1933, **15**, 75—83).—The variation with p_H of [α] of dialysates of the blood of rabbits or dogs (A., 1931, 858) is almost completely eliminated by addition of HCN. This is due to formation of the cyanohydrin of glucose; NH_2-acids and lactic acid play a secondary and far less significant part. F. O. H.

Silica in the organism, and siliceous particles of the blood. L. LEMATTE and E. KAHANE (Compt. rend., 1933, **196**, 575—578).—SiO_2 of the order of 1 mg. may be determined in org. matter to within 0·1—0·2 mg. by the authors' method (A., 1931, 926, 1201). Smaller quantities are detected qualitatively as gelatinous solubilised SiO_2. Ox, horse, pig, dog, and human fibrins contain 0—1 mg. of SiO_2 per 100 g.; these vals. are much < those recorded in the literature. In addition, fibrin also contains traces of insol. SiO_2. A. C.

Phosphorus fractions in blood of the growing organism. C. BOMSKOV and H. NISSEN (Z. ges. exp. Med., 1932, **85**, 142—147).—Figures are given for the P fractions of the blood of rabbits and dogs at various ages. As adult life approaches there is a fall in all the fractions except the acid-insol., which shows a tendency to rise. NUTR. ABS.

Determination of blood- and urine-sulphur. A. LESURE and A. THOMAS (J. Pharm. Chim., 1933, [viii], **17**, 114—130).—In the benzidine method, LiOH is used for neutralisation in place of NaOH, allowing phosphates to be removed by filtration. This is considered indispensable in determination of SO_4'' and advantageous in the case of ethereal sulphates. H. G. R.

Blood-iodine. I. I. NITZESCU and E. BINDER (Compt. rend. Soc. Biol., 1931, **108**, 279—280; Chem. Zentr., 1932, ii, 2481).—Blood-I is normally 8·7—9·4 ($\times 10^{-6}$ g.-%) (Jan.—Mar.), 11·7—12·3 (June—Dec.); in goitre it is 4—5. A. A. E.

Antigenic properties of cholesterol and its derivatives. A. J. WEIL and F. BESSER (Z. Immunität., 1932, **76**, 76—82; Chem. Zentr., 1932, ii, 3428).—Various cholesterol derivatives with pig serum were used to immunise rabbits. The antibodies have a high structure specificity. Oxycholesterol (Lifschütz), dihydrocholesterol, and cholesterol are antigenic, whilst cholesteryl oxide (Westfalen), dibromide, acetate, and palmitate do not give antibodies. A. A. E.

Adsorption and elution of the Forssman heterogenetic antigen. E. BRUNIUS (Biochem. Z., 1933, **258**, 207—220; cf. Rudy, A., 1932, 1153).—Forssman heterogenetic antigen (from guinea-pig and horse kidney) is readily adsorbed by kaolin (I), $Al(OH)_3$ (II), colloidal $Fe(OH)_3$ (III), and animal C (IV), but cannot be removed from the adsorbent by elution [with physiological NaCl, even for long periods, dil. AcOH, aq. NH_3 for (I), H_2O, Na_2HPO_4 for (II) and (III), NaCl, octyl alcohol, 96% EtOH, C_6H_6, 0·001*N*-HCl, 0·001*N*-NaOH for (IV)]. Adsorption with (III) is most effective at high temp. (70°). W. McC.

Specificity of antibodies towards lipins. Sterols. E. BERGER and H. SCHOLER (Z. Immunität., 1932, **76**, 16—35; Chem. Zentr., 1932, ii, 3428).—Various sterols (non-irradiated and irradiated) were injected with pig's serum into rabbits. The sera were highly sp., reacted only with the homologous antigens, and permitted the serological differentiation of irradiated and non-irradiated ergosterol. Even small impurities are detectable. A. A. E.

Effect of heparin and germanin on immunoreactions. F. KLOPSTOCK (Z. Immunität., 1932, **75**, 348—354; Chem. Zentr., 1932, ii, 3112).—A discussion. A. A. E.

Specific combination of arsanil-protein and arsanilic acid with immune serum. F. HAUROWITZ and F. BREINL (Z. physiol. Chem., 1933, **214**, 111—120; cf. A., 1930, 1608).—The ppt. from arsanil–azoprotein and homologous anti-serum contains the more antigen the greater is its concn. in the fluid, unsp. adsorption being excluded. The inhibitory action of arsanilic acid on the pptn. is lost when As^{V} is replaced by Sb^{V} or As^{III} or by conversion of the primary into the secondary arsinic acid (replacement of OH by the $NPhMe_2$ radical). The binding of the anti-serum by the arsanilic acid is directly proved by compensation dialysis (cf. Marrack and Smith, A., 1932, 184). J. H. B.

Kinetics of hæmolysis in colloidal silicic acid–complement systems. E. PONDER (Proc. Roy. Soc., 1933, **B**, **112**, 298—315).—Previously described methods (A., 1932, 413) have been applied to systems containing ox red blood-cells sensitised by silicic acid (I), and guinea-pig complement. The systems are characterised by "hæmolytic zones." The cells absorb some of the sensitising agent, and if the free (I) is removed, the complement acts as a simple hæmolysin. The "zones" are accounted for by a reaction between the free (I) and part of the complement, whereby the latter is inactivated. A. C.

Phosphorescence in human tissues. I. Proof of the phosphorescence in normal human tissues and its measurement. S. HOSHIJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 109—113).—By a modified Bequerel phosphoroscope, phosphorescence has been detected in human bones, teeth, cartilage, nails, and tendons, but not in various other organs. Calcined bone and tooth, but not bone or cartilage decalcified by dil. HNO_3, show phosphorescence. The phosphorescence with most tissues lasts about 0·2 sec. (excitation time 0·04 sec.), but with calcined bone and tooth it lasts about 15 sec. The phosphorescence spectrum has been photographed and measured. W. O. K.

Sulphur and cystine content of egg-membrane of Chinese hens. P. P. T. SAH and C. S. CHEN (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 285—287).—The egg-membrane contained 80·5% protein and 2·83% S. S was present only as cystine. H. G. R.

Identification of *l*-(+)-norleucine as constituent of proteins of the spinal marrow and peripheral nerves. E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1933, **214**, 262—266).—*l*-(+)-Norleucine (I) was obtained from peripheral nerve hydrolysate and was identified by conversion into the corresponding α-bromo-fatty acid, then into the trimethylamino-acid (*chloroaurate*, m.p. 137°). The smaller amount of (I) obtained from spinal marrow was identified by means of the *benzenesulphonyl*, m.p. 113°, and *formyl*, m.p. 114—116°, derivatives. The *phenylcarbimido-*, m.p. 133°, and *phenylhydantoin*, m.p. 110—111°, derivatives of (I) were also prepared. J. H. B.

Distribution of lipin-phosphorus in the adrenals of mammals. A. LEULIER and L. REVOL (Compt. rend. Soc. Biol., 1931, **106**, 667—668; Chem. Zentr., 1932, ii, 2990).

Arginine. III. Arginine content of vertebrate and invertebrate muscle. A. ARNOLD and J. M. LUCK (J. Biol. Chem., 1933, **99**, 677—691).—Arginine (free or as phosphate) is present in small amounts in the thigh muscles of rats and rabbits, but is absent from the muscles of pigeons, cats, frogs, and gopher snakes. Amongst the invertebrates the highest content occurs in the *Crustacea*, a high content occurring in the cephalopod *Paroctopus apollyon*. It is present in the *Echinodermata*, *Platyhelminthes*, and *Phoronidea*, but absent from the *Cœlenterata*, marine *Annelida*, *Echiuroidea*, and *Sipunculoidea* (cf. A., 1932, 532). F. O. H.

***am*-Hexose which occurs in the organism.** Y. KOTAKE and M. NISHAGAKI.—See this vol., 378.

Mineral content of cartilage. W. SILBER (Biochem. Z., 1933, **257**, 363—370).—Air-dried cartilage of rabbit's ear has a 4% ash content containing Na 22, K 12, Ca 3, Mg 2, SO_4 40, P_2O_5 7, and Cl 15%. Aq. extraction for 3 weeks removes 90% of the ash together with 10% of the org. substances. P. W. C.

Copper, iron, and manganese content of fish. T. B. PARKS and E. R. ROSE (J. Nutrition, 1933, **6**, 95—98).—20 species of fresh- and salt-H_2O fish contained 1·4—4·1 mg. Cu, 3·4—9·6 mg. Fe, and 0·1—0·5 mg. of Mn per kg. of moist material. About 12% more Fe was found in salt- than in fresh-H_2O fish, and about 75% more Fe in fish with dark- than in fish with light-coloured tissue. E. B. H.

Red dye of the lobster shell. H. WILLSTAEDT (Biochem. Z., 1933, **258**, 301—303; cf. Verne, A., 1920, i, 680).—The dye is obtained (not quite pure) by extraction with EtOH and CS_2, evaporation of the solvent, dissolution in EtOH, pptn. with alkali hydroxide, dissolution in dil. H_2SO_4, and extraction with Et_2O. The product does not crystallise or yield a cryst. Me derivative with CH_2N_2, but this treatment produces a cryst. *by-product*, $C_{29}H_{41}\cdot CO_2Me$. The dye resembles carotene. W. McC.

Diastase content of cerebrospinal fluid. A. MARCHIONINI and B. OTTENSTEIN (Klin. Woch., 1932, **11**, 1345—1348; Chem. Zentr., 1932, ii, 2482).—A mixture of the fluid (0·1 c.c.), H_2O (2 c.c.), 0·3% glycogen solution (9·1 c.c.), 1·1% NaCl solution (0·1 c.c.), and $N/15$-KH_2PO_4+$N/15$-Na_2HPO_4, p_H 6·8, (0·3 c.c.) is kept for 2 hr. at 40° and cooled. The reducing val. is determined (Hagedorn–Jensen) without deproteinisation, and that of the fluid alone is

subtracted from it.. In non-syphilitic disease the val. is 11—40 mg. per 100 c.c., and in syphilis 0—10 mg. A. A. E.

Mechanism of salivary secretion. V. E. Henderson and M. H. Roepke (J. Pharm. Exp. Ther., 1933, **47**, 193—207).—Stimulation of the chorda tympani leads to the peripheral production of a substance which decreases the contractility of the frog's heart. This effect is overcome by atropine. The active principle is destroyed by alkali and is insol. in Et_2O. It is thought to be acetylcholine. A. L.

Gastric lipase. H. Lichtenberg (Klin. Woch., 1932, **11**, 2117).—Whereas the gastric lipase of older children and adults shows an optimum p_H about 5, the activity at this p_H being five times that at 7, the gastric lipase of infants may show equal activities at p_H 5 and 7. When sugar solution is taken there are equal activities at p_H 5 and 7, but when 1% "plasmon" solution is taken there is an inhibition at p_H 7. The addition of proteins and peptides to the gastric contents of infants results in an inhibition of activity at p_H 7. Apparently the fasting gastric secretion of achlorhydric individuals shows p_H characteristics similar to those of infants. Nutr. Abs.

Lactic acid of gastric juice. L. Norpoth and E. Kaden (Arch. exp. Path. Pharm., 1933, **169**, 414—428).—The gastric juice (I) of a no. of hospital cases contained 0·006—0·025% of lactic acid (II). The highest vals. occurred with gastric diseases. An increase of (II) in the blood induced by injection of adrenaline is not accompanied by an increase of (II) in (I) and, whilst the level of (II) in the blood approximates to that in (I), the (II) of (I) is not due to a simple process of diffusion, but probably to glycolysis in the cells of the stomach tissue. F. O. H.

Gastric secretion of normal Chinese. H. C. Chang and H. L. Chang (Chinese J. Physiol., 1932, **6**, 321—331).—The vol., acidity, and total Cl′ of the gastric juice of 200 normal Chinese, fasting and after histamine stimulation, showed little deviation from the normal Occidental standard except in the incidence of achlorhydria, this being 4% of the fasting cases examined. A. L.

Gastric acidity with special reference to the pars pylorica and pyloric mucosa. J. T. Priestley and F. C. Mann (Arch. Surg., 1932, **25**, 395—403). Nutr. Abs.

Effect of acetylcholine on gastric acidity and its relationship to degree of acidity. P. Merklen, J. Warter, and J. Kabaker (Compt. rend. Soc. Biol., 1932, **111**, 1013—1015).—Injections of 0·2 g. of acetylcholine increased the acidity of the gastric juice of a- and hypo-chlorhydrics, but lowered that of hyperchlorhydrics, *i.e.*, those with free acid $>$ 0·2% HCl. Nutr. Abs.

Gastro-intestinal p_H in rats. I. Eastman and E. G. Miller, jun. (Proc. Soc. Exp. Biol. Med., 1932, **30**, 332—334).—The p_H vals. of the gastro-intestinal tract of rats fed on a normal diet were on the average: stomach, 3·6; small intestine, upper third, 5·9; middle third, 6·3; lower third, 6·8; cæcum, 6·2; colon, 6·6. The vals. were slightly higher in young rats. Diets of suet, potato, or lard had no distinct effect on the reaction, but rachitogenic diets increased intestinal alkalinity slightly. Nutr. Abs.

Chemical differentiation of nervous and hormonal pancreatic secretion. T. F. Zucker, P. G. Newburger, and B. N. Berg (Proc. Soc. Exp. Biol. Med., 1932, **30**, 166—167).—The secretion of pancreatic juice is continuous even when secretin is eliminated by complete removal of the intestine. The inhibiting and stimulating effects of atropine and pilocarpine (I), respectively, indicate that the flow is influenced by the parasympathetic nervous system. A comparison of secretin juice with spontaneous or (I) juice shows that the latter is richer in enzymes and other solids with the exception of HCO_3'. Nutr. Abs.

Reaction of human milk. W. Partridge (Analyst, 1933, **58**, 88—89).—In agreement with Richmond, the acidity usually varies from 2·0 to 5·5 "dairy" degrees. Analyses of 15 samples of human milk are given. T. McL.

Composition and heat of combustion of Danish cow's milk. A. C. Andersen, P. Langmack, and J. E. Winther (Proc. World's Dairy Cong., 1931, ii, 122—123).—For mixed milks, $P=1{\cdot}597+0{\cdot}446F\pm 0{\cdot}11$; $D=7{\cdot}627+1{\cdot}346F\pm 0{\cdot}12$; $R=6{\cdot}03/0{\cdot}1F\pm 0{\cdot}13$; $C=300+113{\cdot}5F\pm 8$, where P is the protein, D the dry substance, F the fat, and R the fat- and N-free dry substance (%), and C is g.-cal. per kg. of milk. Ch. Abs.

Effect of dietary fat on the fat of cow's milk. E. J. Sheehy (Proc. World's Dairy Cong., 1931, i, 76—94).—Cottonseed, olive, and soya-bean oils ($>$30 oz. daily) had no effect. Cod-liver oil (6—8 oz.) and linseed oil (15 oz.) had a depressant effect. Ch. Abs.

Source of the primary catalase of cow's milk. A. Zeilinger (Biochem. Z., 1933, **257**, 450—462).—Milk-catalase is partly derived from the animal (primary) and partly from its bacterial content. Daily determination in cows showed an unmistakable parallelism between blood- and primary milk-catalase. The amount of primary milk-catalase also varies directly with the fat content of the milk and inversely with its d and with the amount of fat-free dry substance of the milk. P. W. C.

Osmotic pressure and milk secretion. W. E. Petersen and T. V. Rigor (Proc. Soc. Exp. Biol. Med., 1932, **30**, 259—264). Nutr. Abs.

Biological relationship between cow's, goat's, and human caseinogens. A. F. Anderson, O. M. Schloss, and H. C. Stuart (Amer. J. Dis. Child., 1932, **44**, 1178—1186).—Cow's (I), human (II), and goat's caseinogens sensitise against each other. Anti-cow's-caseinogen sera gave positive pptn. reactions to (II), and animals that were passively sensitised to (I) exhibited evidence of anaphylaxis when given (II) intravenously. In each case the converse was equally true. Nutr. Abs.

Effect of heat on antigenic properties of milk. J. H. Lewis and H. C. Hayden (Amer. J. Dis. Child., 1932, **44**, 1211—1220).—The serological reactivity of raw (I) and pasteurised (II) milks was $>$ that of evaporated milk (III) and a manufactured sample of

" hypo-allergic fat-free " milk (IV), known as Smaco 303. The caseinogen from (I) and (II) reacted in a higher dilution with all antisera than that derived from (III) and (IV). The reverse is true for the whey-proteins. Although the isolated whey-proteins are extremely heat-labile, showing a decrease in antigenic reactivity even at 60°, caseinogen from (I) is relatively heat-stable, no change occurring in its reactivity until the temp. exceeds 100°. With (I) little change occurs in its antigenic reactivity until the temp. exceeds 110°. There is some evidence that immunisation with heated milks produces antisera that appear to be sp. for the heated antigens.

NUTR. ABS.

Presence in the bile of an enzyme which dehydrogenates stearic acid. G. QUAGLIARIELLO (Atti R. Accad. Lincei, 1932, [vi], **16**, 387—389).—Bile brought to 7·5 by mixed phosphates, saturated with PhMe, and shaken in O_2 absorbs O_2. In presence of Na stearate, the absorption is increased.

T. H. P.

Changes in the secretion and composition of bile during alimentation. S. LEITES and W. JUSSIN (Arch. exp. Path. Pharm., 1933, **169**, 365—384).—The feeding of glucose (I), peptone, flesh (II), nuclein (III), or hempseed oil (IV) or linseed oil (V) to dogs with biliary fistulæ has no influence on the quantity of bile secreted, whilst with butter (VI) there is a decrease. The abs. and relative contents of bile acids are increased with (II) and decreased with (VI); with (III), (IV), and (V) the concn. is slightly increased, whilst with (I) the concn. increases during the first 3 hr. and then decreases for the following 2 hr. In no instance is the concn. of cholesterol or of lipin-P affected.

F. O. H.

Changes in the bile-calcium and -potassium after alimentation. S. LEITES and A. KOSLOWA (Arch. exp. Path. Pharm., 1933, **169**, 385—391).—In dogs with biliary fistulæ the bile-Ca is relatively const., whilst the K level varies considerably. Lesions or inflammation of the gall-bladder or -duct result in an increase of the Ca and, to a greater extent, of the K level. Various types of alimentation have no action on the Ca and K levels.

F. O. H.

Simultaneous study of constituents of urine and sweat. H. H. MOSHER (J. Biol. Chem., 1933, 99, 781—790).—The composition of human sweat (I) qualitatively resembles that of the urine (II) from the same subject. (II) is the more conc. solution containing 3—5 times the amount of total solids and 5—9 times the amount of org. matter. The uric acid-N content of (I) is 0·2—0·5 and the creatinine-N 0·2—0·8 mg. per 100 c.c., whilst the p_H is 5·02—5·71.

F. O. H.

Total analysis of unknown urinary substances. K. HAGENGUTH (Biochem. Z., 1933, **257**, 484—491).—A table summarises the urea content, the total N, C, and vacate O before and after removal of urea and after pptn. also with phosphotungstic acid (I) of five samples of human and rabbit urine. The results suggest that the urinary residue contains substances extremely rich in O and that after pptn. with (I) a mixture of N-containing and N-free substances still remains.

P. W. C.

Detection of β-hydroxybutyric acid in urine and other physiological liquids. J. KHOURI (J. Pharm. Chim., 1933, [viii], **17**, 161—165).—The detection of β-hydroxybutyric acid in urine (after removal of ketones by boiling with a few drops of H_3PO_4) is effected by its oxidation with Na_2O_2 (avoiding excess) in the cold and detection of $COMe_2$ so formed by Frommer's reaction with salicylaldehyde. Preliminary purification and removal of glucose by usual methods are necessary unless the sample is free from sugars and colouring matter.

J. W. B.

Lead in urine. T. C. BOYD and H. D. GANGULY (Indian J. Med. Res., 1932, **19**, 75—80).—Urine of Indians was free from Pb.

CH. ABS.

Examination of urinary ash and uric acid in Wood's light after incomplete ashing. Detection of uric acid. A. HADJIOLOFF and T. KRESTEFF (Compt. rend. Soc. Biol., 1931, **106**, 663—664; Chem. Zentr., 1932, ii, 3128).—A bluish fluorescence, differing from that of fresh urine, is observed after incomplete ashing. Uric acid, slowly ignited until decomp. begins, shows a similar fluorescence. The blue fluorescence becomes yellowish-green on addition of KOH. The test is more sensitive and sp. than the murexide reaction.

A. A. E.

Examination of human and vertebrate animal urine in Wood's light. A. HADJIOLOFF and T. KRESTEFF (Compt. rend. Soc. Biol., 1931, **106**, 662; Chem. Zentr., 1932, ii, 3128).—Fluorescence cannot be due entirely to urochrome or urobilin.

A. A. E.

Organic fraction of urinary phosphorus. B. S. WALKER and E. W. WALKER (J. Lab. Clin. Med., 1932, **18**, 164—166).—An improved method for the determination of org. P in urine is described. The normal output of org. P per 24 hr. is 6—13 mg. (mean 9 mg.). In leucæmia the output is high (up to 23 mg.).

NUTR. ABS.

Excretion of creatinine by the frog's kidney. R. HOBER (Pflüger's Archiv, 1932, **230**, 327—330; Chem. Zentr., 1932, ii, 3115).

Excretion of lipin-insoluble acid dyes through the frog's kidney. R. HOBER and A. MEIROWSKY (Pfluger's Archiv, 1932, **230**, 331—343; Chem. Zentr., 1932, ii, 3115).

Detection of hæmatophorphyrin in, and extraction from, fæces. R. GOIFFON and J. WALTZ (Compt. rend. Soc. Biol., 1931, **108**, 663—664; Chem. Zentr., 1932, ii, 3447).—Garrod's procedure is applied to the separation of hæmato- and coproporphyrin and to the determination by means of fluorescence in $CHCl_3$ solution.

A. A. E.

Correlative regulation of organic and inorganic constituents of venous blood in disease. Parallel determination of lactic acid, ketones, phenols, carbon dioxide, sodium, chlorine (potassium, calcium, phosphorus), and p_H. R. STURM (Arch. exp. Path. Pharm., 1933, **169**, 633—654).—The following mean figures have been found per 100 c.c. of venous blood from healthy individuals: lactic acid 12·66 mg., ketones 7·58 mg. (calc. as $COMe_2$), phenols 39 m.-mol., combined HCO_3 21 m.-equiv., and p_H 7·38. When blood from pathological

cases is abnormally acid, increase of org. anions (lactic acid and ketone) is mainly responsible, whilst when the change is of the opposite type, it is usually due to increase in the concn. of $Na^{\cdot}$. W. O. K.

Physico-chemical and clinical studies of cholesterol metabolism. W. SCHEMENSKY and J. MRUGOWSKY (Z. ges. exp. Med., 1932, **85**, 329—368).—There is very little correlation between serum-cholesterol (I) and rise of blood-pressure; any that exists is to be attributed to the greater age of the patients with hyperpiesia. With increasing age there is a rise in the average (I). In 20 patients with arteriosclerosis the (I) was raised in 11; the rise is attributed to relative impermeability of the vessels through which (I) leaves the blood. Residence at high altitude produced an increase, possibly the result of splenic action. In infectious diseases there is a fall in (I) at the height of infection and a rise during convalescence. The initial fall is attributed to (I) being fixed by toxins. In diabetes the level of the (I) is related in great part but not entirely to general fat metabolism. In nephritis there was no correlation between (I) and blood-pressure or ability to excrete water or concentrate solids. In patients with neoplasms the level of (I) varies, and it is suggested that the rate of tumour growth is the deciding factor. NUTR. ABS.

Antibody to ovalbumin in the blood of allergic subjects. P. WORINGER (Ann. Inst. Pasteur, 1933, 270—281).—Two antibodies (A and B) to ovalbumin have been characterised, only one of which (A) is characteristic of congenital allergy. The optimal zones for the fixation of complement by A and B differ widely. An approx. idea of the content of A of a serum is obtained as follows. Egg-white is added in proportions varying from 1 : 500 to $1 : 5 \times 10^6$ and the mixtures are injected in a normal subject. The following day an injection of egg-white is given and the limits are noted within which an urticarial reaction is produced. There is no fundamental difference between allergy and immunity. P. G. M.

Anæmia. I. Gas metabolism in muscles in experimental anæmia. II. Lactic acid metabolism in muscle in experimental anæmia. III. Resynthesis of lactic acid in anæmic patients. H. SAITO (Tohoku J. Exp. Med., 1932, **19**, 296—307, 308—325, 326—336).—I. In anæmic dogs the O_2 unsaturation of arterial blood entering the gastrocnemius muscle is increased and that of venous blood is normal.

II. In anæmic and normal dogs the venous blood leaving a muscle contains less sugar (I) and more lactic acid (II) than arterial blood. In $NHPh{\cdot}NH_2$ or blood-letting anæmia the arterial and venous (II) are high. In such dogs muscular work causes a less pronounced rise in O_2 consumption and blood-flow and a less pronounced fall in blood-(I) than in normal animals.

III. The blood-(II) in human anæmia is at the upper level of normal limits, and the blood-(I) is normal. Intravenous injection of Na lactate (3 g.) causes a less pronounced but more prolonged rise in blood-(II) than the normal. CH. ABS.

Consumption of oxygen by anæmic blood. K. SIMIDU (Japan. J. Med. Sci., Biochem., 1932, 267—281).—The O_2 consumption of the blood-corpuscles, intact or hæmolysed, of anæmic rabbits is > that of normals. The content of the deproteinised corpuscles in cysteine and cystine, as measured by I titration before and after reduction, is markedly greater in anæmic than in normal rabbit's blood. This difference probably accounts for the change in O_2 consumption. W. O. K.

Test for liver extract [for use in pernicious anæmia]. C. W. EDMUNDS, H. H. BRUECKNER, and A. I. FRITZELL (J. Amer. Pharm. Assoc., 1933, **22**, 91—99).—The method is based on the measurement of the reticulocyte count of pigeon's blood. It is yet only qual. E. H. S.

Intensity of augmented adrenaline liberation elicited by asphyxiating the non-anæsthetised dog. H. SAITO, T. INABA, and W. TAKAHASHI (Tohoku J. Exp. Med., 1932, **19**, 421—439).—Asphyxia in dogs causes hyperglycæmia and increased liberation of adrenaline. The former is partly and the latter entirely inhibited by previous splanchnicotomy. CH. ABS.

Magnesium and cancer in Indochina. J. BABLET and H. BADER (Bull. Assoc. Franç. Cancer, 1932, **21**, 570—573).—In regions where cancer is prevalent the soil and surface H_2O are poor in Mg. NUTR. ABS.

Lactic acid content of normal and carcinomatous tissue. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1933, **214**, 271—280).—The anaerobic glycolysis of normal and cancerous tissue is of the same order. Cancerous tissue and rat's brain tissue both show an aerobic lactic acid (I) content higher than the normal. The rate of formation of (I) is not greater in carcinomatous than in normal tissue. The lessened respiration in the diseased tissue chiefly affects resynthesis, and hence produces an accumulation of (I). J. H. B.

Action of complex-formers and *X*-rays on the partition of lead in organs and tumours. E. FLINT, P. L. GÜNTHER, and F. EICHHOLTZ (Arch. exp. Path. Pharm., 1933, **169**, 618—624).—The partition of an active Pb isotope (I) (from radioactive Th) in normal and sarcomatous rats is not influenced by simultaneous administration of complex-formers. The fate of (I) may be closely followed by the use of multiple inoculation sarcoma (A., 1931, 976). *X*-Irradiation of tumours (II) does not lead to an increased deposition of (I); in old rats the Ca content of (II) increases, whilst the Pb decreases. Thus the division of Pb is not parallel with the increase in the Ca level. F. O. H.

Biochemistry of Rous chick sarcoma. II. V. MORAVEK (Z. Krebsforsch., 1932, **35**, 492—508, 509—522, 626—640; **36**, 386—398; Chem. Zentr., 1932, ii, 3120).—Sarcomatous tissue contains less dry substance and ash than normal tissue. Fowl muscle contains about 100 mg., Rous sarcoma tissue about 300 mg. Na per 100 g. Organs of normal and sarcomatous fowls contain similar amounts of K. The K content of the sarcoma is low (46, normally 300, mg. per 100 g.). Rous sarcoma contains ⩾200, and

surrounding muscle 65, mg. Ca per 100 g. Blood-serum-Ca is rather high, and blood-Ca rather low, in sarcomatous animals. A. A. E.

Inorganic elements in malignant tumours (Rous chick sarcoma). V. Moravek (Biochem. Z., 1933, **258**, 340—346).—In advanced stages of the sarcoma (I) the surface tension, [H·], H_2O content, and contents of inorg. elements (K, Na, Ca, Mg, Cl, S, P) differ, often very greatly, from those of healthy tissue (II) from the same chicks and from those of the tissue of healthy chicks (III), and in the case of some of these factors (II) also differs from (III). The tissue in the immediate neighbourhood of the tumour also has abnormal composition. W. McC.

Extraction of specific substances from mouse sarcoma *in vitro*. P. Mendeleev (Compt. rend. Soc. Biol., 1932, **107**, 901—902; Chem. Zentr., 1932, ii, 3120).—An extract of comminuted mouse sarcoma with Locke solution containing agar, when injected into a growing tumour, arrests its growth or reduces it. A. A. E.

Calcium and phosphorus content of the blood in children with caries-free and carious teeth. I. Jundell and H. Magnusson (Acta paediat., 1932, **14**, 13—18).—In children free from caries serum-P varied between 4·2 and 6·2 mg. per 100 c.c. (average 5·01) and serum-Ca between 9·6 and 12·0 mg. per 100 c.c. (average 10·55), and for those with very advanced caries P was between 4·1 and 5·3 mg. (average 4·71) and Ca between 8·9 and 11·0 mg. (average 9·92). The differences are not significant. Nutr. Abs.

Theory of dental caries; chemical procedures for determining immunity and susceptibility. W. D. Price (Dental Cosmos, 1932, **74**, 1139—1156).—In persons immune to caries Ca and P tend to deposit into the tooth structure from the saliva; in susceptible persons the movement of P, and even Ca, is zero or reversed. The Ca and P in diet can be reinforced sufficiently to control caries by use of sources of vitamins and of ash-forming elements. Ch. Abs.

Mottled enamel and brown stain. J. F. McIntosh, G. Montelius, and Y. C. Ma (Chinese Med. J., 1932, 1099—1103).—The stained and mottled enamel of human teeth, frequently found in North China, contains the normal amount of org. material and of Ca and P, so that decalcification is apparently not involved in its formation. The brown stain does not contain Fe, and therefore does not arise from hæmoglobin. W. O. K.

Lysine excretion in the urine in cystinuria. F. A. Hoppe-Seyler (Z. physiol. Chem., 1933, **214**, 267—270).—From an evaporated urine of cystinuria there was isolated 5-δ-*carbamidobutylhydantoin* (I), $NH_2{\cdot}CO{\cdot}NH{\cdot}[CH_2]_4{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH$, m.p. 198—200°, decomp. 202—205°, affording with HNO_2 5-δ-aminobutylhydantoin, $NH_2{\cdot}[CH_2]_4{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH$ [*chloroplatinate*, m.p. 234—238° (decomp.); *hydrochloride*, m.p. 198—200°; *chloroaurate*, m.p. 189—190° (decomp.)]. (I) is probably an artefact, since it is obtained on evaporation of a mixture of *d*-lysine sulphate, $Ba(CNO)_2$, and aq. H_2SO_4. J. H. B.

Occupation and insulin action in diabetes. F. Brauch (Deut. Arch. klin. Med., 1932, **174**, 352—365).—Of 13 diabetics 10 showed a lower blood-sugar level, diminished urinary excretion of sugar, and a greater response to insulin during bodily work as compared with rest. Nutr. Abs.

Protein, fat, and enzyme chemistry in relation to diabetes. W. Dyes (Chem.-Ztg., 1933, **57**, 133).—A brief summary of recent work on the source of ketonic substances in diabetes. P. G. M.

Ketogenic–antiketogenic relation in the treatment of infantile diabetes. F. Puchulu (Semana med., 1932, ii, 1260—1265).—A diet with a high ketogenic : antiketogenic quotient does not disturb development in children. A const. ketosis is dangerous even in absence of glycosuria. Ch. Abs.

Serum-proteins and -lipins in infantile eczema. H. K. Faber and D. M. Brown (Proc. Soc. Exp. Biol. Med., 1932, **30**, 335—336).—There is an increase in serum-albumin, albumin : globulin ratio, total protein, protein osmotic pressure, and cholesterol; there is a doubtfully significant decrease in serum-globulin and no change in lipin-P. Nutr. Abs.

Blood-glutathione in fever. H. Waelsch and E. Weinberger (Arch. exp. Path. Pharm., 1933, **169**, 625—632).—Fever experimentally induced in man leads to an increase in the I-reducing titre (I) of the blood, the extent of which is dependent on the initial val. of (I). That the increase appears to be limited indicates that the greater part of (I) is due to glutathione (II) and ergothioneine. Injection of (II) into normal or febrile rabbits has no action on the body-temp. F. O. H.

Blood-, tissue-, and urine-protein in kidney diseases. E. G. Schenck and H. Schlüter (Arch. exp. Path. Pharm., 1933, **169**, 343—364).—The constitution of human urine-proteins (I) is different from that of the blood-proteins (II), whilst that of (II) differs from day to day. With kidney disease the kidney- and liver-proteins differ from those of the normal organs both in constitution (III) and distribution (IV). The (III) and (IV) of (I) are changed by administration of urea or protein. The quotient albumin/globulin is of no diagnostic val. F. O. H.

Glycogen-storing [liver] disease. L. Schall (Münch. med. Woch., 1932, **79**, 2078—2080).—Observations are made of an obscure condition involving greatly enlarged liver with abnormally high glycogen content, slight hypoglycæmia, and defective glycogen mobilisation with adrenaline. Nutr. Abs.

Intermediary fructose metabolism in experimental liver damage. H. Steinitz (Z. ges. exp. Med., 1932, **82**, 180—190; Chem. Zentr., 1932, ii, 2990).—$CHCl_3$, but not N_2H_4,H_2SO_4, pulegone, or cocaine, intensifies and prolongs fructosæmia after ingestion of fructose. A. A. E.

Metabolism of the fatty liver. I. Respiration and respiratory quotient. R. Meier and E. Thoenes. **II. Formation and utilisation of lactic acid.** E. Thoenes (Arch. exp. Path. Pharm.,

1933, **169**, 655—666, 667—676).—I. The O_2 consumption of sections of liver from guinea-pigs poisoned with P or $CHCl_3$ and showing fatty degeneration is 40—50% > that of normal starving animals, whilst the R.Q. is markedly < normal. Addition of glucose to Ringer's solution in the case of the fatty livers does not alter the O_2 consumption or the R.Q.

II. Sections of livers from animals poisoned with P probably produce smaller quantities of lactic acid than similar normal liver sections. The isolated liver cell does not appear to vary from the normal in its power to convert lactic acid into carbohydrate.

W. O. K.

Mastitis and carbohydrate deficiency. F. WIEDMANN (Z. Unters. Lebensm., 1933, **65**, 186—198).—A sufficiency of carbohydrates is important for the production of fat and lactose by the cow, and a deficiency causes a fall in these constituents in the milk, and increases in Cl content and (Trommsdorff) sediment-val. In extreme cases the milk loses its emulsifying properties, and contains blood corpuscles.

J. G.

***X*-Ray irradiation in mongolism and its effect on blood-cholesterol level.** A. MADER and E. BINGENHEIMER (Jahrb. Kinderheilk., 1933, **138**, 9—20).—The blood-cholesterol is ordinarily much lower in mongolism than normal and is increased on *X*-ray irradiation. NUTR. ABS.

Ammonium chloride decalcification as modified by calcium intake. Relation between generalised osteoporosis and ostitis fibrosa. H. L. JAFFE, A. BODANSKY, and J. P. CHANDLER (J. Exp. Med., 1932, **56**, 823—834).—Dogs receiving an adequate Ca diet and NH_4Cl showed less decalcification than those receiving a low-Ca diet with or without NH_4Cl. CH. ABS.

Viosterol in experimental fibrous osteitis. A. J. ABELOFF and I. P. SOBEL (Arch. Pathol., 1932, **14**, 471—490).—Lesions of fibrous osteitis, produced in young guinea-pigs by repeated injections of parathormone, were not significantly affected by the administration of vitamin-*D*. NUTR. ABS.

Phosphorus metabolism in general diseases of the bones. M. LABBÉ and M. FABRYKANT (Compt. rend. Soc. Biol., 1931, **108**, 381—382; Chem. Zentr., 1932, ii, 2483).—In osteomalacia and Recklinghausen's disease the blood-P (all fractions except -lipin) is low; in Paget's disease normal vals. are obtained. A. A. E.

Chemical diagnosis of pregnancy. E. O. MANOILOV (Compt. rend. Soc. Biol., 1931, **106**, 913—915; Chem. Zentr., 1932, ii, 3447).—Colour reactions given by serum with diuretin and Nile-blue solutions are attributed to differences in acidity, or to the presence in pregnancy serum of an enzyme which decomposes Nile-blue. A. A. E.

Metabolism after oral administration of glucose to non-pregnant, pregnant, and carcinomatous women. GUTHMANN, GENTZSCH, GOEBEL, and GRÜTZMACHER (Arch. Gyn., 1932, **150**, 78—125; Chem. Zentr., 1932, ii, 3115).—The effects of *X*-irradiation and of administration of glucose on the basal metabolism are described. In pregnancy the blood-sugar reached a higher level and remained high longer than in non-pregnant women. A. A. E.

Arsenic content of the blood of women. Influence of menstrual cycle, pregnancy, and carcinoma. H. GUTHMANN and H. GRASS (Arch. Gynakol., 1932, **152**, 127—140).—The average As content of woman's blood in the inter-menstrual period is 63·8 ($\times 10^{-6}$ g. per 100 c.c.) (range 20·5—113·4) with little variation in the individual. During menstruation there is a 50% increase to an average of 92·5. During pregnancy the increase is still greater, reaching its max. (average 220) between the 5th and 6th months. In the later months of pregnancy there is a gradual fall, but at full term the val. is still above the inter-menstrual val. Carcinomatous subjects have a blood-As content approximating to that found during menstruation. The increase in blood-As may be related to growth processes and cell proliferation.

NUTR. ABS.

Mechanism of the glycosuria of starvation and of under-nourishment. M. SAKAUCHI (J. Biochem. Japan, 1932, **16**, 259—316).—Moderate starvation in rabbits often produces a glycosuria (I) due to a decrease both in insulin secretion and in the kidney threshold val. With more severe starvation this phenomenon does not occur, whilst administration of glucose orally is followed by a very slight hyperglycæmia (II) and intravenously by a prolonged (II) together with (I). Hence severe starvation decreases intestinal absorption of sugar, a decrease which is accompanied by a lowering of the O_2-consumption. F. O. H.

Serum-proteins in infancy and in childhood. Effects of malnutrition and of acute and chronic infections on serum-proteins in infancy and in childhood. C. H. WEBB (Amer. J. Dis. Child., 1932, **44**, 1239—1248).—Normal infants up to 6 months showed low vals. for total protein (I) and particularly for serum-globulin (II), but in older children (2 years and upwards) the vals. for (I) were at the same level as those in the adult. There was no regular relation between the state of nutrition and serum-albumin (III) content, and acute infections were found to produce only comparatively mild and temporary changes in (I). During chronic infections the alterations in the vals. of (I) varied with the type of infection. The most pronounced changes were seen in (*a*) chronic osteomyelitis, which gave high vals. for (II), and (*b*) renal involvement, especially nephrosis, which was accompanied by lowered (III) and lowered total (I), but increased (II). NUTR. ABS.

Vitamin therapy in pulmonary tuberculosis. II. Activated ergosterol hypercalcæmia. P. D. CRIMM (Amer. Rev. Tuberc., 1932, **26**, 112—123).—A cumulative effect on serum-Ca (probably by mobilisation of Ca from the osseous system) is accompanied at first by a brief rise in P concn., and then a gradual fall. After return of Ca to normal, a repetition of the same (massive) dosage produces hypercalcæmia for a longer period. Disagreeable conditions of calcio-toxæmia are alleviated by intravenous injection of $NaHCO_3$. Activated ergosterol increases the Ca, and often the P, in pleural fluid. CH. ABS.

Transmineralisation in the lymphatic glands. P. REINEMER (Biochem. Z., 1933, **257**, 442—449).—Investigation of normal and tuberculous guinea-pig lymphatic glands shows that the K, Ca, Cl, and often the H_2O contents were increased in the pathological glands, and that the Ca content further increased, whereas the K and Cl contents decreased on caseation. Investigation of human glands gave less uniform results. P. W. C.

Chemistry and nutrition. W. R. SIBBALD (Chem. and Ind., 1933, 173—178).—A review.

Action of methylene-blue on cell respiration. W. FLEISCHMANN and S. KANN (Biochem. Z., 1933, **257**, 293—300).—Respiration of the retina *in vitro* is considerably increased by methylene-blue (I). If the oxidation of fructose in neutral PO_4''' solution by atm. O_2 is partly inhibited by KCN, it is increased again by addition of (I), whereas the normal rate of oxidation without KCN is unaffected. The system fructose phosphate–(I) is discussed as a model double respiratory system, a CN′-sensitive Fe respiration and a CN′-insensitive system depending on the oxidation–reduction powers of (I). P. W. C.

Energetics of the mammalian heart. H. GREMELS (Arch. exp. Path. Pharm., 1933, **169**, 689—723).—In a heart–lung prep., the efficiency of the conversion of the energy of oxidation into mechanical energy increases as the rate of mechanical work done becomes greater when this is brought about through increasing the min. vol., but it remains const. when the increase in mechanical work is the result of high aortic pressure. Adrenaline decreases the O_2 uptake specifically and independently of the heart frequency and decreases the mechanical efficiency. Strophanthin and lanadigin decrease the O_2 uptake, whilst the mechanical work remains const. or even increases. W. O. K.

Metabolism of cartilage and callus-tissue. G. KUWABARA (J. Biochem. Japan, 1932, **16**, 389—402).—Cartilage (I) and callus-tissue (II) contain no oxidase, whilst the dehydrogenase activity (III) of (I) is > that of bone (IV). The epiphyseal (I) of rachitic rabbits has a sub-normal (III). Glycolysis by way of hexose phosphate formation provides energy during the formation of (I), (II), and (IV). The val. of (III) is greatest in (II) when calcification is most rapid, whilst with both (I) and (II) advanced development is accompanied by a decrease in (III). F. O. H.

Influence of calcium on cartilage-phosphatase. G. KUWABARA (J. Biochem. Japan, 1932, **16**, 403—406).—The phosphatase of callus-tissue, unlike that of the kidney, is activated by Ca salts. Mg salts are ineffective. F. O. H.

Metabolism of the developing egg of the sea-urchin. J. RUNNSTROM (Biochem. Z., 1933, **258**, 257—279).—In the eggs of the sea-urchin, on fertilisation under aerobic (I) and anaerobic (II) conditions production of acid occurs. Such production also occurs in a hypertonic medium, and is then greater under (II) than under (I). There is a close connexion between the respiration of the eggs and the synthetic processes which occur in them. The production of hexose monophosphate (but not that of lactic acid) is an important factor in the process of development, but normal aerobic fertilisation causes no change in the phosphate fraction or lactic acid content. Under (I), in hypertonic and still more in hypotonic media, changes occur in that fraction. Extracts of both fertilised and unfertilised eggs contain cozymase. W. McC.

Diffusion of atmospheric oxygen into oil-covered water. Development of eggs of *Rana fusca* and *Triton tæniatus* in mineral oil. S. LALLEMAND (Bull. Soc. Chim. biol., 1933, **15**, 91—109).—When covered by a layer (10—40 mm.) of pure paraffin oil, O_2-free H_2O attains equilibrium with the atm. O_2 in approx. 50 hr. With less pure oils, periods of 150—200 hr. are necessary owing to the greater oxidation of the protective oil. An anaerobic condition of the aq. layer is maintained only for the first 3—4 hr. The eggs of *R. fusca* and *T. tæniatus* develop normally when immersed in oil of various degrees of purity or in oil-covered H_2O. F. O. H.

Nutrition of flesh fly larvæ, *Lucilia sericata* (Meig). I. Adequacy of sterile synthetic diets. A. E. MICHELBACHER, W. M. HOSKINS, and W. B. HERMS (J. Exp. Zool., 1932, **64**, 109—128) NUTR. ABS.

Fat metabolism. P. E. VERKADE, M. ELZAS, J. VAN DER LEE, H. H. DE WOLFF, A. VERKADE-SANDBERGEN, and D. VAN DER SANDE (Z. physiol. Chem., 1933, **215**, 225—257).—The use of "intarvin" and of a prep. containing undecoic and tridecoic acids in the treatment of diabetes is discussed (cf. A., 1930, 1206). When normal fat in the diet of diabetics is replaced by glyceryl triundecoate (I), the disordered fat catabolism is partly corrected. Absorption of (I) in the alimentary tract is practically complete, whilst ketonuria and acidosis of the blood are decreased. The lactic acid excretion is unchanged, and no pyruvic acid appears in the urine. Ingestion of 100 g. of (I) is followed by the excretion of approx. 4 g. of nonane-αι-dicarboxylic acid. The possibility of an ω-oxidation occurring in fat catabolism is discussed. F. O. H.

Diet and blood-cholesterol in normal women. R. OKEY and D. STEWART (J. Biol. Chem., 1933, **99**, 717—727).—Variations in the free and total cholesterol (I) of the blood were followed in women fed on diets of low (II) and moderate content (III) of (I). Substitution of (III) by (II) to which was added an amount of (I) equiv. to the deficiency, resulted in slightly lower blood vals. Increased intake of (I) produced an increased level of esterified (I) in the blood. With (III) there was little difference from the menstrual variations in (I) due to (II). F. O. H.

Diurnal cycle in the liver. I. Periodicity of the cycle, with analysis of chemical constituents involved. G. M. HIGGINS, J. BERKSON, and E. FLOCK (Amer. J. Physiol., 1932, **102**, 673—682).—The changes in the liver of the white rat after a 2-hr. feeding and drinking period include the actual wt. of the liver, as well as the increase or decrease in the amount of H_2O, glycogen, protein, and fat for a 2-day period after a single feeding. NUTR. ABS.

Chemical role of normal liver in intermediary metabolism. S. J. THANNHAUSER (Klin. Woch., 1933, **12**, 49—54).—Nucleic acids are broken down in the liver by enzymes which split off PO_4''' and NH_2 groups, leaving oxypurine glucosides. Deamination of NH_2-acids takes place in other organs besides the liver, and actually with greatest rapidity in the kidney. This is presumably to facilitate the excretion of fixed acids as NH_4 salts. Excess NH_3 is also converted by the liver into urea. In conjunction with CO_2, it is linked up with ornithine to form citrulline, which takes up a further mol. of NH_3 to form arginine. This is then hydrolysed by arginase into the original ornithine and urea. The liver is the principal site of production of sugar from non-carbohydrate material. The hæmin of the blood cannot be directly converted by the liver into the bilirubin of the bile, since they are related to ætioporphyrins of different structure. A rupture and re-closure of the pyrrole ring must therefore be assumed. NUTR. ABS.

Energy of urea synthesis. H. BORSOOK and G. KEIGHLEY (Science, 1933, **77**, 114).—The synthesis of urea from NH_3 and CO_2 by liver slices is accompanied by a definite increase in O_2 consumption: one O_2 appears to be used for each $CO(NH_2)_2$ synthesised. Similar results were obtained with glucose and *dl*-lactate and with and without ornithine. L. S. T.

Partition of nitrogenous constituents of urine and its physiological significance. II. Minimal specific excretion of endogenous nitrogen during growth. E. F. TERROINE, G. BOY, M. CHAMPAGNE, and G. MOUROT (Bull. Soc. Chim. biol., 1933, **15**, 42—62).—The total endogenous excretion of N in pigs is proportional to the energy production (A., 1927, 276). When restricted to a protein-free diet, creatine (I) tends to disappear completely from the urine, whilst with growth the excretion of NH_3-, NH_2-acid-, and allantoin-N decreases parallel with the total N. During growth the proportion of excreted (I) to body-wt. is fairly const., the increase in muscle counterbalancing the decrease of functional activity. F. O. H.

Origin of creatine. VII. K. THOMAS, A. T. MILHORAT, and F. TECHNER (Z. physiol. Chem., 1933, **214**, 121—137; cf. A., 1932, 422).—The tolerance of the rabbit for ε-guanidohexoic acid (I) (*picrate*, m.p. 152°; picrolonate, m.p. 236°), ε-methylguanidohexoic acid (II) (*picrolonate*, m.p. 249—251°), γ-methylguanidobutyric acid (III) (*picrolonate*, m.p. 252—255°), and δ-methylarginine (IV) [*diflavianate*, m.p. 231° (decomp.); *picrolonate* $+1{\cdot}5H_2O$, m.p. 227—228°], taken *per os* is about the same as for creatine. A human patient with progressive muscular dystropy can tolerate 3—5 times as much of (I) as of creatine, of (II) and (III) about the same amount. Glycine and γ-aminobutyric acid increase the creatinuria in muscular dystrophy; glutamic and hydantoic acids are without effect. In recovery of (IV) from the urine a small amount of *N*-methyl-2-aminopiperidone was isolated. J. H. B.

Is the capacity to break down exogenous creatine a specific function of the sexually mature organism? O. MÜHLBOCK and C. KAUFMANN (Arch. Gynakol., 1932, **151**, 706—709).—The excretion of creatine and creatinine after intravenous injection of 0·3—1 g. of creatine into women (*a*) during menstruation, (*b*) between menstrual periods, (*c*) with the ovaries removed or functionless by previous operation or disease, (*d*) after the menopause was inconst., creatinuria being sometimes present and sometimes absent. NUTR. ABS.

Effect of administration of tryptophan on the weight and the carbon and nitrogen excretion of the adult animal. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1931, **106**, 590—591; Chem. Zentr., 1932, ii, 2986).—In dogs the N excretion was unchanged, but the C excretion increased. A. A. E.

Effect of administration of histidine on the weight and the carbon and nitrogen excretion of the adult animal. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1931, **106**, 590—591; Chem. Zentr., 1932, ii, 2986).—No effect was observed. A. A. E.

Effect of simultaneous administration of tryptophan and histidine on the weight and the carbon and nitrogen excretion of the adult animal. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1931, **106**, 593—595; Chem. Zentr., 1932, ii, 2987).—The C excretion is const.; the N excretion is const. or diminished. A. A. E.

Variation in the protein intake of sheep in relation to wool growth. A. H. H. FRASER and J. A. F. ROBERTS (J. Agric. Sci., 1933, **23**, 97—107).—Wool characteristics (fineness, length, fibre-wt.) were not significantly different from sheep receiving high- and low-protein diets. The synthesis of cystine is suggested as a special function of the wool follicle. A. G. P.

Covering of nitrogen and sulphur balances by cystine at the level of endogenous protein metabolism. E. F. TERROINE, P. MEZINCESCO, and S. VALLA (Compt. rend., 1933, **196**, 502—504).—Ingestion of cystine slightly reduces the negative N balance of pigs on a carbohydrate diet at the level of min. expenditure of N; the S balance becomes positive simultaneously. There is therefore no parallelism between N and S metabolism. A. C.

Comparative excretion of neutral sulphur in endogenous and exogenous nitrogen metabolism, and its significance. O. V. AMANN and G. MOUROT (Compt. rend., 1933, **196**, 504—506).—The urinary N (I) and neutral S (II) of pigs are 4·85 g. and 0·137 g. daily, respectively, on a carbohydrate diet containing only 1·65 g. of protein-N per day. If the latter is increased to 30·7 g., (I) rises to 14·93 g., whilst (II) is almost stationary. On a protein diet, however (100 g. of protein-N and 5·63 g. of S per day), (I) is 70·96 and (II) shows a distinct rise to 0·427 g. There appears to be no essential difference between endogenous and exogenous protein metabolism, although, in the latter, production of neutral S is lower. A. C.

Effect of age on metabolism, especially on sulphate excretion in urine. M. MÜHLMANN

(Deut. Arch. klin. Med., 1932, **174**, 432—443).—A fall in the urinary excretion of SO_4'' occurs with advancing age. NUTR. ABS.

Influence of thiol on the formation of aberrant disorganised overgrowths in the regenerating right chela of the hermit crab (*Pagurus longicarpus*). F. S. HAMMETT and D. W. HAMMETT (Protoplasma, 1932, **17**, 321—358).—The growth and differentiation of overgrowths are accelerated by ·SH and retarded by :SO. The SH group is specifically responsible for the formation of certain typical emergent disorganised growths. A. G. P.

Chemical basis of nerve stimulation. H. WINTERSTEIN (Naturwiss., 1933, **21**, 21—23).—NH_3 is produced at the rate of $13{\cdot}5\times10^{-6}$ g. per g. of nerve tissue per hr. The average increase in NH_3 production by the action of reflex stimuli is 24%. Its production is a vital process in nerve metabolism. P. G. M.

Ammonia formation in mammalian nerve. K. HALTER (Biochem. Z., 1933, **257**, 313—324).—Rabbit's isolated surviving sciatic nerve eliminates $4—5\times10^{-6}$ g. of NH_3 per g. per hr. Temp. does not but electric stimulation does lead to the formation of a considerably increased amount of NH_3. Mechanical stimulation also increases and asphyxiation decreases NH_3 formation. When the nerve is still connected with the central nervous system, NH_3 formation in the first 0·5—1·5 hr. is $13{\cdot}56\times10^{-6}$ g. per g. per hr., 2—3 times as great as in the isolated prep. Reflex stimulation by mechanical means increases the NH_3 formation by 24% of the resting val. Urethane narcosis of the animals and asphyxiation of the nerves cause considerable decrease. P. W. C.

Formation of carbon dioxide and ammonia by non-medullated mammalian nerves. H. ROSENBAUM and K. HALTER (Biochem. Z., 1933, **257**, 325—332).—Repetition of former work (A., 1932, 770) confirms the fact that for ox splenic nerve at body temp. the CO_2 elimination is much < would correspond with the O_2 absorption, leading to a R.Q. of 0·335, whereas the R.Q. at room temp. is 0·78. The excess utilisation is probably involved in dehydrogenation processes. The formation of NH_3 at room temp. is of the same order as for medullated nerves and is dependent on the temp., being increased at body temp. P. W. C.

Dependence of the oxygen utilisation of the intercostal nerves of the ox on the oxygen tension. A. PRAGER (Biochem. Z., 1933, **257**, 301—306).—The O_2 utilisation of a nerve (diam. 1·9 mm.) reaches a limiting val. at 15—18% O_2 and decreases below this val. approx. proportionally with the O_2 tension. P. W. C.

Elimination of carbon dioxide by nerves under reflex stimulation. J. VON LEDEBUR (Biochem. Z., 1933, **257**, 310—312).—Reflex stimulation of mammalian nerve under physiological conditions does not increase the elimination of CO_2. P. W. C.

Sugar metabolism of non-medullated mammalian nerves. H. ROSENBAUM (Biochem. Z., 1933, **257**, 307—309).—The previously discovered (A., 1932, 770) increased utilisation of O_2 by ox splenic nerves on addition of glucose is confirmed. The excess utilisation is greatest in the first hr., the mean val. being four times that of medullated nerve under the same conditions, and then rapidly falls away. P. W. C.

Specific dynamic action of food. II. Gas exchange after administration of carbohydrates in different animals. U. LOMBROSO and S. DI FRISCO (Arch. internat. Pharmacodyn., 1932, **44**, 50—66).—Sucrose (3—4 g.) given in H_2O by mouth had no appreciable effect on the gas exchange of pigeons or rats. In dogs orally given sucrose or intraperitoneally given glucose raised the metabolism by as much as 30%. NUTR. ABS.

Absorption rates of galactose and mannose. C. E. BURGET, R. LLOYD, and P. MOORE (Proc. Soc. Exp. Biol. Med., 1932, **30**, 368—370).—Using closed jejunal loops in dogs and unanæsthetised rats the relative rates of absorption of galactose and mannose were: in dogs, 108 : 49; in rats, 115 : 64. Mannose cannot be accurately determined by the Shaffer–Hartman method. NUTR. ABS.

Metabolism of lactose. II. Blood-sugar during lactation. L. B. WINTER (J. Physiol., 1933, **77**, 100—103).—Analysis of combined blood samples from nursing women showing lactosuria gave no evidence of the presence of either lactose or galactose. There is therefore no renal threshold for lactose. NUTR. ABS.

Effect of glucosamine on metabolism in the pigeon. D. C. ZUMMO (Arch. Internat. Pharmacodyn., 1932, **44**, 40—49).—Oral administration of 3—4 g. of glucosamine to pigeons caused the O_2 consumption to fall by as much as 30%. It returned to normal in about 2 hr. Subcutaneous or intramuscular injections of smaller doses into pigeons or rats also caused the O_2 consumption to fall, and it did not return to normal in 4—5 hr. NUTR. ABS.

Lactic acid formation in liver cells. M. OKUYAMA (J. Biochem. Japan, 1932, **16**, 237—258).—Isolated liver cells (A., 1932, 428) neither consume O_2 nor form lactic acid (I) owing to the absence of hexose degradation. With unwashed cells the effect of various dyes on the O_2 consumption is parallel to that on the glycolysis, but not to that on the formation of (I). On keeping, the formation of (I) rapidly decreases owing to decomp. of glyoxalase (II) coenzyme (III), whilst the O_2 consumption is only slightly changed. The liver-(II) is more stable than (III). F. O. H.

Resynthesis of lactic acid in man. S. DIETRICH and M. ZEYEN (Z. klin. Med., 1932, **120**, 517—548; Chem. Zentr., 1932, ii, 2991).—Injection of Na *r*-lactate proportionally increases the O_2 demand and the CO_2 produced. 2% is excreted by the kidneys; 20·9% is burnt. In liver diseases and diabetes the quantity burnt is greater. A. A. E.

Bile acids and carbohydrate metabolism. XXIII. Influence of bile acids and of adrenaline on experimental glycocholia. T. TANAKA (J. Biochem. Japan, 1932, **16**, 407—416).—The glycocholia induced in dogs with biliary fistulæ by intravenous injection of glucose is reduced by simultaneous

administration of cholic acid (I) and increased by that of adrenaline (II). Unilateral splanchnicotomy increases the action of (I), but reduces that of (II). The differences between glycosuria and glycocholia are discussed. F. O. H.

Glutathione, iodoacetic acid, and glucose metabolism. J. H. QUASTEL (Nature, 1933, **131**, 206; cf. this vol., 314).—The toxicity of $CH_2I{\cdot}CO_2H$ (I) *in vivo* is diminished or eliminated by admixture with $Na_2S_2O_3$ (II). One mol. of (I) combines with 1 of (II). The inhibitory action of small amounts of (I) on the oxidation of glucose by brain tissue is decreased or inhibited by the addition of glutathione (III), cysteine, or (II) to the tissue. There is a direct action between the S compounds and (I). (III) markedly affects the relationship between fermentation and the respiration of yeast in the presence of glucose. The toxicity of (I) towards biological processes appears to be connected with its power to combine readily with SH compounds, and (III) plays a part in processes inhibited by (I). L. S. T.

Resistance of glucoseureide to urease and other enzyme action; non-absorbability of glucoseureide from the jejunum. F. A. CAJORI (Proc. Soc. Exp. Biol. Med., 1932, **30**, 184—186).—Glucoseureide (I) was not attacked by urease or by yeast. (I) was not hydrolysed or absorbed when placed in Thiry-Vella loops, and when injected into the blood it was excreted unchanged almost quantitatively in the urine. NUTR. ABS.

Relative fatigue recovery values of different carbohydrate mixtures. D. A. LAIRD (J. Ind. Hygiene, 1933, **15**, 89—97).—In the acceleration of the recovery from mental and physical fatigue, ingestion of milk (I) containing 70% maltose (II) is superior to (I) containing the carbohydrate equiv. as 20% (I) +48% sucrose, which, in turn, is superior to milk alone. The phenomenon is explained by the greater rates of absorption and assimilation of (II). F. O. H.

Glucose and the moulting of crustaceans. A. DRILHON (Compt. rend., 1933, **196**, 506—508).—The blood-glucose (I) of crabs rises during moulting, then falls and rises again in the adult stage, but to a lower level. (I) is slightly higher in females than in males. The total glucose of crabs is approx. const. at 3·4—3·6 g. per kg., at all stages of development and in both sexes. A. C.

Phosphorus [in the blood] and moulting of crustaceans. A. DRILHON (Compt. rend., 1933, **196**, 725—726).—Although the total P in the blood of *Maia* remains const. at all stages of the animals' development (the quantity in the blood of the female being twice that of the male), the proportion of org. P increases rapidly after moulting at the expense of inorg. P, and, in adults, may then represent 84% of the total P. J. W. B.

Natural phosphates in cattle-feeding. H. VELU (Rev. vet. et J. Méd. vet. et Zootech., 1932, Nov.).—Experiments on sheep show the toxic effects of (*a*) prolonged addition of small doses of natural phosphate to the ration (3% of the grain ration for 2 years); (*b*) providing H_2O containing PO_4'''. NUTR. ABS.

Mechanism of adaptation to varying salinity in the common eel; osmotic regulation in fishes. A. KEYS (Proc. Roy. Soc., 1933, **B**, **112**, 184—199).—H_2O swallowing plays an essential role in the adaptation of eels to sea-H_2O (I), but not in fresh H_2O (II). Transference of eels from (II) to (I) causes a loss in wt. due to a passive outward flow of H_2O which is counteracted after about 10 hr. by an active process, delayed by narcosis, in which H_2O is taken up, adaptation being complete in 2 days. The change from (I) to (II) results in the reverse order of wt. change. In adaptation to (I), osmotic regulation is effected by the gills which excrete excess salt due to ingested (I), whilst the kidney is responsible for adaptation to (II). The euryhaline teleost is considered a typical fresh-H_2O fish in (II) and typically marine in (I). A. C.

Increased permeability [of larvæ] to acetic acid in narcosis. M. A. VAN HERWERDEN (Protoplasma, 1932, **17**, 358—375).—The permeability of the tail membranes of larvæ of *Rana temporaria* and *R. esculenta* to AcOH increases and that to neutral-red and other dyes decreases during narcosis. A. G. P.

Cellular toxicity of ethyl alcohol. S. LALLEMAND (Bull. Soc. Chim. biol., 1933, **15**, 84—90).—Fresh eggs of hens, when exposed to air saturated with EtOH at 18° for periods of 9 hr. or more, are rendered sterile. The rate of penetration of EtOH vapour through the shell agrees approx. with Graham's law of diffusion, the toxic action occurring when the concn. within the egg reaches approx. 0·4%. F. O. H.

Influence of narcotics on the sugar-excretion threshold. Y. IWANAGA (J. Biochem. Japan, 1932, **16**, 417—431).—Administration of morphine, Et_2O, or $CHCl_3$ to dogs produces an increase of blood-sugar and a lowering of the kidney threshold val. The sympathetic origin of the hyperglycæmia (I) is demonstrated by its inhibition following bilateral splanchnicotomy (II) or injection of ergotamine. (I) due to adrenaline is not influenced by (II), but in such animals it is partly inhibited by narcotics. F. O. H.

Optically active hydantoins as hypnotics. H. SOBOTKA, S. M. PECK, and J. KAHN (J. Pharm. Exp. Ther., 1933, **47**, 209—215).—*l*-Phenylethylhydantoin (I) is as effective as *r*- but 1·25—1·5 times as active as the *d*-isomeride (II) in regard to the min. effective and lethal doses. The toxicity of (II) is, however, only one third that of *r*- as judged by the incidence of nirvanol disease after oral administration in humans. The curative effect therefore does not depend on the appearance of the nirvanol disease. It is suggested that the mechanism of the drug eruption may be explained on the assumption that the (I) is a "spontaneous haptene." A. L.

Piperidinopropanediol diphenylurethane hydrochloride—a new local anæsthetic. T. H. RIDER (J. Pharm. Exp. Ther., 1933, **47**, 255—267).—The hydrochloride ("diothane"), m.p. 195—196°, gives unstable saturated aq. solutions containing 1·3%; $\geqslant$ 1·0% aq. solutions are stable below p_H 5·6; above this val., the free base is pptd. The aq. solutions may be sterilised without loss of activity and have considerable antiseptic power. With rapid

intravenous injection diothane is thrice as toxic as, but on subcutaneous injection less toxic than, novocaine. On mucous membrane the anæsthetic activity is twice that of cocaine; when injected it is thrice as active as novocaine. A. L.

Biological assay of analgesics and their mixtures. III. E. Hesse and H. Reichelt (Arch. exp. Path. Pharm., 1933, **169**, 453—458). F. O. H.

Complex constant of the reaction between novocaine and caffeine. R. Labes and H. Rutenbeck (Arch. exp. Path. Pharm., 1933, **169**, 557—575).—Caffeine (I) and novocaine hydrochloride (II) form a 1 : 1 complex, the complex const. being 20—30. Hence the retardation by high concns. of (II) of the rigor in frog's muscle due to (I) depends on this phenomenon, whilst the action of (II) at low concns. must depend on a sp. action of (II). A parallelism appears to exist between the affinity for adsorption and that for complex-formation when these affinities are correlated with the constitution. F. O. H.

Application quotient and the pharmacological differentiation of similarly acting drugs. P. Pulewka (Arch. exp. Path. Pharm., 1933, **169**, 482—497).—The ratio between the doses of a drug necessary to cause death, anæsthesia, mydriasis, etc. when administered to the same animal by two different routes is termed the "application quotient." Its use in differentiating similarly acting drugs is exampled by various mydriatics and local anæsthetics. F. O. H.

Purification of visceral extracts. New method of toxicological examination for alkaloids. J. A. Pinto (Anal. Asoc. Quím. Argentina, 1932, **20**, 168—175).—The extract of the macerated viscera (100 g.), obtained with dil. H_2SO_4, is neutralised, KOAc (8 g.) is added, and then a solution of an equal amount of $SnCl_4$. This pptn. is repeated, and alkaloids are extracted from the filtrate and washings in the usual way. 90—98% of alkaloid is recovered. R. K. C.

Pharmacology of *Clerodendron*. H. C. Hon (Chinese J. Physiol., 1932, **6**, 353—356).—A variety of Huang-teng from South China, identified as *Clerodendron commersonii*, Spreng., contained only a trace of alkaloids, the amounts being too small to cause any physiological effect. No other active principle was present. A. L.

Toxic action and elimination of nicotine. I. Toxic action of nicotine and oxynicotine. II. Elimination and cutaneous absorption of nicotine and caffeine. N. Sabatucci (Atti R. Accad. Lincei, 1932, [vi], **16**, 520—523, 524—527).—I. For a frog of 20 g., the min. dose of nicotine causing complete paralysis and recovery after a few hr. is 1·2 mg. and the min. lethal dose 3 mg. With oxynicotine the min. lethal dose is 15 mg. The toxic action of nicotine thus depends, at least partly, on the chemical function blocked by the O in oxynicotine.

II. If a frog (20 g.) is placed in 200 c.c. of H_2O immediately after subcutaneous injection of nicotine, the min. lethal dose falls to 1·5 mg., but such dose remains at 3 mg. if the animal is placed in 200 c.c. of H_2O containing the alkaloid. Similar differences are found with caffeine. T. H. P.

Tar in cigarette smoke and its possible effects. W. D. McNally (Amer. J. Cancer, 1932, **16**, 1502—1514).—The tar contains nicotine, phenols, C_5H_5N bases, and NH_3. Physiological effects are discussed. Ch. Abs.

Tobacco tar: alleged carcinogenic action. E. Bogen and R. N. Loomis (Amer. J. Cancer, 1932, **16**, 1515—1521).—Tobacco tar did not produce cancer when painted on the skin of mice and rabbits over periods in which gas tar produced cancer. Ch. Abs.

[Pharmacological effect of] milk. N. J. Modi (Arch. internat. Pharmacodyn. Thér., 1932, **43**, 111—121).—Frog hearts were perfused with Ringer to which were added different quantities of milk, raw, heated, or dried, or milk derivatives, casein, whey, lactose, or alcohol extract of milk. Whole milk in all cases acted as a powerful stimulant. Nutr. Abs.

2-Amino-1-hydroxyhydrindene, an ephedrine-like substance. W. Augstein (Arch. exp. Path. Pharm., 1933, **169**, 114—118).—The action of the compound (I) on the frog's heart and on the blood-vessels, and intestinal and bronchial muscles of homeotherms, resembles that of ephedrine (II). The toxicities for guinea-pigs and rats are equal, but for mice that of (I) is < that of (II). (I) is rapidly absorbed from the intestine. F. O. H.

Rôle of the augmented adrenaline secretion in dogs after guanidine on the fluctuation of the blood-sugar concentration simultaneously occurring. H. Tada (Tôhoku J. Exp. Med., 1932, **20**, 1—13).—Contrary to results obtained with normal dogs, intravenous administration of guanidine hydrochloride (I) to doubly splanchnotomised animals brought about a lowering of the blood-sugar level. Simultaneous administration of (I) and adrenaline was followed by an effect which resembled in degree and duration the algebraic sum of the results obtained from the separate administration of these two substances. Nutr. Abs.

Effect of acetylcholine on the carbohydrate metabolism. Blood-sugar; muscle-glycogen. H. Ernould (Compt. rend. Soc. Biol., 1931, **108**, 434—435, 436—440; Chem. Zentr., 1932, ii, 2483).—In normal rabbits acetylcholine (2·5 mg., subcutaneous) produces slight hyperglycæmia. In vagotomised and nephrectomised rabbits with high blood-sugar following ingestion of glucose (0·6 g. per kg.) the same quantity of acetylcholine produces hypoglycæmia.

In cats after destruction of the brain and spinal cord glycogen is not regenerated in fatigued muscle; it is regenerated, however, when acetylcholine is injected into such animals. This formation of glycogen is independent of the secretion of insulin. A. A. E.

Carbamylcholine. III. Action on gastric and uterine muscle. Habituation or accumulation. W. Velten (Arch. exp. Path. Pharm., 1933, **169**, 223—237).—Carbamylcholine chloride (A., 1932, 301) increases the tonus of and excites single contractions in the gastric musculature which are accompanied

by an increased secretion of gastric juice. It produces a contraction of the isolated uterus (cat, pig), and whilst intravenous injection of large doses increases the blood-sugar of rabbits, that of small doses has no effect. Repeated dosage is attended neither by accumulative action nor by habituation. F. O. H.

Physiological-chemical analysis of the depressor action of organ extracts. II. K. FELIX and A. VON PUTZER-REYBEGG (Arch. exp. Path. Pharm., 1933, **169**, 214—222).—The compound $C_4H_{12}N_6$ from mesentery (A., 1932, 414) [*diflavianate* (I), sinters 226—227°, decomp. 230—231°; *dipicrate*, m.p. 196—197° (decomp.); *dichloroaurate*, m.p. 204°] has a marked depressor activity on the atropinised cat, that of (I) being significant with $2·5—5\times10^{-6}$ g. F. O. H.

Assay of antipyretics. Comparison of an optically active antipyretic with its racemate. W. HEUBNER and W. SILBER (Arch. exp. Path. Pharm., 1933, **169**, 530—536).—Selected mice, kept at a const. external temp., or rabbits in which fever has been induced by subcutaneous injection of bacteria-rich hay infusions, are suitable subjects for the testing of antipyretics. The two optical isomerides of 1-(3-methyl-Δ^1-*cyclo*hexenylphenyl)-2 : 3-dimethylpyrazolone are equal in their blood-temp. lowering action. Bis-*p*-phenetylphenylacetamidine exhibits neither antipyretic nor methæmoglobin-forming activity. F. O. H.

Action of condiments on the movement of the intestinal villi and glucose absorption. E. VON KOKAS and G. VON LUDANY (Arch. exp. Path. Pharm., 1933, **169**, 140—145).—Pimento, garlic, pepper, paprika, onion, cinnamon, and caraway accelerate the movement of the villi of the isolated or *in situ* dog's or pigeon's intestine. The rate of absorption of glucose is also increased to an approx. proportional degree. These two factors lead to an increased val. of the nourishing power of a diet on addition of condiments. F. O. H.

Toxic effects of large amounts of sugar in the blood. C. EVANS (J. Physiol., 1933, **77**, 189—193).—Nine rabbits were injected intravenously with 4·5—30 g. of sugar in 10—15% solution. Blood-sugar vals. were obtained up to 1·90%. No pathological effects could be attributed to the raised blood-sugar content. NUTR. ABS.

Pharmacology of soaps. J. MANGER (Arch. exp. Path. Pharm., 1933, **169**, 268—274).—Aq. Na oleate (I), but not Ringer's solution, removes the effects of poisoning by quinine from the isolated frog's heart. With the normal heart, dil. aq. (I), palmitate, or stearate is more harmful than more conc. solutions. This phenomenon is contrary to the behaviour of soaps in hæmolysis, to their toxicity to tadpoles, and to their action on frog's ciliated epithelium. The growth-accelerating properties of (I) on implants of fowl embryonic tissue are not observed with plants (lupin and wheat). F. O. H.

Avoidance and termination of pregnancy in white rats by means of fission products of fats. B. A. KUDRJASHOV (Arch. exp. Path. Pharm., 1933, **169**, 275—289).—In rats fed on a diet containing lard which has been exposed to the air for 12—18 months, egg-implantation fails or an absorption of the embryos occurs. The fertilised egg is not killed prior to implantation. Rancid lard on saponification and extraction with org. solvents yields two fractions which, on administration to pregnant rats on a normal diet, result in termination of pregnancy, especially between the 6th and 9th day. Sterility due to the action of fatty degradation products is not identical with that due to lack of vitamin-*E*. F. O. H.

Spermicidal powers of chemical contraceptives. V. Comparison of human and guinea-pig sperms. J. R. BAKER (J. Hyg., 1932, **32**, 550—556). CH. ABS.

Experimental variation of the toxicity of digitalis. I. Influence of hypertonic solutions and of experimental uræmia. R. KOHN and B. C. COSTOPANAGIOTIS (Arch. exp. Path. Pharm., 1933, **169**, 146—163).—Intravenous injection of hypertonic aq. NaCl, urea, or glucose into cats produces definite changes in the blood-pressure (I) without injuring the circulatory system. Injection of such solutions simultaneously with or followed by continuous or single dosage of digitalis extract (II) produces similar changes in (I) and, even with 60—70% of the normal min. lethal dose of (II), death. This effect is due to osmotic changes in the blood and tissues due to the hypertonic solution; thus uræmia resulting from $HgCl_2$-poisoning or ligature of the ureters has the same action. F. O. H.

Glucosides acting on the heart. I. Elimination of strophanthin under various conditions. L. LENDLE (Arch. exp. Path. Pharm., 1933, **169**, 392—413).—Injection of 70—80% of the lethal dose of strophanthin (I), followed by slow continuous injection at the rate of 0·006 and 0·03 mg. per kg. per hr. into cats (II) and rabbits (III), respectively, just fails to cause death. Hence the rate of elimination or detoxication of (I) is five times as great in (III) as in (II). Experimentally induced fever in (III) increases the rate of elimination by 20—30%, whilst it is decreased by thyroidectomy and increased by administration of thyroxine. F. O. H.

Pharmacology of *Adonis vernalis*. R. A. HATCHER and H. B. HAAG (J. Pharm. Exp. Ther., 1933, **47**, 217—232).—The average activity of four specimens of *Adonis* (I), as tested by the method of Hatcher and Broody, was < that of good quality digitalis (II). The fatal dose was 100—140 mg., the leaves being more active than the stems. A mixture of the leafy portions deteriorated 35% in 9 months. The infusion, the tincture, and the fluid extract were absorbed irregularly from the gastro-intestinal tract of the cat. (I) is an active emetic, its action being similar to that of (II). The active principles of (I) are sol. in H_2O and 70% EtOH, and a $CHCl_3$ extract of the infusion gives a substance resembling digisol, the purified extract being half as active as cryst. digitoxin. The results indicate that (I) might be used in cases of cardiac disease if (II) were not available. A. L.

Nitrobenzene poisoning. W. BONDE (Pharm. Zentr., 1933, **74**, 113—114).—An account of a fatal case. S. C.

Infiltration of fat into the liver. A. LOEWY and G. CRONHEIM (Biochem. Z., 1933, **257**, 267—288).—The body-wt. of starving guinea-pigs decreases less on keeping at reduced pressure than at normal air pressure. The liver decreases relatively far more than the body-wt. In fed guinea-pigs, keeping at reduced pressure leads to fatty liver, the lipin-sol. P being found chiefly in the $COMe_2$ fraction, but in starving guinea-pigs has not this action, and the Et_2O-sol. P is increased relative to the total P. Similar experiments with rabbits, hens, and geese are reported and differences noted. P. W. C.

Influence of rarefaction of air on the glutathione content of the liver. S. L. MALOWAN (Biochem. Z., 1933, **257**, 437—441).—Seasonal variation of the glutathione content (I) of rat's and guinea-pig's liver could not be detected. (I) increases on keeping the animals at diminished pressure, during surgical shock, and in certain diseases. P. W. C.

Effect of magnesium salts on content of reduced gluthathione in the organs of the dog. R. WOLFF and S. MANJEAN (Compt. rend. Soc. Biol., 1932, **111**, 779—781).—The livers of dogs which had been receiving 2 g. daily of $MgSO_4$ contained larger amounts of reduced glutathione than did livers of control dogs. NUTR. ABS.

Properties and biological action of complex salts of the alkaline earths. K. MULLI and F. STAUDENATH (Arch. exp. Path. Pharm., 1933, **169**, 605—617).—The toxicities of Mg salts and Na citrate (I) are mutually decreased on their admixture, due to the formation in the blood of (I)–Ca citrate complexes. Determinations of the max. effect of this phenomenon, together with those of conductivity etc., indicate that in aq. solution complex salt formation occurs with 36% of (I) and 25% of $MgSO_4$, 20·6% of $MgCl_2$, 29·6% of $MgBr_2$, or 26% of $Mg(NO_3)_2$. F. O. H.

Microscopic study of tissues of the albino rat following the ingestion of aluminium salts. E. SCOTT and M. K. HELZ (Amer. J. Hyg., 1932, **16**, 865—870).—No deleterious effects were caused by Al salts (≯ 3·6% of feed). CH. ABS.

Cobalt-proteins of serum and liver and their distribution in the organism. Affinity between proteins and their parent organs. P. MASCHERPA and L. CALLEGARI (Arch. exp. Path. Pharm., 1933, **169**, 206—213).—Subcutaneous injection into rabbits of small amounts of Co in combination with liver-protein (I) results in a greater accumulation of Co in (I) than in the serum-protein (II). Administration of the Co compound with (I) leads to a lower content of Co in the urine and a greater content in the fæces than that of the compound with (II). The theory that this partition is due to the natural affinity of the protein for its parent organ is discussed. F. O. H.

Spectro-analytical detection of bismuth in tissue and determination of mercury in urine. R. PROBST (Arch. exp. Path. Pharm., 1933, **169**, 119—129).—Very small amounts of Bi are detectable by means of a method using a high-frequency current. Determination of amounts $> 16\times10^{-6}$ g. of Hg is also possible; with urine 50 c.c. are required. With gum-tissue localised occurrence of traces of both Bi and Cu was established, those parts free from Bi being also free from Cu. F. O. H.

[Physiological] action of copper. S. ODA and T. OSUKA (Z. ges. exp. Med., 1932, **82**, 128—142; Chem. Zentr., 1932, ii, 2990).—Parenteral or enteral administration of Cu produces general metabolic changes similar to those produced by Fe. A. A. E.

Distribution of arsenic in the organism after cutaneous resorption of therapeutic doses. L. FUCHS (Deut. Z. ges. gerichtl. Med., 1932, **19**, 280—284; Chem. Zentr., 1932, ii, 2497).—As (≯ 0·1 mg. per 100 g.) was found chiefly in the liver and kidneys, but also in the brain and heart. In bones (lower leg) 6 mg. per 100 g. was found. A. A. E.

Microchemical determination of lead in organic material [urine]. A. NECKE and H. MULLER (Arch. Pharm., 1933, **271**, 81—92).—Separation of 0·1 mg. Pb from 500 c.c. of urine cannot be effected electrolytically, but it may be pptd. together with PO_4'' with $CaCl_2$ and NH_3, as PbC_2O_4 or as PbS, especially in presence of added $CuSO_4$. Titrimetric methods based on separation of PbO_2 or $PbCrO_4$ are inaccurate for < 0·1 mg. Pb. Nephelometric methods with $PbSO_3$ (Badham and Taylor, Rep. of Dir.-Gen. of Public Health, N.S.W., 1925) and PbS (Danckwortt and Uhde, A., 1927, i, 277) are more satisfactory, but not entirely so, neither are the usual colorimetric methods based on pptn. as PbS or the blue colour produced by PbO_2 on tetramethyldiaminodiphenylmethane (I). The most satisfactory method is as follows: 1 litre of slightly acid urine is pptd. with $K_2C_2O_4$ and $CaCl_2$, the ppt. ignited, and dissolved in HNO_3 with addition of 15 mg. $CuSO_4$ or $FeSO_4$, and metals are pptd. with H_2S. The sulphide ppt. is treated successively with EtOH–H_2SO_4 and KCN solution and the residue dissolved in HNO_3. Pb is finally separated electrolytically as PbO_2 and the latter determined colorimetrically with (I). The error is $< \pm 0{\cdot}02$ mg. Pb. S. C.

Effect of thallium on metabolism. M. KOJIMA-KIOTO (Arch. Gynakol., 1932, **152**, 82—88).—Administration of Tl acetate to rats resulted during the first three weeks in a deterioration of the hair and disturbance of the sexual cycle. A qual. increase in the oxidative powers of the organism was indicated by a diminution of the urinary quotients C : N, vacate-O ($KMnO_4$ val.) : N, and vacate-O : C. NUTR. ABS.

Action of intravenous injection of sodium hydrogen carbonate on kidney-fat in the dog. C. ACHARD, J. VERNE, M. BARIETY, and E. HADJIGEORGES (Compt. rend. Soc. Biol., 1933, **112**, 30—31).—When $NaHCO_3$ is intravenously injected into dogs, the alkaline reserve is increased, the total blood-lipins, cholesterol, fatty acid, and lipæmic index show slight variations (usually a decrease), but the kidney-fat does not appear to be altered in spite of the alkalosis. NUTR. ABS.

Pharmacology of inorganic thiocyanates. E. G. JAHR (Arch. exp. Path. Pharm., 1933, **169**, 429—452).—The properties of the Li (I), Na (II), NH_4 (III), and Ca (IV) salts were investigated in rabbits, dogs, cats, and guinea-pigs. Those of (I), (II), and (III) are

similar, being characteristic of SCN′, whilst those of (IV) are modified by Ca″. F. O. H.

Pharmacology of metaphosphoric acids. B. BEHRENS and K. SEELKOPF (Arch. exp. Path. Pharm., 1933, **169**, 238—245).—Moderate amounts of Na hexametaphosphate (I) or of $Na_4P_2O_7$ (II) cause no marked injury when fed to mice. Trimetaphosphate (III) occasionally leads to a loss in body-wt. When introduced by stomach-tube to mice or intravenously to rabbits, (II) is more toxic than (I) or (III). The action on blood-pressure and -coagulation indicates that the toxicity of (I) and (II) on intravenous injection is due to pptn. of Ca in the organism and that (I) and (II) are finally converted into non-toxic orthophosphate. F. O. H.

Blood of rabbits in experimental sodium fluoride poisoning. M. VALJAVEC (Z. ges. exp. Med., 1932, **85**, 382—386).—Acute NaF poisoning causes a fall in serum-Ca and -P, a reduction in white cells, especially lymphocytes, and a shift of polymorphs to the left, but no const. changes in red cells or hæmoglobin. Chronic NaF poisoning causes a fall in serum-Ca, great variations in P, normal or increased numbers of white cells, and a fall in red cells and hæmoglobin. NUTR. ABS.

Iodine tolerance in sheep and lambs. S. WEISER and E. VEGHELYI (Fortschr. Landw., 1932, **7**, 289—291; Chem. Zentr., 1932, ii, 3437).—Sheep receiving daily 4 mg. I as KI had normal body-wt.; the wool yield (normal quality) was 3·14 (control 2·84) kg. per animal, and its I content (1372×10^{-6} g. per 100 g.) 87 times the normal val. The milk contained 97×10^{-6} g. per 100 g. (control 3·4) and the cheese prepared from it 948 (3·5) $\times10^{-6}$ g. per 100 g. The wt. of the lambs was (average) 17·17 kg. (15·70 kg.). Long administration of much higher doses (40 mg. daily) had no injurious effect. A. A. E.

Iodine metabolism in man. I. Blood-iodine and urinary excretion of iodine after single intravenous injection of inorganic iodine in cases with normal thyroids. A. W. ELMER (Deut. Arch. klin. Med., 1932, **174**, 390—398).—After determination of the fasting blood-I level, intravenous injections of 1300×10^{-6} g. I as KI were given and blood- and urinary I determined at intervals for 24 hr. Blood-I fell rapidly from about 40 to 19×10^{-6} g. on the average, in 4 hr. and was normal at 24 hr. Percentage urinary excretion was 13—17 in the first 6 hr. and 21—30 in 24 hr. After injection of 2 mg. of thyroxine giving the same amount of I, only 13% was excreted in the urine in 24 hr. NUTR. ABS.

Effect of high altitudes on total iodine content of the thyroid. A. RABBENO and E. VALLESI (Arch. internat. Pharmacodyn. Ther., 1932, **43**, 448—460).—The I content of guinea-pig thyroids rises for 2 weeks, returning to normal at the end of the third week when the animals are taken to high altitudes (3000 m.). NUTR. ABS.

Changes in blood metabolism under quartz lamp irradiation. I. TEPLOV and R. MESCHERITSKAJA (Deut. Arch. klin. Med., 1932, **174**, 399—414).—Systematic irradiation of healthy animals, and of healthy and diseased men, resulted in an increased destruction of red cells, as shown by a greater excretion of urobilin in the fæces, accompanied by increased erythropoiesis with resultant reticulocytosis. The hæmoglobin content of the red cells generally was unchanged. NUTR. ABS.

Biological action of homogeneous and heterogeneous *X*-rays. C. M. SCOTT (Proc. Roy. Soc., 1933, B, **112**, 365—383).—The responses of the allantois of the chick to homogeneous and heterogeneous *X*-rays are identical. There is no antagonism between components of different λ in mixed radiation, controverting the findings of Moppett (A., 1931, 122). A. C.

Hypoglycæmia after *X*-irradiation of the pancreas. A. TERBRUGGEN and H. HEINLEIN (Klin. Woch., 1932, **11**, 1139—1142; Chem. Zentr., 1932, ii, 3267).—The hypoglycæmia produced was accompanied by unchanged or hypertrophic islets and degeneration of the other pancreatic tissue. In lethal hypoglycæmia there was complete disappearance of glycogen from the liver, musculature, and other organs. The symptoms were prevented by injection of glucose. A. A. E.

Chemical nature of enzymes. J. B. SUMNER (J. Nutrition, 1933, **6**, 103—112).—A review. E. B. H.

Discontinuity of hydration processes. II. Enzyme action. J. V. EYRE and W. A. DAVIS (J. Inst. Brew., 1933, **39**, 103—125).—A no. of enzymic processes are analysed and the hydrolysis–time curves are shown to be composed of a series of parabolas of the type which show abrupt changes at definite points. This holds good up to > 90% hydrolysis. The fact that the "drag" or retarding force is const. (as evidenced by the parabolic nature of the curves) indicates that the deflexion from the straight-line path is not due only to accumulation of the products of the reaction. The hydrogenation of oils in the presence of a Ni catalyst appears to be governed by similar laws. P. G. M.

Yellow oxidation enzyme. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1933, **257**, 492).—The cryst. pigment derived from the oxidation enzyme (this vol., 313) sublimes in high vac. unchanged, m.p. 329°, C 60·98, H 5·04, N 21·4%, S, ash, and halogen nil, agreeing best with the formula $(C_{13}H_{10}N_4O_2)_n$ or $(C_{12}H_{12}N_4O_2)_n$. P. W. C.

Energy relationships in biological dehydrogenations. W. FRANKE (Biochem. Z., 1933, **258**, 280—300).—A discussion of the relationship between free and total energy and heat of reaction of org. substances based on recent data concerning compounds and reactions (particularly dehydrogenations) of biological importance. W. McC.

Specificity of dehydrogenases. T. THUNBERG (Biochem. Z., 1933, **258**, 48—64; cf. A., 1920, i, 784).—The specificity of succinodehydrogenase is not abs., since it activates the H of pyrotartaric acid (I) as well as of succinic (II) and methylsuccinic acids. (I) is probably converted thus into mesaconic acid. Alkylsuccinic acids (Me_2, MeEt, Et_2) are very slightly or not at all affected. Oxalic and malonic acids fix

the enzyme and reduce its effect on (II), but glutaric, adipic, alkylmalonic (Me_2, Et, Et_2, allyl), the alkylsuccinic acids, and (I) produce little or no such result. The H of *d*-malic acid is scarcely or not at all activated by malicodehydrogenase. W. McC.

Determination of diffusion coefficients of substances of high mol. wt. Diffusion of catalase. K. Zeile (Biochem. Z., 1933, **258**, 347—359; cf. A., 1929, 587).—Since the mol. wt. of hæmoglobin determined by the method of Northrop and Anson agrees with the accepted val., Einstein's formula (Ann. Physik, 1906, **19**, 371) is valid, in this case at least. The method cannot be applied to the determination of the mol. wt. of catalase because it decomposes on the filter. This decomp. is a species of dissociation, study of which throws light on the nature of the enzyme. W. McC.

Determination of liquefying power of diastase. J. J. Willaman, E. W. Clark, and O. B. Hager (Biochem. Z., 1933, **258**, 94—101).—The procedure of Jozsa and Gore (B., 1930, 389) is improved by modifying the pipette in a manner described and by using CH_2O as inhibitor of the enzyme action. A formula for calculating liquefying power is also given. W. McC.

Adsorption of malt-amylase on starch. O. Holmberg (Biochem. Z., 1933, **258**, 134—140; cf. Arkiv Kemi, Min., Geol., 1932, **11B**, No. 4, 1).—For the selective adsorption (I) on starch of α-amylase from malt extracts the starch should be finely powdered. The extracts, which should be prepared with 40—50% EtOH, must contain low concn. of maltose. Low concn. of enzyme gives much better results than does high. The extent of (I) is much greater at low (0°) than at higher (20°) temp. Within the range p_H 7·65—4·7 the [H·] has no effect on (I). W. McC.

Amylases of malt and barley. K. Myrbäck and S. Myrbäck (Biochem. Z., 1933, **258**, 158—171; cf. A., 1930, 955; 1931, 1089).—The diastatic power of Swedish brewer's barley (50 samples) is between 50 and 250; its content of free and total amylase (I) varies from year to year, the order of richness of the samples remaining unchanged. Barleys rich in protein are often but not always rich in (I). On malting, the free (I) increases two- to four-fold, but the total (I) increases by $<30\%$. As regards the effect of [H·] on them, the two amylases of malt and that of barley do not differ. W. McC.

Relation between amount of enzyme and its reaction velocity. N. Taketomi and T. Horikoshi (Waseda Appl. Chem. Soc. Bull., 1932, **18**, 4—6).—The velocity of hydrolysis of sucrose by invertase of *Aspergillus oryzæ* is not proportional to quantity or (quantity)$^{\frac{1}{2}}$ of enzyme. Ch. Abs.

Invertase action as a heterogeneous reaction. T. A. White.—See this vol., 357.

Action of formaldehyde on emulsin and invertase. M. Mascré and R. Paris (Compt. rend., 1933, **196**, 438—440).—The hydrolytic effect of emulsin is retarded in media containing 0·65—3·25% CH_2O. The enzyme recovered after 4 days is only slightly less active than that recovered from the usual aq. medium. The retardation occurs mainly during the second hr., but is not due to fixation of CH_2O by the enzyme, although there is an immediate liberation of acid which changes the reaction of the medium from p_H 6·8 to 5·6. The inhibition is probably a physical phenomenon, and is less marked in 70% EtOH. Invertase is similarly affected. P. G. M.

Emulsin. IX. B. Helferich, H. Heyne, and R. Gootz (Z. physiol. Chem., 1933, **214**, 139—144; cf. A., 1932, 1063).—The ratio of the activities of emulsin heated at 45° for varying lengths of time and at different p_H towards phenol-β-*d*-glucoside and phenol-β-*d*-galactoside is const.; hence one enzyme only, β-glucosidase, probably effects both fissions. On the other hand, the α-mannosidase is obviously different, since it is much more stable to heat and is attacked only moderately at 70°. J. H. B.

Emulsin. X. B. Helferich, H. Appel, and R. Gootz.—See this vol., 379.

Glycolytic degradation of carbohydrates. R. Nilsson (Biochem. Z., 1933, **258**, 198—206; cf. A., 1932, 192).—None of the hexose phosphates so far isolated has properties which indicate that it is an intermediate product in glycolysis. All results so far obtained are best explained by supposing that, during the process, the polysaccharides are first converted into hexose phosphate (I), but that in the further degradation an equilibrium is set up between the normal and the active forms of the hexose produced, this equilibrium greatly favouring the normal form. Probably (I) is an enolic form. Thus are also explained the production of glyceraldehyde phosphate (II) and of the compound $C_3H_6O_3$ (possibly $AcCHO,H_2O$) especially since 2 mols. of (II) yield hexose diphosphate (A., 1932, 364). On the assumption that an activator for galactose (III) similar to Meyerhof's hexokinase exists, the production of Harden and Young's ester from (III) is also explained. W. McC.

Fermentation of methylglyoxal. C. Neuberg and M. Kobel (Biochem. Z., 1933, **258**, 365—370; cf. A., 1931, 662; 1932, 1235).—Yeast converts the H sulphite compound of AcCHO, in presence of O_2, first into $AcCO_2H$ and then into MeCHO. W. McC.

Glyoxalase and its co-enzyme. I. M. Ariyama and Y. Kobayashi (J. Biochem. Japan, 1932, **16**, 317—337).—Contrary to Giršavičius (A., 1930, 814; 1931, 1455; 1932, 650), the destruction of AcCHO by liver extracts is not due to its reaction with proteins or NH_2-acids present in the enzyme sample. The rate of decrease in glyoxalase (I) in liver during starvation varies with different species of animals. Enzyme preps. on keeping decrease both in (I) and in co-enzyme. Formation of lactic acid from AcCHO by blood-(I) proceeds quantitatively (cf. A., 1931, 1455). F. O. H.

Specificity of kidney-phosphatases. E. Waldschmidt-Leitz and F. Köhler (Biochem. Z., 1933, **258**, 360—364; cf. Levene and Dillon, A., 1931, 123).—The phosphatase of pig-kidney hydrolyses glycerophosphate, PhH_2PO_4, hexose diphosphate, and adenosinephosphoric acid. The results give no support to

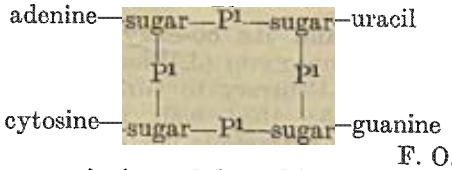
the view of Uzawa (A., 1932, 650) that a phosphodiesterase exists, but it seems that a sp. phosphoamidase is responsible for the hydrolysis of NH_2-acids (creatine-phosphoric acid), even although the enzymic hydrolyses of both phosphoric esters and phosphoric amides are inhibited in the same way by SH compounds. W. McC.

Activation by magnesium of phosphatases at low concentration. I. C. Hommerberg (Biochem. Z., 1933, **258**, 154—157; cf. Jenner and Kay, A., 1931, 1456).—During the hydrolysis of PhH_2PO_4 (Na salt) by low concn. of phosphatase in presence of $MgCl_2$ the activating effect of the Mg and its effect on the spontaneous decomp. of the ester are in some degree additive. W. McC.

Monophosphatases of animal organs and blood. W. Hori (J. Biochem. Japan, 1932, **16**, 433—445).—With Na glycerophosphate as substrate, the following p_H optima were obtained: pig's kidney, 8·8; rabbit's kidney, 8·7; defibrinated, hæmolysed, and dialysed rabbit's blood, 4; hæmolysed erythrocytes (I), 5; serum, 8·7; leucocytes, 8·8. The action of papain or trypsin on (I) decreased the optimum to approx. 4, that of a hæmolysing snake venom to approx. p_H 3, whilst that of 1% $CaCl_2$ produced a marked increase. F. O. H.

Pyrophosphatase and its activator. H. Takahashi (J. Biochem. Japan, 1932, **16**, 447—461).—Three monophosphatases exist with p_H optima at 3 (from taka-diastase or kidney), 5·6 (from rice-bran), and 8·8—10 (from kidney). There are also at least three pyrophosphatases, p_H optima for the hydrolysis of $Ph_2H_2P_2O_7$ occurring at 4, 5, and 8·7 (cf. A., 1932, 305). F. O. H.

Enzymic dephosphorylation of nucleic acid. H. Takahashi (J. Biochem. Japan, 1932, **16**, 463—481).—Neither monophosphatases (I) nor pyrophosphatases hydrolyse yeast-nucleic acid (II), whilst diphosphatases (III) in presence of (I) produce rapid diphosphorylation. By the use of a suitable type of (III) the hydrolysis can be carried out in both acid and alkaline media. The four H_3PO_4 residues in (II) are therefore of the diester type and the following formula [where P^1=·O·P(:O)(OH)·O·] for (II) is advanced.



F. O. H.

Enzymic scission of lysochitin and lecithin. Isomeride of lecithin. A. Contardi and A. Ercoli.—See this vol., 374.

Action of esterase. III. E. A. Sym (Biochem. Z., 1933, **258**, 304—324; cf. A., 1930, 1475; 1931, 520).—In both one- and two-phase systems the H_2O content (I) of preps. (II) containing esterase has a powerful activating effect (III) on the enzyme, (III) being proportional to (I) for low (I). In two-phase systems containing little H_2O (but not in one-phase systems or in two-phase systems rich in H_2O) the rate of action of the ground (II) increases greatly with increase in the fineness of grinding. (II) withstand temp. up to 75° without loss of activity, and activity lost at higher temp. (90—120°) returns after some weeks. In two-phase systems the p_H optimum (within the range 4·4—8·5) is 6·8. W. McC.

Problem of the identity of pancreas-lipase and pancreas-esterase. G. Lo Monaco (Arch. Int. Pharm. Thér., 1932, **42**, 387—399; Chem. Zentr., 1932, ii, 3424).—In pancreatic extracts thermal inactivation of lipase is strictly parallel with that of esterase; for pancreatic juice different results were obtained with different animals (dog). A. A. E.

Effect of certain chemicals on the hydrolytic activity of *Ricinus* and pancreatic lipase. R. H. Clark and R. M. Archibald (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 87—92).—Over long periods of time I may act as an accelerator, whilst most of the other substances tested act as inhibitors. Br acts similarly to I, but larger concns. are required and the return of the activity of the lipase is slower. HCl is a marked and lactic acid a complete inhibitor. CH_2O inhibited, although some aldehydes activated at low concns. and inhibited at higher. *Ricinus* lipase was more sensitive than pancreatic. H. G. R.

Histochemistry of enzymes. III. Proteinases of *Drosera rotundifolia*. H. Holter and K. Linderstrøm-Lang (Z. physiol. Chem., 1933, **214**, 223—240; cf. A., 1932, 427).—The micro-method was used to investigate the activity of the proteinases using edestin as substrate. *Drosera* leaves contain two proteinases, one present in the gland secretion, optimum 3·2, and the other as endo-enzyme in the leaf tissue, optimum p_H 4·3. The secretion proteinase probably differs from animal pepsin. J. H. B.

Rennin. A. Heiduschka and W. Schmidt (Biochem. Z., 1933, **257**, 463—466).—All relishes and spices modify the action of rennin on milk, either inhibiting coagulation by basicity or accelerating through acidity, viscosity, and dispersion. PhOH and tannic acid are exceptions, inhibiting although acidic. The substances also modify the degree of fineness of coagulation. P. W. C.

Action of papain on barley and malt and extracts of these. Ageing of amylase solutions. H. Luers and R. Lechner (Woch. Brau., 1933, **50**, 33—38).—When papain acts on macerated barley, an increase occurs in the saccharifying amylase (I), but no significant development of liquefying amylase (II) can be detected. When malt is treated in a similar way, the increase in (I) is less marked, and again no development of (II) takes place. The protease apparently liberates the (I) from an insol. combination with protein, but is unable to effect any change in its type. When papain activated with HCN is employed, smaller increases of saccharifying power are observed, apparently due to the inhibiting action of HCN on (I), and again no development of (II) is detected. Barley or malt preps. kept aseptically for many days at 0°, room temp., and 35° show no development of (I) or (II), but malt-macerates kept for more than 100 days, in contrast to the fresh material, are able to carry the hydrolysis of starch beyond the point at which colour is developed with I. W. O. K.

Degradation of ovalbumin with papain. T. SVEDBERG and I. B. ERIKSON (Biochem. Z., 1933, **258**, 1—3).—The sedimentation const. of ovalbumin (ultra-centrifuge) decreases following treatment with papain activated with HCN. W. McC.

Action of gastric juice and pancreatic juice on trypsin coated with fatty acid. BOURCET and RAYMOND-HAMET (Bull. Acad. Med., 1931, [iii], **105**, 690—691; Chem. Zentr., 1932, ii, 2476).—"Enzypan" loses only 25% of its potency after 24 hr. treatment with human gastric juice. Pancreatic juice completely hydrolyses the fatty acid. A. A. E.

Enzyme content of pancreas-substitute preparations. E. WALDSCHMIDT-LEITZ and W. SCHAFFNER (Klin. Woch., 1932, **11**, 1175—1176; Chem. Zentr., 1932, ii, 2475).—Tests with commercial preps. are reported. A. A. E.

Destruction spectrum of urease. F. KUBOWITZ and E. HAAS (Biochem. Z., 1933, **257**, 337—343).—Dil. solutions of urease are irradiated with ultra-violet light of known intensity (196—366 mμ) and the decrease of urease activity is followed. The absorption coeffs. calc. from the destruction closely correspond with those directly measured. P. W. C.

Uricolysis. III. W. SCHULER and W. REINDEL (Z. physiol. Chem., 1933, **215**, 258—266).—Amongst artificial oxidising agents, alkaline $KMnO_4$ and mol. O_2 in presence of alkaline MnO_2 react with uric acid (I) in a manner practically identical with that occurring during enzymic uricolysis (cf. A., 1929, 217; 1932, 882). With both reagents hydroxyacetylenediureincarboxylic acid (II) (A., 1932, 864) is formed. Decomp. of (II) yields CO_2 and allantoin (III). During the formation of uroxanic acid or carbonyldiurea from (I), (II) is not formed, nor does the conversion of (II) into (III) by NH_2Ph yield *iso*-allantoin at any stage. The optical inactivity of enzymically produced (III) and the relation of the intermediate products of enzymic to those of catalytic oxidation of (I) indicate that the *in vivo* formation of (III) from (I) is through (II). F. O. H.

Purification of cocarboxylase. Its occurrence in the animal organism. E. AUHAGEN (Biochem. Z., 1933, **258**, 330—339; cf. A., 1932, 967).—Methods for preparing dry, stable, active ætiozymase and for determining cocarboxylase (I) are described. (I) obtained in 10% yield in a form 200 times as active as is yeast extract contains cozymase (II) (which it is impracticable to remove) in the proportion 1 : 10, is free from S, and is adsorbed by $Al(OH)_3$ and animal C. The P content suggests that it is a nucleotide like (II). Uranyl acetate ppts. it, but it becomes progressively less easy to ppt. with various reagents as its purity increases. It is destroyed, although not so rapidly as is (II), during the autolysis of yeast. The liver, kidney, and heart of the pig and the blood (but not the muscle) of the guinea-pig contain small amounts of it or of a substance having similar effects. W. McC.

Yeast asparaginase. W. GRASSMANN and O. MAYR (Z. physiol. Chem., 1933, **214**, 185—210).—Yeast asparaginase (I) is extremely sensitive to acid. It is best prepared by autolysis at weakly alkaline reaction in presence of PhMe or $(NH_4)_2HPO_4$ and is purified by adsorption on kaolin and elution. It is not sensitive to enzyme poisons such as HCN, H_2S, and P_2O_7'''', which may therefore be used to suppress peptidases. Glutathione inhibits slightly, 0·1% solutions of Fe^{III} and Ni^{II} scarcely at all, of Cu^{II} considerably, and of Ag and Hg^{II} completely. (I) is a highly sp. amidase. Substitution in or removal of the NH_2-group of asparagine prevents the hydrolysis. The four isomeric hydroxyasparagines are inactive. Replacement of CO_2H by Me inhibits fission. Aspartic acid diamide is hydrolysed, but much more slowly and only at the amido-linking β to the free NH_2 group. Glutamine is not hydrolysed by (I), but is slowly attacked by fresh yeast autolysate. (I) activity seems to demand the group, $\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO\cdot NH_2$.

The following substrates, amongst others, were prepared: aspartic acid diamide, m.p. 141° (*acetate*, m.p. 144—145°), β-aminobutyramide (*sulphate*, m.p. 238°; hydrochloride, m.p. 142°), *bromopropionyl*-l-*asparagine*, m.p. 154°, $[\alpha]_D$ +18·5° in EtOH, dl-*asparagylglycine*, m. p. 147°, *fumaryl*-l-*dialanine*, m.p. 265° (decomp.) (*Et* ester, m.p. 211·5°, $[\alpha]_D$ +88·3° in EtOH), dl-*asparagyl*-l-*dialanine*, m.p. 213° (decomp.). J. H. B.

Specificity of the electric charge of yeast cells. E. A. MOLDAVSKAJA (Biochem. Z., 1933, **257**, 480—483).—Pretreatment of yeast cells with gelatin enables them to migrate to the cathode both in solutions containing 0·005*N*-HCl and on addition of 0·005% $AlCl_3$. P. W. C.

Determination of hydrogen-ion concentration in living yeast and bacterial cells. M. GUTSTEIN (Protoplasma, 1932, **17**, 454—470).—Colour changes shown by certain indicators absorbed from nutrient solutions by living cells suggest that cells of particular species have an internal p_H which is fixed within narrow limits and is different from that of the nutrient. A. G. P.

Growth of yeast. T. PHILIPSON (Biochem. Z., 1933, **258**, 244—250; cf. A., 1932, 550).—The material (I) from green peas which promotes the growth of yeast consists of at least two components. It is sol. in H_2O and EtOH–Et_2O mixture, but insol. in Et_2O. Inositol, mannitol, and dulcitol do not increase the growth-promoting effects of (I). (I), but not its components separately, promotes growth in various strains of yeast. W. McC.

Effect of inositol, of bios II, and of both together in the culture medium, on the reproduction of twelve kinds of yeast. H. STANTIAL (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 163—164).—Yeasts, the growth of which is greatly increased by media containing both bios I and II, are: Wildier's yeast, *S. cerevisiæ*, *S. validus*, *Sch. octosporus*, baker's and brewer's yeasts. Growth of *S.* and *Zyg. mandschuricus* is increased by bios II only. *S. pastorianus* is unsuited for determination of bios. H. G. R.

Fractionation of bios II. W. L. MILLER, E. V. EASTCOTT, and E. M. SPARLING (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 165—169).—Large-scale prep. of relatively pure bios II from malt combings is described. The product is easily fractionated into bios IIa and IIb by shaking with C in acid solution.

There is no reason to assume more than one IIa and one IIb. H. G. R.

Yeast cozymase. K. Myrbäck, H. von Euler, and H. Hellström (Z. physiol. Chem., 1933, **214**, 184; cf. this vol., 95).—The priority of Dhéré (A., 1905, ii, 783) is recognised. J. H. B.

Synthetic hexose phosphates. II. K. Josephson and S. Roffe (Biochem. Z., 1933, **258**, 147—153; cf. A., 1930, 1166; 1929, 1044).—γ-Acetyl-ζ-triphenylmethyl-αβ-*iso*propylideneglucose, treated with $POCl_3$ in C_5H_5N, yields the *ε-phosphate* (*Ba* salt), which, on hydrolysis with H_2SO_4, yields *glucose ε-phosphate* [*Ba* salt, $[\alpha]_D^{20}$ +15·8; *strychnine* salt, m.p. about 160° (decomp.)]. The behaviour of the phosphate on fermentation indicates that it cannot occur as an intermediate product in the fermentation of glucose to EtOH and CO_2. W. McC.

Putrefactive products of beer yeast. K. Nishida (Bull. Chem. Soc. Japan, 1933, **8**, 14—22).—8 kg. of dried beer yeast, when putrefied in H_2O at 10—28°, yielded $CH_2Ph{\cdot}CH_2{\cdot}NH_2$ (7·2 g. of hydrochloride), adenine (11·5 g. of nitrate), hypoxanthine (13·7 g. of hydrochloride), histamine (9·1 g. of hydrochloride), tyramine (12·4 g. of hydrochloride), putrescine (1·1 g. of hydrochloride), cadaverine (4·1 g. of hydrochloride), leucine (324·9 g.), and NH_3 (128·74 g.). R. S. C.

Cytochrome spectra of brewer's yeasts. H. Fink and E. Berwald (Biochem. Z., 1933, **258**, 141—146; cf. A., 1932, 1167).—Yeasts having two-banded cytochrome spectra are converted into those having four-banded cytochrome spectra by long-continued cultivation in air in large shallow dishes containing shallow layers of nutrient media (preferably containing sucrose). The converted yeast sometimes reverts to the original type on further propagation. W. McC.

Influence of oxygen on alcoholic fermentation. A. J. Kluyver and J. C. Hoogerheide (Compt. rend., 1933, **196**, 443—445).—When a large excess of O_2 is present relative to the amount of yeast, fermentation is partly inhibited as indicated by Meyerhof, but the reverse holds good, as shown by Windisch, when the O_2 is kept const. at a lower level. P. G. M.

Influence of iron on aerobic alcoholic fermentation. A. Malkov (Ukrain. Chem. J., 1932, **7**, [Sci.], 75—83).—The fermentation of sucrose by yeast is stimulated by the presence of 0·6—4·8 mg. of Fe^{II} per 100 c.c. of medium; higher concns. (9·6 mg. per 100 c.c.) retard fermentation. The quality of yeast grown in media containing Fe is normal, whilst the yield is higher, as is also assimilation of N and of P. R. T.

Acceleration by arsenate of fermentation by yeast. A. Harden (Biochem. Z., 1933, **258**, 65—68).—The accelerating effect of Na_2HAsO_4 on the fermentation of hexose diphosphate (I) by zymin is > that of K_2HPO_4, although the effect of the two substances acting simultaneously is < the calc. val. The results support the view that arsenate accelerates the direct fermentation of (I). W. McC.

Method of action of Euler's *Z*-factor. K. Myrbäck and H. Larsson (Biochem. Z., 1933, **258**, 118—133; cf. A., 1925, i, 209). The factor, which is very stable and is not destroyed by long boiling, greatly activates aerobic and anaerobic fermentation by certain fresh and dried yeasts. The smaller is the amount of yeast the greater is the effect of the factor, which, however, has little effect on the respiration. As regards respiration, fermenting power, effect of hexose phosphate, effect of KCN, and period of induction, differences, sometimes great, are found between the different kinds of yeast. W. McC.

Large-scale laboratory cultivation of moulds. W. H. Petersen, L. M. Pruess, H. J. Gorcica, and H. C. Greene (Ind. Eng. Chem., 1933, **25**, 213—215).—A steriliser–incubator is described capable of growing 9 sq. m. of mould mycelium in pure culture.

Resorption of potassium by *Penicillium glaucum* growing in Raulin's solution with increasing additions of potassium chloride. P. Bretin, P. Manceau, and J. Rey (Compt. rend. Soc. Biol., 1931, **106**, 652—653; Chem. Zentr., 1932, ii, 2981).

Behaviour of *Penicillium glaucum* growing in Raulin-type solutions with increasing additions of aluminium chloride. P. Manceau (Compt. rend. Soc. Biol., 1931, **106**, 654—655; Chem. Zentr., 1932, ii, 2981—2982).—No effect on the sugar metabolism was observed. A. A. E.

Action of certain fungi on solutions of aldoses and other carbohydrates. VI. Formation of oxalic acid from *d*-gluconic acid. A. Angeletti and D. Ponte (Annali Chim. Appl., 1933, **23**, 33—37).—When grown in solutions of Ca *d*-gluconate, *Penicillium crustaceum* (L.), Fries, yields CaC_2O_4 and a little $CaCO_3$. In Na citrate solution, this mould gives Na_2CO_3 in small quantity, but no $H_2C_2O_4$, whilst *P. luteum-purpurogenum*, st. 2A, does not attack the citrate. Hence the $H_2C_2O_4$ is formed from *d*-gluconic acid directly. T. H. P.

Oxygen requirements of *Neurospora sitophila* for formation of perithecia and growth of mycelium. F. E. Denny (Contr. Boyce Thompson Inst., 1933, **5**, 95—102).—Perithecia were produced in atm. containing < 1% of O_2. The growth-rate of mycelium was not retarded until the O_2 concn. was reduced to 0·1%, and ceased only in the presence of alkaline pyrogallol. CO_2 up to 30% did not retard mycelial growth. A. G. P.

Susceptibility of *Bilharzia miracidia* to different salts and different p_H. A. Hasan (J. Egypt. Med. Assoc., 1933, **16**, 229—231).—Slight acidity (p_H) killed them in 30 min. Salt solutions at 0·5—0·9% are effective in 4 hr. H. G. R.

***Pseudomonas Lindneri*–*Kluyver* (*Termobacterium mobile*, Lindner). Aerobic and anaerobic fermentation. Alcohol formation.** K. Schreder, R. Brunner, and R. Hampe (Woch. Brau., 1933, **50**, 43—48).—The bacterium (I) ferments sugar in inorg. media, producing EtOH and lactic acid (II) under both anaerobic (III) and aerobic conditions (IV). The fermentation CO_2 production is the same for (III) and (IV), whilst the production of EtOH and that of (II) are respectively smaller and greater with (IV) than with (III). With (IV) addition of EtOH has no significant effect on the fermentation,

although a small additional amount of EtOH is metabolised by (I). The amount of (I) added to the culture influences to a certain extent the respiration and the formation of (II) and EtOH. Max. assimilation occurs with (IV) following the addition of EtOH. This assimilation continues, although at a reduced rate, to the end of the fermentation.

F. O. H.

Assimilation of carbonic acid. F. M. Muller (Chem. Weekblad, 1933, **30**, 202—207).—Under the action of light, red S bacteria are able to reduce CO_2 to CH_2O in presence of various H donors. They contain pigments related to carotene and xanthophyll, and a parallel exists between the reduction of CO_2 by these organisms and assimilation in green plants, from which it is concluded that reduction of CO_2 depends on the presence of a H donor, in this case H_2O. Carotenoids are absent from green S bacteria, and the latter reduce CO_2 only in presence of H_2S. The presence of carotenoids in photosynthesis is connected with the occurrence of less active donors than H_2S. From a consideration of the energy relationships, it follows that four light quanta are absorbed per mol. CO_2 assimilated, and the reduction to CH_2O takes place in two stages by way of HCO_2H. Accepting the fact that both chlorophyll and carotene are loosely combined in the chloroplast with protein, it is suggested that CO_2 becomes attached to Mg in chlorophyll and H_2O to a double linking in carotene. The absorption of light quanta causes an electronic disturbance in the chlorophyll, which is passed on through the protein to the carotene forming + and — poles at the absorbed CO_2 and H_2O, respectively. $H^{\cdot}$ and OH' ions are subsequently discharged at these poles, giving HCO_2H and H_2O_2 and finally CH_2O and O_2.

S. C.

Influence of inorganic salts on the multiplication of *Gonococcus*. C. P. Miller, jun., A. B. Hastings, and R. Castles (J. Bact., 1932, **24**, 439—455).—In the effects on the growth of *Gonococcus* Na and K were interchangeable and non-toxic even at high concns. Ca and Mg were non-essential and inhibited growth in concns. > 30 millimols. per litre. The toxic action of Ca, but not that of Mg, was prevented by addition of citrate or oxalate. The growth range of the organism was p_H 6·0—8·2 with optimum 7·0—7·6. Substitution of Cl' for NO_3' or SO_4'' in the media did not affect growth. Nutrients must be well buffered with HCO_3' or phosphates.

A. G. P.

Effects of various neutral salts on the growth of bacteria. I—III. Sodium and potassium salts. G. Kobayashi (Japan. Z. Mikrobiol. Path., 1932, **26**, 1—15, 16—31, 32—42).—Experiments with *S. aureus, B. pyogenes, Eb. typhi, Es. coli*, and *V. aquatilis* are described. Ch. Abs.

Production of hydroxylamine by the reduction of nitrates and nitrites by various pure cultures of bacteria. G. A. Lindsey and C. M. Rhines (J. Bact., 1932, **24**, 489—492).—Organisms of diverse types produce NH_2OH from NO_3' and NO_2'.

A. G. P.

Carbohydrate common to the group of acid-fast organisms, including the tubercle bacilli. A. Branch (Tubercle, 1932, **13**, 481—488).—The common (precipitin) carbohydrate is not related to the pathogenicity or virulence of acid-fast bacilli.

Ch. Abs.

Influence of silica on the growth of the tubercle bacillus. R. M. Price (Canad. J. Res., 1932, **7**, 617—621).—0·01 mg. of SiO_2 (colloidal or as Na silicate) per c.c. of Dorset's egg medium increases the growth of the tubercle bacillus *in vitro*.

R. S. C.

(*a*) Non-specific complement fixation reaction due to ion antagonism. (*b*) Mechanism of complement fixation. A. Hambleton (Canad. J. Res., 1932, **7**, 583—595, 596—605).—(*a*) The complement fixation test for tuberculosis gives a non-sp. (falsely positive) reaction with Petroff's whole bacillus antigen (but not with the " fat-free " antigen), if the plain saline solution be replaced by a solution containing the following salts in the molar concns. stated: NaCl 0·152, $CaCl_2$ 0·0005—0·0025 (optimum 0·0008), and $MgCl_2$ 0·0002—0·001 (optimum 0·0003). It is considered that the antagonistic effects of Na and Ca ions produce at the surface of the antigen particles a state of unstable equilibrium which leads to agglutination and hence complement fixation.

(*b*) Complement fixation is not due to sp. chemical affinity; it is produced by modification of the physical properties of the tuberculo-antigen, either by immune serum or by non-sp. means. R. S. C.

Composition of the active principle of tuberculin. XV. Precipitated purified tuberculin protein suitable for the preparation of a standard tuberculin. F. B. Seibert and B. Munday (Amer. Rev. Tuberc., 1932, **25**, 724—737).—The protein is obtained by growth on a non-protein synthetic medium, ultrafiltration, and one pptn. with $CCl_3{\cdot}CO_2H$. This protein is relatively stable and its potency varies almost within the range of experimental error of the skin test. Pptn. with $(NH_4)_2SO_4$ affords a pure product, but is tedious. Ch. Abs.

Toxicity of toxins after treatment with aluminium hydroxide or tapioca. S. Schmidt (Compt. rend. Soc. Biol., 1932, **107**, 330—332; Chem. Zentr., 1932, ii, 3429).—Diphtheria and tetanus toxins can be detoxicated, with preservation of antigenic properties, by treatment with $Al(OH)_3$ (Willstatter) or tapioca powder, thus permitting hyperimmunisation. $Al(OH)_3$ added to the anatoxin stimulates the formation of antibodies. A. A. E.

Adsorption of bacteriophage with kaolin and infusorial earth. M. L. Rakieten and G. A. Hunt (Amer. J. Hyg., 1932, **16**, 823—831).—Prep. of protein-free phage of high titre was not accomplished.

Ch. Abs.

Photodynamic action of methylene-blue on bacteriophage. J. R. Perdrau and C. Todd (Proc. Roy. Soc., 1933, **B**, **112**, 277—287; cf. Clifton, A., 1931, 1461).—Phages for two staphylococci and a dysentery strain are inactivated by methylene-blue (optimal concn. 1 in 100,000) in the presence of light and O_2, both of which are necessary. The phages are not reactivated by reducing agents; they are rendered resistant to inactivation by previous union with living bacteria, not necessarily homologous. A. C.

Photodynamic action of methylene-blue on certain viruses. J. R. PERDRAU and C. TODD (Proc. Roy. Soc., 1933, **B**, **112**, 288—298).—Similar phenomena of sensitivity of several viruses to methylene-blue are observed (cf. preceding abstract). Some are protected by living cells from infected animals. The photodynamic action appears to be an oxidative process. A. C.

Bacterial detoxification. R. S. HARRIS and J. W. M. BUNKER (Proc. Amer. Acad. Arts Sci., 1932, **67**, No. 5, 147—168).—The action of Na ricinoleate (I) is due to mol. structure as well as surface tension effects. (I), tri(hydroxyethyl)amine ricinoleate (II), and ephedrine ricinoleate afforded evidence of detoxification of tubercle bacillus. (II), but not Me ricinoleate, detoxified *S. aureus*. CH. ABS.

Effect of organic substances on the toxic action of hypochlorite in *B. coli*. A. ROUSLACROIX, L. BOYER, and J. BOIRON (Compt. rend. Soc. Biol., 1931, **108**, 102—104; Chem. Zentr., 1932, ii, 2478).—Peptone and sewage rich in org. matter diminish the disinfective action of NaOCl; glucose and urea do not affect it. A. A. E.

Action of iodopyridone derivatives on streptococci. A. BINZ and H. MAIER-BODE (Biochem. Z., 1933, **257**, 351—360).—A table shows the disinfecting power against streptococci of a large no. of C_5H_5N derivatives. 4- and 2-Hydroxy- and 5-iodo-4-hydroxy-pyridine are inactive, but 5-iodo-2-hydroxy-pyridine in 0·5% solution has the disinfecting power of PhOH, whilst the more sol. Na salt is less active. Iodopyridones in considerable doses are often non-toxic (cf. A., 1932, 1060). P. W. C.

Oligodynamic action of silver on bacteria and bacteriophage. E. WOLLMAN and (MME.) E. WOLLMAN (Compt. rend. Soc. Biol., 1931, **108**, 111—113; Chem. Zentr., 1932, ii, 2477).—The action increases with rise of temp. Bacteriophages are more resistant than bacteria. A. A. E.

Effect of adrenaline on liver- and muscle-glycogen. I. I. NITZESCU and N. MUNTEANU (Compt. rend. Soc. Biol., 1931, **108**, 294—296; Chem. Zentr., 1932, ii, 2481).—Hyperglycæmia following injection of adrenaline into the portal vein is produced by mobilised liver-glycogen, and hyperlactacidæmia by that of muscle-glycogen. A. A. E.

Effect of adrenalectomy on sugar tolerance. E. HILL and A. E. KOEHLER (Proc. Soc. Exp. Biol. Med., 1932, **30**, 244—247).—Removal of the adrenals lowers sugar tolerance. NUTR. ABS.

Basal metabolism in thyroidectomised, bilaterally adrenalectomised, and castrated rabbits. T. KAIWA (Tohoku J. Exp. Med., 1932, **10**, 440—444).—Thyroidectomy, with castration and/or adrenalectomy, causes a fall in the basal metabolism of rabbits. CH. ABS.

Influence of thyroxine on tissue oxidation. G. MYHRMAN (Acta med. Scand., 1932, **79**, 323—330).—Thyroxine does not increase the oxidation intensity of tissue pulp as shown by methylene-blue technique. NUTR. ABS.

Effect of thyroxine on blood-cholesterol and -lipin. C. I. PARHON and I. ORNSTEIN (Compt. rend. Soc. Biol., 1931, **108**, 303—304; Chem. Zentr., 1932, ii, 2481).—Intramuscular injection of thyroxine (1 mg. every other day) diminishes the blood-cholesterol, -fatty acid, and -total fat in old age. A. A. E.

Effect of thymus preparations on experimental hyperparathyroidism. H. G. SCHOLTZ (Z. ges. exp. Med., 1932, **85**, 547—558).—Administration of thymus extract to rats led to a fall in serum-Ca. Simultaneous administration of thymus extract and parathormone prevented a rise in serum-Ca and decalcification of bones. Splenic extract did not prevent parathormone hypercalcæmia. NUTR. ABS.

Effect of splenectomy and splenic extracts on blood-sugar in the dog. N. FIESSINGER and R. CATTAN (Compt. rend. Soc. Biol., 1933, **112**, 53—55).—Splenectomised dogs show a tendency to high normal fasting blood-sugar levels, prolonged but not intensified alimentary hyperglycæmia, and diminished sensitivity to insulin, although their hyperglycæmic response to adrenaline is unchanged. Injection of a purified extract of spleen causes a transient hypoglycæmia in splenectomised, but not in normal, dogs. This action occurs even in the absence of the pancreas, but the active agent is thought not to be insulin. NUTR. ABS.

Conversion of urinary folliculin into an ether-extractable form. B. ZONDEK (Klin. Woch., 1932, **11**, 812; Chem. Zentr., 1932, ii, 3265).—A claim for priority. A. A. E.

Effect of hormones on blood-sugar regulation. L. ELEK (Z. ges. exp. Med., 1932, **85**, 227—234).—The blood-sugar curve (I) after oral administration of glucose is the same in the pregnant and non-pregnant woman; glycosuria is more frequent in the former. A second dose of glucose 1—1½ hr. after the first often leads to the Staub effect [second peak in (I)] both in the pregnant and non-pregnant. Previous administration of folliculin leads to a rise in the height of (I) in the female rabbit and a fall in the male, increases the hypoglycæmic effect of insulin, and reduces the hyperglycæmic effect of adrenaline. Anterior pituitary extract increases the hyperglycæmic effect of the adrenaline. NUTR. ABS.

Relation between mouse- and rat-unit of the œstrus-producing hormone. H. KREITMAIR (Arch. exp. Path. Pharm., 1933, **169**, 576—584).—The ratio mouse unit : rat unit for any œstrin prep. depends on the medium in which the prep. is suspended or dissolved. Thus for aq. sols (with lecithin as protective agent) the ratio is 1 : 1, whilst for solutions in oil it is 1 : 4. F. O. H.

Purification of the gonadotropic hormone (prolan). B. ZONDEK, H. SCHEIBLER, and W. KRABBE (Biochem. Z., 1933, **258**, 102—105).—Fresh pregnancy-urine (or such urine preserved with Et_2O) is treated with EtOH, the ppt. is extracted with Et_2O, and the insol. portion is dissolved in H_2O. To the aq. solution phosphomolybdic acid is added and the ppt. produced, after separation in the centrifuge, is treated with $Ba(OH)_2$, excess of which is then

removed by CO_2. The filtrate from the $BaCO_3$ is then evaporated in a vac. Further purification is achieved by dialysis, which yields a product having activity of 10^6 rat units per g. 100% of the hormone is thus extracted. The crystals obtained by Claus and those described by Lejwa (this vol., 194) are probably not pure hormone. W. McC.

Gonad-stimulating principle of the anterior lobe of the pituitary. H. B. Van Dyke and Z. Wallen-Lawrence (J. Pharm. Exp. Ther., 1933, **47**, 163—181).—The gonad-stimulating principle retains its activity for 5 months if kept in aq. solution at p_H 3·7—6·4. At p_H 7·5, the solutions are stable for at least 2½ months. Boiling in aq. solution at p_H 4·9—5·4 causes inactivation, but no deterioration is caused at acid p_H by 0·25% *m*-cresol after 6 weeks. Filtration through Berkefeld candles does not remove the hormone. The posterior lobe pressor principle is removed by treatment of the dry pituitary body with aq. 0·02*N*-NH_3 for 24 hr. at room temp. After bringing to p_H 5·0 with AcOH, the solution is centrifuged and EtOH added until the concn. is 35%; from the supernatant liquid the gonad-stimulating principle is pptd. by adding EtOH until concn. is 70%. Gonad-stimulating powders are free from Mn. A. L.

Growth-promoting action of anterior pituitary extracts. H. Lucke and R. Huckel (Arch. exp. Path. Pharm., 1933, **169**, 290—297).—Continuous intramuscular injection of anterior pituitary extract into rats produces a rate of growth, but in only a few cases a final wt., > normal. The changes occurring in the articular cartilage of the tibial epiphysis are typical of the sp. arthritis of acromegaly in man. F. O. H.

Thyreotropic hormone of the anterior pituitary gland. H. Horsters (Arch. exp. Path. Pharm., 1933, **169**, 537—556).—Injection of the hormone into normal persons produces a decrease in the blood-sugar and -pressure. In cases of deficient glycogen metabolism this action is enhanced and, as with insulin, the assimilation of carbohydrate and phosphate is improved. The hormone, the mechanism of which involves the central nervous system, appears to be concerned with the genesis of "pituitary diabetes." F. O. H.

Isoelectric point of insulin. Electrical properties of adsorbed and crystalline insulin. O. Wintersteiner and H. A. Abramson (J. Biol. Chem., 1933, **99**, 741—753).—Insulin (I) has a fairly const. solubility of 0·0004% in *M*/30-acetate buffer of p_H 4·8—6·5. In the same media, nephelometric determination of flocculation gives a max. of p_H 5·4, whilst electrophoresis of (I) adsorbed on quartz particles or pptd. in an amorphous form indicates an isoelectric point of p_H 5·3—5·35 (cf. A., 1932, 1292). Suspended crystals of (I) have a zero mobility at p_H 5·0. The difference in the surface behaviour of adsorbed and cryst. (I) is discussed. F. O. H.

Reduction of toxicity of insulin. E. M. Walter (Z. ges. exp. Med., 1932, **85**, 495—500).—The addition of physiological saline, serum, or 5% red-cell suspensions lessened the hypoglycæmic action of insulin in rabbits. The greatest effect was produced when an insulin and red-cell mixture was kept in a thermostat for 1 hr. before injection. Nutr. Abs.

Observations on various insulin mixtures administered *per os*. E. S. Gais (Proc. Soc. Exp. Biol. Med., 1932, **30**, 216—218).—To prevent enzymic destruction of insulin administered by mouth, an extract from *Ascaris lumbricoides*, containing an anti-protease which prevents the destruction of insulin by peptic and tryptic proteases *in vitro*, has been mixed with it. When administered to fasting rabbits by stomach tube, this mixture caused no hypoglycæmia. Whether the hormone was unabsorbed or destroyed was not ascertained. Nutr. Abs.

Ketosis in the pancreatic and phloridzin diabetes of hypophysectomised dogs. C. T. Rietti (J. Physiol., 1932, **77**, 92—96).—The removal of the pituitary body in the fasting dog reduces phloridzin glycosuria and results in a fatal hypoglycæmia (I), which is prevented by a diet of meat or sugar but not of fat. Removal of the thyroid or the posterior lobe of the pituitary body or lesions of the tuber cinereum do not produce this (I), which is therefore attributed to removal of the anterior lobe of the pituitary. Analysis shows that, following hypophysectomy, the capacity to form blood-sugar at the expense of endogenous protein is diminished, as also is ketosis. Nutr. Abs.

Changes in phosphate fractions and glycogen of muscle in fasted cats and in diabetes without and after insulin. V. M. Vesselkina (Z. ges. exp. Med., 1932, **85**, 463—476).—Starvation led to a fall in hexose phosphate (I), creatine phosphate, and glycogen (II), a rise in adenyl phosphate (III), and no change in total P (IV). In depancreatised animals there was a fall in (I) and (II), a rise in (III) and lipin-P, and no change in (IV). In depancreatised animals treated with insulin (V) there was a return of all the P fractions to normal, but the (II) remained low. During hypoglycæmia there was a rise in (I) above normal and a fall in (III). The fall in muscle-(II) after administration of (V) is not to be interpreted as evidence against the glycogenetic function of (V); the fall is probably due to increased formation of (I). (V) apparently regulates the initial stage of carbohydrate and P metabolism in muscle. Nutr. Abs.

Biochemical and physiological action of carotene and vitamin-*A*. H. von Euler (Ergeb. Physiol., 1932, **34**, 361—405).—A review.

Carotenoids. P. Karrer (Ergeb. Physiol., 1932, **34**, 812—847).—A review.

Vitamin of growth. IV. γ-Carotene. R. Kuhn and H. Brockmann (Ber., 1933, **66**, [*B*], 407—410).—Fractional adsorption of purified carotene by activated Al_2O_3 followed by elution with MeOH–light petroleum permits the isolation, as most readily adsorbed material, of *γ-carotene* (I), $C_{40}H_{56}$, m.p. 178° (vac., corr.), which is optically inactive. It differs from other carotenes in absorbing $12H_2$ and yielding $COMe_2$ when degraded with O_3. In absorption spectrum and adsorptive behaviour it occupies a position intermediate between β-carotene and lycopene. The

constitution $CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH_2-CMe\end{matrix}>C\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot$ $\cdot CH{:}CH\cdot[CH{:}CMe\cdot CH{:}CH]_2\cdot CH{:}CMe\cdot[CH_2]_2CH{:}CMe_2$ is suggested. The growth-promoting action of (I) is approx. the same as that of α- or β-carotene. Activity appears to depend not on the no. of double linkings, but on the presence of at least one C ring of the ionone type. H. W.

Carotene derivative giving with antimony trichloride an absorption band at 610—630 mμ. M. VAN EEKELEN and A. EMMERIE (Nature, 1933, **131**, 275).—The prep. of a carotene derivative which gives a strong absorption band at 610—630 mμ with $SbCl_3$, and has no growth-promoting power, is described. L. S. T.

Inhibitor of the antimony trichloride test for vitamin-*A* in cod-liver oil. A. EMMERIE (Nature, 1933, **131**, 364).—After saponification cod-liver oil gives a stronger Carr–Price reaction in the unsaponifiable fraction. The inhibitor $C_{21}H_{36}O_3$ (I) is a pale yellow viscous substance, b.p. 203°/1 mm., mol. wt. 332. In the catalytic hydrogenation with Pt 4H per mol. are absorbed, yielding a product with no inhibiting power. (I) readily absorbs Br and gives an orange-yellow colour with $C(NO_2)_4$, but the inhibiting power is not due entirely to unsaturation. L. S. T.

Colpokeratosis method of demonstrating the action of vitamin-*A*. E. KLUSSMANN and P. E. SIMOLA (Biochem. Z., 1933, **258**, 194—197).—*A*-Avitaminosis in castrated female rats and in guinea-pigs results in colpokeratosis (I), which is readily and rapidly cured by administration of vitamin-*A*. Since (I) does not accompany scurvy in guinea-pigs or *B*- or *D*-avitaminosis in rats, a sp. and sensitive method (which can be used when the growth method fails) of testing for vitamin-*A* potency is provided. (I) is not cured by giving xanthophyll although the latter is resorbed by rats and stored in their livers. W. McC.

Carotene and vitamin-*A*. H. GOLDBLATT and H. M. BARNETT (Proc. Soc. Exp. Biol. Med., 1932, **30**, 201—204).—The whole of the vitamin-*A* activity of carrot oil was due to carotene and not to the presence of vitamin-*A*. The dose of carotene which appeared to be equal to one Sherman unit of vitamin-*A* was $0{\cdot}5\times10^{-6}$ g. NUTR. ABS.

Relation between vitamin-*A* potency and carotene content of green plant tissue. W. C. RUSSELL, M. W. TAYLOR, and D. F. CHICHESTER (Proc. Soc. Exp. Biol. Med., 1932, **30**, 376—377).—Lucerne had a higher vitamin-*A* potency than could be accounted for by its carotene content. NUTR. ABS.

Vitamin-*A* content of yellow-tissued and white-tissued apples. M. T. POTTER (J. Nutrition, 1933, **6**, 99—102).—There is practically no difference in the vitamin-*A* content of the varieties of apples tested. E. B. H.

Comparison of apricots and their carotene equivalent as sources of vitamin-*A*. A. F. MORGAN and E. O. MADSEN (J. Nutrition, 1933, **6**, 83—93).—The vitamin-*A* vals. corresponded approx. with the carotene contents of the apricots. E. B. H.

Vitamin-*A* content of the blood of cows and oxen. M. LUNDBORG (Biochem. Z., 1933, **258**, 325—329; cf. A., 1931, 644, 988).—The method previously described gives quant. results when applied to the determination of vitamin-*A* in dil. cow- and ox-blood. In cow's blood (which contains three times as much vitamin-*A* as does ox-blood) all the vitamin is found in the serum, but defibrinated ox-blood has two thirds as much vitamin-*A* as has the serum. W. McC.

Growth-promoting action of xanthophyll. M. RYDBOM (Biochem. Z., 1933, **258**, 239—243).—Daily doses of 0·015 mg. of xanthophyll (I) do not promote growth in rats receiving diet free from vitamin-*A* even when the treatment is begun before the special diet is commenced. In guinea-pigs receiving a diet almost free from the vitamin, daily doses first of 0·225 and then of 0·300 mg. of (I) promote growth almost to the same extent as do daily doses of 0·0225 and 0·030 mg. of carotene. W. McC.

Vitamins and immunity. Complement content [of blood-serum] and production of hæmolysin in *A*- and *B*-avitaminosis. P. E. SIMOLA and E. BRUNIUS (Biochem. Z., 1933, **258**, 228—238).—As regards the complement content (I) of their blood-serum and their power to produce immune hæmolysin (II) guinea-pigs suffering from *A*- and *C*-avitaminosis do not differ appreciably from healthy guinea-pigs. Administration of vitamin-*D* (irradiated ergosterol) to the diseased guinea-pigs does not affect either (I) or (II). It is probable that the lowered resistance to infection which accompanies avitaminosis is due simply to lowered vitality. W. McC.

Avitaminosis. XIII. Effect of vitamin-*A* deficiency and vitamin-*D* deficiency on differential leucocyte count of the albino rat. XII. Influence of vitamin-*B* deficiency on differential leucocyte count of the albino rat during lactation. B. SURE and K. S. BUCHANAN (Proc. Soc. Exp. Biol. Med., 1932, **30**, 173—174, 174—175). NUTR. ABS.

The *B*-vitamins. H. SIMONNET (Z. Vitaminforsch., 1933, **2**, 28—47).—A review.

Vitamin-B_2 values of pasteurised milk, evaporated milk, and eggs. E. N. TODHUNTER (J. Amer. Dietet. Assoc., 1932, **8**, 42—46).—The materials are good sources of vitamin-B_2. NUTR. ABS.

Muscle-phosphate during *B*-avitaminosis. S. NAGAI (J. Biochem. Japan, 1932, **16**, 351—358).—In rats (I) and pigeons (II) suffering from *B*-avitaminosis, the muscle-acid-sol. and -inorg. PO_4 are normal, whilst the P_2O_7 level in certain muscles [heart in (I), leg in (II)] is decreased. The phosphagen and hexose monophosphate+adenylic acid contents are subnormal in all muscles. F. O. H.

Adrenal phosphate during *B*-avitaminosis. S. NAGAI (J. Biochem. Japan, 1932, **16**, 377—382).—In fowls suffering from *B*-avitaminosis, the adrenals hypertrophy, the abs. content of acid-sol. PO_4 increases, whilst the abs. and relative content of inorg. PO_4 remains const. and decreases respectively. The abs. contents of P_2O_7 and hexose phosphate+adenylic acid also increase. F. O. H.

Phosphatese and phosphatase action during *B*-avitaminosis. S. NAGAI (J. Biochem. Japan, 1932, **16**, 359—370).—In pigeons suffering from *B*-avitaminosis, the phosphorylating activities of the tissues of the heart (I), kidney (II), liver (III), and pectoral muscle (IV) are increased by 14·6—77·7%, whilst that of the brain-tissue (V) remains normal. The phosphatase activities of (IV) and (V) are increased, that of (III) is decreased, whilst those of (I) and (II) are unchanged. F. O. H.

Glutathione and *B*-avitaminosis. S. NAGAI (J. Biochem. Japan, 1932, **16**, 371—375).—The oxidised form of glutathione (I) occurs in the heart (II) but not in the liver (III) or leg-muscles (IV) of normal rats. During *B*-avitaminosis the content of reduced (I) is markedly lowered in (II), (III), and (IV) of rats and in (II) and (IV) of pigeons, whilst in (III) of pigeons it is increased. F. O. H.

Co-enzyme content of the adrenals of fowls during *B*-avitaminosis. S. NAGAI (J. Biochem. Japan, 1932, **16**, 383—387).—The adrenals of fowls suffering from *B*-avitaminosis have a higher content of the co-enzyme accelerating the anaerobic decomp. of hexose phosphate than those of normal birds. That this increase is associated with the accompanying symptom of hypertrophy of the adrenal cortex is indicated by the delay of the onset of the disease on feeding adrenal cortex. F. O. H.

Role of avitaminosis-*B* and of alimentary equilibrium in the utilisation of lactose by the rat. R. LECOQ (Compt. rend., 1933, **196**, 565—567).—Rats maintained on strictly equilibrated diets free from vitamin-*B* complex, and containing (*a*) 72% of sucrose, (*b*) 72%, (*c*) 38%, and (*d*) 55% of lactose survive for 20—40 days, 10—25 days, 3—5 months, and >6 months, respectively. Addition of 5% of vitamin-*B* complex causes increase in wt. on diets (*a*), (*c*), (*d*), but not on (*b*). As in the case of the pigeon (A., 1929, 726), utilisation of lactose is determined not only by the presence of vitamins-*B*, but also by the alimentary equilibrium. A. C.

Relation of the vitamin-*B* complex to renal enlargement caused by cystine and protein in the diet of the rat. B. B. LONGWELL, R. M. HILL, and R. C. LEWIS (J. Nutrition, 1932, **5**, 539—550).—The kidneys of rats on a diet deficient in the vitamin-*B* complex were slightly larger than those of rats receiving a whole yeast extract. This difference was augmented by the addition of cystine to the diet, or by increasing the caseinogen. NUTR. ABS.

Experimental cataract in vitamin-B_2 deficiency. C. S. O'BRIEN (Arch. Ophthalmol., 1932, **8**, 880—887).—Cataracts were noted in young rats fed on diets deficient in vitamin-B_2, in which vitamin-B_1 was supplied in the form of an EtOH extract of rice polishings. NUTR. ABS.

Avitaminosis and intoxication. I. Experimental polyneuritis and chemical intoxication by metals and metalloids. II. Experimental scurvy and chemical intoxication by metals and metalloids. M. MITOLO (Atti R. Accad. Lincei, 1932, [vi], **16**, 451—455, 528—531).—I. Ingestion of a mixture of salts of metals and metalloids in doses non-poisonous to normal animals enhances nutritional deficiency in pigeons suffering from experimental polyneuritis, the injurious effect of the salts being also increased.

II. Ingestion by guinea-pigs suffering from avitaminosis-*C* of a mixture of salts of metals and metalloids in doses non-toxic to normal animals accelerates and intensifies the effects of the deficiency. T. H. P.

Identification of vitamin-*C*. A. SZENT-GYORGYI (Nature, 1933, **131**, 225—226).—A lecture. L. S. T.

Hexuronic (ascorbic) acid as the antiscorbutic factor and its chemical determination. T. W. BIRCH, L. J. HARRIS, and S. N. RAY (Nature, 1933, **131**, 273—274).—Evidence is produced which is considered to establish the identity of vitamin-*C* and hexuronic acid. L. S. T.

Hexuronic (ascorbic acid) as the antiscorbutic factor and its chemical determination. W. J. DANN (Nature, 1933, **131**, 274; cf. preceding abstract).—Zilva's data (A., 1932, 1294) are analysed and shown not to be contrary to the view that hexuronic acid and vitamin-*C* are identical. L. S. T.

Indophenol-reducing capacity of lemon juice and its fractions in relation to vitamin-*C* activity. S. S. ZILVA (Nature, 1933, **131**, 363).—A criticism of Dann's interpretation (preceding abstract) of the author's previous results. L. S. T.

Vitamin-*C* and ascorbic acid. A. L. BACHARACH (Nature, 1933, **131**, 364).—The view that vitamin-*C* and ascorbic acid are identical is supported. L. S. T.

Reducing power of plant foodstuffs and its relation to vitamin-*C*. VI. Purification of the reducing substance from [potatoes and] hipberries and its identity with vitamin-*C*. J. TILLMANS, P. HIRSCH, and R. VAUBEL (Z. Unters. Lebensm., 1933, **65**, 145—168).—Determinations of the reduction val. (A., 1932, 310, 658), solids, ash, and "apparent equiv. wt." indicate that extraction of the reducing substance from potato is most complete after 2·5 hr. in a mixture containing 60% $COMe_2$ and 40% 0·05*N*-H_2SO_4. Various physical and chemical methods of purification are described for hipberries. The best procedure is extraction with H_3PO_4 in CO_2, followed by evaporation, pptn. in succession with $COMe_2$ and $Pb(OAc)_2$ (excess being removed with H_2S), evaporation, extraction with MeOH, pptn. with Et_2O, and extraction with H_2O of the residue after a final evaporation. Pptn. with $Pb(OAc)_2$ and $COMe_2$ is repeated, and an evaporated extract of the residue in light petroleum is finally extracted at −5° with $COMe_2$ and then with Et_2O, all operations being carried out in an atm. of N_2. The residue is recryst. from MeOH and gives a yield of 0·0016%, the substance being very similar to "hexuronic acid" (this vol., 196). Feeding experiments on guinea-pigs show that 0·5 mg. per day suffices to prevent scurvy. J. G.

Vitamin-*C*. Addendum. H. VON EULER and E. KLUSSMANN (Svensk Kem. Tidskr., 1932, **44**, 310).—With 2 : 6-dichlorophenol-indophenol the ad-

renal glands of scorbutic guinea-pigs give a titration val. of 0·6—0·9 (see this vol., 325), whereas those of normal animals give 1·2—3, a val. which is still further increased by injection of vitamin-*C*.

F. O. H.

Scorbutic dental changes and their modification by synthetic vitamin-*C* preparations. G. Westin (Z. Vitaminforsch., 1933, **2**, 1—24).—A study of histo-pathological changes in teeth of guinea-pigs after administration of orange-juice, narcotine derivatives, or glycuronic acid (I) in experiments of prophylactic or curative type lasting 10—31 days or 3—10 days, respectively [with A. Rygh and O. Rygh]. (I), narcotine, and narcotine irradiated or treated with germinating seeds, had no action. β-Gnoscopine, anhydrohydrastininephthalide, nor-narcotine, and dimethylnornarcotine showed slight antiscorbutic action. Methylnornarcotine showed action in daily doses of 10—30 (prophylactic) and 100×10^{-6} g. (curative), and a synthetic preparation was active in doses of 1—3×10^{-6} g. (curative). Simultaneous administration of (I) was without effect. R. K. C.

Preservation of vitamins of the fodder of cattle. A. I. Virtanen (Biochem. Z., 1933, **258**, 251—256).—Fodder for farm animals (cows, calves, horses, pigs, poultry) loses most or all of its vitamin-*C* on storage (for 5—10 months), whereas such fodder maintained at p_H 3—4 during storage by admixture of acid (HCl, H_2SO_4) loses only 40—60% during that time. Similarly, whilst the carotene content of the fodder stored in the customary ways decreases by as much as 55% this content in the acidified fodder either remains unchanged or increases on keeping for 1½—5 months.

W. McC.

Determination of vitamin-*C* standard and the requirement of healthy individuals by measurement of the strength of skin capillaries. G. F. Gothlin (Skand. Arch. Physiol., 1931, **61**, 225—270; Chem. Zentr., 1932, ii, 2989).—A scorbutic diet produces a marked fall in the strength of skin capillaries; the condition disappears on administration of fresh orange juice. The protective dose is calc.

A. A. E.

Products obtained by heating vitamin-*D* and their hydro-derivatives. P. Busse (Z. physiol. Chem., 1933, **214**, 211—222).—The product obtained by heating vitamin-*D* at 180—190° for 4 hr. consists of a mol. *compound*, m.p. 122—124°, of pyrocalciferol (I) and an isomeride, iso*pyrovitamin* (II), m.p. 112—115°, $[\alpha]_D^{20}$ +332° (*acetate*, m.p. 113—115°, $[\alpha]_D^{20}$ +333°). (II) is reduced by Na in EtOH to *dihydro*iso*pyrovitamin* (III), m.p. 129—130°, $[\alpha]_D^{15}$ +11·85° (*acetate*, m.p. 145—146°, $[\alpha]_D^{18}$ +30·2°). Catalytic hydrogenation (spongy Pt in Et_2O–EtOH) of the acetate of (III) and hydrolysis gives *hexahydro*iso*pyrovitamin*, sinters 68—80°, $[\alpha]^{20}$ −6·9° (2 : 6-*dinitro*-p-*toluate*, m.p. 164—165°, $[\alpha]_D^{20}$ +1·37°). Reduction of (I) with Na in EtOH gives *dihydropyrocalciferol* (IV), m.p. 121—122°, $[\alpha]_D^{18}$ +70·3° (*acetate*, m.p. 131—133°, $[\alpha]_D^{15}$ +44·7°), and when heated for 11 hr. at 190°, epi*dihydropyrocalciferol* (V), m.p. 138—139°, $[\alpha]_D^{6}$ +54·3° (*acetate*, m.p. 98—99°, $[\alpha]_D^{19}$ +35·6°). Catalytic reduction of the acetate of (IV) and hydrolysis affords *hexahydropyrocalciferol* (VI), m.p. 130—131°, $[\alpha]_D^{18}$ +34·35°. Catalytic reduction of (V) or heating (VI) gives *hexahydro*epi*pyrocalciferol*, m.p. 137°, $[\alpha]_D^{18}$ +30·15° (m-*dinitrobenzoate*, m.p. 197—198°, $[\alpha]_D^{18}$ +20·9°): all rotations in $CHCl_3$. (I) and (II) are antirachitically inactive in 10^{-6} g. dose and less toxic than vitamin-*D*.

J. H. B.

Origin of vitamin-*D* in the organism. F. Venulet and F. Goebel (Compt. rend. Soc. Biol., 1932, **111**, 1026—1028).—Vitamin-*D* (I) was absent from the fæces of rats fed either on normal diet or on McCollum's diet (3143). Ultra-violet irradiation caused (I) to appear in the fæces of the normally fed rats but not in the fæces of those fed on rachitogenic diet. The dried flesh of the rachitic rats contained the precursor of (I), but not (I) itself.

Nutr. Abs.

Vitamin-*D* and the blood-phosphate curve. C. Bomskov and G. Rath (Z. ges. exp. Med., 1932, **85**, 400—404).—Na β-glycerophosphate was injected subcutaneously into rabbits given vitamin-*D* or treated with ultra-violet light. In both cases the resulting increases of blood-phosphate were < in similarly injected but otherwise untreated control animals.

Nutr. Abs.

Comparison of bone-ash of rachitic rats treated with viosterol and with phosphate ion. C. A. Lilly (Proc. Soc. Exp. Biol. Med., 1932, **30**, 175—176).—Addition of phosphate or of vitamin-*D* to Steenbock's low-phosphate, rachitogenic diet raised the bone ash of young rats consuming the diet.

Nutr. Abs.

Effect of irradiated ergosterol on the parathyroidectomised rat. T. von Spreter (Z. ges. exp. Med., 1932, **85**, 19—45).—Irradiated ergosterol (I), in daily amounts of 150 rat units, exerted no influence on the progress of the symptoms in parathyroidectomised rats. A daily dose of 500 units, while producing no symptoms of overdosage, prolonged the life of the animals and prevented the development of such defects in the enamel and dentine of the teeth as were found in animals receiving the lower amounts of (I).

Nutr. Abs.

Effect of viosterol on excretion of lead. F. B. Flinn and A. R. Smith (Proc. Soc. Exp. Biol. Med., 1932, **30**, 367—368).—Large doses of viosterol (I) caused an increased elimination of Pb in cats. In two cases the elimination was 10 and 30 times as great as during the period previous to the administration of (I). Only a slightly increased elimination was produced in guinea-pigs, due possibly to their relatively greater resistance to (I). (I) had no protective action against Pb poisoning in the case of four guinea-pigs.

Nutr. Abs.

Relation between hormones and vitamins, with special reference to the thymus and irradiated ergosterol. M. Coppo (Arch. internat. Pharmacodyn. et Ther., 1932, **43**, 123—185).—Young rabbits, from which the thymus had been recently removed, received daily doses of 0·25 c.c. of a 1% solution of irradiated ergosterol (I), and survived, whilst intact controls, receiving the same toxic doses, died. Far larger doses were needed to kill the former. *X*-Ray examination of the bones of such rabbits revealed typical decalcificatory lesions, following extirpation of the thymus. Dosage with (I) in

no way prevented the development of these, although intact controls similarly dosed showed enhanced calcification of the bone. Extirpation of the thymus did not affect the rise in blood-sugar or -phosphate, observed to occur in normal animals, following administration of (I). NUTR. ABS.

Activated ergosterol. D. BEALL and J. BIELY (Trans. Roy. Soc. Canada, 1932, [iii], **26**, III, 57—60).—1/40 c.c. of viosterol, having a potency of 250*D*, is as effective as 1 c.c. of cod-liver oil (112 units per g.) in prevention of rickets. H. G. R.

Unirradiated ergosterol and vascular sclerosis. T. GORDONOFF and S. ZURUKZOGLU (Z. Vitaminforsch., 1933, **2**, 25—28).—Sclerotic patches in the aorta with lesions in the media were observed in rabbits fed with ergosterol and exposed either to alpine sunlight or an ultra-violet lamp. R. K. C.

A thermodynamic law of life. K. STERN (Ber. deut. bot. Ges., 1933, **51**, 44—52).—In order to maintain the living organism, the "chemical potential" (Gibbs) of the essential nutrients must lie within certain well-defined limits, otherwise the nutrient becomes non-effective however great the amount supplied. A. G. P.

Plant growth substances. IV. Phytohormone of cell elongation. Isolation of auxin from human urine. F. KÖGL, A. J. HAAGEN-SMIT, and H. ERXLEBEN (Z. physiol. Chem., 1933, **214**, 241—261).—Cryst. *auxin*, m.p. 196°, activity 50 million units per mg., and its *lactone*, m.p. 172—173°, activity 35 million units per mg., were obtained from normal and mixed human urine. Lactonisation was accomplished by treatment with HCl in MeOH prior to distillation. The activity was followed by means of the Went technique (bending of oat coleoptile). Substances showing the Went reaction obtained from various sources appear to be identical. J. H. B.

Auxin; its occurrence in the plant and animal kingdoms. F. KÖGL (Naturwiss., 1933, **21**, 17—21).—Precise details are given for extracting auxin from urine (see preceding abstract). Auxin has $[\alpha]_D$ −3·18° and its lactone, m.p. 173°, $[\alpha]_D$ −3·42°, activity 50 million units per mg. The following *derivatives* have been prepared; dihydro-, m.p. 199°; tri(dinitrobenzoyl)-, m.p. 169°; Me ester, m.p. 150°; dihydroauxin-lactone, $C_{18}H_{32}O_4$, m.p. 191°; *p*-phenylphenacyl ester, $C_{32}H_{42}O_6$, m.p. 166°; *ψ*-auxin, $C_{18}H_{32}O_5$ (inactive). The auxin content of urine during pregnancy is normal. P. G. M.

Plant respiration. IV. Relation of the respiration of potatoes to the concentration of sugars and to the accumulation of a depressant at low temperatures. (i) Effect of temperature-history on the respiration/sugar relation. (ii) Form of the normal respiration/sugar relation and the mechanism of depression. J. BARKER (Proc. Roy. Soc., 1933, **B**, **112**, 316—335, 336—358).—The effect of varying sugar concn. on the respiration rate (I) of potatoes has been studied, and curves are given, showing the R/S relation at different temp. In addition to the direct retardation of (I) at low temp., a sp. temp. effect is observed as a result of which (I) is also dependent on the temp. history of the potato. Thus exposure to cold causes the accumulation of a (I)-depressing substance, max. at −1° and approx. nil at 8°. The development and operation of the effect of this substance, however, have a temp. coeff. in the opposite sense, being observed maximally at the higher temp. (10°) and negligibly at −1°. A. C.

Large respirometer. W. B. BALCH (Science, 1933, 77, 116—117). L. S. T.

Starch formation in cane leaves. W. E. COLLINGH and V. J. KONINGSBERGER (Arch. Suikerind. Ned.-Indie, 1932, **40**, Meded. No. 19, 1325—1340).—In CO_2 assimilation by the leaves of the cane variety POJ 2878 much starch is formed and is stored in the starch sheath surrounding the vascular bundles. This is much less marked in the leaves of some other varieties, viz., Striped Lahaina, or in those of sorghum. An excised leaf of cane which is caused to absorb sugar solution (sucrose, maltose, glucose, or fructose) converts part of the sugar into starch. J. P. O.

Maturity of sugar cane. II. Life history of "Hayaue" plant canes. III. Sucrose accumulation in the sugar cane. IV. Significance of water in "maturity." V. Utilisation of solar energy in the cane. VI. Changes in chemical composition of cane stalks deprived of their leaves. S. OZAWA and S. KOMATSU. **V. Utilisation of solar energy in the cane.** S. OZAWA. **VI. Changes in chemical composition of cane stalks deprived of their leaves.** S. OZAWA and Y. MAKINO (Mem. Coll. Sci. Kyoto, 1933, *A*, No. 1, 125 pp.).—II. Variations in the H_2O and chlorophyll contents of leaves with age and climatic conditions are recorded. In the expressed sap of the canes high titratable acidity and low p_H are especially marked in the upper sections, where active transformation of sugars into org. acids occurs. Variations with age of the total solids and non-reducing sugars of the sap and of fibre in the cane are of a similar character. Non-reducing and reducing sugars show an approx. inverse relationship.

III. The sprouting of stem cuttings of cane involves the utilisation of stored sucrose. Shoots developing from over-mature crowns left in the soil withdraw very little reserve sucrose from the parent plant. Tasselling and side-shoot production necessitate the consumption of stored sucrose, to an extent which depends on the general activity of the cane.

IV. In the early stages of maturity canes from poorly drained soils contained a higher proportion of reducing sugars than those from more porous soils. Irrigation may increase sugar yields by curtailing vegetative growth and in this respect is more effective than drainage.

V. A mathematical discussion of the photosynthesis and metabolism of carbohydrates.

VI. Removal of all but the tip leaves of canes causes, in the expressed sap, a decrease of total solids and sp. rotation to vals. which remain approx. const. until new leaves have developed and are actively functioning. Subsequently these vals. rise to the normal. Growth of the cane continues slowly in the absence of leaves, stored carbohydrate serving as an energy source. During this period the reducing sugar content of the sap is not greatly reduced. A. G. P.

Relation between water content, chlorophyll content, and the rate of photosynthesis in some tropical plants at different temperatures. R. H. DASTUR and B. L. DESAI (Ann. Bot., 1933, **47**, 69—88).—The "assimilation no." (*W*), *i.e.*, ratio of H_2O content : rate of assimilation, in plants increases with rising temp. up to a max. point and subsequently declines. Willstatter's "assimilation no." (CH), *i.e.*, ratio of chlorophyll content : CO_2 assimilated, showed no such regularity with temp. changes. The assimilation of CO_2 is more closely related to the H_2O content than to the chlorophyll content of leaves. A. G. P.

Fat metabolism of leaves. II. Fats and phosphatides of the runner bean (*Phaseolus multiflorus*). R. C. JORDAN and A. C. CHIBNALL (Ann. Bot., 1933, **47**, 163—186).—All organs of the plant contain lecithin and kephalin, in amounts which decrease in order from the cotyledons to the pinnate leaves. Cotyledons and embryo axes also contain a small amount of Mg phosphatidate. On germination the proportion of this compound increases rapidly until the prophylls begin to expand, when there is a steady transition to the Ca salt which is the principal phosphatide of the mature prophylls and pinnate leaves. The transition of the (fat-sol.) Mg salt to the Ca salt coincides with the onset of chlorophyll synthesis. The disappearance of phosphatides from the cotyledons during germination is more rapid than the appearance of phosphatides in the growing organs. Evidence is advanced that glyceride fatty acids in mature pinnate leaves can function as food reserves, but that phosphatides form integral parts of the protoplasm. Waxes and unsaponifiable materials in plants are probably the end-products of metabolism. A. G. P.

Metabolism of certain sea-weeds. P. HAAS and T. G. HILL (Ann. Bot., 1933, **47**, 55—67).—Examination of a no. of sea-weeds shows the contents of fats and fat-like substances and also the saturation of the fats to increase with the degree of emergence of the plants. The unsaponifiable residue of the fatty matter increases with the depth of immersion. The sugar content of marine algæ is small, but sugar alcohols (mannitol, sorbitol, dulcitol) are of general distribution. These compounds are probably the secondary products of sugars. NH_3 is present in all but certain exposed algæ. In exposed plants of high zones the amide-N content is usually > the NH_3-N. The reverse is the case in plants bathed with or frequently immersed in H_2O. NMe_3 occurs in several species; an octapeptide of glutamic acid is found in *Phæophyceæ* of the higher zones and a pentapeptide in other species. A. G. P.

Synthesis of protein by green plants. L. LOOSE and W. H. PEARSALL (Nature, 1933, **131**, 362—363).—In *Chlorella* the velocity of protein synthesis is approx. five times as great in the light as in the dark. If sufficient carbohydrate be present, the final equilibrium is similar in both cases. L. S. T.

Formation of tubers and other storage organs. Influence on translocation of the period of light and the supply of potassium. M. A. H. TINCKER and F. V. DARBISHIRE (Ann. Bot., 1933, **47**, 27—53).—Accumulation of carbohydrates in certain tubers varied with the period of exposure of the plants to light. Replacement of K by Na in nutrient solutions did not effect as much change in growth habit as did variations in light exposure. K-deficient plants wilted at higher levels of H_2O supply than those receiving adequate K. In dahlias the total dry-matter production was markedly reduced by K deficiency. The rate of formation and translocation of starches was influenced by the K supply. A. G. P.

Effect of chemical treatment of dormant potato tubers on the conductivity of the tissue and on the leaching of electrolytes from the tissue. J. D. GUTHRIE (Contr. Boyce Thompson Inst., 1933, **5**, 83—94).—Treatment of potato tubers with $CH_2Cl{\cdot}CH_2{\cdot}OH$ increased by small but significant amounts the conductivity of the tissue and the ease of leaching of electrolytes from it. KCNS produced similar but smaller changes. The action of thiourea was less definite. A. G. P.

Absorption and accumulation of solutes by living plant cells. IV. Surface effects with storage tissue : quantitative interpretation with respect to respiration and salt absorption. F. C. STEWARD (Protoplasma, 1932, **17**, 436—453).—High respiration rates in potato discs exposed to air occur only in a surface zone of cells which is deeper than in the case of discs exposed to salt solutions. Salt absorption is confined to cells exhibiting high respiration rates and from which there is a marked disappearance of starch. A. G. P.

Plant buffer systems in relation to the absorption of bases by plants. T. C. DUNNE (Hilgardia, 1932, **7**, No. 5, 207—234).—Examination of the expressed sap of frozen and thawed tissues indicates that org. acids, amides, NH_2-acids, sugars, and phosphates are the principal buffering agents present. Low supplies of K and P to the plant result in a decreased p_H and increased buffer power in the sap, probably due to relative increases in the proportions of org. acids, amides, and NH_2-acids. Plants grown with low Ca supplies are not necessarily injured nor do they show more acid saps. Under these conditions more K is absorbed and serves as a base in the buffer system. Treatment with $CaCO_3$ may produce an injurious alkalinity in the sap of certain plants. In buckwheat treatment with $CaCO_3$ reduced the oxalate content of the sap. Much of the oxalate in buckwheat is in an insol. form. A. G. P.

Antagonism. I. Effect of the presence of salts of univalent, bivalent, and tervalent cations on the intake of calcium and ammonium ions by potato tuber tissue. G. F. ASPREY (Proc. Roy. Soc., 1933, **B**, **112**, 451—472).—Absorption of $Ca^{\cdot\cdot}$ and $NH_4^{\cdot}$ from aq. solutions of $CaCl_2$ and NH_4Cl, respectively, is at first rapid (for 3 and 10 hr., respectively), and then proceeds slowly. The similar initial rates of absorption are due to their dependence during this period on physical properties (*e.g.*, mobility) of the ions, which are similar. Experiments with added NaCl, $MgCl_2$, and $LaCl_3$ show that the antagonistic action of an ion to absorption varies directly as the valency and concn. of the added ion. Mixtures of $CaCl_2$ and NH_4Cl exhibit mutual antagon-

ism. 0·02*N* and more conc. solutions of $AlCl_3$ have an anomalous effect, causing considerable initial reduction in absorption of $NH_4^{\cdot}$, which increases for 9 hr., and then decreases again. LiCl increases the absorption of $NH_4^{\cdot}$, possibly due to the exosmosis induced by Li salts. The intake of Cl' is not greatly affected by Na or K, but is reduced by Li. The increased absorption of $NH_4^{\cdot}$ and Cl' caused by sucrose may be due to an increase in tissue respiration. The " antagonism " of an ion may be regarded as due to a balance between its sp. effect on the tissue and ionic competition for absorption. A. C.

Growth and differentiation. IV. Distribution of some solutes in the tissues of *Kleinia articulata*. D. Thoday and H. Evans (Ann. Bot., 1933, **47**, 1—20).—In the stem tissues of *K. articulata* $Ca^{\cdot\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, NO_3', and malate are the predominant ions with PO_4''', SO_4'', Cl' in small amounts. The proportions of $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $NH_4^{\cdot}$, and $Fe^{\cdot\cdot\cdot}$ are small. The amount of $Ca^{\cdot\cdot}$ is nearly equiv. to that of $Na^{\cdot}+K^{\cdot}$. In the separated zones of the stem the ratio $Ca^{\cdot\cdot}$: $(Na^{\cdot}+K^{\cdot})$ averages 4 : 1 in the pith and 1 : 4 in the cortex. No $Ca^{\cdot\cdot}$ was detectable in the outer cortex. The cortex contains approx. two thirds of the total $K^{\cdot}$ and the pith two thirds of the total $Ca^{\cdot\cdot}$. There is a general distribution of NO_3' in stems with a tendency to decrease towards the outer cortex and in the centre of the pith. Largest amounts occur in the bundle zone. Inulin and PO_4''' accumulate in the bundle zone in which the sugar concn. is low. Cl' is evenly distributed throughout the tissues. SO_4'' is less in the pith than in the cortex or bundle zone. Sol. $Mg^{\cdot\cdot}$ occurs mainly in the pith centre where $Ca^{\cdot\cdot}$ is low. In cortex and pith the relative excess of bases indicates high proportions of malates. Diurnal changes in acidity occur in those parts of the stem in which malic acid and K are associated. A. G. P.

Initiation and stimulation of roots from exposure of plants to carbon monoxide. P. W. Zimmermann, W. Crocker, and A. E. Hitchcock (Contr. Boyce Thompson Inst., 1933, **5**, 1—17).—Exposure of a no. of plants to an atm. containing 1% of CO induced root production from young stems and in other cases stimulated the growth of pre-existing root primordia on older parts of stems. Root hairs were more abundant on CO-treated plants and cuttings of tobacco plants rooted much more rapidly after exposure to CO. A. G. P.

Water-permeability of protoplasm. B. Huber (Ber. deut. bot. Ges., 1933, **51**, 53—64).—Plasmolysis by neutral salt solutions of the mesophyll cells of *Vallisneria* is much less rapid than in those of the epidermis. This effect is not the result of differences in cell size, but of differences in the permeability of the protoplasm to H_2O. A. G. P.

Artificial nutrition of cultivated plants. I. Nutrient media of stable p_H. C. Zinzadze (Ann. Agron., 1932, **2**, 809—853).—Nutrient media are stabilised with respect to p_H by the use of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2,22H_2O$. Addition to the media of active C improved the growth of plants by the adsorption of toxic material which tends to accumulate in the medium. A. G. P.

Health condition of cultivated plants in relation to their nutrition. F. Labrousse (Ann. agron., 1932, **2**, 774—808).—The influence of physical and chemical soil conditions, of unbalanced nutrition, and of the absence of certain essential nutrients, on the distribution of plant disease and the susceptibility of plants to infection is discussed. An extensive bibliography is appended. A. G. P.

Nitrate storage by higher marine algæ. S. Suneson (Z. physiol. Chem., 1933, **214**, 105—108).—Many species were tested for nitrate ($NHPh_2$ reaction). NO_3' is present in some green, but absent from most brown, algæ. The red species show the greatest differences. J. H. B.

Fixation of nitrogen by the bacteria of legumes. H. Burgevin (Compt. rend., 1933, **196**, 441—443).—Soya beans grown in soil inoculated with *B. radicicola*, Beij., are more able to utilise N both from the air and as NH_4NO_3 than those grown in soil not inoculated. The foliage is greener, the plants are healthier, and the harvest is better, typical nodules being formed on the roots. P. G. M.

Legume-bacteria and plants. XII. Utilisation by non-leguminous plants of the nitrogen compounds from the root-nodules of leguminous plants. A. I. Virtanen, S. von Hausen, and H. Karstrom (Biochem. Z., 1933, **258**, 106—117; cf. A., 1931, 1101).—The org. compounds which diffuse from root-nodules produced by inoculation in otherwise sterile leguminous plants (clover, peas) grown from seed in a N-free medium consist almost entirely of NH_2-acids. Non-leguminous plants (barley) grow very well while utilising these compounds as their sole source of N, and it is very probable that under natural conditions such utilisation occurs to a great extent. The view that higher plants utilise only inorg. compounds for their N supply is thus controverted. Org. N compounds (aspartic acid, asparagine, caseinogen hydrolysates, urea, alanine) exhibit great differences as regards their capability to serve as N sources for red clover, peas, and barley. Aspartic acid is an excellent N source for leguminous plants but is not so for the Gramineæ. W. McC.

After-ripening of *Rhodotypus kerrioides* seeds. F. Flemion (Contr. Boyce Thompson Inst., 1933, **5**, 143—159).—During the after-ripening period there is an increase in catalase, peroxidase, and lipase activity, in H_2O-absorbing power, and in the contents of N sol. in 80% EtOH, titratable acid, and sucrose, and a steady decrease in Et_2O-sol. constituents. A. G. P.

Is elementary nitrogen absorbed by nodules on the roots of Leguminosæ in the assimilation of atmospheric nitrogen ? G. J. A. Galestin (Chem. Weekblad, 1933, **30**, 207—209).—An apparatus is described in which a limited supply of air or other gas can be circulated over approx. 500 g. of nodules. Experiments with detached nodules from *Lupinus luteus* show that no absorption of N_2 takes place. S. C.

Drying and fermentation of tobacco. II Relationship of enzyme content (peroxidase oxygenase, catalase) of tobacco and the dis-

appearance of nicotine during fermentation. L. BARTA (Biochem. Z., 1933, **257**, 406—410).—In tobacco poor in peroxidase and oxygenase, loss of nicotine (I) by fermentation does not occur and in tobaccos rich in these enzymes there is no relationship between the enzyme content and loss of (I). There is, however, a definite relationship between the catalase content and the loss of (I) by fermentation. P. W. C.

Biological introduction to the cellulose symposium [Delft, May 1932]. G. VAN ITERSON (Chem. Weekblad, 1933, **30**, 2—19).—A survey of the production of cellulose in plants, and of the structure, optical and mechanical properties, swelling, and chemical behaviour of cellulose. An extensive bibliography is given. H. F. G.

Robinoside in the flowers of *Vinca minor*, L. (*alba*). J. RABATÉ (Bull. Soc. Chim. biol., 1933, **15**, 130—134).—The flowers of *V. minor*, L. (*alba*), but not of the blue variety or of *V. major*, L., contain 0·4% of robinoside (A., 1926, 1183). F. O. H.

Starch and alkaloid content of leaves. M. JANICSEK (Mezog.-Kutat., 1932, **5**, 283—292; Chem. Zentr., 1932, ii, 3277).—For the determination of starch the leaves are freed from colouring matter and reducing substances by extraction with EtOH and the residual starch is determined colorimetrically with I. The alkaloid content of leaves of *Datura stramonium* and *D. metel* increases relatively at night, since starch is then saccharified and passes to other parts of the plant. A. A. E.

Physico-chemical heterogeneity of plastids. A. MAIGE (Compt. rend., 1933, **196**, 424—426).—Starch grains are entirely evolved in the plastid vacuoles in the unilocular type, but the plastid walls exhibit a variable permeability to sugars over different portions of their surfaces, which explains the formation of starch mainly by the plastid cap. P. G. M.

Chinese "dragon eyes." P. P. T. SAH and T. W. LI (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 277—283).—The dried fruit (*Euphoria longana*, Lam.) contains no vitamin-*A* or -*B*. An analysis of the fresh fruit is given. H. G. R.

Chinese peanuts and peanut oils. P. P. T. SAH, K. PING, T. S. MA, and J. CHOW (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 289—294).—Analyses are given. H. G. R.

Sativic and tetrabromostearic acids derived from lumbang oil and their significance in relation to naturally occurring linoleic acid. D. M. BIROSEL (Univ. Philippines Nat. Appl. Sci. Bull., 1932, **2**, 103—117).—Only two isomeric sativic acids have been obtained by oxidation of the free fatty acids from lumbang oil and of linoleic acid from α-linoleic acid tetrabromide. The compounds usually designated β- and δ-linoleic acid are, respectively, almost pure Me ester and a mixture of the acid and ester. CH. ABS.

Phosphatide content of apples, pears, plums, and peaches. B. REWALD and A. SCHWIEGER (Biochem. Z., 1933, **257**, 289—292).—No characteristic differences could be detected between the phosphatide contents of peel and pulp with any of the fruits, the contents ranging from 0·03% in peach to 0·009% in apple pulp and from 0·066% in plum to 0·011% in apple peel. The highest vals. (0·41%) were obtained in the pips (plum). In pulp, the total crude fat is highest in plum (0·37%) and lowest in pear (0·11%), whilst in peel it is highest in peach (1·57%) and lowest in pear (0·54%). P. W. C.

Change of colour of *Boletus strobilaceus*, Scop. G. BERTRAND (Biochem. Z., 1933, **258**, 76—78; cf. A., 1902, i, 220).—The fungus yields a cryst. phenolic *substance*, strobilomycol, which is easily attacked by laccase with production of a red and then a black colour. W. McC.

Effects of sulphur deficiency on metabolism in tomato. G. T. NIGHTINGALE, L. G. SCHEMMERHORN, and W. R. ROBBINS (Plant Physiol., 1932, **7**, 565—595).—Tomatoes grown in S-deficient media slowly developed symptoms resembling those of N starvation except that stem growth of a thin and woody character continued. The carbohydrate content of these plants was very high and they contained more NO_3' than corresponding plants in a complete nutrient. This results from a retardation of the normal NO_3'-reducing and carbohydrate-oxidising processes. Starch digestion and sugar translocation took place freely in S-deficient plants (I). The latter were further characterised by thick cell walls containing a high proportion of fibre and lignin, reduced amounts of protoplasm, and a much reduced content of ·SH compounds in the meristematic tissue. Proteolysis, normally associated with decreased carbohydrate contents, was active in (I). Whereas the org. S of normal plants existed mainly as insol. protein complexes, that of (I) was largely H_2O-sol. and contained little or no cystine, cysteine, or glutathione. In tomato the reduction $SO_4'' \longrightarrow SO_3'' \longrightarrow$ ·SH and of $NO_3' \longrightarrow NO_2' \longrightarrow NH_3$ occurred in the relatively alkaline phlœm-regions of roots and tops. In apple, narcissus, and asparagus NO_3' reduction is confined chiefly to fibrous roots and SO_4'' reduction mainly to the tops and only to a small extent in roots. A. G. P.

Determination of protein by sulpho-chromic oxidation. A. BOUTROUX (Bull. Soc. Chim. biol., 1932, **14**, 1343—1349).—The method is satisfactory for purified proteins, but cannot be used directly on sera owing to interference of lipins. A. L.

Micro-Kjeldahl method. S. BALACHOVSKI and B. BRUNS (Biochem. Z., 1932, **256**, 292).—An apparatus is described which permits the NH_3 to be distilled off by evaporating to dryness in vac., the vol. of distillate being always the same. P. W. C.

Alternative reagent for the determination of galactose. V. J. HARDING, T. F. NICHOLSON, and G. A. GRANT (J. Biol. Chem., 1933, **99**, 625—628).—*Saccharomyces marxianus*, being, in contrast to galac yeast, without action on maltose, can be used for the determination of galactose mixed with certain other sugars in urines and Folin–Wu blood-filtrates. The technique of the method is described. A. L.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1933.

General, Physical, and Inorganic Chemistry.

Precision measurements with high dispersion of the Stark effect in hydrogen. L. KASSNER (Z. Physik, 1933, **81**, 346—362). A. B. D. C.

Current–intensity relation of the 600 Å. band of helium. J. L. NICKERSON (Physical Rev., 1931, [ii], **38**, 1907). L. S. T.

Characteristics of the carbon arc in chlorine. W. KANGRO and E. JEEP (Physikal. Z., 1933, **34**, 300—303).—Using a pressure of Cl_2 of 700 mm., the arc potential was considerably smaller than that in air. At the temp. of the arc, the Cl is entirely in the at. form. The conductivity can be regarded as transport of electricity by negatively-charged Cl atoms, or due to the formation of positive atom ions by thermal dissociation. A. J. M.

Predissociation in nitrogen and excitation of the green auroral line. J. KAPLAN (Physical Rev., 1931, [ii], **38**, 1079—1080). L. S. T.

New criterion for predissociation. J. KAPLAN (Physical Rev., 1931, [ii], **38**, 1079, 1792). L. S. T.

Continuous absorption of oxygen between 1750 and 1300 Å. and its bearing on the dispersion. R. LADENBURG and C. C. VAN VOORHIS (Physical Rev., 1933, [ii], **43**, 315—321; cf. this vol., 10).—The absorption coeff.-wave no. relation is shown graphically. The max. absorption coeff. reduced to n.t.p. is approx. 490 cm.$^{-1}$ The calc. f val. is 0·193 compared with 0·202 calc. from dispersion measurements. N. M. B.

Alternating intensities of Na_2 bands. H. C. UREY (Physical Rev., 1931, [ii], 1074—1075).—An alternating intensity is detectable in Na bands and the spin of the nucleus is probably $\geq 5/2$. L. S. T.

Spectra of potassium and sodium in the mercury arc. D. A. WELLS and I. BALINKIN (J. Opt. Soc. Amer., 1933, **23**, 105—108; cf. A., 1932, 924).—The construction of Hg–K and Hg–Na amalgam lamps with regard to % of K or Na, dimensions, wattage input, and evacuation is described, and spectrograms obtained are reproduced. N. M. B.

Determination of light yield in the sodium spectrum. G. HAFT (Physikal. Z., 1933, **34**, 287—288, and Z. Physik, 1933, **82**, 73—91).—The excitation function (intensity of line as a function of accelerating potential of electrons) was determined for Na lines by a new method. A. J. M.

Predissociation and pressure effects in the band spectrum of aluminium hydride. E. HULTHÉN and R. RYDBERG (Nature, 1933, **131**, 470—471). L. S. T.

Electrodeless discharges in argon. I. Electrical properties. S. P. MCCALLUM and L. KLATZOW (Phil. Mag., 1933, [vii], **15**, 829—839). H. J. E.

Spectra of calcium I-like ions: manganese VI, iron VII, cobalt VIII, and nickel IX. W. G. CADY (Physical Rev., 1933, [ii], **43**, 322—328).—Wavelengths, frequencies, transitions, and term vals. are tabulated for the vac. spark spectra. The analysis is compared with theoretical predictions. N. M. B.

Nuclear moments of indium and gallium. J. S. CAMPBELL and R. F. BACHER (Physical Rev., 1931, [ii], **38**, 1906—1907).—The nuclear moment of In is $> I\frac{1}{2}$, whilst that of Ga appears to be $\frac{1}{2}$. L. S. T.

Hyperfine structure of the lines of the arc spectrum of rubidium. D. A. JACKSON (Proc. Roy. Soc., 1933, **A**, **139**, 673—682).—The two resonance lines, 7947 and 7800 Å., possess the same fine structure, and each has four components. The lines 4215 and 4201 Å. possess three components, that of longest wave-length being slightly broadened. The observed structure is explained on the assumption that each isotope (Rb^{85} and Rb^{87}) has its $5S_{1/2}$ level split up into two levels. There is an appreciable isotope shift; the centre of gravity of the levels of Rb^{85} is 0·2 cm.$^{-1}$ higher than that of those of Rb^{87}. I is 3/2 for Rb^{85}, the most probable val. for Rb^{87} being 5/2. The magnetic moment of the nucleus of Rb^{87} is about 2·5 times that of Rb^{85}. This indicates a considerable difference in the structure of the two nuclei. L. L. B.

Determination of intensity of the members of the principal series of rubidium and cæsium. H. KOHN and H. J. HUBNER (Physikal. Z., 1933, **34**, 278—282).—The intensity ratios of doublet components of the higher members of the principal series of Rb and Cs were determined by a photographic-photometric method. There is a deviation from the Burger–Dorgelos intensity rule, probably due to hyperfine structure. A. J. M.

Zeeman effect of the terms of Zr I and Zr II. P. M. SANCHO (Anal. Fís. Quím., 1932, **30**, 867—875).—Theoretical. The magnetic factors are calc. by Russell's formula. H. F. G.

Action of a magnetic field on absorption spectrum of iodine. I. I. AGARBICEANU (Compt. rend., 1933, **196**, 760—763).—The effects of a mag-

netic field of 1400 gauss, transverse to the direction of observation, on the absorption spectrum of I vapour at 90° and also with addition of O_2 at 86° are compared. The broadening effect of the O_2 is reversed by that of the magnetic field, supporting Van Vleck's explanation of the action of a magnetic field (cf. A., 1932, 787). C. A. S.

Arc spectrum of iodine. W. E. CURTIS (Nature, 1933, **131**, 398—399).—A criticism (cf. this vol., 200). L. S. T.

Broadening of the ultra-violet absorption bands of xenon under pressure. J. C. MCLENNAN and R. TURNBULL (Proc. Roy. Soc., 1933, **A**, **139**, 683—698).—Experiments are described to show how the absorption coeff. for various wave-lengths in the band varies with pressure. The results indicate the pressures at which collisions between > two atoms become effective in the absorption, as suggested by Franck. L. L. B.

Hyperfine structure and nuclear moment of rhenium. W. F. MEGGERS, A. S. KING, and R. F. BACHER (Physical Rev., 1931, [ii], **38**, 1258—1259; cf. A., 1931, 993).—Most of the lines of the spectrum of Re I have 2—6 components. Both isotopes of Re appear to have the same nuclear moment $2\frac{1}{2}$ $(h/2\pi)$. L. S. T.

"Quantitative" [spectral] lines of rhenium. S. PIÑA DE RUBIES (Anal. Fís. Quim., 1932, **30**, 918—921).—Quant. lines are defined as those visible in the arc spectrum of 5×10^{-4} g. of an element. The lines emitted by Re at concns. of 1·0 and 0·1% (2322—2399 Å.) under standard conditions are recorded, 14 being new lines below 2500 Å. H. F. G.

Deepest term in the Au II spectrum. R. A. SAWYER and K. THOMSON (Physical Rev., 1931, [ii], **38**, 2293—2294).—Three lines locating $^1S_0$ are recorded. L. S. T.

Fluorescent excitation of mercury by the resonance frequency and by lower frequencies. V. (LORD) RAYLEIGH (Proc. Roy. Soc., 1933, **A**, **139**, 507—517).—When Hg is made fluorescent by wave-lengths > a few Å. longer than the resonance line, neither 2^3P_1 nor 2^3P_0 atoms are formed at any stage. It is concluded that with this kind of excitation the mechanism of fluorescence producing the 3300 and 4850 max. is concerned solely with excited Hg mols. L. L. B.

Dependence of the intensity of mercury [spectral] lines on temperature and the production of continuous bands. O. MASAKI (J. Sci. Hiroshima Univ., 1932, **A**, **3**, 61—65).—The change of colour with temp. of excited Hg vapour containing Ne has been analysed spectroscopically. The intensity of some lines decreases with rising temp., with a min. at about 160°. The resonance line shows max. intensity at about 80°. Above 160° all bands become stronger. F. L. U.

Zeeman effect of lead II, III, and IV. J. B. GREEN and R. A. LORING (Physical Rev., 1933, [ii], **43**, 459—466).—Various minor corrections are made. N. M. B.

Arc spectrum of radium emanation. E. RASMUSSEN (Z. Physik, 1933, **80**, 726—734).—Lines between 10,000 and 3000 Å. are tabulated. A. B. D. C.

Absorption of metals in the visible and ultra-violet. H. FROHLICH (Z. Physik, 1933, **81**, 297—312).—The width and position of the forbidden energy regions of Kronig can be determined from the optical consts. of a given metal. Available measurements for Cu, Ag, and Au are discussed; the proper function of the electron in these deviates to a greater extent from that of the free electron than in alkali metals. A. B. D. C.

High-frequency electric discharges in gases. J. C. WILSON (Nature, 1933, **131**, 546—547).—Discharges of an unusual type are described. L. S. T.

Distribution of radiation in the arc. K. BRUCKERSTEINKUHL (Z. wiss. Phot., 1933, **32**, 3—62).—The spectra of 13 metals were examined with a quartz spectrograph, and of 38 metals with a concave grating. Most spectra have a greater intensity at the poles, and the lines are classified into 6 groups, according to their intensity distribution, which may be greater at one pole than at the other. This distribution affords a method for differentiating arc and spark lines. Certain Cu lines (cf. Sommer, A., 1927, 83) are spark, not arc, lines. The temp. groupings of King (Astrophys. J., 1922, **56**, 318) above and below λ 2810 are not identical. Comparison with the arc types shows the latter to correspond with a series of energy levels. The effects produced by impurities are described, and a method for the quant. analysis of mixtures is suggested. J. L.

Electron and proton spin moments and the possibilities of their orientation as a consequence of the quantum-dynamical, relativistic, invariant differential equation of the many-body problem. H. SEYFARTH (Ann. Physik, 1933, [v], **16**, 636—646). W. R. A.

Spectrum of the night sky as observed in India. K. R. RAMANATHAN (Indian J. Physics, 1932, **7**, 405—410).—The spectrum does not differ markedly from that observed in other parts of the world. W. R. A.

Transformations in the theory of complex spectra. G. H. SHORTLEY (Physical Rev., 1933, [ii], **43**, 451—458; cf. A., 1932, 668).—Mathematical. N. M. B.

Corrected relative intensities of the *X*-ray lines in the tantalum *L* series. V. HICKS (Physical Rev., 1931, [ii], **38**, 572—573).—Corr. vals. are recorded (cf. A., 1931, 3). L. S. T.

***X*-Ray scattering power of silver for *Kα* copper radiation.** L. CHROBAK (Z. Krist., 1933, **84**, 475—477; cf. A., 1930, 1491).—Ag powder was used, and the observed intensities were plotted. C. A. S.

Structure of *K* line of boron. A. HAUTOT (Compt. rend., 1933, **196**, 688—689; cf. A., 1931, 4, 889).—The *K* line of B consists of a more intense component 2 Å. wide with centre at 67·9 Å., and a weaker one 0·6 Å. wide separated from the former by 1·25 Å. C. A. S.

M levels of magnetised iron. PRIVAULT (Compt. rend., 1933, **196**, 854—856).—The greatest difference detectable in λ of $K\beta_1$ and $K\beta_5$ on applying a field of 5000 gauss to an Fe anti-cathode was $+0{\cdot}12$ X, average $+0{\cdot}025$ X, and in the energies of the levels M_3 and M_5 of 0·2 and 0·4 ev., respectively. C. A. S.

Chemical and physical conditions of hydrogen in platinum and palladium when influencing photo-electric activity. G. BETHE (Z. Physik, 1933, **80**, 701—725).—Mol. H_2 influences photo-electric activity of Pt and Pd only when O_2 and H_2O are present; at. H, obtained from glow discharges, increased the photosensitivity. A. B. D. C.

Absorption of energy in ionised gases. T. V. IONESCU and (MME.) I. MIHUL (Compt. rend., 1933, **196**, 682—684; cf. this vol., 9).—Curves are deduced showing that the absorption of energy is a function of the intensity of the current in the tube containing the gas, the nature and pressure of the gas, the wave-length, and the length of the tube. C. A. S.

Thermionic and adsorption characteristics of thorium on tungsten. W. H. BRATTAIN and J. A. BECKER (Physical Rev., 1933, [ii], **43**, 428—450).—The dependence of the thermionic emission of W on the temp. and surface density of Th deposited on a W ribbon was investigated. The variation of emission with applied field, and the evaporation and migration of Th on the W surface were studied. N. M. B.

Relative ionisation of air, nitrogen, oxygen, and argon with the Cu-$K\alpha$ line. O. GAERTNER (Ann. Physik, 1933, [v], **16**, 613—624).—The ionisation vals. at various pressures were determined with A as a standard and using two ionisation chambers. The following vals. are given: A 28·8, air $35{\cdot}49\pm0{\cdot}17$, N_2 $39{\cdot}31\pm0{\cdot}20$, O_2 $32{\cdot}95\pm0{\cdot}22$ volts per ion pair. W. R. A.

Photo-electric emission in a magnetic field. R. SCHMID (Ann. Physik, 1933, [v], **16**, 647—656). W. R. A.

Standing light waves; repetition of an experiment by Wiener, using a photo-electric probe surface. H. E. IVES and T. C. FRY (J. Opt. Soc. Amer., 1933, **23**, 73—83).—An active layer of Cs is formed on a Pt surface, and, supported on quartz, at an angle with the surface. Variations in the photo-electric current for different angles of incidence, conditions of polarisation, and wave-lengths indicate the photo-electric sensitivity along the inclined layer, corresponding with variations of the standing wave pattern. N. M. B.

Electron emission of thin metal layers under X-rays. J. KLEIN (Z. Physik, 1933, **81**, 101—120).—The electron emission was studied in relation to the layer thickness and frequency of the incident X-rays. Variation of the "true absorption coeff." with frequency is deduced, including the regions of absorption edges. A. B. D. C.

Trajectories of electrons in a longitudinal magnetic field. B. KWAL (Compt. rend., 1933, **196**, 758—760; cf. A., 1929, 231). C. A. S.

Positive electron. C. D. ANDERSON (Physical Rev., 1933, [ii], **43**, 491—494).—Out of 1300 Wilson chamber cosmic-ray tracks 15 were of positively-charged particles of mass $<$ that of the proton, and producing curvatures and ionisations requiring the mass to be <20 times the electron mass. These "positrons" are concluded to be secondary particles ejected from at. nuclei. N. M. B.

New evidence for the positive electron. J. CHADWICK, P. M. S. BLACKETT, and G. OCCHIALINI (Nature, 1933, **131**, 473).—Expansion photographs obtained when Pb is exposed to γ-rays and neutrons afford strong evidence of positive particles with the same mass and magnitude of charge as a negative electron. L. S. T.

Photographs of tracks of penetrating radiation. P. M. S. BLACKETT and G. P. S. OCCHIALINI (Proc. Roy. Soc., 1933, **A**, **139**, 699—718).—A method is described by which the high-speed particles produced by certain penetrating radiations take their own Wilson cloud-track photographs. Suitable tracks are found on 80% of the photographs. Measurements are made of the $H\rho$ of a track (ρ is the radius of curvature of a track) and the ionisation along it, from which the mass of the particle is determined. Photographs of tracks, definitely curved, some bent slightly in one direction and some in the other, are obtained; *i.e.*, some of the particles are positively charged, some negatively. The salient features of 500 photographs are described, and it is considered that the showers of particles producing the complex tracks are due to some nuclear disintegration process stimulated by particles or protons of high energy associated with the penetrating radiation. It is concluded that particles exist with a positive charge and a mass comparable with that of an electron. The frequency of occurrence of the showers, and their possible relation to the bursts of ionisation observed by various workers, are discussed. It is suggested that the positive and negative electrons in the showers are created during a collision process. The subsequent fate of the positive electrons is discussed in the light of Dirac's theory of "holes" (A., 1930, 271). The probable existence of non-ionising neutrons or photons in the showers is discussed. L. L. B.

New method of producing negative ions. J. S. THOMPSON (Physical Rev., 1931, [ii], **38**, 1389).—Negative ions are formed at metal surfaces bombarded by positive ions. Positive Li ions bombarding Pt produce negative ions of $OH'=17$ and $Cl'=35$; secondary electrons and ions, probably H_1' and H_2', are also formed. L. S. T.

Reflexion of mercury molecular rays at crystal cleavage faces. B. JOSEPHY (Z. Physik, 1933, **80**, 755—762).—Diffuse reflexion, but not deviation of max. intensity from the line of geometrical reflexion (cf. Ellett and Olson, A., 1928, 566), was observed for Hg mol. rays incident on cleavage faces of NaCl and LiF. A. B. D. C.

Proton reflexion and stationary radiation from impact of solids. C. RAMSAUER and R. KOLLATH (Ann. Physik, 1933, [v], **16**, 560—569).—

Experimental methods are described by which protons of 30—1500 volts impinge on brass and lampblack. The no. of reflected protons and the emitted secondary radiation have been investigated. W. R. A.

Scattering of slow protons by gas molecules. C. RAMSAUER and R. KOLLATH (Ann. Physik, 1933, [v], **16**, 570—587).—Protons of 30—120 volts velocity in He, A, H_2, and CH_4 have been investigated throughout a scattering region of 15—167°. W. R. A.

Positive ion work function of tungsten for the alkali metals. R. C. EVANS (Proc. Roy. Soc., 1933, A, **139**, 604—617).—Determinations have been made of the rate of evaporation of K, Rb, and Cs ions from a clean W surface, under conditions such that the surface concns. are very small and the particles deposited on the surface with low kinetic energy. The temp. coeff. of the rate of evaporation is a measure of the positive ion work function. This is $2{\cdot}4_3$, $2{\cdot}1_4$, and $1{\cdot}8_1$ volts for K, Rb, and Cs, respectively. By considering these vals. in terms of the Born cycle it is concluded that the surface ionisation potential of all three elements is about −0·3 volt, and the at. work function about 2·2 volts. L. L. B.

Collision of slow positive ions in inert gases. I. Ion sources. II. Ionisation by K^+ ions in argon. M. NORDMEYER (Ann. Physik, 1933, [v], **16**, 697—705, 706—719).—The production of suitable ions is discussed and the ionisation function of K^+ ions at 1000 volts in A has been investigated. Deviations from the results of Beeck (A, 1930, 1494) are discussed. On extrapolation the input potential of the ionisation function is 75 volts. W. R. A.

Revision of the at. wt. of arsenic. I. Analysis of arsenic tribromide. II. Analysis of arsenic trichloride. G. P. BAXTER, W. E. SHAEFER, M. J. DORCAS, and E. W. SCRIPTURE, jun. (J. Amer. Chem. Soc., 1933, **55**, 1054—1066).—The at. wt. of As is 74·91 from determinations of the ratios $AsBr_3 : 3Ag$ and $AsCl_3 : 3Ag$ with specially purified materials. J. G. A. G.

Isotope of hydrogen. G. N. LEWIS (J. Amer. Chem. Soc., 1933, **55**, 1297—1298).—H_2O, d 1·035, of which about 1/3 of the H consists of the heavier isotope, has been obtained by electrolysis. The refractive index is < that of ordinary H_2O. J. G. A. G.

Masses of Ne^{20} and B^{11}. The mass of Ne^{22} and the disintegration of F^{19}. K. T. BAINBRIDGE (Physical Rev., 1933, [ii], **43**, 424—427).—Masses obtained by measurements of spectra are: Ne^{20} 19·9967±0·0009; B^{11} 11·0107±0·001; Ne^{22} 21·9947±0·0009. The max. val. of Ne^{22} calc. from Aston's val. for F^{19} and the disintegration of F^{19} is 21·9925±0·0015; this discrepancy is discussed. N. M. B.

Periodic system of atomic nuclei and the principle of regularity and continuity of series. A correction. W. D. HARKINS (Physical Rev., 1931, [ii], **38**, 1792; cf. A., 1931, 1349). L. S. T.

Diagram of the periodic table. F. W. RIXON (Chem. and Ind., 1933, 260—261).—At. nos. of the elements are plotted as abscissæ and the ordinates are the no. of electrons of the respective elements in excess or defect of the nearest rare gas. The two short periods are duplicated to represent electrons both above and below the inert gas structure. The relation between the sub-groups A and B of the usual table is brought out clearly. E. S. H.

Radioactive phenomena of second order and artificial origin. G. REBOUL (J. Phys. Radium, 1933, [vii], 4, 73—89; cf. A., 1932, 672).—A method is described for the activation, by exposure to radiation in a resistance cell, of paper, cloth, ebonite, and other insulators so as to produce effects analogous to those of radioactive substances. The properties of the activated substances, the relation to ordinary radioactivity, and the mechanism of activation are discussed. The phenomena are attributed to orbital electrons. The wave-lengths of the emitted radiation are of the order of 25—350 Å. N. M. B.

New radioactive substances. A. DEBIERNE (Compt. rend., 1933, **196**, 770—771).—If a Ra-containing Ba prep. be repeatedly fractionated either by pptn. of the carbonate or crystallisation of the bromide, marked differences in the activity–time curve of the head and tail fractions are observed. It is suggested that this is due to formation of neo-radium (Ne-Ra) thus: Ra⟶Ne-Ra⟶Rn, and that this is the explanation of peculiarities in the emission of β-rays by Ra, and in its magnetic spectrum (cf. A., 1932, 318, 895). C. A. S.

Parent of protoactinium. O. A. GRATIAS and C. H. COLLIE (Proc. Roy. Soc., 1933, A, **139**, 567—575).—Experiments are described which show that when U-I decays it forms a radioactive element which has similar chemical properties to protoactinium and emits α-particles. Its half-val. period, $7{\cdot}8\times10^4$ years, is sufficiently close to that of protoactinium ($3{\cdot}2\times10^4$ years) to establish the identity of the two elements. L. L. B.

Range of radiation from samarium. G. VON HEVESY and M. PAHL (Nature, 1933, **131**, 434—435).—The range of Sm radiation (this vol., 4) is 1·1 cm. at 15°; the calc. velocity of particles is $1{\cdot}05\times10^9$ cm. sec.$^{-1}$ 1 g. of Sm emits 75 α-particles per sec., giving half-period of $1{\cdot}2\times10^{12}$ years. The activity is not due to an isotope present only in small amounts. The activity attributed to La and Nd (this vol., 204) is due to radioactive impurities. L. S. T.

Radioactivity of a fraction from a neodymium-samarium mixture: element 61. M. CURIE and S. TAKVORIAN (Compt. rend., 1933, **196**, 923—925; cf. A., 1931, 890).—Spectral examination of the middle fractions resulting from fractionating 5 kg. of $Nd_2O_3+Sm_2O_3$ showed no trace of element 61, but a radiation was observed more penetrating than that attributable to Sm (cf. this vol., 204) and attaining a max. in the fraction in which element 61 is to be expected. Nd and La are not radioactive. C. A. S.

Conservation of energy and the disintegration of Ra-*E*. L. W. MCKEEHAN (Physical Rev., 1931, [ii], **38**, 2292—2293). L. S. T.

Analysis of α-rays by an annular magnetic field. (LORD) RUTHERFORD, C. E. WYNN-WILLIAMS, W. B. LEWIS, and B. V. BOWDEN (Proc. Roy. Soc., 1933, **A**, **139**, 617—637).—An account is given of a new method, involving the use of an electromagnet to bend the α-rays into a circle, by means of which the relative velocities of a no. of important α-particle groups have been determined with an accuracy of 1 in 5000. The weak group of α-rays from Ra-*C* (about 1 in 4000 of the main Ra-C′ group) is found to comprise two distinct components. The main long-range groups from Th-*C′* and Ra-*C′* have been observed. The differences of energy between the main group and two of the long-range groups from Ra-*C′*, deduced from the measurements, are in close agreement with the γ-ray energies found by Ellis (this vol., 4). L. L. B.

Relative velocities of the α-particles from thorium-*X* and its products and from Ra-*C′*. G. H. BRIGGS (Proc. Roy. Soc., 1933, **A**, **139**, 638—659).—An account is given of measurements by the direct magnetic deflexion method of the relative velocities of the α-particles from Th-*X*, -*Em*, -*A*, -*C* (mean), -*C′*, and Ra-*C′*; the probable error is 1 in 20,000. Preliminary results, correct to 1 in 2000, are also given for the relative velocities of Ra-*A* and -*Em*. The results are combined with the range measurements of Lewis and Wynn-Williams (A., 1932, 671) to give a new correction curve to the Geiger relation V^3-kR for ranges between 8·6 and 4 cm. For ranges >5 cm. the relation between range and velocity is accurately given by $V^{3\cdot26}=kR$. L. L. B.

Range of α-particles from thorium by the Wilson chamber. F. N. D. KURIE and G. D. KNOPF (Physical Rev., 1933, [ii], **43**, 311—314).—At 0° and 760 mm. the extrapolated no.-distance range from 300 tracks is $2\cdot72\pm0\cdot03$ cm. The low val. of Henderson (cf. A., 1931, 16) is discussed. N. M. B.

Quantitative theory of radioactive α-emission. T. SEXL (Z. Physik, 1933, **81**, 163—177).—Radioactive disintegration consts. are calc. from the diffuseness of α-particle levels. Gamow's work is criticised. A. B. D. C.

Absorption of β-rays by, and molecular structure of, organic compounds: halogen derivatives. G. FOURNIER and M. GUILLOT (Compt. rend., 1933, **196**, 698—700; cf. this vol., 334).—Δ being the difference between the observed and calc. vals. of the mass absorption coeff. for β-rays (μ/ρ), the differences between Δ for a series of org. compounds and their Cl- and Br-derivatives are 0·6—0·9 and 1·85—1·9, respectively, and that between Δ for corresponding Cl- and Br-derivatives is 1·1—1·2. Δ increases with no. of atoms of Cl. Δ for Br′ is zero (cf. A., 1932, 210); for liquid Br it is 3·0, indicating a behaviour approximating to that of the latter in Br in org. substances. C. A. S.

Maximum energy of β-rays from uranium-*X* and other bodies. B. W. SARGENT (Proc. Roy. Soc., 1933, **A**, **139**, 659—673).—The range of the β-rays of U-X_2 is 1·10 g. per sq. cm. in C and in Al. The end-point of its spectrum is $2\cdot32\times10^6$ volts. No β-rays were found having energies from 3 to 7×10^6 volts, and an upper limit on their no. was determined. A survey of the data on the end-points of 12 β-ray spectra, together with a list of preferred vals., is given. L. L. B.

Nuclear scattering of β-rays. T. SEXL (Z. Physik, 1933, **81**, 178—185).—Theoretical. A. B. D. C.

γ- and *X*-Ray spectra of the thorium family. M. VALADARES (Compt. rend., 1933, **196**, 856—858).—Using Frilley's crystal diffraction method (cf. A., 1929, 971) and (*a*) a metal plate activated with thoron, and bulbs containing (*b*) mesothorium, and (*c*) radiothorium, the γ-ray spectra showed the lines λ 103, 143, 160, and 165 X from (*a*), (*b*), and (*c*), 285, 320, 330, and 387 from (*b*) and (*c*), and 118 from (*b*); 103, 285, 320, and 330 are the second order lines corresponding with 52, 143, 160, and 165, respectively. Three faint lines occur between 165 and 285; 143 is a doublet (139 and 143), probably due to Th-*B*⟶Th-*C*. 160 and 165 belong to $K\alpha_1$ and $K\alpha_2$ of element 83. C. A. S.

Temperature effect and its elimination in Geiger–Müller tube counters. L. F. CURTISS (Bur. Stand. J. Res., 1933, **10**, 229—232).—The decrease in rate of counting with rise in temp. is attributed to evaporation of volatile matter from the hard rubber insulators usually employed. A new form of counter in which only glass and metal are used is described and is claimed to be free from temp. effects. A. R. P.

Determination of emanation content of the atmosphere and its application to investigations of the relation with meteorological factors, and influence of emanation content of the atmosphere on measurement of cosmic rays. W. MESSERSCHMIDT (Z. Physik, 1933, **81**, 84—100).—The annual mean content of emanation in the atm. is 300×10^{-18} curie per c.c. A. B. D. C.

Spectrum and latitude variation of penetrating radiation. E. J. WILLIAMS (Nature, 1933, **131**, 511—512). L. S. T.

Nuclear energy levels. G. GAMOW (Nature, 1933, **131**, 433).—The level system of the Ra-*C′* nucleus is constructed from various data and compared with the theoretical. L. S. T.

Scattering power of many-electron atoms. F. BLOCH (Z. Physik, 1933, **81**, 363—376).—The Thomas–Fermi method is used and agrees with experiment for elements from H to Au. A. B. D. C.

Theory of atomic nuclei. II. E. N. GAPON (Z. Physik, 1933, **81**, 419—423).—The method previously developed (this vol., 111) is extended to atoms between A and Nd. A. B. D. C.

Structure of atoms and molecules revealed by *X*-rays. J. WEIGLE (Arch. Sci. phys. nat., 1932, **14**, 351—362).—A lecture. N. M. B.

Recent researches on the transmutation of the elements. (LORD) RUTHERFORD (Nature, 1933, **131**, 388—389). L. S. T.

Heights of nuclear potential barriers and nuclear structure. E. C. POLLARD (Nature, 1933, **131**, 398).—Theoretical. The view that the heights

of the potential barriers of light nuclei are proportional to at. nos. (this vol., 205) agrees with Heisenberg's suggestion that nuclei are composed of protons and neutrons with certain attractive forces between them. L. S. T.

Diffuse double layer. J. LENS (Proc. Roy. Soc., 1933, **A**, **139**, 596—603).—Mathematical. L. L. B.

Application of the double-layer theory of Otto Stern. F. URBAN and H. L. WHITE (J. Physical Chem., 1933, **37**, 399).—Corrections (see this vol., 122).

Exchange energy. V. FOCK (Z. Physik, 1933, **81**, 195—208).—An exchange energy operator is set up for alkali atoms; the operator is linear, and the motion of even a single electron in a given electrostatic field is specified only when the exchange field is included. The classical analogue of this operator vanishes when h becomes zero, but an approx. expression is given from which an estimate of the exchange energy may be made. A. B. D. C.

Density distribution of unipolar ion currents. W. DEUTSCH (Ann. Physik, 1933, [v], **16**, 588—612).—Mathematical. W. R. A.

Quantum mechanics of beryllium hydride. C. E. IRELAND (Physical Rev., 1933, [ii], **43**, 329—336; cf. Furry, A., 1932, 319).—Mathematical. N. M. B.

Variable-scale atomic wave functions. J. P. VINTI and P. M. MORSE (Physical Rev., 1933, [ii], **43**, 337—340).—Mathematical. N. M. B.

Corpuscular mechanics. F. J. DE WISNIEWSKI (J. Phys. Radium, 1933, [vii], **4**, 90—104).—Mathematical. A generalised corpuscular mechanics is co-ordinated with wave mechanics so as to take into account the properties of neutral He and its analogues, and other anomalies in classical corpuscular mechanics. N. M. B.

Wave equations and the conservation of energy. A. LEES (Nature, 1933, **131**, 402).—Theoretical. L. S. T.

Atomistic conception of space and time. L. SCHAMES (Z. Physik, 1933, **81**, 270—282). A. B. D. C.

Determination of e/m for an electron by a new deflexion method. F. G. DUNNINGTON (Physical Rev., 1933, [ii], **43**, 404—416).—An improved method, avoiding measurement of acceleration voltage and eliminating contact potential errors, gives the val. $(1{\cdot}7571\pm0{\cdot}0015)\times10^7$ e.m.u. N. M. B.

Determination of e/m by photo-electrons excited by X-rays. G. G. KRETSCHMAR (Physical Rev., 1933, [ii], **43**, 417—423).—A magnetic deflexion method applied to electrons ejected from thin evaporated or sputtered films of Au, Ag, Cu, and Pt by Mo K radiation gives the val. $(1{\cdot}7570\pm0{\cdot}0026)\times10^7$ e.m.u. N. M. B.

Zeeman effect in solids. F. H. SPEDDING (Physical Rev., 1931, [ii], **38**, 2082). L. S. T.

Absorption of light by ozone between λ 3050 and 2150 A. N. T. ZE and C. S. PIAW (Compt. rend., 1933, **196**, 916—918; cf. A., 1932, 869).—The coeffs. of absorption of 194 lines (λ 3053·5—2135·9) have been recorded, including many new ones (cf. A., 1927, 607). C. A. S.

Interpretation of the BeF bands. R. S. MULLIKEN (Physical Rev., 1931, [ii], **38**, 836—837).—The $^2\Pi$ state is inverted (cf. A., 1930, 520). The bearing of this inversion on the electron configuration is discussed. L. S. T.

Emission and absorption spectra in sulphur dioxide. T. C. CHOW and H. D. SMYTH (Physical Rev., 1931, [ii], **38**, 838).—A correlation of data. L. S. T.

Band spectrum due to the molecule N_2O_3. E. H. MELVIN and O. R. WULF (Physical Rev., 1931, [ii], **38**, 2294).—An absorption spectrum of apparently diffuse bands and probably due to N_2O_3 has been observed in the near ultra-violet in mixtures of NO and NO_2. L. S. T.

Reflexion spectrum of halides of rare earths, especially erbium. F. EPHRAIM, G. JANTSCH, and C. ZAPATA (Helv. Chim. Acta, 1933, **16**, 261—267; cf. A., 1929, 864).—Reflexion spectra of anhyd. $ErCl_3$, $ErBr_3$, and ErI_3 have been measured. The displacement due to change of halogen is markedly smaller than is the case with Pr and Nd. Data are given for HoI_3. Narrow absorption bands are absent from the spectrum of YbI_2, whence it is concluded that the colour resides in the outer electron shell. F. L. U.

Light absorption and lattice energy for the alkali hydrides. J. H. DE BOER and C. J. DIPPEL (Naturwiss., 1933, **21**, 204—205).—Cs atoms adsorbed on the surface of CaF_2 layers rapidly take up H_2, in contrast to ordinary Cs. If a colourless layer is irradiated with light (2500—3000 Å.), the blue colour returns and H_2 is set free. There is an absorption at a much greater wave-length than for halides of other alkali metals. The small electron affinity of the H atom is the chief cause of this. The failure of the equations of Hilsch and Pohl and of Wolff and Herzfeld to explain the facts for LiH may be due to a specially strong red displacement owing to adsorption of H in the lattice. A. J. M.

Band spectra of barium oxide. P. C. MAHANTI (Nature, 1933, **131**, 402).—An arc between C electrodes containing $BaCl_2$ or $Ba(NO_3)_2$ gives red-degrading bands between 4300 and 8000 Å. attributed to BaO. L. S. T.

Line absorption of chromic salts in relation to co-ordination. C. H. JOHNSON and A. MEAD (Nature, 1933, **131**, 399).—Aq. solutions of Cr^{III} compounds show only one narrow band. This band moves farther into the red as the three electrically neutral mols. of $C_2H_4(NH_2)_2$ in $[Cr(en)_3]^{\cdots}$ are successively replaced by negatively-charged C_2O_4 radicals. The band for $[Cr(en)_3]^{\cdots}$ is near that of $Cr^{\cdots}$, presumably $[Cr(H_2O)_6]^{\cdots}$ in violet solutions of Cr^{III} salts. The position of the band for green solutions of $Cr_2(SO_4)_3$ is in agreement with the view that when a solution of $Cr_2(SO_4)_3$ is boiled SO_4'' displaces H_2O mols. and the green colour is due to $[Cr(H_2O)_4SO_4]^{\cdot}$. The linkings uniting en and C_2O_4 radicals are considered to be predominantly covalent. L. S. T.

New band in the spectrum of the OH molecule. H. L. JOHNSTON, D. H. DAWSON, and (MISS) M. K. WALKER (Physical Rev., 1933, [ii], **43**, 473—480).—91 new lines were observed. 44 of these are extensions of λ 3428, 54 lines (including 11 in common with λ 3428) form a new band with a head at λ 3484, and 4 lines are unidentified. N. M. B.

Absorption spectra of cobaltous compounds. IV. The alkali oxide–boric oxide glasses. W. R. BRODE (J. Amer. Chem. Soc., 1933, **55**, 939—947).—The position of the absorption bands in the blue glasses is independent of the alkali oxide (Li, Na, K, or Cs) and therefore the alkali metal is not attached to or part of the chromophore. The substitution of alkali chloride or sulphide for oxide produces characteristic bands, indicating that the CoO blue glasses belong to the system of co-ordinated Co blue compounds investigated previously (A., 1931, 1109). Pink glasses, with high $[B_2O_3]$, contain un-co-ordinated $Co^{\cdot\cdot}$. By adjusting the relative concn. of oxides, glasses can be prepared which change from pink to blue on raising the temp.; the effect is most evident with K_2O glasses and is due to change of relative intensity of the absorption bands. J. G. A. G.

Orientation of co-ordination water molecules about rare-earth ions in solution. F. H. SPEDDING and G. C. NUTTING (Physical Rev., 1931, [ii], **38**, 2295).—Absorption spectra of the $Gd^{\cdot\cdot\cdot}$ ion in solutions of $GdCl_3,6H_2O$ and $Gd(EtSO_4)_3,9H_2O$ show that the H_2O mols. take up definite positions about the $Gd^{\cdot\cdot\cdot}$ ion to give a field of definite symmetry. L. S. T.

Optical absorption of substituted benzenes. II. Xylidines and xylenols. III. Calculation of displacement of bands by substituents. H. CONRAD-BILLROTH (Z. physikal. Chem., 1933, **B**, **20**, 222—226, 227—236; cf. A., 1932, 1188).—II. The ultra-violet absorption spectra of the xylidines consist of a single band, but with the xylenols there is separation into two bands.

III. A method of calculating the displacement of the ultra-violet absorption bands of C_6H_6 caused by substituents from vals. characteristic of the latter by a kind of vector addition is described, and its validity demonstrated from experimental data. Discrepancies, which are allowed for, occur when a Me group is in the *o*-position or a OH group in the *p*-position to any second substituent. R. C.

Optical absorption of some carbon compounds in Schumann ultra-violet. G. SCHEIBE, F. POVENZ, and C. F. LINSTROM (Z. physikal. Chem., 1933, **B**, **20**, 283—304).—Measurements have been made down to about 1500 Å. with alkyl iodides, MeCHO, $COMe_2$, various aliphatic acids and esters, and C_6H_6. The results are correlated with Raman frequencies. R. C.

New long-wave absorption band of carbon disulphide. D. M. DENNISON and N. WRIGHT (Physical Rev., 1931, [ii], **38**, 2077—2078). L. S. T.

Selection principle in oscillation spectrum of calcite. F. MATOSSI (Physikal. Z., 1933, **34**, 230—232). There are two special cases in which the rule put forward by Dennison (Rev. mod. Phys., 1931, **3**, 280) can be tested: (1) the linear XY_2 mol. (*e.g.*, CS_2), and (2) the plane trigonal XY_3 group (*e.g.*, CO_3). For CS_2 results are in agreement with theory, but for CO_3 in $CaCO_3$ there are some discrepancies, which, it is suggested, may be due to asymmetry in the CO_3 group. A. J. M.

Infra-red interference spectra. J. W. ELLIS (J. Opt. Soc. Amer., 1933, **23**, 88—91).—Series of 60 or 70 interference max. and min. observed in an investigation of the infra-red transmission of thin sheets of cellophane and mica are recorded and discussed. N. M. B.

Infra-red absorption spectra of certain alkaloids. (MISS) M. E. O'BYRNE (J. Opt. Soc. Amer., 1933, **23**, 92—100).—Data are recorded, with rock-salt and fluorite prisms, in the range 1—12 μ for 2 : 3′-dipyridyl, methylanabasine, nicotine, sparteine, sparteine sulphate, pelletierine, arecoline, arecoline hydrobromide, pilocarpine, pilocarpine hydrochloride, anabasine (plant product), and neonicotine (synthetic; probably identical). N. M. B.

Rotation–vibration spectrum of water vapour. I. R. MECKE (Z. Physik, 1933, **81**, 313—331).—17 Bands of H_2O vapour are analysed, and the necessary series formulæ, sum rules, symmetry properties, selection and intensity rules are discussed in relation to mol. consts. In the ground state of zero vibrational quantum nos., the vertical angle for H_2O is 105° 6′ and the OH distance is 0·970 Å. A. B. D. C.

Infra-red absorption bands of methane. W. V. NORRIS and H. J. UNGER (Physical Rev., 1933, [ii], **43**, 467—472).—In the region 1—2 μ new bands were located at 1·135, 1·187, 1·330, and 1·734 μ, and fine structure data are tabulated. 14 new lines were observed for the 1·66 μ band (cf. Moorhead, A., 1932, 212). N. M. B.

Bibliography of the Raman effect, 1930—1932. S. C. SIRKAR (Indian J. Physics, 1932, **7**, 431—490).

Removal of continuous background from Raman spectrum of carbon tetrachloride. M. E. HIGH and M. L. POOL (Physical Rev., 1931, [ii], **38**, 374—375).—The continuous spectrum of CCl_4 is almost completely removed by small amounts of m-$C_6H_4(NO_2)_2$. L. S. T.

Raman effect. XXIV. Raman spectrum of organic substances (molecules with C:C:X linking). H. KOPPER and A. PONGRATZ (Monatsh., 1933, **62**, 78—89; cf. A., 1931, 284; this vol., 144).—Raman frequencies are given for the following: $CH_2Br{\cdot}CHBr{\cdot}CH_2Br$, $CH_2{:}CBr{\cdot}CH_2Br$, $CH_2{:}C{:}CH_2$, $CH_2{:}CH{\cdot}CHEt{\cdot}OH$, $CH_2{:}C{:}CHEt$, $CHMe{:}C{:}CHMe$, MeNCO, EtNCO, and $Pr^{\beta}NCO$. The Raman spectrum of allene corresponds with that calc. for a symmetrical linear mol. containing a :C: linking. F. L. U.

Raman spectra of cyclenes. M. GODCHOT, E. CANALS, and (MLLE.) G. CAUQUIL (Compt. rend., 1933, **196**, 780—781; cf. A., 1932, 559).—The Raman spectra of *cyclo*-C_nH_{2n-2} for n=5—8 (11, 18, 13, and 14 lines, respectively) closely resemble each other. All contain lines near 1600, 1440, and 1200

cm.$^{-1}$ characteristic respectively of the double linking, CH_2, and the cyclic structure; the frequencies < 1000, characteristic of C–C, diminish as n increases; all show a strong line near 1000. C. A. S.

Rotation structure of Raman bands of polyatomic molecules. G. PLACZEK and E. TELLER (Z. Physik, 1933, **81**, 209—258, 839).—Placzek's polarisation theory of the intensity of Raman lines due to oscillation (cf. A., 1931, 893) is extended to rotation lines and their envelopes. Examples discussed are: H_2, CO_2, N_2O, C_2H_2, NH_3, CO_3, mols. of types ZXY_3 and XY_4, and H_2O. A. B. D. C.

Raman spectrum of gaseous ammonia. E. AMALDI and G. PLACZEK (Z. Physik, 1933, **81**, 259—269).—Observations previously recorded (A., 1932, 897) are interpreted according to Placzek's theory (cf. preceding abstract). A. B. D. C.

Depolarisation of Raman radiation in diffusion spectra of liquids. J. CABANNES and A. ROUSSET (Ann. Physique, 1933, [x], **19**, 229—303).—The polarisation of Raman radiation was studied in 23 liquids, and conclusions are reached concerning the symmetry of various types of mols., including XY_2, XY_3, XY_4, ZXY_3, Z_2XY_2, and the C_6H_6 nucleus, which possesses only a ternary axis. A. J. M.

Calculation of characteristic frequencies of organic chain-molecules by means of models. K. W. F. KOHLRAUSCH (Z. physikal. Chem., 1933, B, **20**, 217—221).—Polemical (cf. this vol., 114). R. C.

Colour in films of sputtered tin. C. J. OVERBECK (J. Opt. Soc. Amer., 1933, **23**, 109—113).—Films sputtered on glass in air or O_2 showed rings or colour cycles attributed to interference effects due to variation in film thickness, probably of SnO_2. Films sputtered in N_2 consist of an opaque brown Sn–N compound, which produces a nearly transparent colour film, similar to the first-mentioned, when heated in O_2. Films produced in H_2 have mirror surfaces of high reflecting power. N. M. B.

Absorption spectra of photochemically coloured alkali halide crystals. H. FROLICH (Z. Physik, 1933, **80**, 819—821).—Mollwo's empirical law (A., 1932, 673, 1074) relating frequency of absorption of coloured alkali halide crystals with the grating const. is deduced theoretically. A. B. D. C.

Artificial colouring of crystals. V. BILLIET (Natuurwetensch. Tijds., 1933, **15**, 52—54).—The staining and change of habit of $H_2C_2O_4$ crystals produced in aq. and $COMe_2$ solutions containing methylene-blue are described. H. F. G.

Effect of temperature on extinction of fluorescence of dye solutions by electrolytes. A. W. BANOV (Z. physikal. Chem., 1933, **163**, 172—184).—Cases of both increase and decrease of extinction with rise in temp. have been observed. If the extinction is due to collisions of the second kind between ions and excited dye mols. it may be expected to increase with rise of temp., whilst the reverse will be true if the cause is increase of the activity of the dye by the electrolyte (A., 1930, 1235). Where there are no collisions of the above kind the influence of ions on the fluorescence intensity apparently runs parallel with their hydration. R. C.

Investigation of the glow of phosphorus with the aid of a photo-electric counter. C. OUELLET (Trans. Faraday Soc., 1933, **29**, 486—494).—The kinetics of the oxidation of P has been investigated with the help of a sensitive photo-electric quantum counter. No radiation < 2800 Å. is emitted outside the explosive limits. The variation of intensity of radiation with pressure of O_2 is explained by a chain mechanism. The glow is composite and the various spectral components vary independently. Some or all of the bands situated above λ 2800 Å., the threshold val. of the counter, are emitted only, or suddenly increase in intensity at a definite pressure which is $>$ that at which the visible glow sets in. The form of the intensity–time curve for the radiation suggests that two chemical reactions, unequally affected by pressure, are involved in the glow. M. S. B.

Luminescence by cathode rays. I. Chromium and other elements as activators for aluminium oxide. S. IZAWA (J. Soc. Chem. Ind. Japan, 1933, **36**, 43—44B).—Traces of various elements were added to Al_2O_3, which was then heated at 1300° for 1 hr. and cooled rapidly. The luminescence to cathode rays of 4000 volts was then observed. D. R. D.

Fluorescence of pure salts of the rare earths. R. TOMASCHEK and O. DEUTSCHBEIN (Nature, 1933, **131**, 473).—Pure salts of certain rare earths fluoresce when excited by violet and ultra-violet light. L. S. T.

Luminescence and crystalline structure. B. E. COHN (J. Amer. Chem. Soc., 1933, **55**, 953—957; cf. A., 1931, 284).—The emission spectrum of fluorescence of Zn borate glass containing Mn is a band extending from 5670 to 6750 Å. (max. at 6100 Å.) which is independent of the wave-length of the exciting (ultra-violet) light. The intensity of fluorescence is max. when the Zn : Mn at. ratio is 23 : 1, whereas the intensity of thermoluminescence, max. at 6050 Å., is greatest with the Zn : Mn ratio 200 : 1. The substituted cryst. lattice theory is not supported by these data. J. G. A. G.

Absorption spectra of naturally coloured fluorites. J. YOSHIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 170—177).—The absorption spectra may be ascribed to the presence of rare earths. No connexion is found between the photoluminescence of fluorites and ultra-violet absorption spectra. C. W. G.

Intensity of the band spectrum of phosphors. H. NITKA (Ann. Physik, 1933, [v], **16**, 720—744).—The intensity of the emission spectrum of SrS–Cu, ZnS–Mn, CaS, and CaS–Bi phosphors was investigated. The dependence of the intensity of individual bands on the method of prep. and of excitation of the phosphor is discussed. W. R. A.

Emission from oxide-coated cathodes. M. BENJAMIN and H. P. ROOKSBY (Phil. Mag., 1933, [vii], **15**, 810—829).—The coating on active cathodes prepared from $BaCO_3$ or $SrCO_3$ has been shown by X-ray analysis to consist of BaO or SrO. The mixed

oxides form solid solutions. Preferential evaporation of BaO may occur on flashing BaO–SrO-coated cathodes poisoned by O_2, with irreversible loss of activity. Such poisoned cathodes are reactivated on bombarding with A or Hg ions. H. J. E.

Reversal of current in rectifier photo-cells. H. H. Poole and W. R. G. Atkins (Nature, 1933, **131**, 547—548; cf. this vol., 338). L. S. T.

Characteristic vibrations and the selective external photo-electric effect. I. Coal-tar dyes in the visible spectral region. II. Metals in the ultra-violet. F. Hlucka (Z. Physik, 1933, **81**, 66—75, 76—79).—I. The selective external photo-electric effect is shown to occur at the same spectral regions as characteristic frequencies for several coal-tar dyes.

II. Characteristic frequencies deduced from optical data are shown to lie in the region of the selective external photo-electric effect. A. B. D. C.

Existence of an inner photo-effect in cuprous oxide. D. Nasledov and L. Nemenov (Naturwiss., 1933, **21**, 205).—No inner photo-effect could be found even at the temp. of liquid air. A. J. M.

Effect of temperature on crystal photo-effect. G. Barth and H. Dember (Physikal. Z., 1933, **34**, 284—286).—Investigation of the dependence of the photo-electric current and potential obtained on illumination of a Cu_2O crystal on the wave-length of the incident light, and comparison with the optical absorption coeff. curve shows that the max. does not lie at the position of strongest absorption, but at the long-wave absorption edge. There is thus a close connexion between the inner and crystal photo-effects. With fall of temp. the crystal photo-potential increases rapidly, and the max. moves towards the shorter waves. The displacement of the max. is due to the shifting of the absorption edge with fall of temp. towards shorter waves. After many observations, the crystal appears to change its properties. The effect is limited at very low temp. by the resistance of the crystal. The difference in behaviour between Zn blende and Cu_2O is explained. A. J. M.

Theory of crystal photo-effect. H. Teichmann (Physikal. Z., 1933, **34**, 283—284). A. J. M.

Dielectric losses in rock salt. P. L. Bayley (Physical Rev., 1933, [ii], **43**, 355—357).—The phase angle, in the range 1—1000 kilocycles, was $< 0{\cdot}0001$. Moisture increases the power factor, especially at lower frequencies. Traces of org. surface contamination may cause apparent dipole properties. N. M. B.

Debye effect in viscous dielectrics. G. Todesco (Nuovo Cim., 1932, **9**, 125—131; Chem. Zentr., 1932, ii, 2602).—With an oscillator working down to λ 9 m. castor oil was shown to have an absorption band with max. at λ 21·60 m. (21°; internal friction 7·7 c.g.s.), whence the mol. has a $1{\cdot}7\times10^{-8}$ cm. The val. calc. from the temp. coeff. of the dielectric const. is $1{\cdot}8\times10^{-8}$ cm. A. A. E.

Cryoscopic rules and dipole theory. W. Fischer (Z. physikal. Chem., 1933, **163**, 257—262).—Empirical rules connecting degree of association as deduced from cryoscopic data with chemical constitution are interpreted in the light of the dipole theory. R. C.

Investigation of the dielectric properties of sodium potassium tartrate by means of *X*-rays. H. Staub (Physikal. Z., 1933, **34**, 292—296).—The intensity of *X*-ray interference produced by a crystal of Na K tartrate is altered by application of an electric field. The dependence of this change on temp. and field strength is investigated, and it is shown that the abnormally high dielectric const. of the salt is accompanied by a high displacement of ions in the lattice. A. J. M.

Determination of static dielectric constant of sodium potassium tartrate. G. Oplatka (Physikal. Z., 1933, **34**, 296—300).—A new method of determining dielectric properties is described and applied to the determination of the effect of duration of charging and field strength on the dielectric const. of Na K tartrate. The results agree with those of Staub (cf. preceding abstract). The fatigue effect was also investigated. A. J. M.

Investigation of dipole moments with molecular rays. I. Estermann and M. Wohlwill (Z. physikal. Chem., 1933, **B**, **20**, 195—208).—The dipole moments of pentaerythritol and some related compounds have been determined by the semi-quant. condensation method (A., 1928, 1309). A method of determining the intensity distribution in mol. rays, depending on measurement of the heat liberated in condensation of the mols., has been worked out, and used for the determination of dipole moments from observations on the deviation of mol. rays in electric fields (cf. this vol., 210). R. C.

Influence of pressure on the dielectric constant of carbon dioxide up to 1000 atmospheres between 25° and 150°. A Michels and (Mrs.) C. Michels (Phil. Trans., 1933, **A**, **231**, 409—434; cf. Keyes, A., 1931, 147).—Using the heterodyne beat method at a frequency of 508 kilocycles results are tabulated for a range of pressures at each of 12 different temp. The val. of the Clausius–Mosotti expression is independent of the temp. and tends to decrease with rise of pressure. N. M. B.

Dielectric constant of liquids. VIII. G. Devoto (Gazzetta, 1933, **63**, 50—58; cf. A., 1932, 794).—Vals. of the dielectric constant–concn. coeff. for aq. solutions of glycine and its homologues are given in more detail, and new measurements for solutions of hydantoin, hydantoic acid, pyrrolidone, C_5H_5N, ethyl- and propyl-carbamide, leucylglycylglycine, and glycyl-leucine are reported. The structure of these substances is discussed. O. J. W.

Dielectric polarisation of solutions of sulphur in carbon disulphide. S. Dobinski (Bull. Acad. Polonaise, 1932, A, 239—247).—From measurements of the dielectric const. and densities of solutions of S in CS_2 of various concn. and at various temp. the polarisation of S is calc. as 0·252 c.c. per g. As the sp. refraction for the D line is 0·262 c.c. per g. the dipole moment of S in CS_2 solution is zero. J. W. S.

Frequency variation of the dielectric constant of dilute non-aqueous solutions. L. J. Oncley

and J. W. WILLIAMS (Physical Rev., 1933, [ii], **43**, 341—354).—To test the dipole theory, data for the frequency variation of the dielectric const. for 14 viscous solutions of various polar substances in non-polar solvent media at frequencies up to 2×10^7 cycles per sec. were obtained. The dielectric consts. of four rosin solutions in mineral oils of varying viscosity are tabulated, and the inner-frictional consts. for these systems are calc. Viscosity had little effect on 16 mixtures of "floricin," paraffin oil, and vaseline. Applications of results to the Debye theory are discussed. N. M. B.

Dipole moments of benzene derivatives with freely rotatable substituents. J. W. WILLIAMS (Z. physikal. Chem., 1933, **B**, **20**, 175—181).—A reply to criticism (A., 1932, 984). R. C.

Dipole moments of benzene derivatives with freely rotatable substituents. H. L. DONLE (Z. physikal. Chem., 1933, **B**, **20**, 182—183).—A reply to Williams (preceding abstract). R. C.

Rotation of molecules or groups in crystalline solids. C. S. HITCHCOCK and C. P. SMYTH (J. Amer. Chem. Soc., 1933, **55**, 1296—1297).—Dielectric consts. of H_2S (cf. this vol., 210), NH_3, and MeOH have been determined between $-190°$ and just above the m.p. The mols. of solid NH_3 do not rotate, but the dipole rotation of MeOH decreases sharply at $-114{\cdot}0°$. J. G. A. G.

Improvements in the photo-electric polarimeter: rotatory dispersion of sucrose in the ultra-violet. G. BRUHAT and A. GUINIER (Compt. rend., 1933, **196**, 762—764; cf. A., 1932, 892).—The improvements described extend its use to λ 2481 Å. This is illustrated by determining the rotatory dispersion of sucrose for 13 vals. of λ. C. A. S.

Molecular rotation in liquids as revealed by the Raman effect. S. P. RANGANADHAM (Indian J. Physics, 1932, **7**, 353—364).—The depolarisation of the scattered light has been determined spectroscopically for Hg radiation of 4046 and 4358 Å. using two associating, nine non-associating, and two viscous liquids. The aggregate intensity of the rotation wing to that of the pure Rayleigh scattering is deduced. W. R. A.

Change of sign of rotatory power and mutarotation of "aluminium emetic." PARISELLE (Compt. rend., 1933, **196**, 918—920; cf. A., 1927, 856).—1 mol. of tartaric acid dissolves 1 mol. of $Al(OH)_3$ to form "Al emetic" (I); with more acid the solution behaves as a mixture of (I) and acid (cf. A., 1900, i, 375; this vol., 240). (I) thus prepared is a vitreous uncrystalhsable solid; in dil. solution it is dextro-, in conc. lævo-rotatory: $[\alpha]^{22}$ for $1{\cdot}85M$ $-13°$, $1{\cdot}3M$ $0°$, $0{\cdot}04M$ $+105°$. Equilibrium on dilution is attained in about 1 hr. $[\alpha]$ varies rapidly with temp.: $[\alpha]^0$ $+12{\cdot}5°$, $[\alpha]^{30}$ $+35°$. These and cryoscopic results indicate hydrolysis or depolymerisation into two compounds with $[\alpha]$ $-305°$ and $[\alpha]$ $+258°$, the lævo-compound producing 2 mols. of the dextro-. C. A. S.

Faraday effect in paramagnetic solutions. C. J. GORTER (Physikal. Z., 1933, **34**, 238—241).—The rotation due to certain ions is considered, especially those of the rare earths and elements of the Fe group. A. J. M.

Faraday effect of camphorquinone. J. VERHAEGHE (Compt. rend., 1933, **196**, 850—852; cf. A., 1927, 8).—A C_6H_{14} solution of camphorquinone shows no anomalous magnetic rotatory dispersion; a C_6H_6 solution gave results scarcely distinguishable from those of pure C_6H_6, and positive ordinary rotation. C. A. S.

Anomalous dispersion of magnetic and electric birefringence. R. LUCAS and M. SCHWOB (Compt. rend., 1933, **196**, 765—767).—The dispersions of the magnetic and electric birefringences between λ 4358 and 5780 Å. of *r*-fenchone are 0·75 (at 16·5°) and 1·30 (20·5°); of Et *r*-phenylsuccinate (I) 1·39 (18°) and 1·05 (24°), respectively. Havelock's formula does not apply. The electric birefringence–temp. curve for λ 5780 Å., from 15° to 80°, of (I) is abnormal. These results indicate in both compounds the presence of two forms in equilibrium (cf. A., 1930, 136; 1932, 679). C. A. S.

Diamminozinc bromide. Crystallographic study. S. KOZIK (Bull. Acad. Polonaise, 1932, **A**, 318—323).—$ZnBr_2,2NH_3$, like $ZnCl_2,2NH_3$, crystallises in the rhombic system. It has a rather high *n* and strong double refraction ($n_\gamma-n_\alpha=0{\cdot}0608$ approx.), but only very slight dispersion in the visible region. The compounds are deposited in Leclanche cells charged with NH_4Br and NH_4Cl. J. W. S.

Refractivity of para-hydrogen. C. CUTHBERTSON and M. CUTHBERTSON (Proc. Roy. Soc., 1933, **A**, **139**, 517—520).—The val. of *n* for a para–ortho-H_2 mixture (47% para), prepared by adsorption of pure H_2 at the temp. of liquid O_2, does not differ from that of ordinary H_2 by >2 or 3 parts in 14,000. L. L. B.

Significance of specific exaltation of molecular refraction and molecular dispersion. K. VON AUWERS (Z. physikal. Chem., 1933, **164**, 44—47; cf. this vol., 211).—The sp. exaltation of mol. refraction is determined solely by structure, whilst the mol. exaltation is influenced also by the mol. wt., and is therefore unsuitable for detecting structural peculiarities. For dispersive power it is immaterial whether sp. or mol. exaltation is used. R. C.

Refractive indices of ammonium nitrate. S. B. HENDRICKS, W. E. DEMING, and M. E. JEFFERSON (Z. Krist., 1933, **85**, 143—155; cf. A., 1932, 986).—The refractive indices for white light and densities of the various forms of NH_4NO_3 are recorded. A modified form of Bragg's method (cf. A., 1924, ii, 373; 1925, ii, 92) gives results closely agreeing with the max. index in all except the rhombic forms. C. A. S.

Formula to represent the dispersion of optical glass. A. BIOT (Ann. Soc. Sci. Bruxelles, 1933, **B**, **53**, 11—13). W. R. A.

Atomic moments of ferromagnetics. E. C. STONER (Nature, 1933, **131**, 433—434).—Theoretical. L. S. T.

Theory of diamagnetism for mono- and poly-nuclear systems. D. P. RAY-CHAUDHURI (Phil. Mag., 1933, [vii], **15**, 797—807).—The susceptibility

of a mol. AB is related to that of the constituent atoms by $-\chi_A$ $-\chi_A-\chi_B+\lambda$. The significance of the term λ is discussed. H. J. E.

Magnetic moments of potassium and lithium in relation to their magnetic nuclear moments. II. W. MEISSNER and H. SCHEFFERS (Physikal. Z., 1933, **34**, 245—252; cf. this vol., 213).—The degree of accuracy of the Rabi method (I) of determining magnetic moments is not so great as that of the Stern–Gerlach method (II), although it is suitable for comparative measurements. (I) gives for Li a val. 0·3% >that obtained by (II). A. J. M.

Susceptibility and electrical conductivity of copper–manganese alloys. S. VALENTINER and G. BECKER (Z. Physik, 1933, **80**, 735—754).—Susceptibility and electrical conductivity were measured for various Cu–Mn alloys between −180° and 20°. A. B. D. C.

Magnetic susceptibilities of lead, silver, and their alloys. C. G. MONTGOMERY and W. H. ROSS (Physical Rev., 1933, [ii], **43**, 358—360).—Magnetic susceptibilities, χ, may be expressed by $10^9\chi=(116{\cdot}44\pm0{\cdot}68)+(0{\cdot}764\pm0{\cdot}012)P$, where P is the % wt. of Ag. N. M. B.

Diamagnetic susceptibility of the rare-gas atoms according to Slater's method. S. C. BISWAS (Physical Rev., 1931, [ii], **38**. 1784—1785). L. S. T.

Constitution of red perchromates. B. T. TJABBES (Z. anorg. Chem., 1933, **210**, 385—388).—The magnetic susceptibility of K_3CrO_8 is $+3{\cdot}98\times10^{-6}$, indicating that the Cr has a valency of 5 or 7. The val. 5 is supported by electronic considerations, isomorphism with perniobates and pertantalates containing Nb^V and Ta^V, and analogy with the magnetic properties of other compounds of Cr^V. For red $Zn(NH_3)_4MoO_8$ $\chi=-0{\cdot}25\times10^{-6}$. D. R. D.

Theory of diamagnetism of conductivity electrons. R. PEIERLS (Z. Physik, 1933, **80**, 763—791).—Conditions are determined for calculation of free energy by quantum statistics without knowledge of the stationary states, and the results applied to the diamagnetism of free electrons and the magnetic behaviour of bound electrons; the influence of collisions, and the limiting field for const. susceptibility, are discussed. A. B. D. C.

Theory of diamagnetism of conductivity electrons. II. Intense magnetic fields. R. PEIERLS (Z. Physik, 1933, **81**, 186—194).—The theory previously developed (cf. preceding abstract) is extended to intense magnetic fields, and explains qualitatively anomalies observed for Bi at low temp. A. B. D. C.

Diamagnetism of free electrons. J. S. MITCHELL (Phil. Mag., 1933, [vii], **15**, 807—810).—Theoretical. The diamagnetic susceptibility of a gas of free electrons is approx. one third of Pauli's val. for the paramagnetic susceptibility due to spin (cf. A., 1927, 288; 1928, 823). H. J. E.

Thermal and magnetic behaviour of gadolinium sulphate at liquid helium temperatures. N. KURTI (Z. physikal. Chem., 1933, **B**, **20**, 305—324).—The magneto-thermal effect has been measured at liquid He and liquid H_2 temp. for field strengths up to 10,000 gauss. The sp. heat has been determined at 1·6—20° abs. Below 7° it begins to show an increasing positive deviation from the T^3 law and at about 4° rises so rapidly that at 1·6° it is about 500 times the theoretical val. From this anomaly it is deduced that in the cryst. state the ground state of $Gd^{\cdots}$ is resolved according to the requirements of Nernst's heat theorem, the term resolution being approx. 0·5 g.-cal. per g.-ion. Sp. heat measurements in a magnetic field of 1800 gauss, made to test Langevin's theory of the connexion of sp. heat with magnetisation, show that the sp. heat of magnetised $Gd_2(SO_4)_3$ exceeds that of the unmagnetised salt by an amount which agrees with the theory. R. C.

Magnetic properties of liquid ozone. P. LAINE (Compt. rend., 1933, **196**, 910—913).—Assuming that O_3 follows Curie's law (cf. A., 1914, ii, 423) its paramagnetism decreases by one seventh between the temp. of liquid O_2 and N_2, thus enabling an admixture of 0·1% of O_2 to be detected in liquid O_3. Pure liquid O_3 indicated slight paramagnetism with susceptibility independent of temp. (cf. A., 1928, 226, 1082). C. A. S.

Crystalline fields of Pr, Nd, and Yb from paramagnetic susceptibilities. W. G. PENNEY (Physical Rev., 1933, [ii], 43, 485—490; cf. A., 1932, 985; this vol., 212).—Calculations on the temp. variation of paramagnetic susceptibility based on crystal fields give agreement with experimental results for $Pr_2(SO_4)_3$, Nd_2O_3, and Yb_2O_3. For $Pr_2(SO_4)_3,8H_2O$ a field of cubic symmetry is necessary. N. M. B.

Role of electron orbit impulses in ferromagnetic lattices. H. LUDLOFF and G. REYMANN (Physikal. Z., 1933, **34**, 233—234).—Theoretical. A. J. M.

Supplement to the theory of magnetisation curves of ferromagnetic single crystals. R. R. GANS and E. CZERLINSKY (Ann. Physik, 1933, [v], **16**, 625—635). W. R. A.

Electronic states of molecules containing the CO group. C. P. SNOW (Chem. and Ind., 1933, 292).—Deductions in extension of Mulliken's treatment (cf. this vol., 339) are discussed. N. M. B.

Arrangement of valency electrons in the nitrogen atom. Rotatory power of unsymmetrical tertiary amines. A. DELAYGUE (Bull. Soc. chim., 1933, [iv], **53**, 80—84).—On the basis of Dupont's view that the outer 5 electrons of N are situated at the corners of a tetrahedron, one corner of which carries 2 electrons, it should be possible to prepare optical isomerides of the unsymmetrical *tert.*-amines. An unsuccessful attempt, probably due to racemisation, has been made to separate these in the case of NPhMe·CH_2Ph by combining with *d*-camphor-β-sulphonic acid. M. S. B.

Complex anion of Buff's and Bunsen's salts. F. HOLZL and W. STOCKMAIR (Monatsh., 1933, **62**, 1—12; cf. A., 1929, 545).—On the basis of conductivity and transference measurements it is concluded that both substances have the same anion,

and are represented by $(ROH,H)_6[Fe(CN)_6Cl_2]$ for Buff's compound (R=Me, Et, or Pr), and $(NH_4)_6[Fe(CN)_6Cl_2]$ for Bunsen's salt. F. L. U.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1932, [v], **18**, 1124—1137; cf. A., 1930, 277, 853; 1931, 685, 1106, 1127, 1215, 1356; 1932, 1078).—Mathematical. A. J. M.

Energy values of linkings in organic substances. J. A. CLOPATT (Soc. Sci. Fennica Comm. Phys. Math., 1933, **6**, No. 23, 18 pp.).—From a study of the heats of combustion of a no. of org. compounds the energy vals. of various linkings are obtained. A. J. M.

Structure of alkali hydride molecules. A. KREBS (Z. Physik, 1933, **81**, 1—2).—The ionic or, alternatively, at. nature of the alkali hydride mols. is discussed. A. B. D. C.

Group theory and valency states. S. C. KAR (Z. Physik, 1933, **81**, 139—142).—Group theory is used to determine valency states of atoms, eliminating Slater's permutation group (cf. A., 1930, 126). A. B. D. C.

Structure of triatomic molecules. A. B. D. CASSIE (Nature, 1933, **131**, 438).—A scheme for obtaining the structures of triangular mols. from the total number of available valency electrons is formulated. L. S. T.

Units of affinity and their specific number among the elements. J. GNEZDA (Bull. Acad. Yougoslav. Sci., 1933, **27**, 1—36).—Assuming the quadrivalency of C, the compound $CO_2,8PhOH$ indicates that O has 6 units of affinity. Two of these units are free in H_2O and are involved in the formation of hydrates. The existence of $HCl,2H_2O$ is held to indicate the tervalency of the H atom. Developing this system, nos. of units of affinity are assigned to the elements. Constitutional formulæ of great complexity are given for simple inorg. compounds. By adopting a valency of 11 for the K atom it is shown that hydrates of KNO_3 cannot exist. The units of affinity are termed "viravals" and are distinguished from "voluvals" which are the units of combination by vol. The viravals are considered in terms of electrons. E. S. H.

Quantum mechanics and chemistry with particular reference to reactions involving conjugate double linkings. H. EYRING (Science, 1933, **77**, 158—160). L. S. T.

Atomic distances in Werner's co-ordinated compounds. II. Hexammine and hexamethylamine halides of Co^{II} and Ni^{II} of the fluorite type. G. BODTKER-NÆSS and O. HASSEL (Z. anorg. Chem., 1933, **211**, 21—27; cf. this vol., 114).—Lattice consts. have been determined for compounds of $[Ni(NH_3)_6]^{\cdot\cdot}$ and $[Co(NH_3)_6]^{\cdot\cdot}$ with Cl′, Br′, and I′. The distances Co–Cl, Co–Br, Co–I, Ni–Cl, Ni–Br, and Ni–I are 4·37, 4·50, 4·73, 4·36, 4·48, and 4·71 Å., respectively. The effective radii of the ions $[Ni(NH_3)_6]^{\cdot\cdot}$ and $[Co(NH_3)_6]^{\cdot\cdot}$ are 2·58, 2·60 Å. The lattices of $Ni(MeNH_2)_6I_2$ and $Co(MeNH_2)_6I_2$ are similar. H. J. E.

Spectrography of *X*-rays by transmission of non-canalised rays across a curved crystal. II. Y. CAUCHOIS (J. Phys. Radium, 1933, [vii], **4**, 61—72).—Full details are given (cf. A., 1932, 246, 553, 892).

Principles of *X*-ray structure results and their possible explanation by tetrahedral domains of atomic influence. R. REINICKE (Z. Krist., 1933, **84**, 468—474).—Recapitulation and extension of the author's theories (cf. A., 1932, 796, 901; this vol., 215). C. A. S.

Topologically equivalent crystal linkings. H. HEESCH (Z. Krist., 1933, **84**, 399—407; cf. A., 1931, 1000). C. A. S.

Determination of crystal orientation. J. THEWLIS (Z. Krist., 1933, **85**, 74—88; cf. A., 1931, 27).—A graphical method. C. A. S.

Accurate method of measuring lattice constants. V. KUNZL and J. KOPPEL (Compt. rend., 1933, **196**, 940—942).—An improvement of Pavelka's method of deducing fairly accurately the lattice const. from observations with an inferior spectrograph is described. Applied to quartz the result is within 0·01% of that with an accurate instrument. C. A. S.

Recrystallisation phenomena with synthetic metallic substances. W. TRZEBIATOWSKI (Naturwiss., 1933, **21**, 205).—The behaviour of Cu powder, hot and cold, under pressures of 30,000 and 15,000 atm. has been studied. For the cold and warm pressing up to 250° the hardness was 150—165 Brinell units. In the Debye diagram a cold deformation was noted. The thread diagram, however, showed no alteration of the rectilinear arrangement of the crystallites. Contrary to Sauerwald (B., 1932, 428), on heating to 300—400° there is a decrease in hardness of > 100 Brinell, and the cold deformation in the *X*-ray diagram disappears, nuclear growth being noticed. For lower pressures it may be assumed that this effect is due to adhesion phenomena. Resistance–temp. curves give a min. for resistance at the recrystallisation temp. Compressed bodies seem to behave in this respect like semi-conductors. A. J. M.

Lattice constant and particle size in gold–silver alloys. P. WEIST (Z. Physik, 1933, **81**, 121—128).—Lattice consts. of single crystals were accurately determined. The polycryst. material obtained by deformation and heating of the single crystals showed different lattice consts., the deviation being greatest for 75% Au. A. B. D. C.

Modifications of phosphorus pentoxide. K. BORATYNSKI and A. NOVAKOVSKI (Compt. rend., 1933, **196**, 691; cf. A., 1932, 217).—Revised determinations give for cryst. P_2O_5 d 2·283, and for the amorphous form 2·207. C. A. S.

Lattice constant of a rhombohedral face of quartz. V. KUNZL and J. KOPPEL (Compt. rend., 1933, **196**, 787—789; cf. A., 1931, 150).—The lattice const., d_{∞}, of a rhombohedral face of quartz is 3336·66 X. A new method of determining the const. of a spectrograph is described. C. A. S.

Crystal structure of aluminium fluoride. J. A. A. KETELAAR (Z. Krist., 1933, **85**, 119—131; cf. A., 1930, 400; 1931, 1359; 1932, 796).—AlF_3 is

rhombohedral with a unit cell which may be either hexagonal, a 4·914, c 12·46 Å., with 6 mols., or rhombohedral, a 5·029 Å., β 58° 31′, with 2 mols.; space-group D_3^7. The structure is a co-ordination lattice consisting of a distorted close packing of F atoms with hollow spaces alternating with the positions of the Al atoms, in which H_2O mols. can fit, thus explaining the stability of the hydrates AlF_3,H_2O and $2AlF_3,H_2O$. The structure is similar to that of FeF_3, CoF_3, RhF_3, and PdF_3. C. A. S.

Habit variation in potassium chlorate crystals produced by dyes. H. E. Buckley and W. Cocker (Z. Krist., 1933, **85**, 58—73).—The effect of 86 dyes on the crystallisation of $KClO_3$ has been examined; many are several hundred times as powerful as any inorg. ion (cf. A., 1932, 681). The active group is SO_3Na, made very much more active if associated with an ·N:N· group unless this is in the *o*- or *peri*-position (cf. A., 1930, 991). C. A. S.

Crystal structure of tetragonal hydrated nickel sulphate. R. B. Corey and R. W. G. Wyckoff (Z. Krist., 1933, **84**, 477; cf. A., 1932, 986).—Previous results are confirmed. C. A. S.

Crystal structure of potassium selenibromide. J. L. Hoard and B. N. Dickinson (Z. Krist., 1933, **84**, 436—441).—K_2SeBr_6 is cubic with a 10·36 Å., and 4 mols. in the unit cell; u=0·245 Å., Se–Br= 2·54 Å., and the "octahedral" electron-pair-linking radius of Se^{IV} is 1·40 Å. The structure is the same as that of K_2SnCl_6 (cf. A., 1922, ii, 287; 1932, 903). C. A. S.

Artificial production of regular crystal intergrowths of potassium alum. M. Schaskolski and A. Schubnikov (Z. Krist., 1933, **85**, 1—16).—The orientation of crystals of K alum grown on larger crystals is examined, and explained by an extension of Rover's epitaxy theory (cf. this vol., 369). C. A. S.

Crystal structure of silver perrhenate. F. Buschendorf (Z. physikal. Chem., 1933, B, **20**, 237—244).—$AgReO_4$ has the scheelite structure, a_0 5·349±0·03, c_0 11·916±0·03 Å., and the space-group is C_{4h}^6. R. C.

Crystal structure of muscovite. W. W. Jackson and J. West (Z. Krist., 1933, **85**, 160—164; cf. A., 1931, 415).—A revised set of diagrams illustrating the structure of muscovite is given. C. A. S.

***X*-Ray examination of boracite.** R. Hocart (Compt. rend., 1933, **196**, 789—791; cf., A., 1929, 749).—Laue and oscillation photographs confirm the rhombic structure of boracite, space-group probably C^{11}, but with very close approximation to face-centred cubic. C. A. S.

Orientation of crystals on hydrargillite, and on twinned calcite. L. Royer (Compt. rend., 1933, **196**, 709—710; cf. A., 1932, 326, 451; this vol., 214).—The parameters of the base of crystals of hydrargillite are almost identical with those of muscovite; crystals that are oriented on mica are equally so on hydrargillite. The direction of orientation of crystals on a mechanically produced twin of calcite is the mirror image of that on the unaltered portion. C. A. S.

Crystal structure of zunyite. L. Pauling (Z. Krist., 1933, **84**, 442—452).—Zunyite, $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$, is cubic, a 13·28 Å., with 4 mols. in the unit cell; space-group T_d^2 ($F\bar{4}3m$). A structure consistent with observed intensities is proposed. C. A. S.

Niccolite. W. Faber (Z. Krist., 1933, **84**, 408—435).—Niccolite is trigonal-pyramidal, C_3, or trapezohedral, D_3, with $a:c$=1 : 1·397$_4$, or by *X*-ray 1 : 1·393; d_1^{25} of a natural crystal 7·784, after fusion d_1^{20} 7·733; m.p. 969—971° analysis Ni 43·25, As 55·10%, and impurities. No trace of any transition point was found to explain heterogeneity between crossed nicols. *X*-Ray investigation confirmed previous results (cf. A., 1907, ii, 553; 1926, 460). C. A. S.

Structure of fibrous zeolites. W. H. Taylor, C. A. Meek, and W. W. Jackson (Z. Krist., 1933, **84**, 373—398).—Natrolite, scolecite, mesolite, and thomsonite are all built up of strings of tetrahedra of SiO_4 and AlO_4, each O being common to two tetrahedra; these strings are parallel to the c axis and strong along their length, but comparatively loosely connected laterally. The structures of the first three are similar with a body-centred unit cell 13×13×6·6 Å., the linking in thomsonite is different. The dehydration and base-exchange properties are due to channels between the strings of tetrahedra; the H_2O mols. and positive ions occupy positions in or near these channels, and can move freely along them without breaking down the framework of tetrahedra. Detailed structures are proposed (cf. A., 1930, 1240; 1931, 550; 1932, 715; this vol., 141). C. A. S.

Structure of methylcarbamide. R. B. Corey and R. W. G. Wyckoff (Z. Krist., 1933, **85**, 132—142).—Methylcarbamide is rhombic with a 6·89, b 6·96, c 8·45 Å., and 4 mols. in the unit cell; space-group V^4. Various structures are discussed. C. A. S.

Polymorphism of paraffins. N. Yannaquis (Compt. rend., 1933, **196**, 784—787; cf. B., 1932, 298; this vol., 116).—The m.p., transition points, and optic axial angles have been determined, and the appearances on cooling between crossed nicols described for various fractions (b.p. 163—208°) of petroleum. There is no trace of the intermediate transition (observed in a pure paraffin) from one to a second rhombic form, but only directly to the hexagonal modification. C. A. S.

Rotation *X*-ray goniometer diagrams. E. Sauter (Z. Krist., 1933, **84**, 461—467).—The use of the new universal *X*-ray camera as an *X*-ray goniometer is illustrated by deducing the reciprocal lattice and unit cell (a 9·95, b 10·1, c 21·4 Å., β 86° 15′) of monoclinic diphenylethylene sulphide from a rotation photograph taken therewith. C. A. S.

Crystal structure of diphenyl series. L. W. Pickett (Nature, 1933, **131**, 513).—Crystal structure analyses of Ph_2, p-$C_6H_4Ph_2$, and p-diphenyldiphenyl indicate that the C_6 rings in each mol. are coplanar and linearly extended. a and b are practically identical in all three cases, whilst c is 9·50, 13·59,

and 17·72 Å., respectively. The length of each mol. is approx. parallel to the *c* axis. L. S. T.

Evaluation of fibre diagrams. E. SAUTER (Z. Krist., 1933, **84**, 453—460).—A graphic method for constructing the reciprocal lattice from a rotation photograph is described, and illustrated by application to cellulose hydrate (cf. A., 1929, 1132; 1923, ii, 1055). C. A. S.

X-Ray fibre diagram as a quantitative measure of change of structural units of cellulose fibre by chemical processes. II. Use of mixed preparations for measurement of partial conversion in action of aqueous sodium hydroxide on cellulose. W. SCHRAMEK [with H. NEUMANN and C. SCHUBERT] (Z. physikal. Chem., 1933, **B**, **20**, 209—216).—The need for caution in the interpretation of the reaction mechanisms of cellulose by means of fibre diagrams is emphasised. In particular, no conclusions can be reached from the sharpness or width of interferences unless it is known that in the transformation of one lattice structure into the other no intermediate stages are possible. In the transformation of Na-cellulose I into hydrocellulose a modification of cellulose not previously observed appears. R. C.

X-Ray examination of rice and potato starches. B. TAKEI (Japan. J. Physics, 1933, **8**, 85—90).—Rice and potato starches were examined by the powder method using Fe *K* radiation. Complete drying causes alteration in the sizes of the lattices of the two starches; on admission of ordinary air into the apparatus, the original lattices are restored. A. J. M.

Magnetic resistance change of a bismuth wire. E. ENGLERT and K. SCHUSTER (Physikal. Z., 1933, **34**, 236).—The magnetic resistance of a Bi wire for high-frequency a.c. (wave-length 1 m.) is the same as for d.c. A. J. M.

Recrystallisation of aluminium crystals. IV. Work-hardening and power of recrystallisation during plastic deformation of metals. W. G. BURGERS (Z. Physik, 1933, **81**, 43—65; cf. A., 1931, 416).—Nuclei of new crystals appear at places of curvature of slip lamellæ, and the no. of these nuclei increases rapidly with increase of localised distortion; hence for a given total deformation the no. of nuclei formed may vary, and this is used to explain contradictory results on the relation of work-hardening and recrystallisation of Al. A. B. D. C.

Strength of polycrystalline materials. W. KUNTZE (Z. Physik, 1933, **81**, 80—83).—The different behaviour of poly- and single cryst. materials under space stress is discussed. A. B. D. C.

Recovery of iron and nickel after cold working. G. TAMMANN and G. MORITZ (Ann. Physik, 1933, [v], **16**, 667—679).—In Fe and Ni the temp. coeff. of the electrical resistance of the hard metal is smaller than for the soft. The temp. of recovery after cold working lies higher for hardness than for electrical resistance. The temp. interval for recovery of electrical resistance is not markedly displaced by the period of working. The influence of the magnetic transition of Ni is discussed. W. R. A.

Determination of electrostriction of gases. J. JAUMANN (Physikal. Z., 1933, **34**, 282).—A new method is described. The highly compressed gas is submitted to an alternating field of 50—700 Hertz, and the corresponding pressure oscillations are measured by a compensation microphone. For He, H_2, N_2, O_2, CO_2, and SO_2 at room temp. there is proportionality between the effect and the square of the field strength. The effect is proportional to density only in the case of H_2 and He. A. J. M.

Cohesion. IV. Cleavability of galena. H. TERTSCH (Z. Krist., 1933, **85**, 17—35; cf. A., 1932, 452). C. A. S.

Plastic torsion, recrystallisation, and solidification of aluminium. A. E. VAN ARKEL and M. G. VAN BRUGGEN (Z. Physik, 1933, **80**, 804—812).—Plastic torsion is related to crystal size in Al rods. A. B. D. C.

A3 point of highly purified iron. F. R. HENSEL and E. I. LARSEN (Met. and Alloys, 1933, **4**, 37—38).—Dilatometric measurements on specimens of Fe containing only traces of solid or gaseous impurities showed that the A3 point is raised, although its intensity, as indicated by length and thermal changes, was not reduced. Similar experiments on still purer Fe are necessary to correlate Yensen's hypothesis that the A3 transformation is due to impurities (A., 1929, 1135). C. A. K.

Mixtures of sterically similar compounds with similar groups as solvents for micro-mol. wt. determinations by the method of molar m.p. depression. J. PIRSCH (Ber., 1933, **66**, [*B*], 506—511; cf. this vol., 342).—The m.p. of mixtures of bornyl chloride (I) and bornyl bromide (II) increases almost rectilinearly within increasing % of (I) from 89° to 131·2° without occurrence of a eutectic or max. The molar depression of m.p. of mixtures of (I) and (II) can be calc. from the simple mixture rule, which is valid even in very dil. solution. H. W.

Molecular size of "fatty" substances. P. PFEIFFER and W. GOYERT (J. pr. Chem., 1933, [ii], **136**, 299—313).—Mol. wt. determinations (f.p. and b.p.) of the following esters in C_6H_6 and occasionally in $COMe_2$, COPhMe, $MeNO_2$, or *cyclo*hexanone (b.p. const.=3·96) show that the compounds undergo no dissociation (cf. Grün, A., 1913, i, 157): cetyl acetate, benzoate, succinate, and *tricarballylate*, m.p. 46·5° (becoming clear at 52°) (from Na cetyloxide and tricarballyl chloride or from cetyl alcohol and tricarballylic acid at 190°/16 mm.); Et stearate, succinate, and tricarballylate; glycol diacetate and distearate; glyceryl triacetate, $\alpha\gamma$-distearate, and tristearate. Slight variations occur with concn. in some cases. H. B.

Temperature dependence of the electrical resistance of pure metals. E. GRÜNEISEN (Ann. Physik, 1933, [v], **16**, 530—540).—Li, Na, Cu, Ag, Au, Al, Pb, W, Rh, Pt, and Pd are discussed in relation to the T^5 and T^4 laws. W. R. A.

Heat capacity of methane. D. P. MACDOUGALL (Physical Rev., 1931, [ii], **38**, 2297—2298).—A recalculation of previous results (A., 1931, 1216). $C_p^{0.98\,1}$ is 8·54 g.-cal. per mol. L. S. T.

Extra specific heat of cuprous sulphide; specific heat of ferrous oxide. W. P. WHITE (J. Amer. Chem. Soc., 1933, **55**, 1047—1053).—The sp. heats have been determined over wide intervals in the range 30—900°. The sp. heat of Cu_2S has a max. at about 300°. J. G. A. G.

Molecular heats and natural frequencies of ethane and ethylene. A. EUCKEN and A. PARTS (Z. physikal. Chem., 1933, **B**, **20**, 184—194).—The mol. heats, C_p, of C_2H_4 and C_2H_6 have been determined at 178—464° and 189—373° abs., respectively. For C_2H_4 the C_p vals. reduced to zero pressure may be represented by the Planck–Einstein formula, using spectroscopically determined natural frequencies, if a frequency of 750—800 cm.$^{-1}$ is assigned to the spin of the CH_2 radicals towards each other. The C_p vals. for C_2H_6 are not inconsistent with free rotation of the Me radicals. R. C.

Helium isotherms at low temperatures and high pressures. E. BUCHMANN (Z. physikal. Chem., 1933, **163**, 461—468).—Measurements have been made at 13·5—20·4° abs. at pressures up to 1800 kg. per sq. cm., and d of liquid He in equilibrium with the solid determined at these temp. Vals. of pv/RT as high as 12·5 have been observed. R. C.

Entropies of methane and ammonia. W. F. GIAUQUE, R. W. BLUE, and R. OVERSTREET (Physical Rev., 1931, [ii], **38**, 196—197; cf. A., 1931, 800).—The entropies of CH_4 and NH_3 at 298·1° abs. and 1 atm. calc. from spectroscopic data are 44·35 e.u. and 46·4 e.u., respectively. When nuclear spin entropy is included the abs. vals. are 49·86 e.u. and 52·7 e.u. L. S. T.

Entropies of methane and ammonia. D. P. MACDOUGALL (Physical Rev., 1931, [ii], **38**, 2074—2075; cf. A., 1931, 800).—The calc. abs. entropy of CH_4 at 298·1° is 49·97 g.-cal. per degree per mol. and the val. less the nuclear spin entropy is 44·46 (cf. preceding abstract). For NH_3 the abs. entropy is 52·10 and that less nuclear spin entropy 45·79. L. S. T.

Nernst theorem. J. E. VERSCHAFFELT (Natuurwetensch. Tijds., 1933, **15**. 33—38).—A brief account. H. F. G.

Pressure of saturated water vapour in the range 100—374°. N. S. OSBORNE, H. F. STIMSON, E. F. FIOCK, and D. C. GINNINGS (Bur. Stand. J. Res., 1933, **10**, 155—188).—The pressure was determined by the static method using a high-pressure calorimeter fitted with a precision piston gauge and Pt resistance thermometers supplemented by thermoelements. The results are tabulated in atm., centibars, and kg. per sq. cm. for each 1° C. and in lb. per sq. in. for each 1° F. The saturation pressure in atm. is given (correct to 3 parts in 10,000) by: $\theta \log_{10} P = a\theta + b + cx^3 + dx^5 + ex^6$, where a, b, c, d, and e are consts. within one or other of the temp. ranges, 100—275° and 275—374°, θ is the abs. temp., and $x = (\theta^2/2{\cdot}98 \times 10^5) - 1$. Within the first temp. range $a = 5{\cdot}4247285$, $b = -2003{\cdot}853$, $c = 87{\cdot}880$, $d = 107{\cdot}35$, $e = -96{\cdot}252$, and within the second $a = 5{\cdot}4231165$, $b = -2002{\cdot}971$, $c = 109{\cdot}54$, $d = -608{\cdot}22$, $e = 1399{\cdot}0$. A. R. P.

Van der Waals' equation. II. K. JABŁCZYNSKI (Rocz. Chem., 1933, **13**, 75—84).—The conclusions reached previously (this vol., 117) for CO_2 and C_2H_4 are extended to CO, N_2, O_2, H_2, and He. The val. of b is in all these cases const. for a given gas, whilst a may possess a negative or positive val., according to the temp. and pressure of the gas. The val. of a is 0 for CO_2 at 1000°, for CO at 450°, for O_2 at 750°, and for N_2 at 800°. R. T.

Physical properties of ethylamine. E. POHLAND and W. MEHL (Z. physikal. Chem., 1933, **164**, 48—54).—The measured v.p. between −61° and 24° may be represented by $\log p_{mm} = 21{\cdot}5535 - 2093{\cdot}686/T - 4{\cdot}61703 \log T - 2{\cdot}74 \times 10^{-4}T$. The d of the solid, liquid, and saturated vapour have been determined at several temp. The Eotvos const. is 1·9, and the mol. heat of the liquid 31·1±0·9 g.-cal. R. C.

Density and compressibility of ammonia. At. wt. of nitrogen. E. MOLES and T. BATUECAS (Anal. Fís. Quím., 1932, **30**, 876—879).—The data previously reported have been corr. (A., 1930, 1357). The mean density, in g. per litre at s.t.p., is 0·77170, and that calc. from measurements at 0·5 atm. is 0·76573; the val. of $1+\lambda$ is 1·0157, and the calc. at. wt. of N is 14·007. H. F. G.

Compressibility of cubic compounds. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1932, **67**, 345—375).—Measurements were made at 30° and 75° at 1—12,000 atm., and the compressibility was expressed by: $V/V_0 = Ap + Bp^2$, where A and B are consts. characteristic of the substance. Vals. of A and B at 30° and 75°, and the mean coeff. of thermal expansion at 30—75°, are tabulated for CaS, SrS, BaS, MgO, CaO, Cu_2O, As_2O_3, $Sr(NO_3)_2$, CuCl, CuBr, CuI, LiI,$3H_2O$, LiI, CsF, CsCl, CsBr, and CsI. Compressibilities for all the alkali halides are tabulated; a break at about 1000 kg. indicates a transition in RbCl. CH. ABS.

Relation between the turbulent internal friction and the constitution of liquids. F. GRIENGL, O. KOFLER, and M. RADDA (Monatsh., 1933, **62**, 131—151; cf. A., 1927, 1133; 1930, 1245).—The viscosities for turbulent flow of Me, Et, Pr^{α}, Pr^{β}, Bu^{α}, *n*-, and *iso*-amyl alcohols, C_6H_6, PhMe, *m*-xylene, $PhNO_2$, NH_2Ph, $NPhMe_2$, and $NPhEt_2$ up to 60—120° have been measured. The results satisfy relations of Thole and Dunstan (J. Chim. phys., 1909, **7**, 205), Porter (A., 1912, ii, 434), and Herz (A., 1928, 229, 943), previously established only for Poiseuille flow. H. J. E.

Effect of temperature on the viscosity of liquids. E. VAN AUBEL (Bull. Acad. roy. Belg., 1932, [v], **18**, 1026—1047).—It is shown that the experimental facts regarding the effect of temp. on viscosity of (1) molten salts ($PbCl_2$ and $AgNO_3$), (2) aq. solutions (sugar), (3) liquids above their b.p. (C_6H_6, PhMe, Et_2O, EtOAc, EtBr), and (4) PhF, PhCl, and CCl_4 are best represented by van Aubel's equation, $\phi - m + n \log (\theta - t)$, where ϕ is the fluidity, t the temp., θ the crit. temp., and m and n are consts., rather than by that of Andrade ($\eta = ae^{b/T}$, where T is the abs. temp., and a and b are consts.). A. J. M.

Dependence of viscosity of air, argon, and hydrogen chloride on temperature. J. R. PARTINGTON (Physikal. Z., 1933, **34**, 289—292; cf. Williams, A., 1926, 234; Shilling and Laxton, A., 1930, 1509).—The method used was based on that of Shilling and Laxton. Anomalous results obtained at low temp. are not to be ascribed to inaccuracy of Sutherland's formula, but to "bent streaming." This effect has vitiated many results previously taken as accurate. A. J. M.

Constitution of binary alloys at room temperature. A. N. CAMPBELL (Nature, 1933, **131**, 438). L. S. T.

***X*-Ray study of copper–cadmium alloys.** E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1933, A, **139**, 526—541).—The phase diagram is similar to that given by Jenkins and Hanson (B., 1924, 298). The *X*-ray method fails to disclose the structure of the pure β-, γ-, and ε-phases, but the structure of the δ-phase is similar to that of γ-brass, having a body-centred cubic lattice with 4 mols. (Cu_5Cd_8) per unit cell. The close analogy suggested by some workers between the corresponding phases of the Cu–Cd system and the analogous Cu–Zn, Ag–Zn, and Ag–Cd systems is not supported. The effects of annealing are studied by precision camera analysis. Lattice distortion in filings is eliminated by a simple annealing, but such annealing does not bring about the true thermal equilibrium. The data relating the α-phase parameter, composition, and temp. of samples in the equilibrium state show that the proportion of Cu in the saturated α-phase decreases with fall of temp. A modification is therefore made in the previously accepted α–(α+β) boundary. L. L. B.

Recovery of electrical resistance of binary mixed crystals of copper, silver, and gold, following cold working. G. TAMMANN and K. L. DREYER (Ann. Physik, 1933, [v], **16**, 657—666).—Crystals of Cu, to which varying small amounts of Zn, Sn, Mn, Ni, and Au were added, have been studied; also crystals of Ag with addition of Zn, Cd, and Au, and crystals of Au with addition of small quantities of Ag. Cu, Ag, and Au are influenced in a similar way. The influence of the crystal structures of the two components of the mixed crystal, and of the at. radius of the added metal is discussed. The temp. of the inflexion point and the appearance of a second inflexion point with larger amounts of the second metal are also considered. W. R. A.

Crystal structure of precipitated copper–tin alloys. H. KERSTEN and J. MAAS (J. Amer. Chem. Soc., 1933, **55**, 1002—1004).—An alloy of composition and crystal structure identical with the Cu_3Sn phase prepared by fusion is pptd. by Sn from hot 1% $CuSO_4,5H_2O$ containing < 12 c.c. of conc. H_2SO_4 per litre. With > 20 c.c. of H_2SO_4 per litre, the alloy pptd. corresponds with the α-phase of the Cu–Sn system. J. G. A. G.

Copper–magnesium alloys examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1933, **29**, 550—553).—Thermodynamic analysis of experimental data confirms the metallographic work of Jones (A., 1931, 1224), and indicates that both the liquid and the solid solutions (Mg in Cu and Cu in Mg) contain only monat. mols. The results give no evidence of the existence of MgCu. F. L. U.

***X*-Ray investigation of copper–aluminium alloys.** A. J. BRADLEY and (MISS) P. JONES (Inst. Metals, Mar. 1933. Advance copy, 27 pp.).—The α-phase is face-centred cubic, *a* 3·608 (pure Cu) to 3·657 Å. [Cu saturated with Al (10%)]. Alloys with 10·5—16% Al consist of α+δ after annealing at 500° and slowly cooling, the eutectoid point occurring at 12·4% Al. The body-centred cubic β-phase is stable only above 530° and decomposes on quenching into homogeneous β′ (cf. Obinata, B., 1930, 105, 1072; Smith and Lindlieff, below). The β′-alloy with 12·5% Al has *d* 7·12 and apparently a face-centred cubic structure from which certain atoms are missing. The δ-phase proper exists only between 16 and 19% Al; its structure resembles that of γ-brass with 52 atoms in the unit cell, corresponding with the composition Cu_9Al_4. The δ′-phase (19—22·5% Al) is pseudo-cubic with 49 atoms in the unit cell, and the ε-phase, obtained by quenching from 700° the alloy with 22·8% Al, is cubic and decomposes on annealing at 530° and slow cooling into a two-phase mixture. Alloys with 22·8—29% Al show many different types of structure, according to the heat treatment, and it is suggested that either the η-phase consists of a no. of phases of small range or a gradual modification takes place. The θ-phase belongs to the tetragonal space-group D_{4h}^{18} and has *a* 6·054±0·001, *c* 4·864±0·001 Å., with 47% Al; *d* is 4·34 and the no. of atoms per unit cell 12. The phase has not a unique composition. A. R. P.

Micrographic study of the decomposition of the β-phase in the copper–aluminium system. C. S. SMITH and W. E. LINDLIEFF (Amer. Inst. Min. Met. Eng., Tech. Publ. No. 493, 1933, 39 pp.).—The mechanism of the decomp. of the β-phase in the Cu–Al alloy with 11·87% Al has been studied. At 565° transformation commences in 1 hr. and is complete in 10 hr., whereas at 535° it is complete in 7 min. At still lower temp. the time of transformation increases, until at 400° the change occupies 5 days. The rapid transformation at 535° proceeds through the formation of a β′-phase which serves as a nucleus for the rapid formation of α-needles or plates. The amount of α formed in the transformation increases with falling temp. of transformation, and below 400° practically the whole specimen is converted into α, although the limit of solid solubility of Al in Cu is 9·8%. A theory is advanced to account for the formation of β′ and supersaturated α. Ordinary etching reagents do not reveal the presence of β′; suitable reagents for this purpose are ammoniacal H_2O_2 or, better, a mixture of 40 g. HNO_3 (*d* 1·42), 25 g. CrO_3, and 35 g. H_2O. Addition of small amounts of Sn to the alloy retards the formation of β′, but larger amounts, *e.g.*, 4%, stabilise the phase. The changes in hardness, electrical conductivity, and *X*-ray diffraction pattern in the transformation of β confirm the existence of β′. A. R. P.

Segregate structures of the Widmanstatten type developed from solid solutions of copper in zinc. M. L. FULLER and J. L. RODDA (Amer. Inst.

Min. Met. Eng., Inst. Met. Div., Preprint, 1933).—The structures are produced by the segregation of the ε-phase from the η-solid solution of Cu in Zn. Both phases are hexagonal close-packed. An orientation of the segregate relative to the matrix, and a mechanism for the segregation, are suggested. CH. ABS.

X-Ray investigations of the mixed crystal system gold–silver and the solvent effect of nitric acid on the system. M. LE BLANC and W. ERLER (Ann. Physik, 1933, [v], **16**, 321—336).—Mixtures containing < 48 mol.-% Ag are practically unaffected by HNO_3 (*d* 1·32 and 1·42) at 49°. The resistance to attack is diminished as the Ag content is increased. *X*-Ray observations show that the metals form an uninterrupted mixed crystal series. W. R. A.

Effect of a deformation (pulverisation) on the superstructure lines and the lattice constant of an iron–aluminium alloy. K. SCHAFER (Naturwiss., 1933, **21**, 207).—The Debye diagram obtained with very finely pulverised Fe–Al alloy does not give the superstructure lines noticed by Bradley and Hope (A., 1932, 669), and the lattice const. is 0·7% > for the ordinary alloy. A. J. M.

Recovery of electrical resistance and hardness of binary mixed crystals of iron after cold working. G. TAMMANN and V. CAGLIOTI (Ann. Physik, 1933, [v], **16**, 680—684).—The effects observed when small amounts of Al, Si, V, Cr, Co, Ni, Mo, and W are added to electrolytic Fe are discussed. W. R. A.

Heat effect of the austenite–pearlite transformation. H. ESSER and W. GRASS (Stahl u. Eisen, 1933, **53**, 92).—From determinations of the total heat content of steel with 0·82% C, 0·1% Si, and 0·12% Mn at 400—900° the calc. heat evolution in the austenite–pearlite transformation is 21·22 g.-cal. per g., but this appears to be too low owing to the formation of a small quantity of sorbite. A more accurate determination by R. Averdieck (Diss., Aachen, 1932) gave 22·54 g.-cal. per g. A. R. P.

Physical and mechanical properties of Mg–Al–Cu alloys rich in magnesium. A. PORTEVIN and P. BASTIEN (Compt. rend., 1933, **196**, 693—696; cf. A., 1932, 989).—Hardness and electrical conductivity data suggest that the alloys examined are solid solutions. The thermal diagram gives slightly different limits for the range of these solutions. Other mechanical properties are discussed with reference to the nature of the phases. C. A. S.

Rate of precipitation of nickel silicide and cobalt silicide in the hardenable copper–nickel–silicon and copper–cobalt–silicon alloys. C. L. WILSON, H. F. SILLIMAN, and E. C. LITTLE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Preprint, 1933).—The change in electrical resistance and Rockwell hardness of Cu alloys containing Ni_2Si and Co_2Si has been determined after annealing at various temp. The rate of pptn. of Ni_2Si increases with rise in annealing temp. to a max. which depends on the % of Ni_2Si. Similar discontinuities are observed with the Co_2Si alloys. The solubility of Co_2Si in Cu is 5% at 970°. CH. ABS.

Magnetic susceptibility of several systems of binary alloys. Y. SHIMIZU (Sci. Rep. Tohoku, 1932, **21**, 826—850).—The relation between magnetic susceptibility (I) and concn. has been investigated for the alloys Au–Ag, Au–Cu, Sb–Bi, Pt–Pd, Sn–Bi, Bi–Pb, Cd–Sn, Sb–Pb, Bi–Te, and Al–Sn, all prepared by fusion and subsequent annealing in vac. Alloys which form solid solutions follow closely the additive law both with respect to (I) and to density. Occluded gases have a large effect on (I) and the rapid decrease observed when a trace of, *e.g.*, Sn, Te, Pb, etc. is added to, *e.g.*, Bi or Sb is not a property characteristic of the alloys, but is due to absorbed gas. J. W. S.

Refractive index of liquid mixtures with pyridine as a component. N. A. PUSHIN and P. G. MATAVULJ (Z. physikal. Chem., 1933, **164**, 80—86; cf. this vol., 119).—For mixtures of C_5H_5N with phenols the deviation of *n* from the simple mixture rule exhibits a max. at 50 mol.-%; in some cases the graph of the temp. coeff. of *n* against composition shows a discontinuity at the same point. R. C.

Influence of cellulose nitrate on the refraction of liquid mixtures. II. Refractometric determination of the alteration in concentration of liquid mixtures by cellulose esters. T. TOMONARI (J. Soc. Chem. Ind. Japan, 1933, **36**, 51—52B; cf. this vol., 119).—For solutions of stable cellulose nitrate (I) in ketone–alcohol mixtures, the change in *n* is proportional to concn. of (I). This is not true for solutions of unstable preps. of (I), which give abnormally high vals. of *n*, owing to reaction with one of the components of the solvent. D. R. D.

Diamagnetic susceptibilities of liquid mixtures with a new apparatus. L. SIBAIYA and H. S. VENKATARAMIAH (Indian J. Physics, 1932, **7**, 393—404).—$COMe_2$–$CHCl_3$ mixtures show max. deviation from the simple mixture rule at 33 wt.-% $COMe_2$ and evidence of the deviation of other physical properties for this mixture is given. For H_2O–AcOH mixtures max. deviation is found at 75% AcOH. W. R. A.

Dynamic azeotropism. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1932, [v], **18**, 1160—1168).—Mathematical. A. J. M.

Classification of zeotropic and azeotropic mixtures. W. SWIENTOSŁAWSKI (Rocz. Chem., 1933, **13**, 125—129).—The classification proposed is based on considerations of miscibility. R. T.

Diffusion of silver and copper in glass. J. HALBERSTADT (Z. anorg. Chem., 1933, **211**, 185—194).—The diffusion coeff. of Ag in glass between 565° and 615° and that of Cu in glass at 650° have been measured. It is shown that metals dissolve in glass in the at. state. The val. of the diffusion coeff. for Ag is abnormally high; this is attributed to solvation of the Ag. H. J. E.

Solubility of nitrogen in water at 50°, 75°, and 100° from 25 to 1000 atm. R. WIEBE, V. L. GADDY, and C. HEINS, jun. (J. Amer. Chem. Soc., 1933, **55**, 947—953; cf. A., 1932, 908).—Data are recorded. At about 70°, the absorption coeff. has a

min. which becomes more pronounced with increasing pressure. Accurate vals. of the solubility at high pressures cannot be calc. from the low-pressure data. J. G. A. G.

Solubility of nitrogen in liquid ammonia at 25° from 25 to 1000 atm. R. WIEBE and T. H. TREMEARNE (J. Amer. Chem. Soc., 1933, **55**, 975—978).—Data are recorded. J. G. A. G.

Solubility of oxygen in gold and in certain silver-gold alloys. F. J. TOOLE and F. M. G. JOHNSON (J. Physical Chem., 1933, **37**, 331—346; cf. A., 1928, 229).—The solubility of O_2 in Au at 900°/70 cm. is approx. 0·010 vol. per unit vol. of Au. The solubility of O_2 in alloys containing 5, 10, and 20% Au has been measured at 200—850° and 5—80 cm. pressure. Above 700° the solubility is approx. proportional to $p^{1/2}$ and is related to the temp. (t) by $1/Q - K_1(A-t)$ (Q=solubility, A=m.p. of the alloy). Below 700°, $Q - ap^k$, in which k diminishes with increase in t. N_2 is insol. in Au and in the Au–Ag alloys. H. J. E.

Solubility of the hydrates of manganous sulphate. J. H. KŘEPELKA and B. REJHA (Coll. Czech. Chem. Comm., 1933, **5**, 67—75).—The solubility curves of $MnSO_4,xH_2O$ (x=1, 4, 5, and 7) have been determined. No other hydrates exist. $MnSO_4,7H_2O$ and $MnSO_4,5H_2O$ melt without decomp. at 24° and 55°, respectively. H. J. E.

Solubility relations of barium sulphate in aqueous solutions of strong electrolytes [at 25°]. E. W. NEUMAN (J. Amer. Chem. Soc., 1933, **55**, 879—884; cf. A., 1932, 801).—The solubility in aq. solutions of the chlorides and nitrates of K, Mg, and La has been determined. The solubility in H_2O is $0{\cdot}957\times10^{-5}M$ and the activity coeff. 0·977. Activity coeffs. are calc., and the data are in accord with the Gronwall and La Mer extension of the interionic attraction theory. J. G. A. G.

Influence of carbon disulphide on the solubility of iodine in water. G. HERRERO (Anal. Fís. Quím., 1932, **30**, 880—885).—The presence of CS_2 has no influence on the solubility of I in H_2O (cf. A., 1932, 803). H. F. G.

Solubility of inorganic compounds in liquid ammonia. I. M. LINHARD and M. STEPHAN (Z. physikal. Chem., 1933, **163**, 185—195).—The solubilities of Na and K halides and nitrates at 0° have been determined. R. C.

Solubility of sodium chloride in liquid ammonia. G. PATSCHEKE (Z. physikal. Chem., 1933, **163**, 340—350).—The solubility has been determined at −77° to 43°. Between the eutectic point, −76·6°, and −9·5° the solid phase in equilibrium with the solution is $NaCl,5NH_3$. Above −9·5°, at which the NaCl concn. in the liquid phase is a max., the solid phase is NaCl. R. C.

Use of non-aqueous solvents in the study of the rare-earth group. B. S. HOPKINS and L. L. QUILL (Proc. Nat. Acad. Sci., 1933, **19**, 64—68).—The solubilities of $NdCl_3$ and $LaCl_3$ in various alcohols, including $C_2H_4(OH)_2$ and $C_3H_5(OH)_3$, and of $Pr(NO_3)_3$ and $Nd(NO_3)_3$ in Et_2O have been determined. Below 22° $Nd(NO_3)_3$ is slightly sol. in Et_2O, whilst $Pr(NO_3)_3$ is insol. This fact may be used as a means of separating the two salts. The solubilities of rare-earth nitrates at 25° in both Et_2O and dioxan have been plotted against at. no. Ce has a similarly anomalous position on the curve for each solvent. M. S. B.

Solubility of palmitic and lauric acids and of their sodium salts in alcohol. P. EKWALL and W. MYLIUS (J. pr. Chem., 1933, [ii], **136**, 133—136).—At −10° to 25° the solubility of the acids in aq. EtOH rises, and that of the salts falls, as the EtOH content of the solvent increases. H. A. P.

Solubility of glutamic acid in water and certain organic solvents. V. A. PERTZOFF (J. Biol. Chem., 1933, **100**, 97—104).—The solubility of *d*-glutamic acid in H_2O, MeOH, EtOH, and $COMe_2$ at 25° has been determined. The calc. heat of dissolution in H_2O is 9600 g.-cal. H. G. R.

Solubility of calcium stearate in solutions containing bile and in water. W. D. LANGLEY, M. G. ROSENBAUM, and M. M. ROSENBAUM (J. Biol. Chem., 1932, **99**, 271—278).—Ca stearate is practically insol. in dil. ox bile, whilst in H_2O the solubility const. is $3{\cdot}61\times10^{-15}$. F. O. H.

Two co-existent phases. A. VLOEK and K. TEIGE (Chem. Listy, 1932, **26**, 65—69, 89—95, 116—120, 161—164, 195—197, 257—266, 281—285, 568—572, 597—600, 614—621; 1933, **27**, 8—13).—A relation is deduced which is said to determine the conditions for homogeneity in ternary liquid mixtures. This rule is shown to hold for the systems H_2O–C_6H_6–$COMe_2$, H_2O–$CHCl_3$–AcOH, and H_2O–C_5H_{11}·OH–EtOH, MeOH, or $COMe_2$. R. T.

Viscosity of mixtures of partly miscible liquids. System phenol–water. R. KREMANN, F. GRIENGL, and H. SCHREINER (Monatsh., 1933, **62**, 28—46).—The viscosity coeffs. of stirred PhOH–H_2O mixtures at 50° reach a well-defined max. within the region of limited miscibility. In presence of NaOH or HCl more conc. than 0·001*N* the val. of the max. viscosity is lowered, and its position displaced towards a higher concn. of PhOH. The results are discussed. F. L. U.

Viscosity anomalies of self-separating systems. I. Structure viscosity of critical liquid mixtures. Wo. OSTWALD and H. MALSS (Kolloid-Z., 1933, **63**, 61—77).—The viscosity of saturated aq. sucrose, and of molten glucose, lauric and stearic acids, $NaOAc,3H_2O$, $COPh_2$, and $C_{10}H_8$ at all the temp. and pressures investigated is in accordance with the Hagen–Poiseuille law. The viscosity anomalies reported for very conc. LiCl solutions at low pressures (cf. Blair, A., 1931, 560) are not confirmed. Experiments with crit. liquid mixtures (C_6H_{14}–$PhNO_2$, C_6H_{14}–MeOH, *iso*butyric acid–H_2O, PhOH–H_2O, PhOH–C_7H_{16}, and C_6H_6–AcOH–H_2O) show the existence of structure viscosity; the Hagen-Poiseuille law is not valid, and the viscosity increases strongly at small velocities of flow. These results demonstrate the emulsoid character of the crit. liquid systems. E. S. H.

Ternary systems water, *tert.*-butyl alcohol, and salts at 25°. P. M. GINNINGS, E. HERRING, and B. WEBB (J. Amer. Chem. Soc., 1933, **55**, 875—

878).—For the 30 salts investigated, the rate of decrease of wt.-% of *tert.*-BuOH with respect to wt.-% of salt in the alcohol-rich liquid phase is a direct function of the wt.-% of *tert.*-BuOH. J. G. A. G.

Absorption of hydrogen by iron. F. KORBER and H. PLOUM (Z. Elektrochem., 1933, **39**, 252—255).—Absorption of H_2 by Fe, when the latter serves as cathode in the electrolysis of aq. H_2SO_4, or when it is dissolved in H_2SO_4, occurs only in presence of catalysts, of which the most powerful are S (especially as H_2S), As, P, and other elements which form volatile hydrides. Ni and Hg have a slight catalytic action, Cu and Ag none at all. D. R. D.

Adsorption. I. Mechanism of the activation of charcoal. II. Mechanism of the adsorption of vapours by unactivated charcoal. L. J. BURRAGE (Trans. Faraday Soc., 1933, **29**, 445—457, 458—476).—I. The characteristics of charcoals in relation to their origin are described and a new theory of activation, based partly on botanical and partly on chemical grounds, is advanced. In the process of activation the charcoal which is formed from the almost pure cellulose of the young cell walls and contains a complex C_XO_Y (A., 1932, 1084) is removed, whilst the charcoal from the lignocelluloses remains untouched. Pitting is caused and the carbonised remnants of the cellulose attached to the walls of these pits or pores are the active centres. Experiments are described in support of this theory.

II. Polar mols. only can be adsorbed by unactivated charcoal. Ten isotherms have been determined at 25° for substances of which the dielectric const. D varies from 81 to 2·2. At high pressures adsorption increases with D. The amounts of a large no. of substances quasi-chemically held have been determined. Only when the substance contains O, S, or N is any appreciable quantity firmly retained, suggesting that the mols. are held by the charcoal surface or by the partly displaced C_XO_Y sponge as oxonium, sulphonium, or NH_4 compounds. Adsorption may take place either by displacement of the C_XO_Y complex or by combination with it.

M. S. B.

Adsorption. III. Effect of activation of charcoal on isothermals of carbon tetrachloride. IV. Effect of activation of charcoal on isothermals of water, and its relation to hysteresis. L. J. BURRAGE (Trans. Faraday Soc., 1933, **29**, 564—569, 570—576; see above and this vol., 221).—III. Adsorption isotherms for CCl_4 vapour at 25° on various charcoals have been determined and compared with respect to the origin of the charcoal and the method of activation. The best material is nut shell for low and peat for high pressures. The capacity for adsorption at either high or low pressures depends entirely on the degree to which activation can be controlled.

IV. Isotherms for H_2O vapour have been similarly compared, and the adsorption capacity is shown to depend in this case also on the degree of activation. A detailed mechanism is suggested to account for the adsorption–desorption hysteresis loop. F. L. U.

Discontinuities [in gaseous adsorption] and the nature of adsorbent solids. G. H. PIPER (Trans. Faraday Soc., 1933, **29**, 538—543).—Theoretical. Irreversible discontinuities in gaseous adsorption isotherms cannot in all cases be due to condensation of gas to liquid. A mechanism is suggested whereby labile links between the atoms of an adsorbent are ruptured and transferred to those of the adsorbed gas. F. L. U.

Method for obtaining data for the sorption of vapours by solids. J. L. PORTER (J. Physical Chem., 1933, **37**, 361—366).—The apparatus and method are described. The adsorption of various liquids on dehydrated chabasite and the sorption isotherms of org. vapours on chabasite and activated charcoal have been measured. The results indicate persorption and not capillary condensation.

H. J. E.

Adsorption of cæsium on calcium fluoride films, and associated swelling phenomena. C. J. DIPPEL and J. H. DE BOER (Chem. Weekblad, 1933, **30**, 221—222).—The adsorption of I on a CaF_2 film (produced by evaporation and condensation) shows the film to be of laminated structure; when the film is heated to about 350° the surface diminishes, the points of greatest adsorption potential being the first to disappear. Analogous diminution, on sintering, of the quantity of material adsorbed is not, however, observed with Cs, and if the adsorbed Cs is subsequently removed, the I adsorption is that of an unsintered film. The Cs thus appears to open up the CaF_2 surface. This does not occur if the film is sintered at a higher temp. The max. absorption of I adsorbed at the most active points of the surface is in the ultra-violet, whereas for less active points the max. is shifted towards the red; the reverse obtains with Cs. H. F. G.

Adsorption of electrolytes by crystalline surfaces. L. DE BROUCKÈRE (Ann. Chim., 1933, [x], **19**, 79—204).—A full account of work previously published (A., 1928, 831; 1929, 757, 874, 1001; 1930, 152, 407, 850; 1931, 298, 1226; 1932, 223, 332, 689).

F. L. U.

Absorption of barium hydroxide, sodium hydroxide, and water by cellulose, from aqueous barium hydroxide and from mixed solutions. S. M. NEALE and W. A. STRINGFELLOW (J. Text. Inst., 1933, **24**, 30—34T).—In pure $Ba(OH)_2$ solutions the absorption of Ba rises steadily with increasing concn., whilst the absorption of H_2O falls. Addition of $Ba(OH)_2$ decreases the absorption of Na, but the addition of NaOH increases that of Ba. B. P. R.

Adsorption and hydrolysis of glycogen. G. BANCROFT and E. G. FRY (J. Biol. Chem., 1933, **100**, 255—265).—Charcoal (I) adsorbs glycogen (II) up to a certain limit from aq. solution, and subsequent dilution produces very little change. 50·9 mg. of adsorbed (II), when hydrolysed for 2 hr., gave only 1·93 mg. of glucose, the hydrolysis being independent of the adsorbed (II). BuOH and $CHCl_3$ have no influence on the hydrolysis of (II) by amylase alone. The latter hydrolyses (II) in the presence of (I) provided neither it nor (II) is completely adsorbed. The increased hydrolysis due to BuOH and $CHCl_3$ in the presence of (I) is not due to their influence on adsorption. H. D.

Adsorbing power of soil for pyrophosphoric acid. A. FABRIS (Atti R. Accad. Lincei, 1932, [vi], **16**, 637—640).—The soils examined adsorb $H_4P_2O_7$ from solutions of its salts. This is attributed mainly to the org. constituents of the soil. Rates of adsorption are recorded. O. J. W.

Formation and structure of adsorption complexes. H. J. C. TENDELOO (Chem. Weekblad, 1933, **30**, 220—221).—A brief review of published work. H. F. G.

Adsorption of colloids by metallic surfaces and its effect on the adherence of electrolytic deposits. P. JACQUET (Compt. rend., 1933, **196**, 921—923; cf. B., 1933, 109).—A clean Cu sheet is steeped in a solution of various colloids for a few seconds, thoroughly washed, and used as cathode with a $CuSO_4+H_2SO_4$ electrolyte. Films of a protein or its degradation products greatly reduce the adhesion of the deposited Cu, but films of gum or dextrin have scarcely any effect. Such a film is not removed by washing in hot H_2O or by stripping off the newly deposited Cu. C. A. S.

Determination of absolute surface area of metals. O. ERBACHER (Z. physikal. Chem., 1933, **163**, 215—230).—The method used depends on effecting an exchange of the atoms of the metal surface for those of a more noble metal under such conditions that a monat. film of the latter is deposited (cf. this vol., 468). Compared with the val. calc. by direct measurement, the surface of a metal is increased by polishing about 1·7 times, and by rubbing with emery-paper, independent of its fineness, 2·5 times. The adsorption of metal ions on more noble metals has been investigated. R. C.

Absolute determination of active surface of noble metals. O. ERBACHER (Z. physikal. Chem., 1933, **163**, 231—239).—If the noble metal is charged with H, it is only the H on the active parts of the surface which is electromotively active and can be exchanged for a metal of more positive electrode potential, forming a monat. film (cf. preceding abstract). From these considerations the active surface of Pt has been determined. The active surface of Pt rubbed with emery-paper is more than twice as great as the directly measured surface, and is about 85% of the true total surface. After polishing, the surface is 5—30 times smaller and after platinising 10—20 times greater than after treatment with emery. The active centres of polished Pt and on Pt rubbed with emery-paper are uniformly distributed over the surface. R. C.

Capillarity. XVIII. Capillary rise and its relations to angle of inclination of the wall. K. SCHULTZE (Kolloid-Z., 1933, **62**, 294—305).—The capillary rise of H_2O and of paraffin has been measured at the surface of glass plates and rods. When the rod is disposed vertically the capillary rise decreases as the diameter of the rod is decreased. When the rod or plate is inclined towards one side, the capillary rise increases on that side and decreases on the other side. E. S. H.

Capillary systems. XII (2). Calculation of material content of homogeneous filter structures. I. Sphere planes and sphere layers as structural elements of homogeneous sphere lattices. II. Building of homogeneous sphere lattices (co-ordination numbers 13—2) from sphere planes and layers and the calculation of their material content. E. MANEGOLD and W. VON ENGELHARDT (Kolloid-Z., 1933, **62**, 285—294; **63**, 12—25).—Mathematical. E. S. H.

Mechanism of the flotation process. D. TALMUD (Kolloid-Z., 1933, **62**, 335—343).—Discussion of published and new data leads to the view that the main features involved are the mechanical rigidity of the adsorption layers and the adhesion of the hydrophobic particles to one another and to the hydrophobic surface of the foam in consequence of the adsorption of surface-active substances from the H_2O. A measure of the adherence is given by the sliding velocity of the particles relatively to the surface of the foam. E. S. H.

Microscopy of flotation phenomena in reflected light. N. KING (Kolloid-Z., 1933, **62**, 343—346).—The observations show that crystallites of Ni dimethyl- and diphenyl-glyoxime collect in the liquid surface and give rise to a definite contact angle, thus establishing the conditions required by Ostwald's theory (cf. A., 1932, 333). The flotation of PbS in presence of xanthates also takes place at the liquid–gas boundary. E. S. H.

Surface tension and adhesion tension. F. J. NELLENSTEYN and N. M. RODENBURG (Chem. Weekblad, 1933, **30**, 189—191).—A general method is derived for calculating the surface tension of a solid; for glass the calc. val. is 135 dynes per cm. H. F. G.

Surface and interface activity of salts of fatty alcohol sulphuric esters. A. LOTTERMOSER and F. STOLL (Kolloid-Z., 1933, **63**, 49—61).—The surface tensions of solutions of salts of the type $C_nH_{2n+1}\cdot O\cdot SO_3M$ (n=12, 14, 16, or 18) have been determined at 20°, 40°, and 60° over a concn. range of 0—10 g. per litre. The surface tension–concn. curves show 1 or 2 minima, which are displaced in the direction of lower concn. and higher temp. as the no. of C atoms increases. The interfacial tension of some of these compounds has been measured against liquid paraffin under the same conditions. The vals. decrease with increasing no. of C atoms and vary little with temp.; the curves show no minima. E. S. H.

Surface tension measurements with non-aqueous colloidal solutions. E. W. J. MARDLES (Trans. Faraday Soc., 1933, **29**, 476—485).—Surface tension (γ) measurements have been made with a large no. of organosols at different temp. and concn. by the drop-wt. and max. bubble pressure methods. In general, colloids lower γ of the liquid when high and raise it when low, as do many crystalloids. The γ of colloids in mixed liquids depends to a large extent on the vals. in the separate solvents, but also on the sp. character of the substances used and the variation of solvent power of the liquid mixture with composition. Increased solvent action with consequent fall in colloidality cause a diminution in the γ-lowering effect. The γ of mixed colloids in single liquids con-

forms fairly closely to the mixture rule. There is no apparent correlation between frothing and γ.
M. S. B.

Investigation of thin surface films on metals by means of reflected light. L. TRONSTAD (Trans. Faraday Soc., 1933, **29**, 502—514).—The application of Drude's optical methods, using reflected polarised light, to the study of films on metallic surfaces is discussed with special reference to passivity, oxidation and atmospheric corrosion, adsorption, and unimol. films such as may be obtained with fatty acids. Its application to the study of heterogeneous catalysis, surface migration, lubrication and friction, casting of alloys, flotation of ores, etc. is suggested.
M. S. B.

Light-sensitive surface layers. III. F. WEIGERT and E. EBERIUS (Kolloid-Z., 1933, **62**, 306—310; cf. A., 1932, 460, 909).—The former experiments are amplified. By melting, so as to mix the red-sensitive layer with the rest of the photographic emulsion, the whole emulsion becomes sensitive to red.
E. S. H.

Heats of wetting of cellulose acetate by aliphatic alcohols and aromatic hydrocarbons. S. E. SHEPPARD and P. T. NEWSOME (J. Physical Chem., 1933, **37**, 389—395).—The heats of wetting of $COMe_2$-sol. cellulose acetate by H_2O, MeOH, EtOH, Pr$^{\alpha}$OH, Bu$^{\alpha}$OH, C_6H_6, PhMe, *m*-xylene, and *cyclo*hexane have been measured at 25°. The respective amounts of adsorption and capillary condensation have been deduced by comparing heats of wetting with adsorption data; pore vol. and sp. surface have also been calc.
H. J. E.

New case of membrane equilibrium. A. N. TSVETKOV (Bull. Acad. Sci. U.R.S.S., 1932, [vii], 1147—1149).—Theoretical.
T. H. P.

Osmosis in systems consisting of water and tartaric acid and containing three liquids separated by two membranes. I. F. A. H. SCHREINEMAKERS and H. H. SCHREINEMACHERS (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1241—1250).—Systems of this type have been investigated experimentally. The influence of the nature of the membrane (cellophane or pig's bladder) is stressed.
D. R. D.

Osmotic systems in which non-diffusing substances may occur also. III. Equilibria with one invariant liquid. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1235—1241).—These systems, which are of considerable biological importance (*e.g.*, the equilibrium between blood and another fluid separated by a membrane), are considered from a theoretical point of view.
D. R. D.

Ionic theory of electro-osmosis, streaming currents, and surface conductivity. J. J. BIKERMAN (Z. physikal. Chem., 1933, **163**, 378—394).—By means of Gouy's theory of the diffuse double layer, equations have been derived for the principal electrokinetic phenomena. These involve the electrokinetic potential, but not the dielectric const. or viscosity or thickness of the double layer. Helmholtz's electro-osmosis equation has been verified and the view that it conflicts with the ionic theory shown to be incorrect. The surface conductivity varies with the frequency used to measure it; equations for the conductivity for the limiting cases of high and low frequency both deviate from Smoluchowski's equation. Equations for transport nos., which are affected by electro-osmosis and ion adsorption, are deduced. Helmholtz's formula for streaming current is valid only when the aperture through which flow occurs is not too narrow. The effect of proximity to the wall on ionic mobility has been worked out; with a high electrokinetic potential at high dilution it is negligible.
R. C.

F.p. of solutions of nitrobenzene in benzene and *cyclo*hexane and their relation to the electrical polarisation. L. G. DAVY and N. V. SIDGWICK (J.C.S., 1933, 281—286).—The degree of association of $PhNO_2$ in C_6H_6 has been calc. from f.-p. data on the assumption that double mols. are formed and the vals. are compared with those derived from polarisation data. The agreement is fairly close. Polarisation data in C_6H_{12} are not available, but association should not be very different from that in C_6H_6. F.-p. data, however, indicate a val. 3—5 times as great. This behaviour is attributed to the tendency of the system to separate into two liquid layers. The results in both C_6H_6 and C_6H_{12} are not in accordance with the law of mass action, the deviation being much more marked in C_6H_{12}. It is inferred that the association is not due to the formation of definite polymerides, but to an orientation of the polar mols. under the influence of their mutual attraction.
M. S. B.

Dielectric constant of solutions of amino-acids and peptides. J. WYMAN, jun., and T. L. McMEEKIN (J. Amer. Chem. Soc., 1933, **55**, 908—914).—Data for aq. solutions of eight α-, β-, γ-, and ε-NH_2-acids and five polypeptides of glycine confirm the zwitter ion hypothesis and show that all of the mols. are rod-like and without tendency to bend or form rings. Zwitter ions predominate in EtOH–H_2O solutions of glycine.
J. G. A. G.

Dipole moments of esters of amino-acids and peptides. J. WYMAN, jun., and T. L. McMEEKIN (J. Amer. Chem. Soc., 1933, **55**, 915—922).—Dielectric consts. of C_6H_6 solutions of Et esters of ten NH_2-acids, and glycylglycine have been determined. The small vals. of the dipole moments support the hypothesis that the large dielectric consts. of aq. solutions of the free acids are due to zwitter ions.
J. G. A. G.

Electrolytes of high mol. wt. E. HEDELIUS and E. REINIUS (Biochem. Z., 1933, **258**, 181—193).—Although glucose produces the depression calc. from its mol. wt. in the f.p. of aq. solutions of electrodialysed serum- and ov-albumin, the depressions produced by strong electrolytes are much smaller than the calc. vals., the extent of the deviations varying with p_H and electrolyte concn. The combining powers of the proteins and the size of the ions produced may account for the abnormalities.
W. McC.

Cryoscopic determination of hydration of ions in solution. F. BOURION, E. ROUYER, and (MLLE.) O. HUN (Compt. rend., 1933, **196**, 1015—1017). C. A. S.

Brownian movement visible with the unaided eye. E. PODSZUS (Kolloid-Z., 1933, **62**, 347).—The movement can be observed in suspensions of finely-powdered Al (containing platelets of colloidal thickness and diameter about 1 μ) in C_6H_6, to which a little gum is added. E. S. H.

Influence of heat flow on Brownian motion. I. M. SATO (Z. Physik, 1933, **80**, 822—826).—Parallel plates heated to different temp. in a gas will appreciably influence the mean Brownian displacement in the gas only at low pressure. A. B. D. C.

Formation, size, and stability of emulsion particles. I. New method of emulsification. C. G. SUMNER (J. Physical Chem., 1933, **37**, 279—302).—Reproducible and homogeneous emulsions of C_6H_6 in H_2O were made by injecting C_6H_6 vapour into H_2O containing Na oleate as a stabilising agent, and the particle-size distribution was studied (cf. A., 1932, 139). The effects of vapour temp., cross-section of jet, pressure, and Na oleate concn. on the particle size were examined. The mechanism of the process of emulsification is discussed. H. J. E.

Aerosols, especially of ferric oxide. G. JANDER and A. WINKEL (Kolloid-Z., 1933, **63**, 5—12).—Aerosols of Fe_2O_3 have been prepared by illuminating with ultra-violet or visible light a mixture containing a small amount of $Fe(CO)_5$ vapour and a large amount of air. Ultramicroscopic observations show that the no. of particles per unit vol. decreases rapidly during the first 30 min., and afterwards very slowly. The particle concn. which can be attained increases linearly with the gas pressure. The aerosols contain charged particles of both signs and can be electrically pptd. by applying high voltages. E. S. H.

Highly-purified ferric oxide sols. H. NEURATH and W. PAULI (Z. physikal. Chem., 1933, **163**, 351—377).—Sols prepared by hydrolysis of $FeCl_3$ and purified by electrodecantation can be kept for long periods without perceptible change and have a $H^{\cdot}$ activity corresponding approx. with neutrality. The filtrate after pptn. with K_2SO_4 shows an increased p_H, due to reaction of a Fe hydroxide on the surface of the particles, $2FeO{\cdot}OH+K_2SO_4 \longrightarrow (2FeO)SO_4+2KOH$, or to reaction of an oxide with H_2SO_4 released from the salt by hydrolysis. The sols contain sufficient Cl to account for their charge and electrocratic character. As purification progresses, secondary particle formation occurs, which causes the bulk of the ionogenic surface complexes to become inaccessible. The low threshold vals. for pptn., the high mobilities of the colloid ions, and the flocculating action of $COMe_2$ show that the stability of the sols does not depend on hydration. Sorum's sols (A., 1932, 461) seem to have been imperfectly purified. R. C.

Constitution of electrically-prepared silver sols. E. EINECKE (Z. Elektrochem., 1933, **39**, 126—131).—Ag electrically dispersed in 0·0001*N*-NaOH contains Ag_2O in a proportion which decreases with increasing concn. of Ag. Reduction by Kohlschütter's method is slow and incomplete in presence of gum arabic, but can be effected readily by electrolysis at 50°. The resulting Ag_2O-free sols with 2% gum arabic are very stable, and when evaporated give a dry residue which can be dissolved unchanged. A certain proportion of unreduced Ag_2O is essential to the stability of unprotected sols. Sols prepared by electrolysis of H_2O between Ag electrodes contain chiefly Ag_2O with about 15% Ag. F. L. U.

Colloidal solutions in metals. E. PODSZUS (Kolloid-Z., 1933, **62**, 346—347).—$Th(NO_3)_4$ is added to a conc. solution of NH_4 tungstate until the content of ThO_2 is about 1·5%. The solution is acidified, dialysed, and then evaporated, the glass-like product being reduced with H_2 and ground to a fine powder. Filaments prepared from this powder by the usual means have little rigidity, but at temp. above 1200° filaments are obtained which have higher resistance and less tendency to sinter than those produced by the usual methods. E. S. H.

Osmotic pressure of solutions of cellulose nitrate. J. GRAD (Compt. rend., 1933, **196**, 773—775; cf. A., 1932, 909).—Samples of the same cellulose nitrate (mol. wt. about 50,000) autoclaved in H_2O at 130° for 0—20 hr. show a linear increase in osmotic pressure with time of heating; the viscosity decreases very rapidly at first, but after 12 hr. tends to a limit not much > that of the solvent. C. A. S.

Viscosity as a function of the particle size and sol concentration in the case of highly-polymerised substances. H. L. BREDEE and L. A. VAN BERGEN [with J. DE BOOYS] (Chem. Weekblad, 1933, **30**, 223—228).—A brief mathematical treatment is given, and the results are compared with the equations of other workers. The validity of the various formulæ is examined in connexion with published data for viscose, cellulose nitrate, gelatin, etc. Emphasis is laid on the importance of the ratio of the total vol. of dispersed particles per c.c. to the concn., expressed as the total vol. of (dry) material per c.c. H. F. G.

Theory of friction in coarsely disperse substances. G. I. POKROVSKI (Kolloid-Z., 1933, **63**, 25—27).—Experiments with sand of different particle sizes support the conclusion that the friction increases as the degree of dispersion decreases. E. S. H.

Friction of disperse systems of different plasticity. B ILJIN, T. MASSILLON, and N. ZACHAROV (Kolloid-Z., 1933, **63**, 27—34).—A pendulum viscosimeter for measuring the friction of plastic masses is described. Data are given for suspensions of $CaCO_3$ in H_2O (with and without Me-violet) and in vaseline oil (with and without oleic acid), and for suspensions of C in H_2O (with and without Me-violet). E. S. H.

Electrical properties of colloids. I. Explanation of activity and conductivity measurements in colloidal solutions. II. Specific behaviour of colloids as electrolytes. J. N. MUKHERJEE (Kolloid-Z., 1933, **62**, 257—268; **63**, 36—47).—I. A theoretical discussion based on the distribution of electric charges in primary and electrical adsorption.

The transport method of determining electrophoretic velocity is criticised and its limitations are pointed out.

II. The activity of $H^{\cdot}$ and Cl', electrophoretic velocity of the particles, and electrical conductivity in sols of $Al(OH)_3$ and $Fe(OH)_3$ cannot be explained by applying to colloid systems the ordinary theory of electrolytes. There appears to be no relation between activity and conductivity, and neither electrophoretic velocity nor equiv. conductivity increases regularly with dilution. Similar results have been observed with SiO_2 sols. The relation between conductivity and activity is further discussed. E. S. H.

Quantitative significance of viscosity and streaming-double refraction in suspensions. W. KUHN (Kolloid-Z., 1933, **62**, 269—285).—A quant. theory is developed which postulates that the individual particles are birefringent, and that the Brownian movement tends to keep them disoriented, whilst streaming motion tends to produce orientation. E. S. H.

Transverse magneto-optic anisotropy of some colloidal solutions. I. W. HELLER and H. ZOCHER (Z. physikal. Chem., 1933, **164**, 55—79).—The magnetic double refraction (I) and dichroism of V_2O_5 sols, whatever their age, are positive. This is true both for the atactosols and diluted tactosols. For normal highly-disperse monodisperse sols (I) increases linearly with the square of the field strength; deviations occur only with sols of a very low degree of dispersity. If the ζ potential is sufficiently small, natural V_2O_5 sols can be pptd. by shaking; at the same time (I) increases considerably and strong double diffraction appears. The magneto-optic behaviour of the secondary particles is qualitatively similar to that of the primary particles. The magnetic anisotropy has no detectable temp. coeff. The rates of orientation and de-orientation are practically independent of the temp. and are each proportional to 1/time. R. C.

Rate of formation of nuclei, and Ostwald's rule of transformation in stages. I. N. STRANSKI and D. TOTOMANOV (Z. physikal. Chem., 1933, **163**, 399—408).—Volmer's theory of the formation of nuclei (A., 1926, 676; 1929, 1399) accounts for the variation with temp. of the no. of nuclei in supercooled melts, and leads to Ostwald's rule relative to the formation of polymorphic modifications. Observations on the crystallisation of NaBr from aq. solution and the sublimation of HgI_2 agree with the theory. Sublimed HgI_2 contains some red crystals formed directly from the vapour. R. C.

Coagulation of strongly solvated sols by organic substances and salts. V. B. JIRGENSONS (Kolloid-Z., 1933, **63**, 78—84; cf. A., 1932, 1202).—Small amounts of $CaCl_2$ have a sensitising influence on the coagulation of albumin sols by MeOH, EtOH, and PrOH at all concns. of the alcohol. As the amount of $CaCl_2$ is increased the discontinuity observed in the pptn. curve due to the alcohol alone disappears. The minimal amount of $CaCl_2$ required for sensitisation is 0·000016 g.-mol. per litre. With K_2SO_4 the sensitivity in acid solution is $>$ in neutral solution, but the reverse behaviour is observed with NaCl, KCl, and $CaCl_2$. The general behaviour can be classified as: (*a*) discontinuities in absence of salts, (*b*) sensitisation by small and medium amounts of salts, and (*c*) stabilisation by high concns. of salts in presence of 40—60 vol.-% of the alcohol. Sensitisation is due to discharge of the particles and stabilisation is due to complex formation and solvation. E. S. H.

Effect of sugars on the inhibition of the precipitation of ceric hydroxide from a solution of ceric ammonium nitrate. M. V. NABAR and M. PRASAD (J. Indian Chem. Soc., 1932, **9**, 609—613).—The amount of sugar or glycerol required to inhibit the pptn. of $Ce(OH)_4$ decreases with increase in (1) total vol., and (2) the amount, of alkali present (up to a certain limit), but increases with $[Ce^{\cdot\cdot\cdot\cdot}]$. The order of inhibiting power is sucrose > fructose > maltose > lactose > glucose > mannitol > glycerol > glycol. E. S. H.

Influence of radiations from radioactive substances on flocculation of colloids. A. BOUTARIC and (MLLE.) M. ROY (Compt. rend., 1933, **196**, 1020—1022).—The rate of flocculation of positive sols, *e.g.*, $Fe(OH)_3$ or mastic+$AlCl_3$, is greatly increased by exposure to the radiation from Ra contained in a thin glass bulb; that of negative sols is unaffected. The effect is due to the primary β-rays. A Pt tube containing Ra is without influence. C. A. S.

Peculiar case of thixotropy. H. HOFFMANN and N. BRUCH (Cellulosechem., 1933, **14**, 53—54).—The thixotropy observed when aq. NaOH is added to a solution of cellulose in aq. $Cu(OH)_2$ and $C_2H_4(NH_2)_2$ is shown almost equally by the addition of H_2O alone. A. G.

Debye–Hückel theory and the electrokinetic potential. R. AUDUBERT (J. Chim. phys., 1933, **30**, 89—101; cf. A., 1932, 911).—In very dil. solution the changes of electrokinetic potential are in conformity with the Debye–Hückel theory. The deviations, which increase with increase of the valency of the ions, may be interpreted as a result of adsorption phenomena. Disperse systems in which the disperse medium is an extremely dil. electrolyte may be considered as electrolytic solutions. H. F. G.

Arrangement for electrophoresis. (MLLE.) CHOUCROUN (Compt. rend., 1933, **196**, 777—780).—An arrangement is described which avoids the difficulties caused by electrolysis and consequent production of H^+ and OH^- in the study of electrophoresis, and also makes it possible with a field of 100 volts per cm. to concentrate colloids without alteration, to separate mixtures of unequally charged particles, etc. C. A. S.

Variation of electrokinetic potential of silver halide colloids on dilution. A. BASIŃSKI (Rocz. Chem., 1933, **13**, 117—124).—The positive charge of colloidal particles of AgCl, AgBr, or AgI diminishes with dilution of the sol and becomes negative at high dilutions. Dilution of positively- or negatively-charged AgI sols with perimicellar fluid leads to diminution but not inversion of charge. These effects are ascribed to elution of adsorbed Ag ions and adsorption of OH' at higher dilutions. R. T.

Kohlrausch–Weber theory of the moving boundary. W. HACKER (Kolloid-Z., 1933, **63**, 47—49).—Theoretical. E. S. H.

Mechanics of gelation. E. G. RICHARDSON (Trans. Faraday Soc., 1933, **29**, 494—502).—The process of gelation has been studied in gelatin and in cellulose nitrate dissolved in $C_5H_{11}\cdot OAc$ and thinned with C_6H_6. The transition from increasing size of suspended particles, usually associated with increased η, to gelation is very sudden. The behaviour of cellulose nitrate, for which the viscosity diminishes before gelation starts, emphasises the independence of the two processes. M. S. B.

Optical absorption and gelatinisation of gelatin. J. H. DE BOER and C. J. DIPPEL [with J. F. H. CUSTERS] (Chem. Weekblad, 1933, **30**, 222—223).—The absorption of gelatin sols between 4000 and 2400 Å. is independent of concn. and of variations of p_H between 2·5 and 8·5; the degree of scattering, however, depends on both these factors. The absorption curve of the sol crosses that of the gel at about 2500 Å. Transition from the one curve to the other is not related to macroscopic gelatinisation, but is associated with change of the optical rotation and of the *X*-ray spectrum. The absorption does not alter with subsequent ageing of the gel. H. F. G.

Interferometric investigations. IV. Swelling of plane gelatin plates. P. KORNMANN (Kolloid-Z., 1933, **63**, 1—5).—The rate of increase in height of a gelatin disc swelling in H_2O, as measured by the interferometer, is interrupted by a sudden contraction at a certain stage, which coincides with a sudden increase in the rate of surface expansion. This contraction depends on the thickness of the gelatin and on its original content of H_2O, and the time of its appearance, t, is related to the thickness μ by $t=\mu^2/c$, where c is a const. depending on temp. and other conditions. The phenomenon is due to the relatively rapid swelling of the outer layer of gelatin; the interior does not swell for some time, and prevents expansion in the plane of the disc. E. S. H.

Silicic acid gels. III. Effect of the addition of some solutes on the time of set. C. B. HURD and D. H. CARVER (J. Physical Chem., 1933, **37**, 321—329; cf. A., 1932, 1202).—Aq. NH_3, NH_2Me, $NHMe_2$, NMe_3, C_5H_5N, and NH_2Ph in concns. up to 0·04*M* decrease the time of set (t) of gels prepared from aq. Na_2SiO_3 and aq. AcOH. This effect is mainly due to the increase of the p_H of the mixture; there is also a sp. effect which is greatest for NMe_3. EtOAc increases t owing to the formation of AcOH by hydrolysis. Sucrose, glycerol, and C_6H_6 are inactive. EtOH, MeCHO, and $COMe_2$ do not alter the p_H, but show a sp. effect in increasing t. H. J. E.

Rhythmic precipitation in stretched gels. A. BOUTARIC and J. RATELADE (Compt. rend., 1933, **196**, 692—693).—When a strip of cellophane or cellulose acetate impregnated with $K_2Cr_2O_7$ is maintained under longitudinal tension with one end immersed in aq. $AgNO_3$ a series of lines of Ag_2CrO_4 is formed, each consisting of minute elliptical spots. The lines are perpendicular, and the major axes of the ellipses are parallel, to the direction of tension. The distance apart of the lines increases with the distance from the solution. C. A. S.

Union of organic bases with proteins. I. II. Peptisation of caseinogen by adrenaline. G. BÜTTNER (Biochem. Z., 1933, **258**, 401—413, 414—419).—I. The dependence on p_H of the union of histamine (I) and adrenaline (II) with gelatin is investigated by the ultra-filtration method. The amount of base combined is very small at p_H 4·5, increases sharply up to p_H 6·4, and then decreases. The combination curves for (II) with gelatin and caseinogen (III) at the same p_H follow a very similar course. (I) can in part displace (II) from its protein compound.

II. (III) is peptised by free (II) and the distribution of the base between the dissolved and undissolved (III) and the intermicellar fluid has been examined. There is no simple relation between the amount of (II) combined with the peptised (III) and that remaining in the intermicellar fluid. In the peptisation with racemic (II) preferential combination with either optical isomeride does not occur. P. W. C.

Lyotropic series in swelling and its extension to organic, non-ionising substances. I. Influence of inorganic salts with different anions on the swelling of potato starch. II. Influence of thiocyanate and organic sulphur compounds on the swelling of potato starch. J. R. KATZ and F. J. F. MUSCHTER (Biochem. Z., 1933, **257**, 386—396, 397—405).—The increase of swelling of starch by H_2O on addition of inorg. salts and org. substances has been investigated. The strongest inorg. swelling agent is NaCNS, which is almost equalled by NaCNSe, but NaCNO is much less effective. Similarly, $CS(NH_2)_2$, $Me\cdot CS\cdot NH_2$, $SH\cdot CH_2\cdot CO_2Na$, and Na thiobarbiturate are all considerably more active than the corresponding O compounds, and there is little difference in swelling power whether the substances are ionised or not. The activity in these compounds is regarded as due to the C:S grouping which is adsorbed by the starch. P. W. C.

Effect of ions in lyotrope series on the swelling of organic matter. Spreading of the ions on ionised and non-ionised organic substances. III. Effect of organic halogen compounds on the swelling of starch. IV. Effect of inorganic salts, thiocyanates, and organic sulphur compounds on the shrinking of collagen. V. Effect of organic halogen compounds containing a hydrophilic group and of the length of the chain in organic compounds containing such group on the shrinking of collagen. J. R. KATZ and A. WEIDINGER (Biochem. Z., 1933, **259**, 76—84, 191—199, 223—230; cf. preceding abstract).—III. The degree of swelling (S) produced in potato starch by ionised and non-ionised org. halogen, CN, and SCN compounds varies with the halogen or other group concerned in the order I>SCN>Br>Cl>CN>H. In the case of ionised and non-ionised halogen and polyhalogen compounds S is proportional to the no. of halogen atoms. The results are parallel to

those of Frumkin (A., 1925, ii, 109). Possibly some form of chemical combination occurs.

IV. The shrinking of collagen by different ions gives the series $CNS' > I' > Br' > ClO_3' > NO_3' > Cl' > BrO_3' > F' > CN' > SO_4''$. From NO_3' to SO_4'' the action is inhibitory, but with the remaining ions it is stimulating. The ions containing the CN group form the series $CNSe'$, $CNS' > CNO' > CN'$. Org. S compounds are more active than the corresponding O compounds. Thioacetate has an abnormally large inhibitory effect. $CN{\cdot}NH_2$ has a strong stimulating effect, but MeCN is inactive. The results are parallel to those with starch and in agreement with those of Frumkin.

V. The stimulating effect, *St*, of org. halogen compounds increases with the no. of halogen atoms; both ionised and non-ionised compounds are active if sufficient halogen atoms are present, although the former are more active than the latter. *St* also increases with the at. wt. of the halogen. For salts of aliphatic and aromatic carboxylic and sulphonic acids, aliphatic alcohols and phenol, and aliphatic carbamates *St* increases with the length of the C chain. This increase is observed also with aromatic substances; these are more active than aliphatic substances with the same no. of C atoms.

W. McC.

Swelling of protein fibres. I. Swelling of collagen. (Miss) D. J. Lloyd, R. H. Marriott, and (Miss) W. B. Pleass (Trans. Faraday Soc., 1933, **29**, 554—563).—The points of resemblance and of difference between the swelling of collagen fibres and that of gelatin jellies can be accounted for by the constraint due to rings of reticular tissue around the former and by the existence of cross linkings binding their mol. chains. Data relating to the swelling of collagen and of 33% gelatin jellies in acid, alkali, and salt solutions are recorded. F. L. U.

Influence of lyotropic substances on the shrinkage temperature of collagen. J. R. Katz and A. Weidinger (Collegium, 1933, 85—88).—The shrinkage temp. (S.T.) is lowered by neutral salts in the order of the lyotropic series, being least with SO_4'', by org. compounds containing a hydrophilic group (NH_2), and by org. halogen compounds containing a halophilic group, in which case the lowering increases with the no. of halogen atoms and their at. wt. The S.T. lowering brought about by Na salts of the fatty and alkylsulphonic acids increases with the length of the hydrocarbon chain, and a greater decrease is caused by those PhOH derivatives which contain a hydrophilic group. The S.T. lowering is explained by the hydration of the collogen micelles as a result of the polar adsorption of the lyotropic substances. D. W.

Behaviour of aqueous solution of the domestic [silk] cocoon. IX. Swelling of sericin. X. Freezing of sericin solution. H. Kaneko (J. Agric. Chem. Soc. Japan, 1932, **8**, 1190—1195, 1196—1200).—IX. Sericin *A* is coagulated by $(NH_4)_2SO_4$, *B* remaining in solution. In distilled H_2O *A* swells $> B$, but *B* swells markedly in solutions of Na salts of fatty acids. In acid solution the min. point for the swelling of sericin is near the isoelectric point. The swelling of sericin in H_2O increases with rise of temp., especially at $> 50°$.

X. After melting the frozen sericin solution a part (irreversible) does not resume the colloidal state. Sericin solution from cocoons having good reelability contains much irreversible sericin (*A*, together with reversible sericin, *B*). The f.-p. depression is generally small in the solution from cocoons having good reelability. The combined H_2O is 4—7% at concns. $> 1\%$ and p_H 6·0. Ch. Abs.

Union of biocolloids. XIV. Adsorption of starch on various emulsion surfaces. Z. Horowicz. **XV. Proteins and nuclein and their degradation products.** S. J. von Przyłecki and M. Z. Grynberg (Biochem. Z., 1933, **257**, 344—350, 389—400).—XIV. Adsorption of starch by olive oil and its variation with p_H, duration of shaking, and addition of surface-active materials, adsorption of starch on liquid paraffin and amyl alcohol, the coagulation of albumin by shaking at room temp., and the effect of the addition of salts are investigated, the results are tabulated, and a theoretical explanation is attempted.

XV. At p_H 3 ovalbumin, globulin, gelatin, and caseinogen form compounds with adenylic, guanylic, and xanthylic acids and with yeast- and thymus-nucleic acids. The compounds are not decomposed by dilution or by addition of solvents, but are degraded when the p_H is increased by addition of salts. Ultra-filtration experiments show that the amount of polynucleotide combined with protein gel is much $>$ that with sol. Albumin and gelatin combine with nuclein at p_H 3 and 7, but globulin, although combining at p_H 3 and 5·9, does not combine at 7·3. The mode of combination is discussed in each case. P. W. C.

Union of biocolloids. XVI. Synthetic nucleoproteins. S. J. von Przyłecki (Biochem. Z., 1933, **258**, 79—93; cf. A., 1932, 1089).—Neutral and acid proteins (glutin, gelatin, ovalbumin, serum-albumin, globulin, caseinogen, horse-serum) combine, at $[H^·]$ below the isoelectric points, with nucleic acids (*e.g.*, yeast- and thymus-nucleic acids) yielding substances (I) which are pptd. by acid (HCl, AcOH) but are sol. in excess and in alkali. The P and N contents of (I) have been determined and their properties (effect of addition of NaCl or Na_2SO_4, $[\alpha]_D$, ratio protein : nucleic acid) studied. (I) do not resemble nucleoprotamines or nucleohistones. A system of classification for nucleoproteins is suggested.

W. McC.

Pasting of potato starch, especially by different heat treatments. E. Wiegel (Kolloid-Z., 1933, **62**, 310—324).—Microscopical observations on the formation of potato-starch paste at different temp. show that the individual grains do not cohere at a definite temp., but over a wide region in which the no. of cohering grains increases and decreases statistically. The viscosimetric and elastic behaviour of the starch paste varies considerably with the degree of swelling of the particles, which in turn depends on the thermal history of the starch. After prolonged hydrothermal treatment, either in H_2O or steam, diminution of swelling and resistance to complete

dispersion are observed. A lower rate of heating is then required for pasting to occur. The dispersion of starch in hot H_2O is the more rapid and complete, the higher is the temp. of pasting. The formation of elastic gels depends on keeping the paste at 80° after raising the temp. slowly, but a higher temp. is required when the starch has been treated previously with reagents. The viscosity curve is said to depend on the material of the viscosimeter. E. S. H.

Physical chemistry of starch and bread-making. XI. Division of starches into groups according to *X*-ray spectrum and properties of amylopectin. M. Samec and J. R. Katz [with R. Klemen] (Z. physikal. Chem., 1933, **163**, 291—311; cf. A., 1932, 338).—The differences between the starches obtained from various plants have been investigated. There is a parallelism between the type of the *X*-ray spectrum and certain properties of the amylopectin prepared from the starch. In the consistency and appearance of the amylopectin, starches giving a *C* spectrum are intermediate between those having *A* and *B* spectra. In respect of the intensity of drying required to produce a given change in the *X*-ray spectrum, starches with *A* spectra are intermediate between those with *B* and *C* spectra. In the [H·] of the amylopectin per g.-atom of P, starches with *B* and *C* spectra are similar, but differ characteristically from starches with *A* spectra (*Gramineæ* starches). R. C.

Dissolution of resins in alkali. III. Dissolution of copals, amber, and other resins in sodium hydroxide. Wo. Ostwald and W. Gamm (Kolloid-Z., 1933, **62**, 324—335; cf. B., 1933, 276).—The dissolution of a no. of resins in aq. NaOH follows the solid-phase rule. Two types of curve, connecting the degree of peptisation with the amount of the solid phase, are recognised. With the copals the solubility for a const. amount of solid phase increases steadily with increasing concn. of NaOH and does not show a max., such as is obtained with colophony. Congo copal has a max. solubility at 50°, which is > twice that at 20°. E. S. H.

Nernst's theory of association of strong electrolytes. J. Zirkler (Z. physikal. Chem., 1933, **164**, 134—137).—The mean heats of dissociation of NH_4NO_3 and $CsNO_3$ have been calc. The degrees of association calc. from conductivity data (cf. this vol., 123) agree satisfactorily with those calc. from f.-p. data, when interionic forces are taken into account. R. C.

Dissociation constant of acetic acid. A criticism. D. J. G. Ives (J.C.S., 1933, 313—314).—The disagreement between the vals. obtained by recent investigators (A., 1932, 695, 1089; this vol., 28, 125, 127) is due to an error on the part of Jeffery and Vogel in the correction for hydrolysis. D. R. D.

Dissociation of acetic acid in water. C. W. Davies and W. H. Banks (Nature, 1933, **131**, 328—329).—A discussion (cf. this vol., 125, 127). L. S. T.

Dissociation constants of acids. W. F. K. Wynne-Jones (Chem. and Ind., 1933, 273).—No conclusions can be reached regarding the variation of the dissociation consts. of a series of similar org. acids with the solvent, when the consts. differ by < a factor of 10. With acids of different types (*e.g.*, BzOH and picric acid) a difference of 10^3 is scarcely significant. E. S. H.

Electrolytic solutions. III. Dissociation constant. R. M. Fuoss and C. A. Kraus (J. Amer. Chem. Soc., 1933, **55**, 1019—1028; cf. this vol., 230, 353).—The dissociation const. of a binary electrolyte, calc. on the hypothesis of Coulomb forces, is an explicit function of the dielectric const. of the solvent and a parameter a, the "ion size." For a sp. val. of a, there is a max. val. of dielectric const., and for a given solvent, there is a max. val. of a beyond which ion-pairs of the solute are unstable. The val. of a varies with the constituent ions of the electrolyte, and for a given electrolyte, with the solvent. J. G. A. G.

Oxidation–reduction. XVIII. Simple safranines. R. D. Stiehler, T. T. Chen, and W. M. Clark (J. Amer. Chem. Soc., 1933, **55**, 891—907).—Data are recorded for five dyes in the p_H range 1·08—12·31 at 30°. Although each system is primarily reversible, after each successive addition of $Cr(OAc)_2$ to the dye, the potential–time curve has a very flat min., thus indicating the absence of true equilibrium. In the p_H range 3—7·5, the leuco-products of the dyes slowly change colour and the e.m.f. deviate considerably from vals. calc. from the characteristic consts. The relation between the "normal potential," E_0, and the concn., C, of the dye is given by $E_0 - E - A \log C$, where A is a characteristic const. and E is the observed val. It is shown spectrophotometrically that change of species of each oxidant is concomitant with change of C. J. G. A. G.

Theory of reversible two-step oxidation. B. Elema (J. Biol. Chem., 1933, **100**, 149—153).—A reply to Michaelis (A., 1932, 809). The latter's observations are essentially identical with the author's (A., 1931, 1371). A. L.

Acidic property of sugars. II. F. Urban and R. D. Williams (J. Biol. Chem., 1933, **100**, 237—241; cf. A., 1932, 231).—The amounts of base bound by glucose, fructose, sucrose, and lactose at various p_H vals. have been determined by the use of a glass electrode and the previously calc. dissociation consts. confirmed. For the first three sugars there is no evidence of a third dissociation const. below p_H 13·6. A. L.

Graphical determination of homogeneous equilibrium between three constituents. P. Montagne (Compt. rend., 1933, **196**, 928—930; cf. A., 1929, 138).—The author's graphical method is extended to the general case of dissociation, $\alpha A \rightleftharpoons \beta B + \gamma C$. C. A. S.

Desiccants, and the rate of evaporation of water. K. A. Borgen (Dansk Tidsskr. Farm., 1933, **7**, 61—71).—Beakers containing H_2O and H_2SO_4, respectively, were placed in a desiccator and the rate of evaporation of the H_2O was measured by the changes in wt. The influence of temp. and surface area was examined. H. F. H.

Vapour pressures of the heptahydrate and the saturated solution of sodium sulphite. K. Arii (Sci. Rep. Tohoku, 1932, **21**, 790—805).—The v.p. of the systems $Na_2SO_3,7H_2O$–Na_2SO_3, $Na_2SO_3,7H_2O$–saturated solution, and Na_2SO_3–saturated solution have been measured at 15—50°. The heat content and free energy changes during hydration are calc. The transition point (33·5°) agrees with previous measurements. J. W. S.

Transition point of sodium sulphite. K. Arii (Sci. Rep. Tohoku, 1932, **21**, 772—782).—Redetermination of the transition point $Na_2SO_3,7H_2O$ Na_2SO_3 by thermometric, dilatometric, and thermobalance methods gives 33·5°. J. W. S.

Dehydration of copper sulphate trihydrate. M. M. Cooper, J. Colvin, and J. Hume (Trans. Faraday Soc., 1933, **29**, 576—583).—The solid reaction $CuSO_4,3H_2O \longrightarrow CuSO_4,H_2O$ has been studied at 40—50° by a method previously described (A., 1931, 1132). The heat of activation is 15·6 kg.-cal. per mol. The observed retardation of the rate of propagation of the interface with increase in % decomp. is attributed mainly to the formation of a barrier of recryst. monohydrate which hinders the escape of H_2O vapour. The effect increases with rise of temp. F. L. U.

Solid–liquid equilibria in some two-component systems involving hydrogen cyanide. A. L. Peiker and C. C. Coffin (Canad. J. Res., 1933, **8**, 114—118).—The f.-p. curves of the systems HCN–H_2O, HCN–HCO_2H, HCN–$HCO{\cdot}NH_2$, and HCN–PhCHO are of the simple eutectic type and show no evidence of compound formation. In the systems HCN–HCl and HCN–HBr a compound is formed. E. S. H.

Fusion curves for the systems ammonia–propyl alcohols and ammonia–butyl alcohols. H. P. Cady and E. A. Jones (J. Physical Chem., 1933, **37**, 303—320).—Fusion curves for NH_3 with $Pr^{\alpha}OH$, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, $Bu^{\beta}OH$, *sec.*- and *tert.*-BuOH have been examined. In each case a compound with 1 mol. of NH_3 and 1 mol. of alcohol is formed, each compound having a congruent m.p. The *tert.*-alcohol–NH_3 compound is the most dissociated and those of the primary alcohols and NH_3 least. The structure of the compounds is discussed. *sec.*-BuOH has m.p. −114·7°. H. J. E.

System palmitic acid–sodium palmitate. P. Ekwall (Z. anorg. Chem., 1933, **210**, 337—349).—The m.-p. diagram over the range 0—75% NaPl indicates the existence of the *compounds* NaPl,2HPl and 2NaPl,HPl (Pl=$C_{15}H_{31}{\cdot}CO_2$), which possibly form mixed crystals. The *compound* NaPl,HPl separates only from supercooled melts. D. R. D.

Effect of isomerism in fusion diagrams of aromatic binary systems. A. L. Bernoulli and P. Lotter (Helv. Chim. Acta, 1933, **16**, 246—259).—Data for the f.p. of binary mixtures of $C_{10}H_8$, phenanthrene, and anthracene with each of the isomerides of $OH{\cdot}C_6H_4{\cdot}NH_2$ and of $C_6H_4(NH_2)_2$ are given. The hydrocarbons combine with the *m*- and *p*- but not with the *o*-compounds. For the 12 *m*- and *p*-compounds (B) examined, the formula of the compound formed with the hydrocarbon (A) is AB_{2n}, where n is the no. of C_6H_6 rings in A, irrespective of their arrangement. F. L. U.

System Ca_2SiO_4–Fe_2SiO_4. N. L. Bowen, J. F. Schairer, and E. Posnjak (Amer. J. Sci., 1933, [v], **25**, 273—297).—An intermediate compound $CaFeSiO_4$ (m.p. 1208±2°) forms a complete series of solid solutions with fayalite (m.p. 1205±2°). $CaFeSiO_4$ and β-Ca_2SiO_4 form a non-continuous series of solid solutions. C. W. G.

Calorimetric analysis of organic systems. I. Apparatus and applications. J. Straub and R. N. M. A. Malotaux (Rec. trav. chim., 1933, **52**, 274—288).—Heating (and, in some cases, cooling) curves are given for ice and various org. compounds and mixtures, temp. being plotted against quantity of heat supplied, instead of against time. The quantity of heat required to raise the vessel alone to each temp. can with advantage be subtracted before plotting the curve. The practical applications of this method are considered (cf. B., 1930, 109). D. R. D.

System nickel oxide–oxygen–water. M. Le Blanc and R. Müller (Z. Elektrochem., 1933, **39**, 204—209).—By the action of aq. K_2CO_3 and Br in aq. KBr on aq. $NiCl_2$, an unstable black ppt. of variable composition, NiO,xO,yH_2O, where x may be as high as 0·9, is obtained. The extra O liberates I from HI and is evolved on treatment with acid or heating in vac. at 360°. The peroxide has no definite dissociation pressure of O_2 or H_2O, and no crystal structure can be detected by the *X*-ray method. D. R. D.

Liquidus and solidus studies. III. Ternary system $Ba(NO_3)_2$–$Ca(NO_3)_2$–KNO_3. K. Laybourn and W. M. Madgin (J.C.S., 1933, 236—240).—The mixture of lowest m.p. is the binary eutectic of KNO_3 and $Ca(NO_3)_2$, there being no ternary eutectic. It is probable that $Ca(NO_3)_2$ and $Ba(NO_3)_2$ form a continuous series of solid solutions, although direct investigation of the binary system is impossible, since the components decompose below their m.p. D. R. D.

Equilibrium of the system sodium sulphite–sodium pyrosulphite–water. K. Arii (Sci. Rep. Tohoku, 1932, **21**, 783—789).—Measurements at 25° and at 35° afford no evidence of the formation of double salts or solid solutions. J. W. S.

Polymorphism. V. Ternary systems α- and β-monochloroacetic acid–phenol–naphthalene. E. Mameli and A. Mannessier-Mameli (Gazzetta, 1933, **63**, 12—16; cf. A., 1923, i, 555).—The behaviour of the two forms of $CH_2Cl{\cdot}CO_2H$ in the ternary systems is analogous to that in the binary systems previously described. They form no additive compounds, and the ternary eutectic temp. are 8·8° and 6·8° for the α- and β-forms, respectively. O. J. W.

System cellulose–copper hydroxide–ethylenediamine. H. Hoffmann and N. Bruch (Cellulosechem., 1933, **14**, 50—53).—1 mol. of $Cu(OH)_2$ is dissolved by 2 mols. of aq. $C_2H_4(NH_2)_2$. Partition experiments show that an equilibrium is probable between Cu $en(OH)_2$, Cu $en_2(OH)_2$, and Cu $en_3(OH)_2$.

The [α] of cellulose in such a solution is approx. independent of its concn., but increases with increasing concn. of Cu. Probably an equilibrium exists between two cellulose compounds with widely different rotations. A. G.

Determination of distribution in gel reactions. K. HESS and O. SCHWARZKOPF (Z. physikal. Chem., 1933, **163**, 395—398).—Champetier's attempts to represent the composition of the solid phase in the systems cellulose–NaOH–H_2O and cellulose–neutral salt–H_2O in terms of definite stoicheiometric ratios (A., 1932, 1022) is condemned on the ground that in such systems the superimposition of surface reactions on vol. reactions renders such a procedure inadmissible. R. C.

Field of saturation of potassium and sodium chloride in quinary sea-salt systems. D. LANGAUER (Rocz. Chem., 1933, **13**, 105—116).—The equilibrium relations in the system NaCl–KCl–$MgCl_2$–$MgSO_4$–H_2O are discussed. R. T.

Heat capacity and related thermodynamic properties of aqueous solutions. II. Lithium and sodium hydroxides at 25°. F. T. GUCKER, jun., and K. H. SCHMINKE (J. Amer. Chem. Soc., 1933, **55**, 1013—1019; cf. A., 1932, 696).—Sp. heat data are recorded for 0·04—2·5*M* aq. solutions. The apparent molal heat capacity of the solute bears a linear relation to $\sqrt{}$molality. Partial mol. heat capacities of solute and solvent have been evaluated. J. G. A. G.

Heat of dilution and partial molal heat capacity of zinc sulphate from the e.m.f. of galvanic cells. V. K. LAMER and I. A. COWPERTHWAITE (J. Amer. Chem. Soc., 1933, **55**, 1004—1013).—From existing e.m.f. data (A., 1932, 126), the change of free energy and the heat content of the reaction Zn (*s*, sat. with Hg)+$PbSO_4$ (*s*)=$ZnSO_4$ (*m*)+Pb (*s*, sat. with Hg) at 298·1° abs. are 18,951 and 34,380 g.-cal., respectively. Failure to include effects due to thermal expansion leads to serious errors in the calculation of partial molal heat capacities. Integral heats of dilution of $ZnSO_4$ are calc. J. G. A. G.

Heat capacity and entropy of calcium oxalate from 19° to 300° abs. Entropy and free energy of oxalate ion. W. M. LATIMER, P. W. SCHUTZ, and J. F. G. HICKS, jun. (J. Amer. Chem. Soc., 1933, **55**, 971—975).—The data refer to CaC_2O_4,H_2O for which the entropy at 298·1° is calc. to be 37·28 E.U. The entropy and free energy of formation of C_2O_4'' are 9·3 E.U. and −158,000 g.-cal., respectively. J. G. A. G.

Thermodynamic properties of fused salt solutions. VII. Zinc bromide in lead bromide. E. J. SALSTROM (J. Amer. Chem. Soc., 1933, **55**, 1029—1036).—The e.m.f. of the cell $Zn(l)|ZnBr_2(l)|Br_2(g)$ at 500° is 1·2702 volt, from which the free energy of the reaction $Pb+ZnBr_2=PbBr_2+Zn$ is 10,990 g.-cal. at 500°. From the e.m.f. of the cell $Pb(l)|PbBr_2(l)|ZnBr_2(l)|Br_2(g)$ at 390—530° with mol. fractions of $PbBr_2$ between 1·0 and 0·2, activities, activity coeffs., free energies of formation, and partial mol. free energies of $PbBr_2$ and $ZnBr_2$ are calc. The positive deviation from Raoult's law is discussed. J. G. A. G.

Effect of ethylene glycol on the activity of sulphuric acid in aqueous solutions [at 25°]. H. M. TRIMBLE and P. F. EBERT (J. Amer. Chem. Soc., 1933, **55**, 958—968).—The activity of H_2SO_4, calc. from the e.m.f., *E*, of the cell $H_2|0·005—1·0M$-H_2SO_4+0·0—10*M*-glycol$|Hg_2SO_4$, Hg, for which *E* is a linear function of the log. mol. fraction of the H_2SO_4, increases regularly with the concn. of glycol. J. G. A. G.

Free energy of iron oxides. J. CHIPMAN and D. W. MURPHY (Ind. Eng. Chem., 1933, **25**, 319—327).—The equilibria in reactions occurring in molten steel, particularly on deoxidation, are difficult to determine directly, and more satisfactory results are given by extrapolation or by other indirect methods. If the free energies of reacting compounds are known, equilibrium consts. are readily obtained. Average vals. for the heat capacity of Fe in its various modifications and for Fe_3O_4 are calc. from published results. Vals. for FeO are deduced on the basis of Kopp's rule. The free energy of FeO is deduced from the equilibrium consts. of the reactions $FeO+H_2=Fe+H_2O$ and $FeO+CO=Fe+CO_2$. All energy data are referred to β-Fe (=δ-Fe) for simplification. An approx. val. is deduced for the heat of fusion of FeO and the free energy of FeO in liquid Fe deduced from its solubility. The free energy of Fe_3O_4 is calc. from the third law of thermodynamics and the reaction $4FeO=Fe_3O_4+Fe$, close agreement in results being obtained. For Fe_2O_3 no trustworthy equilibrium data are available and thermal data involve a doubtful extrapolation to high temp. Results are tabulated and compared with previously recorded data. C. I.

Heat of formation of silicon carbide. O. RUFF and P. GRIEGER (Z. anorg. Chem., 1933, **211**, 145—149; cf. A., 1907, ii, 738).—Errors in previous work are pointed out. The heat of formation of SiC from α-graphite and cryst. Si is 26·7±2·1 kg.-cal. H. J. E.

Thermochemical constants of the hexafluorides of sulphur, selenium, and tellurium. D. M. YOST and W. H. CLAUSSEN (J. Amer. Chem. Soc., 1933, **55**, 885—891; cf. A., 1932, 905).—Heats of formation of the gases are: SF_6 262 kg.-cal., SeF_6 246, and TeF_6 315. SeF_6 reacts with NH_3 slowly at 200° and more rapidly at 330°, forming Se, N_2, and HF. The inertness of the hexafluorides towards reducing agents is not attributable to a lack of thermodynamic tendency to react. Lower fluorides of Se and Te have been obtained. J. G. A. G.

Perylene and its derivatives. XXXVIII. Heats of combustion of perylene derivatives. A. PONGRATZ, F. GRIENGL, and J. CECELSKY (Monatsh., 1933, **62**, 71—77; cf. A., 1929, 1387).—The relations between the heats of combustion (which are determined) of some perylene derivatives and related substances are examined. J. L. D.

Transport numbers in mixed aqueous solutions of alkali chlorides. I. Theoretical. P. VAN RYSSELBERGHE. **II. Transport numbers of the potassium, the rubidium, and the cæsium ions in concentrated solutions of sodium chloride, and of the potassium ion in concentrated solutions of lithium chloride.** P. VAN RYSSELBERGHE

and L. NUTTING (J. Amer. Chem. Soc., 1933, **55**, 990—996, 996—1001).—I. Existing transport data for mixtures of alkali chlorides are consistent with the hypothesis that the mobilities of the various ions are proportional to their vals. in solutions of the separate salts which are of the same concn. as the total concn. of the mixture. The MacInnes formula (A., 1925, ii, 872), which follows from this hypothesis, has an unrestricted range of validity for these cases.

II. The data, which refer to 25° and total concns. up to 5*M*, are consistent with the MacInnes formula for the transport no. of one of the two metallic ions in a mixture of alkali chlorides. These chlorides are dissociated to the same extent in all the mixtures investigated. J. G. A. G.

Transport numbers in membranes. Measurements by means of electromotive force. S. OKA (J. Soc. Chem. Ind. Japan, 1933, **36**, 65—66B).—The transport no. of KCl in various membranes has been calc. from the e.m.f. of the following cells: (1) Hg|HgCl, 0·1*N*-KCl|membrane|0·01*N*-KCl, HgCl|Hg, and (2) a similar cell with K amalgam in place of the membrane. $n_K=E_1/E_2$. The vals. calc. thus agree well with those deduced from the e.m.f. of cells of the type (3) Hg|HgCl, KCl(sat.)|0·1*N*-KCl|membrane|0·01*N*-KCl|KCl(sat.), HgCl|Hg, for which $E_3=(2n_K-1)(RT/F)\log_e a_1/a_2=(1-2n_{Cl})(RT/F)\log_e a_1/a_2$, where a_1 and a_2 are the activity coeffs. of KCl in 0·1 and 0·01*N*-KCl, respectively. True vals. are obtained only when the solutions are streamed rapidly through the apparatus. The vals. obtained bear little or no relation to the electrokinetic potential of the membrane. D. R. D.

Transport numbers in membranes. S. OKA (J. Soc. Chem. Ind. Japan, 1933, **36**, 66—67B).—The transport nos. of KCl, HCl, KOH, $CaCl_2$, and K_2SO_4 in various membranes (paper, collodion, gelatin, and cellophane) have been determined by the second method described in the preceding abstract. The transport no. of the anion is always lowered by the membrane, except in the case of amphoteric membranes (chromated gelatin, collodion impregnated with hæmoglobin). For membranes of similar material, the depression is greatest for the membrane of least permeability to H_2O. D. R. D.

Conductivity of alkylammonium picrates in aqueous solution at 0°, 25°, and 90°. II. P. EKWALL (Z. physikal. Chem., 1933, **163**, 442—460; cf. A., 1932, 1092).—The conductivity data are, on the whole, in good agreement with the Debye–Huckel–Onsager theory. The mobilities of the alkylammonium ions in aq. solution have been calc. Stokes' law is valid for migration of some of these ions, but for NH_4^+ and the methylammonium ions the temp. coeff. of the mobility is smaller than that of the fluidity of H_2O, whilst for $NH_2Pr_2^+$, $NHPr_3^+$, and NPr_4^+ it is greater. This latter type of deviation is ascribed to the open structure of the ions. R. C.

Conductivity measurements in nitro-compounds. I. Conductivity measurements in nitromethane. II. Conductivity measurements in nitrobenzene. III. Behaviour of electrolytes in nitro-compounds. P. WALDEN and E. J. BIRR (Z. physikal. Chem., 1933, **163**, 263—280. 281—290, 321—339).—I. Conductivity measurements have been made at 25° with various org. and inorg. salts at dilutions up to 20,000 litres. The viscosity of $MeNO_2$ has been measured at 0—50°.

II. Conductivity measurements have been made at 25° with solutions of org. salts at dilutions up to 50,000 litres. Measurements with solutions of some amines and hydrazines show that with these $PhNO_2$ forms very weak electrolytes.

III. $PhNO_2$ and $MeNO_2$ are differentiating solvents which show differences in the strength of dissolved salts. For the alkali and halogen ions the strength of the salts increases with the at. wt. Ionic mobilities, and from them ionic solvations, have been calc. For alkali and halogen ions the degree of solvation decreases with increasing at. wt. A review of conductivity data for various solvents shows that the Debye–Hückel theory of strong electrolytes is valid only for solvents of high dielectric const. and electrolytes with large ions. The sp. influence of solvent on solute, which becomes apparent with differentiating solvents, is largely determined by chemical considerations, and cannot be covered by the consts. of the Debye–Hückel–Onsager equation. R. C.

Electrical resistance of palladium wires charged with hydrogen between 160° and 310°. H. BRÜNING and A. SIEVERTS (Z. physikal. Chem., 1933, **163**, 409—441).—The resistance of Pd–H alloys has been measured during isothermal changes of H_2 pressure, *P*, at 160—310°, and the amount of H taken up has been determined at 200—310°. The resistance is measured by the ratio (*Q*) of the resistance of the wires charged with H to the resistance of the H-free wire at the same temp. Below 300°, the *C*–*P*, *Q*–*P*, and *C*–*Q* isotherms (*C*=concn. of H in Pd) all have a middle portion which is more or less horizontal, and is considered to correspond with the presence of two solid phases in equilibrium, $PdH_\alpha+\frac{1}{2}(\beta-\alpha)H_2\rightleftharpoons PdH_\beta$. The hydrogenation and dehydrogenation isotherms coincide only over those portions which correspond with the presence of a single solid phase; over the middle parts of the isotherms there is hysteresis, probably due to internal strains occasioned by the vol. change involved in the α–β transformation. The fact that the middle parts of the isotherms are not perfectly horizontal is attributed to imperfect establishment of equilibrium. When two solid phases are present the resistance is additively constituted of their separate resistances. The ends of the horizontal parts of the isotherms are much more sharply defined on the *Q*–*P* and *C*–*Q* diagrams than on the *C*–*P* diagram. There is no reason for supposing that the β phase is Pd_2H. Above about 300° the flat portions of the isotherms and the hysteresis disappear, and there is then no difference between the α and β phases. R. C.

Electrical conductivity and diffusion in solid silver sulphide, selenide, and telluride. Mechanism of the formation of these compounds from their elements. C. TUBANDT, H. REINHOLD, and (FRL.) A. L. NEUMANN (Z. Elektrochem., 1933, **39**. 227—244).—Pure solid α-Ag_2S, -Ag_2Se, and -Ag_2Te conduct electrolytically, the conductivity being

abnormally high, although the diffusion coeffs., D, are of the same order as those of other solid electrolytic conductors. If excess of Ag is present, some metallic conduction occurs, whilst if free S or Se is present the conductivity is lowered. The β-forms are metallic conductors. $D=13{\cdot}37e^{-1470/T}$ for α-Ag_2Se, $3{\cdot}33e^{-1330/T}$ for α-Ag_2Te, $5{\cdot}19\times10^{-4}$ cm.^{2} per day for β-Ag_2Se at 107°, and $6{\cdot}86\times10^{-4}$ cm.^{2} per day for β-Ag_2Te at 107°. When α-Ag_2X (where X=S, Se, or Te) is formed in the solid state from its elements, the Ag becomes covered with a film of Ag_2X. Further formation of Ag_2X occurs by diffusion of Ag through the Ag_2X to X, and not by diffusion of X. It is suggested that Ag^+ and electrons move through the Ag_2X, and combine with X when they reach the X phase, forming Ag_2X. The excess X left in the Ag_2X layer then combines with Ag at the surface of the metallic Ag phase. D. R. D.

Conductivity of binary or ternary partly miscible liquid mixtures with one very weak electrolytic component. M. Pestemer and O. Platten (Monatsh., 1933, **62**, 152—159).—Conductivities of the two layers have been measured for PhOH–H_2O, PhOH–aq. HCl (0·001—0·1N), PhOH–0·1N aq. NaOH, NH_2Ph–H_2O, and NH_2Ph–20% aq. sucrose. On interdispersion of the two layers by stirring, the conductivity is approx. additive. The effect of the addition of cresol was also examined. H. J. E.

Shape of the electro-capillary curve of mercury in capillary-inactive electrolytes. R. M. Joshi (Indian J. Physics, 1932, **7**, 427—430).—The electro-capillary curve of Hg in contact with N-$NaNO_3$ does not agree with the Lippmann–Helmholtz theory. W. R. A.

Boundary layer and diffusion potential of dilute electrolytes. S. T. Chang (Ann. Physik, 1933, [v], **16**, 513—529).—The change in diffusion potential with time at the contact surfaces, 0·01N-KCl|N-HCl, 0·01N-LiCl|N-HCl, 0·1N-LiCl|N-HCl, and N-KCl|N-HCl have been investigated. The effect of disturbing the boundary layer has also been examined. The results show that the Planck stationary state is established after the disturbance. W. R. A.

Application of Gronwall, La Mer, and Sandved's extension of Debye's theorem to solutions of cupric sulphate. (Mlle.) Quintin (Compt. rend., 1933, **196**, 767—769).—When applied to the cell Cu (amalgam two phases)|$CuSO_4(C)$|Hg_2SO_4(sol.)|Hg a const. val. is obtained for the at. radius, a, only when $C < 0{\cdot}01N$. This is probably due to a being different for the two ions. C. A. S.

Glass electrode determination of the dissociation constant of hypochlorous acid. H. T. S. Britton and E. N. Dodd (Trans. Faraday Soc., 1933, **29**, 537—538).—Potentiometric titrations with NaOH, using a glass electrode, are reproducible, and give $K=3{\cdot}2\times10^{-8}$ at 15°. F. L. U.

Rôle of finely-divided mercury in the depolariser of the standard cell. R. B. Elliott and G. A. Hulett (J. Physical Chem., 1933, **37**, 271—277).—Cells with very finely-divided Hg have a low e.m.f., due to the effect of increased solubility of the finely-divided Hg on the reaction $Hg^{++}+Hg=Hg_2^{++}$. With time, as the globules of Hg grow, the e.m.f. increases to a normal val. H. J. E.

Theory of simultaneous discharge of several ionic species at the same electrode. O. Essin (Z. physikal. Chem., 1933, **164**, 87—96).—Theoretical relations are derived which agree with published experimental data. R. C.

Mechanism of exchange of metal atoms for more noble ions. O. Erbacher (Z. physikal. Chem., 1933, **163**, 196—214).—If the exchange which occurs when a metal is brought in contact with a solution containing more noble ions depends solely on the difference in electrode potential of the two elements, the film of more noble metal deposited is monat. On the surface of the less noble metal, however, the solubility at active points is not the same as it is elsewhere (A., 1915, ii, 156; 1929, 759), and if the e.m.f. corresponding with the resulting local action is > the discharge voltage, E, of the more noble ion it assists in the separation of the latter and a deposit many atoms thick results. By preliminary treatment of the metal with the solvent, the e.m.f. of this local action can be depressed below E, in which case only a monat. deposit is formed. R. C.

Electrocrystallisation of metals. II. V. A. Kistiakovski and P. D. Dankov (Bull. Acad. Sci. U.S.S.R., 1932, [vii], 993—996).—Preliminary addition of colloidal Cu does not modify the structure of the Cu ppts. obtained by electrolytic pptn. Hence electrocrystallisation of Cu does not proceed with intermediate formation of colloidal particles of the same type as those of ordinary colloidal Cu sols (cf. A., 1930, 1381). T. H. P.

Hydrogen over-voltage and structure of double layer. A. Frumkin (Z. physikal. Chem., 1933, **164**, 121—133).—Taking into account the potential distribution in the double layer, Erdey-Gruz and Volmer's theory of over-voltage (A., 1930, 1376) leads to the relation $\zeta=(2RT/F)\log_e[H^+]-(2RT/F)\log_e i$ +const. between the discharge voltage, ϕ, and the current strength, i. Heyrovsky's theory (A., 1927, 1145) gives a similar relation, but with $(2RT/F)\log_e i$ replaced by $(RT/F)\log_e i$. Since these equations reduce to $\phi+\zeta$=const. for const. $[H^+]$ and i, it has been possible to calculate ζ from data for the effect of neutral salts on H over-voltage. The vals. obtained agree fairly well with those calc. by Stern's theory for certain concns. of HCl. R. C.

Anodic behaviour of cobalt. K. Georgi (Z. Elektrochem., 1933, **39**, 209—219).—The influence of c.d., p_H, temp., time, and dissolved O_2 on the p.d. of a Co anode in aq. $CCl_3{\cdot}CO_2H$, HCl HBr, $HClO_4$, H_2SO_4, H_3PO_4, AcOH, and their Na salts, is closely analogous to that observed in the case of Ni (A., 1932, 1000, 1093). D. R. D.

Results of the kinetic investigation of passivity phenomena. W. J. Muller (Angew. Chem., 1933, **46**, 197—198).—A lecture, summarising the laws of growth of the protective anodic film. E. S. H.

Types of chemical reactions. W. A. Noyes (J. Amer. Chem. Soc., 1933, **55**, 656—661).—A survey. J. G. A. G.

Reaction velocities. K. POSTHUMUS (Rec. trav. chim., 1933, **52**, 241—250).—A mathematical treatment of the theory of activated mols. D. R. D.

Combination of hydrogen and oxygen in a silver vessel. C. N. HINSHELWOOD, E. A. MOELWYN-HUGHES, and A. C. ROLFE (Proc. Roy. Soc., 1933, **A**, **139**, 521—525).—The explosion phenomenon shown by H_2–O_2 mixtures in vessels of porcelain or SiO_2 from about 450° upward, if the pressure lies between certain limits, is not observed in Ag vessels (A., 1928, 483, 960). Reaction chains are not developed in the gas, and it is concluded that the active species which would normally propagate the chains are destroyed at the Ag–Ag_2O surface. L. L. B.

Combustion of hydrocarbons. W. A. BONE (J. Roy. Soc. Arts, 1933, **81**, 550—571).—A lecture.

Effect of an electric field on the flame temperature of combustible gas mixtures. B. LEWIS and C. D. KREUTZ (J. Amer. Chem. Soc., 1933, **55**, 934—938; cf. A., 1932, 808).—An electric field applied transversely across a flame of Pittsburgh natural gas, C_2H_4, *iso*butane, and butylene in air reduces the flame temp. The effect is greatest for low gas velocities and mixtures containing excess of air. Whilst the high-temp. flame of CS_2 is deflected toward the negative electrode by an electric field, the low-temp. flame is not affected. J. G. A. G.

Determination and calculation of the flame temperatures of complex mixtures of combustible gases. B. LEWIS, H. SEAMAN, and G. W. JONES.—See B., 1933, 291.

Coil ignition of some explosive gaseous mixtures. B. W. BRADFORD, G. I. FINCH, and (MISS) A. M. PRIOR (J.C.S., 1933, 227—232).—Determination of the igniting power (I) of induction coil sparks toward explosive gaseous mixtures, varying the amount of energy associated with the inductance component of the spark, shows that (I) is associated with the whole of the discharge, and not only the capacity component. Variations in primary capacity at const. primary current have little effect on (I), but progressive suppression of the inductance component decreases (I). In the ignition of relatively insensitive mixtures ($2CO+O_2$+5% H_2; $2H_2+O_2$) the inductance component, particularly its first oscillation, is more effective than the capacity component. With CH_4+2O_2 mixtures, the (I) of the inductance component is relatively less. J. S. A.

Sulphur–hydrogen reaction. E. E. AYNSLEY, T. G. PEARSON, and P. L. ROBINSON (Nature, 1933, **131**, 471—472).—N_2 increases the velocity of the gaseous reaction between H_2 and S. No heterogeneous reaction on the glass walls of the vessel could be detected, but such a reaction confined to the surface of S and proportional to its area has been observed (cf. J.C.S., 1923, **123**, 696). L. S. T.

Reaction regions. XXIII. Prevention of explosive reactions in gas and vapour mixtures by small amounts of various substances. II. W. P. JORISSEN and J. J. HERMANS (Rec. trav. chim., 1933, **52**, 271—274).—The following substances have a pronounced inhibitive action on the explosion of CH_4–air mixtures, increasing approx. in the order indicated: $Bu^{\beta}Br < Bu^{\alpha}Br < iso\text{-}C_5H_{11}Cl < Pr^{\beta}I < Pr^{\alpha}Br$ (I) $< iso\text{-}C_5H_{11}Br$ (II). 1·5 vol.-% of (II) is sufficient to prevent explosion of all CH_4–air mixtures, but owing to its high v.p. inhibition is most readily effected by means of (I). D. R. D.

Kinetics of the unimolecular dissociation of gaseous ethyl bromide. E. L. VERNON and F. DANIELS (J. Amer. Chem. Soc., 1933, **55**, 922—934; cf. A., 1932, 1002).—The dissociation of gaseous EtBr into C_2H_4 and HBr is a homogeneous reaction at pressures between 12 and 364 mm. in the range 395—420°, and is accompanied by a bimol. recombination. The unimol. velocity coeff., $k=3{\cdot}85\times 10^{14}e^{-54,800/RT}$, decreases at pressures below 100 mm. and at lower pressures the reaction becomes of second order. O_2 accelerates the reaction. The data are consistent with the theory that the energy of activation of a unimol. reaction must be localised in a particular degree of freedom, or a particular linking, before the mol. will disrupt. J. G. A. G.

Velocity of reaction between potassium dichromate and potassium iodide in absence of acids. A. SCONZO (Gazzetta, 1933, **63**, 58—69).—When $K_2Cr_2O_7$ and KI are mixed in aq. solution the reaction is $2K_2Cr_2O_7+2KI=3K_2CrO_4+CrO_2+I_2$. $CrO_2,2H_2O$ is gradually deposited as a yellowish-brown powder. K_2CrO_4 has no action on KI. The velocity of the reaction between $K_2Cr_2O_7$ and KI is of the first order and at every instant is proportional to the [H·] resulting from hydrolysis of $K_2Cr_2O_7$. O. J. W.

Velocity of reaction between chromic acid and potassium iodide. A. SCONZO (Gazzetta, 1933, **63**, 70—75; cf. preceding abstract).—The velocity of reaction between $H_2Cr_2O_7$ and KI in aq. solution is proportional to the [H·]. O. J. W.

Mechanism of the ferricyanide–iodide reaction. A. VON KISS [with I. BOSSANYI] (Rec. trav. chim., 1933, **52**, 289—297).—The velocity of the reaction $2Fe(CN)_6'''+2I'=2Fe(CN)_6''''+I_2$ in presence of S_2O_3'' has been studied at 25°. The S_2O_3'' reduces the I to I′ so long as any S_2O_3'' remains, the time required for the formation of a blue colour with starch being thus an indication of the velocity of the first reaction, which is unimol. with respect to $Fe(CN)_6'''$ and bimol. with respect to I′. The reaction is accelerated by H·. D. R. D.

Kinetics of the reaction between iodine and ferrous salts. A. BERTHOUD and S. V. ALLMEN (J. Chim. phys., 1933, **30**, 102—129).—Previous views are discussed. The rate of the reaction between $FeSO_4$ and I in presence of H_2SO_4 and of KF (to remove as K_3FeF_6 the Fe''' formed) has been studied. At high KI concns. a unimol. velocity coeff. is obtained, but at lower KI concns. the reaction tends to become semimol., and, finally, unimol. again. KF accelerates the reaction. The velocity coeff. is approx. proportional to the $FeSO_4$ concn. and inversely proportional to the [H·]. At high KI concns. KCl and KBr have little influence, but at lower KI concns. they cause considerable acceleration. The

temp. coeff. of the reaction velocity is about 3 (20—30°), and is independent of the KI concn. H. F. G.

Diffusion of hydrogen peroxide in various solvents. K. G. STERN (Ber., 1933, **66**, [*B*], 547—554).—The rate of diffusion of H_2O_2 (I) in H_2O, EtOH, MeOH, $COMe_2$, and Et_2O, with and without stabilisers (II) [mainly $CO(NH_2)_2$ and NHPhAc] has been measured at 0—40° according to the method of Northrop and Anson (A., 1929, 587). Complex formation does not appear to occur between (I) and (II). (I) diffuses in relatively dil. solution more slowly than other substances of similar, true mol. wt., probably on account of association. Above 5°, the rate of diffusion has a normal temp. coeff., but increases below 5°, thus possibly accounting for the simple mol. wt. found by determining the f.p. of solutions in H_2O. *M* in various solvents is calc. according to Euler, Herzog, and Sutherland. H. W.

Velocities of reduction of ceric and perceric salts by sugars. G. LEJEUNE (Compt. rend., 1933, **196**, 772—773; cf. A., 1930, 1520).—The rates of reduction by various sugars of a solution containing $CeO^{\cdots\cdot}$ and of one containing a perceric salt (I), determined electrometrically, are similar save that that of (I) is somewhat more rapid. The similarity is attributed to equality of degree of ionisation. C. A. S.

Kinetics of reactions in solutions. Interaction of potassium hydroxide and the alkyl halides in ethyl alcohol. G. H. GRANT and C. N. HINSHELWOOD (J.C.S., 1933, 258—261).—Some reactions in solution take place at the theoretical rate, no. of mols. reacting=no. of mols. colliding$\times e^{-E/RT}$. Others are many powers of ten slower. Reactions of the former class appear almost invariably to involve an ion. The reaction between KOH and alkyl halides belongs to this group, and is governed by OH′. J. S. A.

Velocity of decomposition of diazo-compounds in water. X. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1933, **36**, 59—64B; cf. this vol., 233).—Data are given for many aromatic diazonium chlorides concerning the velocity of decomp. and of hydrolysis to phenols at various temp. D. R. D.

Velocities and heats of hydrolysis of the amides. II. E. CALVET (J. Chim. phys., 1933, **30**, 140—166; cf. A., 1929, 1389).—The heat of the reaction NH_2Ac $(3N)$+NaOH (N)=NaOAc,$3H_2O$ (solid)+NH_3 $(0{\cdot}8N)$ is $11{\cdot}2\times10^3$ g.-cal. The heat of dissolution of NH_2Ac is $2{\cdot}05\times10^3$ g.-cal., and the heat of hydrolysis of cryst. NH_2Ac by H_2O (liquid) is $3{\cdot}0\times10^3$ g.-cal. The velocity coeff. of the hydrolysis at 0° is 0·0139, and the temp. coeff. of the velocity (0—17°) is 2·57. The heat change on hydrolysis in solution in 200 mols. H_2O, and the velocity coeff. of the reaction are given also for $HCO{\cdot}NH_2$, $EtCO{\cdot}NH_2$, $PrCO{\cdot}NH_2$, valeramide, hexamide, NH_2Bz, and mono-, di-, and tri-chloroacetamide. H. F. G.

Constitutional factors controlling prototropic changes in carbonyl compounds. IV. Carbethoxyl and allied groups. H. B. WATSON and E. D. YATES (J.C.S., 1933, 220—223).—The velocity of bromination of $AcCO_2Et$ (I) with Br in 0·5*M*-solution in 75% AcOH at 25° when (I) is in excess, at first decreases (due to initial basic catalysis, since addition of a small amount of mineral acid prevents the initial period of higher velocity) and then becomes const., and is independent of [Br]. In agreement with the $-I$ effect of the CO_2Et group which decreases the tendency of carbonyl O to co-ordinate $H^{\oplus}$, the reaction is but weakly catalysed even by high concn. of HCl. Similar bromination of $CH_2Ac{\cdot}CO_2Et$ is very rapid and is catalysed by HCl (no HCl, v=240; *M*-HCl, v=5180, the respective vals. of v for $COMe_2$ being 0·90 and 134), but no basic catalysis is detectable, whereas bromination of $CO(CH_2{\cdot}CO_2Et)_2$ is so rapid (corresponding vals. of v=2480 and 4380±10%) that it can be measured only by a flow method. These results and earlier ones dealing with the bromination of acid bromides (A., 1927, 1168; 1928, 716) are discussed on an electronic basis. J. W. B.

Thermal decomposition and detonation of mercury fulminate. W. E. GARNER and H. R. HAILES (Proc. Roy. Soc., 1933, **A**, **139**, 576—595).—The conditions controlling the beginning of detonation of single crystals of $Hg(CNO)_2$ (I) at 100—150° have been investigated. The thermal decomp. below the ignition temp. occurs in three stages: (1) a quiescent period, with slight browning of the crystal; (2) a period of acceleration of the reaction, for which log $(dp/dt-dp_0/dt)=kt$+const. holds; and (3) a region where the equation for reactions of the first order holds. Stages (2) and (3) also occur in the decomp. of crushed and ground (I) and in that of Pb styphnate. The results are interpreted as due to the beginning of thermal decomp. in the Smekal cracks of the (I) crystal and the spread of the reaction to crystallites isolated by the destruction of the cementing material. Detonation, which occurs during the second stage of the reaction, probably arises within the crystal on the surfaces of the Smekal cracks. The heat of detonation is 113 kg.-cal. and the crit. increment about 30 kg.-cal. L. L. B.

Thermal decomposition of lead styphnate. H. R. HAILES (Trans. Faraday Soc., 1933, **29**, 544—549).—The velocity of decomp. of Pb styphnate above 200° follows the same law as does that of crushed and ground Hg fulminate (cf. preceding abstract). A branching chain mechanism accounts for the reaction during the period of acceleration. Detonation occurs above 225°. F. L. U.

Phenomena associated with detonation of explosives. T. URBANSKI (Rocz. Chem., 1933, **13**, 130—139).—Mixtures of NH_4NO_3 with $C_6H_2Me(NO_2)_3$ or with glyceryl nitrate yield on detonation in glass tubes spirally propagated explosion flames. The velocity of propagation of the flame varies at different parts of the tube at the same distance from the origin. These effects are ascribed to asymmetrical action of the detonator, and to heterogeneity of the medium. A thin layer of explosive in contact with the walls of the tube may explode after the central mass, or may even remain intact after the explosion. R. T.

Measurement of the rate of adsorption at constant pressure. P. V. McKINNEY (J. Physical

Chem., 1933, **37**, 381—387).—An apparatus for measuring the rate of adsorption of H_2 on a MnO–Cr_2O_3 catalyst at const. pressure is described. Greater and more rapid adsorption occurs than in experiments at const. vol. The effect on the adsorption of alternately treating the surface with H_2 and evacuating is described. The significance of these results in the calculation of activation energies is discussed. H. J. E.

Catalysed decomposition of nitroamide. IV. Nitroamide catalysis in *iso*amyl alcohol solution. J. N. Brønsted and J. E. Vance (Z. physikal. Chem., 1933, **163**, 240—256; cf. A., 1931, 1134).—In *iso*-C_5H_{11}·OH solution at 20° $H_2N_2O_2 \longrightarrow H_2O + N_2O$ is a basic catalysis, the catalytic action being ascribable to the base mols., not the anion base corresponding with the solvent as acid. The velocity coeff., k_1, is related to the strength of the base, K_B, by $k_1 = G_2 K_B^{1-x}$. The catalytic action, G_2, of base mols. with a single negative charge is about 1000 times > that of electrically neutral bases having in H_2O the same strength, and positively-charged bases are still more active. Strong acids have a small catalytic effect. R. C.

Hydrogen sulphate ion catalysis in the hydrolysis of esters. H. M. Dawson, E. R. Pycock, and E. Spivey (J.C.S., 1933, 291—296).—Measurement of the rate of hydrolysis of EtOAc in presence of H_2SO_4, $NaHSO_4$, $H_2SO_4 + NaHSO_4$, and $NaHSO_4 + Na_2SO_4$ shows that HSO_4' possesses considerable catalytic activity. Observed velocities are given by the expression $v = k_h[H^·] + k_a[HSO_4']$: no measurable effect due to undissociated H_2SO_4 is observable, consistent with practically complete first-stage dissociation. For the second-stage dissociation const. of H_2SO_4 in salt-free solutions, the val. $K_2 = 1{\cdot}0 \times 10^{-2}$ is calc. from the kinetic data. J. S. A.

Poisoning of a nickel catalyst by thiophen. G. Roberti (Gazzetta, 1933, **63**, 46—49).—In the poisoning by C_4H_4S of a Ni catalyst for the hydrogenation of C_6H_6 to C_6H_{12}, the extent of poisoning is a function of the partial pressure of C_4H_4S in the gaseous phase and, within certain limits, is independent of the amount of C_4H_4S passed over the catalyst. Different parts of the catalyst surface are poisoned to different extents. O. J. W.

Activation of oxides by foreign oxides. R. Schenck and H. Roters (Z. anorg. Chem., 1933, **211**, 65—82; cf. A., 1932, 819).—Addition of Al_2O_3 to MnO promotes the reduction of CO_2 to CO at 725°. Al_2O_3 and ZrO_2 promote the oxidation of CO to CO_2 by CeO_2 at 700°; TiO_2 has a smaller effect, and ThO_2, La_2O_3, and MgO are inactive. The active added oxide lowers the O_2 dissociation pressure in the system MnO–Mn_2O_3–Mn_3O_4 and raises it for the system CeO_2–Ce_2O_3. H. J. E.

Catalysts for synthesis of aliphatic alcohols. M. Strada.—See B., 1933, 259.

[Catalytic] hydrogenation of cresols and dihydric phenols. C. M. Cawley.—See B., 1933, 260.

Catalytic reduction of aromatic nitro-compounds. S. J. Green.—See B., 1933, 260.

Catalytic effect of alkali hydroxide on alcoholysis and hydrolysis of fats. G. K. Rowe.—See B., 1933, 274.

Influence of the conditions of preparation on the activity of a nickel–manganese–aluminium catalyst. E. Fischer and K. Meyer.—See B., 1933, 305.

[Catalytic] action of water vapour on methane. G. Matignon and M. Séon.—See B., 1933, 291.

Platinised silica gel as an oxidation catalyst in gas analysis. I. Oxidation of hydrogen and carbon monoxide. K. A. Kobe and E. J. Arveson (Ind. Eng. Chem. [Anal.], 1933, **5**, 110—112).—Reaction of H_2 with O_2 is quant. at 100° in presence of commercial platinised SiO_2 gel. H_2–CO mixtures can be oxidised completely by O_2 at 300°, but at 100° CO acts as a catalyst poison. Hydrogen may be determined in a mixture with hydrocarbons by fractional combustion with O_2 in presence of the catalyst at 100°; the gases are passed 4—6 times at the rate of 30—50 c.c. per min. E. S. H.

Velocity of catalysed hydrogenations. III. A. Kailan and O. Stüber (Monatsh., 1933, **62**, 90—100; cf. A., 1931, 1376; 1932, 347).—In the hydrogenation of oleic acid at 180° with Ni as catalyst on different substrata, the efficiency of the latter is in the following order: kieselguhr > Al_2O_3 > CeO_2 > talc, animal- and limewood-C. As active metals Ni and Co are equally effective, Fe is less so, and Cu less so than Fe. No addition of H was observed with Zn, Pb, Ag, Sb, UO_2, Mg, Ca, or Hg. With a 20% Ni–SiO_2 catalyst the velocity coeff. is doubled for a rise of 20° between 100° and 180°. Velocity measurements have also been made with Et oleate, ricinoleic acid, $C_{10}H_8$, anthracene, cymene, $PhNO_2$, and NH_2Ph. F. L. U.

Anodic formation of peroxides. J. M. Gallart (Anal. Fís. Quím., 1932, **30**, 922—943).—Electrolysis of H_2SO_4, HNO_3, H_3PO_4, and $HClO_4$ yields, in addition to the recognised per-acids, yet more active compounds similar to those formed by the action of F on the solutions (A., 1927, 741). Favourable conditions for the formation of these products have been investigated, using a Pt electrode for measuring the oxidation potential of the solutions, and their constitution and mode of decomp. by per-acids or by H_2O are discussed. R. K. C.

Electrolysis of molten alkali cyanides. M. Centnerszwer and J. Szper (Bull. Acad. Polonaise, 1932, **A**, 267—270).—The electrolysis of molten NaCN has been studied in Pyrex glass vessels and with anodes of Ni, Cu, Fe, Al, and C, the highest efficiency being attained with the two last. The Na liberated floats on the surface of the metal, forming no metallic fog, whilst the $(CN)_2$ can be efficiently recovered by passage through solutions of NaOH and Na_2CO_3. KCN behaves similarly, except that the Pyrex glass is attacked. J. W. S.

Electrolysis of silver-bearing thiosulphate solutions. K. Hickman, W. Weyerts, and O. E. Goehler.—See B., 1933, 313.

Metals and alloys. VI. Formation of negative ions by elements. E. ZINTL and H. KAISER (Z. anorg. Chem., 1933, **211**, 113—131; cf. A., 1932, 455).—On electrolysis of alkali halides or NEt_4I in liquid NH_3 with cathodes of Pb, Tl, Sn, and Ge, only Pb gave evidence of anion formation, yielding coloured solutions near the cathode containing polyplumbides [*e.g.*, Na_4Pb_9]. K_4Sn_9 was formed on adding Sn to a solution of KNH_2 in liquid NH_3. Pb gave a similar result, but Ge did not react. A Na–Ge alloy extracted with liquid NH_3 formed a brown solution containing Ge in the anion. Na–Ga, Na–In, Cs–Ga, and Cs–In alloys gave negative results. The position in the periodic table of elements forming negative ions is discussed. Lattice consts. were measured for the fluorite structures Mg_nPb (*a* 6·836 Å.), Mg_2Sn (*a* 6·765 Å.), and Mg_nGe (*a* 6·378 Å.). H. J. E.

Electrochemistry of rhenium. II. Electrochemical reduction products in solutions containing chloride and fluoride ions, and the chemical formation of lower valency stages in sulphuric acid solution. H. HOLEMANN (Z. anorg. Chem., 1933, **211**, 195—203; cf. A., 1932, 236).—No H_2ReCl_6 was formed on electrolysis of $KReO_4$ in HCl solution. The cryst. compound with 2-hydroxyquinoline may be used to test for $ReCl_4''$ in presence of $KReO_4$. Electrolysis of $KReO_4$ with NH_4F or HF gave good yields of almost pure Re. Electrolysis of K_2ReCl_6 with a Hg cathode gave Re amalgam. The formation of coloured H_2SO_4 solutions of lower valency Re compounds is described. H. J. E.

Short-circuit electrolysis. I. Electrolytic decomposition of a liquid layer hanging freely between rotating cylindrical electrodes. E. MANEGOLD and R. HOFMANN (Z. Elektrochem., 1933, **39**, 244—251).—With the apparatus described, a liquid can be electrolysed with the electrodes only 1 mm. apart, and the cathodic and anodic products collected separately. The quant. side of the problem is considered mathematically. Data are given for aq. NaCl, Na_2SO_4, $NaNO_3$, NaOH, and HCl. D. R. D.

Electrodeposition of metals on cathodes covered by insulating layers. C. MARIE and N. THON.—See B., 1933, 271.

Electrolysis of molten beryllium–copper alloy with 10% beryllium. L. LAMMERMAYR (Monatsh., 1933, **62**, 67—70; cf. A., 1930, 1510).—At 1050° with a c.d. of 6 amp. per sq. mm., Be migrates to the cathode, Cu to the anode. F. L. U.

Anode process in the lead accumulator. E. H. RIESENFELD and H. SASS (Z. Elektrochem., 1933, **39**, 219—227).—Measurements of $[H_2SO_4]$ and *X*-ray examination of the plates indicate that during the discharge of the Pb accumulator a basic sulphate, $PbO_x(SO_4)_{1-x}$, is formed at the anode, and not $PbSO_4$ as is commonly supposed. On recharging, alternate addition of SO_4 and hydrolysis produce successively $Pb_3O_{3x}(SO_4)_{4-3x}$, Pb_3O_4, $Pb_3O_4SO_4$, Pb_3O_5, $Pb_3O_5SO_4$, and PbO_2. The process is reversed on discharging. Sulphation is due to the conversion of the basic sulphate into $PbSO_4$ by the action of H_2SO_4. D. R. D.

Electrodeposition of alloys. I. Nickel–cobalt alloys. S. A. PLETENEV and V. V. KUSNEZOVA (Z. Elektrochem., 1933, **39**, 201—204).—The electrodeposition of Co–Ni alloys from acid solutions of $NiSO_4$ and $CoSO_4$ in which Ni : Co = 15 : 1 has been studied. The influence of p_H (kept const. during electrolysis by addition of H_2SO_4 or NH_3), temp., c.d., velocity of rotation of cathode, and agitation by means of a stream of air on the composition of the deposit and the % of the total Co deposited has been investigated. Under the optimum conditions (Ni 80, Co 5·33 g. per litre, c.d. 100 amp. per sq. m., p_H 3·5, *t* 20°, 2000 r.p.m.) 90% of the Co is deposited as a 41% alloy in 26 hr. D. R. D.

Electrolysis of aluminium–tin alloys containing iron, as an example of the electrolytic purification of molten aluminium from iron. R. KREMANN and L. LAMMERMAYR (Monatsh., 1933, **62**, 61—66; cf. following abstract).—Electrolytic migration of Fe in Al–Sn alloys containing about 1% Fe decreases steadily as the proportion of Al increases. It is concluded that purification of Al by this method would not be possible. F. L. U.

Electrolysis of molten binary alloys of aluminium, and solubility of iron in molten aluminium at different temperatures. R. KREMANN, E. I. SCHWARZ, and S. LE BEAU (Monatsh., 1933, **62**, 47—60; cf. A., 1930, 1510).—Data are given for the linear distribution of the components in Al–Cu and Al–Sn alloys when electrolysed at various c.d. Dissolution of the Fe electrodes is partly anodic and partly independent of the passage of current. It is very slight below 700°. F. L. U.

Photochemical kinetics. R. WEGSCHEIDER (Monatsh., 1933, **62**, 101—112; cf. A., 1929, 776).—Theoretical. Formulæ for photochemical changes are derived, in which the absorption due to all substances present is taken into account. F. L. U.

Photo-sensitised decomposition of ozone by chlorine. R. G. W. NORRISH and G. H. J. NEVILLE (Nature, 1933, **131**, 544—545).—With pressures of O_3 and $Cl_2 > 100$ mm. and light of 365 mμ, a red liquid oxide of Cl [ratio Cl : O in agreement with $(ClO_3)_n$] is formed. Separation is marked at 0°, but decomp. occurs with a rise in temp.; temp. coeff. 2·4 per 10°. Heidt and co-workers' (this vol., 237) dark reaction is explicable in terms of the separation of this oxide. L. S. T.

Autoxidation of stannous chloride. III. The photochemical reaction. R. C. HARING and J. H. WALTON (J. Physical Chem., 1933, **37**, 375—380; cf. this vol., 232).—Aq. $SnCl_2$ (32 g. per litre: 0·8*N* in HCl) absorbs continuously below 3000 Å. The absorption does not obey Beer's law. This is attributed to the complexes $HSnCl_3$ and H_2SnCl_4, which are the active agents in absorbing light. The photochemical oxidation has a quantum yield of 10—30. Picric acid inhibits, and various other substances accelerate, both the thermal and photo-reactions, for which a chain mechanism is suggested. H. J. E.

Photochemistry of hydrogen sulphide. N. O. STEIN (Trans. Faraday Soc., 1933, **29**, 583—591; cf. A., 1931, 1109).—When H_2S is decomposed by ultra-

violet light S is formed in the gaseous phase. The quantum yield increases from 2 mols. of H_2 at >250 mm. to 3·8 at 1350 mm. The mechanism of the primary reaction is discussed. F. L. U.

Photochemistry of phosphine. H. W. MELVILLE (Proc. Roy. Soc., 1933, **A**, **139**, 541—557).—The absorption spectrum of PH_3, photographed at room temp., is found to be of the pre-dissociation type, and similar to that of NH_3. The photo-decomp. of PH_3 by light from Zn and Al sparks has been investigated. PH_3 is dissociated into PH_2 and H, which diffuse to the walls and undergo secondary reactions [$PH_2+PH_2=P_2$ (red P)$+2H_2$, $H+H=H_2$, and $PH_2+H=PH_3$] such that the net quantum yield (γ) is about 0·5 in a 2-cm. tube. The reaction PH_2+H is slightly favoured by increase of surface and by an increase in the no. of H atoms adsorbed on the walls. Temp. up to 300° have little effect. On adding O_2 to PH_3 and illuminating, a stable chain reaction occurs. With pressures of $PH_3=O_2=0·05$ mm., $\gamma=200$. The probability of branching at any one cycle is <1 in 200. L. L. B.

Fog formation [in photographic emulsions] by chemical reactions. E. FUCHS (Z. wiss. Phot., 1933, **32**, 63—64).—Contrary to Luppo-Cramer (A., 1932, 479) $CuSO_4$ causes some fogging, even in total darkness, if the treatment is short (*e.g.*, 1—2 sec. in 3% solution); this action is greatly increased by exposure to red light. Longer treatment causes desensitisation, and no fog appears, even in red light; this may partly be due to oxidation of the fog nuclei. Previous work (Phot. Ind., 1931, 993, 1140) is upheld. J. L.

Photochemical chlorination of methane. C. PADOVANI and F. MAGALDI.—See this vol., 370.

Photochemical polymerisation of methylacetylene and allene. S. C. LIND and R. LIVINGSTON (J. Amer. Chem. Soc., 1933, **55**, 1036—1047).—Allene, CH:CMe, and isoprene are converted into white polymerides in the complete radiation of the hot Hg arc. The quantum efficiencies of the first two reactions are 2·5 and 3·5, respectively, and are independent of pressure and intensity of the absorbed light. The absorption spectra of allene and CH·CMe, in contrast to C_2H_2, are continuous and have no band structure. J. G. A. G.

Interaction of ethyl alcohol and oxygen photosensitised by hydrogen peroxide. Haber–Willstatter mechanism of enzyme reactions. H. S. TAYLOR and A. J. GOULD (J. Physical Chem., 1933, **37**, 367—374).—Direct oxidation of EtOH by O_2 occurs on illumination with a quartz–Hg arc. The action is autocatalytic, which is attributed to accumulation of H_2O_2. Addition of H_2O_2 to the EtOH photosensitises the reaction, for which a chain mechanism with short chains involving the OH radical is suggested. The photo-oxidation of MeCHO is a reaction with longer chains. The effect of inhibitors was examined. H. J. E.

Photochemical transformation of *o*-nitrobenzaldehyde. II. R. WEGSCHEIDER (Monatsh., 1933, **62**, 113—118; cf. A., 1929, 895).—The results obtained by Weigert and Brodmann (A., 1925, ii, 1075) are more satisfactorily explained by partial inactivation of activated mols. through collisions of the second kind, than by assuming a change in photochemical efficiency due to orientation of the mols. F. L. U.

Photo-change of *N*-chloroacetanilide in various solvents. F. W. HODGES (J.C.S., 1933, 240—246).—In addition to *p*-chloroacetanilide, acetanilide, diacetylhydrazobenzene, and chlorinated solvent may be formed. In solvents containing H, the quantum efficiency was very high, interaction with the solvent giving rise to reaction chains. In CCl_4, the quantum efficiency is 5—6. In $CHCl_3$, C_6H_6, PhCl, and PhBr the temp. coeff. (24—34°) was 1·34—1·39; in CCl_4, *cyclo*hexane, and decalin, zero; in PhMe, apparently negative. Little relation between reaction velocity and the physical properties of the solvents is apparent; in related solvents, velocity diminishes with increasing dielectric const. J. S. A.

Decomposition of cyclic nitrogen compounds by light from the quartz lamp. F. LIEBEN and V. GETREUER (Biochem. Z., 1933, **259**, 1—7; cf. A., 1931, 1251).—In one group (all members of which have OH or CO in the ring; uric acid, xanthine, uracil, alloxan, hydantoin, α-hydroxynicotinic acid) very little or no NH_3 is eliminated, but the opening of the ring caused by the irradiation results in production of NH_2 groups. In another group of the cyclic nitrogenous compounds (histidine, proline, glyoxaline, guanine, C_5H_5N, nicotinic acid) the NH_3 eliminated on irradiation comes exclusively from the ring, no free NH_2 being produced. Na thymonucleate resists decomp. by the light, and the small amount of NH_3 eliminated is derived from NH_2 groups originally present. W. McC.

Action of ultrasonic waves on photographic plates. N. MARINESCO and J. J. TRILLAT (Compt. rend., 1933, **196**, 858—860; cf. this vol., 224).—Exposure of plates or paper to such waves in H_2O before development or in the developer causes increased blackening, and formation of a slight veil even on an unexposed plate. There is also some colloidal dispersion of the sensitive layer. C. A. S.

Effect of ultrasonic waves on chemical processes. H. BEUTHE (Z. physikal. Chem., 1933, **163**, 161—171).—Reactions in aq. solution initiated by these waves are due to H_2O_2 formed from dissolved O_2 by some secondary action of the waves. The formation of HNO_2 and NH_3 from dissolved N_2 is recorded. R. C.

Acceleration of the decomposition of crystals of barium azide by the emission from radium emanation. W. E. GARNER and C. H. MOON (Nature, 1933, **131**, 513).—Anhyd. cryst. BaN_6 decomposes above 100° giving N_2. After an induction period the reaction spreads from nuclei of Ba formed on the surface of and in the crystal. The period of induction is shortened and the rate of nuclei formation increased about three times by exposure to radon. L. S. T.

Solid polyiodides of the alkali metals. N. S. GRACE (J. Physical Chem., 1933, **37**, 347—360; cf. A., 1931, 580).—RbI_3, CsI_3, and CsI_4 are the only true binary polyiodides of the alkali metals formed

at 25° and 1 atm.; others reported have been shown to contain combined solvent. The ternary compounds $2CsI_9,3C_6H_6$, $RbI_9,2C_6H_6$, $RbI_7,2C_6H_6$, and $KI_9,3C_6H_6$ have been isolated from the system I–alkali iodide–C_6H_6. Na and Li form no solid polyiodides, unsolvated or solvated with H_2O or C_6H_6 at 25°, but there is evidence of polyiodides solvated with H_2O below 25°. H. J. E.

Chloro-complex salts of univalent copper. H. Remy and G. Laves (Ber., 1933, **66**, [*B*], 571—576; cf. this vol., 360).—The following *compounds* are prepared from their components in the mol. proportion shown in parentheses, the dry salts being brought under EtOH–HCl (A) or H_2O–HCl (B) in an atm. of CO_2. All are very sensitive to air. $[NH_3Me][CuCl_3]$ (A, 1 : 1), m.p. 87—90° (indef.); $[NH_3Me]_2[CuCl_3]$ (A or B, 1 : 2 or 1 : 3), m.p. 89—90°; $[NH_2Me_2][Cu_2Cl_3]$ (A or B, 1 : 1), m.p. 129—130° (decomp.); $[NH_2Me_2][CuCl_2]$ (A, 1 : 2 or 1 : 3), m.p. about 80—87° after blackening; $[NHMe_3][Cu_2Cl_3]$ (A, 1 : 1), m.p. about 145° after softening and darkening at 100°; $[NHMe_3]_2[CuCl_3]$ (A, 1 : 2 or 1 : 3); $[NMe_4][Cu_2Cl_3]$ (A, 1 : 1), m.p. 230° (decomp.) after darkening at 200°. H. W.

Cupric and cadmium ammines. M. Aumeras and A. Tamisier (Bull. Soc. chim., 1933, [iv], **53**, 97—113).—It has been shown spectrophotometrically that $Cu^{\cdot\cdot}$ forms a complex ion in solution by combining with 4 mols. of NH_2Me, C_5H_5N, and $C_5H_4N{\cdot}C_5H_{10}N$, thus following the general rule for cupriammines. The dissociation consts. are, respectively, $1{\cdot}6\times10^{-8}$, $3{\cdot}1\times10^{-4}$, and $2{\cdot}2\times10^{-3}$, and comparison with the data for other cupriammines shows that the stability diminishes with increasing mol. wt. and substitution. Quinoline, although containing the C_5H_5N nucleus, does not form the same type of complex, probably owing to the presence of the C_6H_6 nucleus; instead, a solid of composition $2Cu(NO_3)_2,3C_9H_7N$ separates. With allylamine the complex $Cu(CH_2{\cdot}CH{\cdot}CH_2{\cdot}NH_2)_4^{\cdot\cdot}$ is formed in solution. When left in the dark for 3 months a slight ppt. of $CuO,4H_2O$ was obtained and the liquid became fluorescent, probably due to condensation of the allylamine. The cadmiammonium ion was investigated by the partition method. The composition is $Cd(NH_3)_4^{\cdot\cdot}$. The dissociation const., $1{\cdot}1\times10^{-7}$, is in good agreement with that usually accepted. The solid salt obtained with $CdSO_4$, $CdSO_4(NH_3)_4,2H_2O$, is much less stable than the corresponding Cu compound ($+10H_2O$) when examined by the method of loss in wt. with increasing temp. Both compounds lose H_2O more rapidly than NH_3. M. S. B.

Silver ferrites. VII. Structure and quantitative separation of aged ferric hydroxide. A. Krause and H. Torno (Z. anorg. Chem., 1933, **211**, 98—112; cf. A., 1932, 1216).—Orthoferric hydroxide ages to form hydrohæmatite at concns. of NaOH or KOH $< 0{\cdot}01N$ or $> 3{\cdot}5N$. Concns. between 0·01 and $3{\cdot}5N$ favour the ageing to goethite. The various stages of the ageing may be followed by analysis by the Ag ferrite method and by the solubility in cold 32·5% HNO_3. H. J. E.

Amphoteric behaviour of metal hydroxides. I. Magnesium pyrocatechol hydroxy-salts. R. Scholder and E. Schletz (Z. anorg. Chem., 1933, **211**, 161—172).—A series of *salts* of the type $[Mg(C_6H_4O_2)_n]Na_m$ (n=2, 3, or 4) was prepared by adding NaOH to aq. $MgCl_2$ and *o*-$C_6H_4(OH)_2$ at 0°. From solutions with 1 mol. or less of $C_6H_4O_2$ per mol. of Mg, salts of the type $[Mg(C_6H_4O_2)_x(OH)_y]Na_2$ were obtained. They decomposed readily, forming $Mg(OH)_2$. These OH-salts illustrate the weak amphoteric character of $Mg(OH)_2$, and support the classification of Mg with Be and Zn. H. J. E.

Magnesium chlorite and double chlorites of copper with magnesium, barium, and thallium. G. R. Levi and D. Ghiron (Atti R. Accad. Lincei, 1932, [vi], **16**, 632—636; cf. A., 1923, ii, 492).—The following *compounds* have been prepared: $Mg(ClO_2)_2,6H_2O$, colourless rhombohedral pseudocubic crystals, d 1·62, a 7·36 Å., c/a 2·45; $2Cu(ClO_2)_2,Mg(ClO_2)_2,8H_2O$, yellowish-brown transparent prisms; $Cu(ClO_2)_2,Ba(ClO_2)_2,4H_2O$, yellowish-green fluorescent crystals; $Cu(ClO_2)_2,TlClO_2,2H_2O$, a pinkish-brown powder. The double salts are more stable than $Cu(ClO_2)_2$. O. J. W.

Reactions between calcium oxide and carbon dioxide and between calcium oxide and sulphur dioxide. J. Zawadzki and S. Bretsznajder (Bull. Acad. Polonaise, 1932, **A**, 271—286).—The initial process in the reaction between CaO and CO_2 is the adsorption of the gas on the surface, in which the mols. move freely and finally combine at active spots. At higher CO_2 pressures nuclei are formed, especially at the active spots, and the velocity of growth of the nuclei governs the velocity of absorption of CO_2. Similar relations hold for the decomp. at very low pressures. Abs. rates of absorption depend on the no. of nuclei and the condition of the surface of the CaO. The behaviour with SO_2 is rather similar and eventually follows approx. the equation $4CaO+6SO_2=4CaSO_4+S_2$. J. W. S.

Hexa-aquo salts of bivalent metals. P. Pfeiffer, S. von Müllenheim, and K. Quehl (J. pr. Chem., 1933, [ii], **136**, 249—256).—The following *salts* of the type $[MX_6]Y_2$ are described: (*a*) X=H_2O, Y=naphthalene-2-sulphonic acid, and M=Hg and UO_2; (*b*) X=H_2O, Y=*d*-camphor-β-sulphonic acid, and M=Cd, Ni and Cu ($+H_2O$); (*c*) X=H_2O, Y=*d*-α-bromocamphor-π-sulphonic acid, and M=Cd, Ni, and Cu; (*d*) X=NH_3, Y=naphthalene-2-sulphonic acid, and M=UO_2; (*e*) X=ethylenediamine, Y=*d*-camphor-β-sulphonic acid, and M=Cd and Ni (both $+H_2O$). The following *salts* are also prepared: $[Hg(NH)_4]$ dinaphthalene-2-sulphonate; $Cu(OH_2)_2$ en_2 di-*d*-camphor-β-sulphonate and di-*d*-α-bromocamphor-π-sulphonate, the latter $+H_2O$. R. S. C.

Large-scale production of radium compounds. E. A. Kolbe (Chem.-Ztg., 1933, **57**, 213—214).—A brief historical account, dealing particularly with the work of Kroupa. H. F. G.

Preparation of boron and its compounds with nitrogen and carbon. E. Podszus (Z. anorg. Chem., 1933, **211**, 41—48).—The prep. of BN by heating B_2O_3 in NH_3 at 1000—2000°, and the formation of B carbide from BN and C are described. The com-

position of the " carbide " varied from B_6C to B_3C, the hardness increasing with the C content. Pure B was prepared by heating Fe in BCl_3 vapour. The resistance of B has a small negative temp. coeft. (cf. Warth, Trans. Amer. Electrochem. Soc., 1925, **47**, 62; Kahlenberg, A., 1925, ii, 425). H. J. E.

Neodymium free from iron and silicon. F. TROMBE (Compt. rend., 1933, **196**, 704—706).—Pure $NdCl_3$ is prepared by heating the crude chloride for 24 hr. at 800° in HCl; a mixture of $NdCl_3$ 60, KCl 35, and CaF_2 (pptd.) 5% is electrolysed at 1040—1060° with a current of 9—10 amp. per sq. cm. in the arrangement used for Ce (cf. A., 1931, 1253). Yields of 7, 12, and 40% were obtained with voltages of 8, 10, and 16, respectively, but the higher voltages introduced K into the Nd, removable by heating in vac. at 1200°. If prepared in a SiO_2 crucible the Nd contains 0·6% Si, but if in a fluorite one (cf. B., 1931, 720) < 0·05% Si with 0·02% Fe and a trace of Ca; d_4^{15} 6·94, Brinell hardness 60. C. A. S.

Preparation of compounds of carbon and nitrogen with metallic elements. A. PERRET.—See B., 1933, 305.

Influence of impurities on properties of lead. I. Introduction. J. N. GREENWOOD. **II. (A) Purification of lead by electrolysis. (B) Comparison of the crystallisation of commercial and electrolytic leads. (C) Photomicrography of lead.** R. S. RUSSELL.—See B., 1933, 309.

Mechanism of precipitation processes. XI. Precipitation of $PbCl_2$ or $Pb(CNS)_2$ with Na_2S and of $PbCl_2$ or $PbBr_2$ with NaOH. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1933, **211**, 16—20; cf. A., 1932, 584).—Pptn. of aq. $PbCl_2$ or $Pb(CNS)_2$ with aq. Na_2S yields Pb_2Cl_2S or $Pb_2(CNS)_2S$ as a secondary product; the amount decreases on keeping and is smaller in more acid solution. Aq. $PbCl_2$ or $PbBr_2$ with aq. NaOH forms PbCl·OH (I) or PbBr·OH (II). (I) is less stable than (II), whilst compounds of the type Pb_2X_2S are less stable than (I) or (II). H. J. E.

Dimetaphosphates. P. PASCAL and (MME.) RÉCHID (Compt. rend., 1933, **196**, 828—830).—To prepare dimetaphosphoric acid, H_3PO_4, is heated at about 320° until crystals (of an insol. polymeride) just appear. The melt is dissolved in H_2O at 0°; at higher temp. $H_4P_2O_7$ is formed. On adding the calc. amount of NaOH a neutral solution is obtained whence $Na_2(PO_3)_2,3H_2O$ is pptd. by excess of EtOH as an oil which rapidly crystallises. It is very sol. in H_2O, and cannot be dehydrated, passing when heated into $Na_2H_2P_2O_7$, and then into Maddrell's insol. salt. The fresh solution at 0° gives a Zn salt sol. in excess of Na salt, and no ppt. with a neutral luteocobaltic salt; when acidified with AcOH it does not ppt. albumin. Cryoscopic determination of the mol. wt. gives 76 for $N/32$ and 130 for $N/10$; equiv. conductivity at 20·5°: λ_{1024} 75, and λ_{32} 55, λ_{1024} for $Na_6(PO_3)_6$ being 142, and for $Na_3(PO_3)_3$ 117. Maddrell's salt is not a dimetaphosphate (cf. A., 1924, ii, 476). C. A. S.

Metaphosphoric acids. (MME.) RÉCHID (Compt. rend., 1933, **196**, 860—861; cf. preceding abstract).—The " insol. polymeride " appears after 20, 1, and 0·5 hr. at 218°, 320°, and 355°, respectively; it gives a definite *X*-ray spectrum, is insol. in H_2O or hot dil. HNO_3, is hydrolysed in boiling aq. NaOH, and unchanged at 800°. The dimetaphosphoric acid (I) at 400° forms a transparent polymeride, which on further heating gradually passes into forms dissolving very slowly in H_2O, with steady increase in mol. wt., *e.g.*, the acid formed in 4 hr. at 600° gives a Na salt of mol. wt. 358. These highly-polymerised acids all ppt. albumin and are uncrystallisable, but volatile, the vapour condensing to (I). Prolonged heating converts them irreversibly into the " insol. polymeride." Ordinary P_2O_5 containing little of the insol. form gives an aq. solution containing much (I); it is only such P_2O_5 that gives on hydration $H_4P_2O_7$ before passing into H_3PO_4. C. A. S.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. XVI. Vanadates and polyvanadates crystallised from solutions of different hydrogen-ion concentrations. G. JANDER and K. F. JAHR (Z. anorg. Chem., 1933, **211**, 49—61; cf. A., 1932, 1204).—Vanadates of Na, Mg, Ca, Sr, and Ba, prepared in acid solution, were of the general type $nM^I_2O,5V_2O_5$,aq. (n=3 or 4). The Na and Mg salts formed mixed crystals. In more acid solutions Ba forms a (3 : 4)- and a (2 : 3)-vanadate. All of the salts are considered as derivatives of pentavanadic acid. H. J. E.

Oxidation of hydrogen sulphide solutions by air. M. KAPP.—See B., 1933, 306.

Sulphur monoxide. I. P. W. SCHENK (Z. anorg. Chem., 1933, **211**, 150—159).—SO has been prepared as an orange-red solid by cooling the gases from an a.-c. discharge at low pressure through streaming S vapour+SO_2. Above −80° it decomposes into S+SO_2. With C_2H_4, S is deposited; Cl_2 yields SCl_2 and SCl_4. The solid behaves as the anhydride of $H_2S_2O_3$. The gases passing from the discharge gave absorption bands between 2700 and 3200 Å., which were attributed to SO. H. J. E.

Preparation and properties of pentathionic acid and its salts; its toxicity to fungi, bacteria, and insects. O. N. LIMING (Phytopath., 1933, **23**, 155—174).—Ba, Na, and K pentathionates (95—98% pure) were prepared by a modification of Raschig's method. $H_2S_5O_6$ prepared from the Ba salt contained small amounts of tri- and tetra-thionic acids. Dil. aq. $H_2S_5O_6$ decomposes only very slowly on keeping. A suspension of hydrophilic colloidal S prepared from H_2S and SO_2 after concn. to a paste contained S 47, $H_2S_5O_6$ 34, and H_2O 19%. It was stable in sealed containers, but liberated SO_2 on exposure to air. No appreciable amounts of SO_2 were formed in a solution containing ½ lb. of paste in 50 gals. H_2O, and the S remained in good suspension for 3 months. The toxicity of $H_2S_5O_6$ and of the colloidal S so prepared was determined. A. G. P.

Selenides. II. Formation of copper selenides by reduction of aqueous selenious acid with cuprous oxide [or copper]. III. Action of copper selenides on solutions of noble metal salts. W. GEHLMANN and F. W. WRIGGE (Z. anorg. Chem., 1933, **210**, 373—377, 378—384).—II. Cu_2O

and Cu react with aq. or slightly acidified SeO_2 solution forming $CuSeO_3,2H_2O$, Cu_2Se, Cu_3Se_2, and CuSe.

III. In presence of H_2O, CuSe undergoes double decomp. with $AgNO_3$ and AgCl, giving Ag_2Se and $Cu(NO_3)_2$ or $CuCl_2$. Cu_3Se_2 and Cu_2Se react similarly, but with liberation of Ag, *e.g.*, $Cu_2Se+4AgNO_3=Ag_2Se+2Ag+Cu(NO_3)_2$. On strongly heating the dry mixture, AgCl reacts slowly with CuSe. The Cu selenides and Se ppt. the metal from aq. Au, Pt, and Pd salts, SeO_2 passing into solution. D. R. D.

Separation of polonium by centrifuging. A. Korvezee (J. Chim. phys., 1933, **30**, 130—139).—The % of Po removed from a solution by centrifuging passes through a sharply-defined max. (up to 100%) as the electrolyte concn. is increased. The form of the curve varies with the nature of the electrolyte present. H. F. G.

Oxygen fluorides : O_2F_2 and OF. O. Ruff and W. Menzel (Z. anorg. Chem. 1933, **211**, 204—208).—O_2F_2, m.p. approx. −160°, b.p. (extrapolated) −57°, is formed as an orange solid on passing F_2+O_2 at 15—20 mm. pressure through a discharge tube partly cooled in liquid air. The formula was determined by analysis and from the gas density. Gaseous O_2F_2 is brown. Above −100° it decomposes into *OF*, a colourless gas of very low b.p. and f.p. OF reacts with HI as follows : $OF+3HI=3I+HF+H_2O$. On cooling it does not re-form O_2F_2, for which the formula $O{:}O{:}F_2$ is suggested. H. J. E.

Role of gaseous oxygen in the thermal reaction between manganic ion and oxalate ion [at 25°]. H. F. Launer (J. Amer. Chem. Soc., 1933, **55**, 865—874; cf. A., 1932, 1002).—Under certain conditions, in the presence of air, O_2 is absorbed during the oxidation of excess of C_2O_4'' by Mn'''; the colour persists longer than and the yield of CO_2 is > in the absence of O_2. The effect is attributed to the regeneration of Mn''' in a reaction between Mn'' and a C peroxide. H_2O_2 is found in solutions in which O_2 has been present, but never if O_2 has been excluded. The data are consistent with the reactions (1) $Mn'''+2C_2O_4'' \rightleftharpoons Mn(C_2O_4)_2'$, rapid, (2) $Mn'''+C_2O_4'' \longrightarrow Mn''+CO_2+CO_2'$, measurable, (3) $Mn'''+CO_2' \longrightarrow Mn''+CO_2$, rapid, (4) $CO_2'+O_2 \rightleftharpoons O_2CO_2'$, rapid, and (5) $O_2CO_2'+Mn''+2H' \longrightarrow Mn'''+CO_2+H_2O_2$, measurable, where (4) and (5) account for the participation of O_2. J. G. A. G.

Mechanism of oxidation processes and the oxidation of ferrous salts by hydrogen peroxide. W. Manchot and W. Pflaum (Z. anorg. Chem., 1933, **211**, 1—15).—Aq. $FeSO_4$ reacts with neutral KI+H_2O_2, 2 equivs. of I being liberated for each equiv. of Fe^{II} oxidised, and 3 equivs. of H_2O_2 being used (cf. Hale, A., 1930, 41). The intermediate formation of $FeSO_4,H_2O_2$ is suggested. In presence of HCl liberation of I is slower and oxidation is incomplete. The mechanism is discussed. H. J. E.

Metal carbonyls. XVIII. Reactions and derivatives of metal carbonyls with substituted nitric oxide. W. Hieber and J. S. Anderson (Z. anorg. Chem., 1933, **211**, 132—140; cf. A., 1932, 1219).—$Fe(CO)_2(NO)_2$ and $Co(CO)_3(NO)$ react with C_5H_5N forming $Fe_2(NO)_4,3C_5H_5N$ and $Co_2(NO)_2CO,2C_5H_5N$. With *o*-phenanthroline in C_6H_6 or MeOH solution they form $Fe(NO)_2,C_{12}H_8N_2$ and $Co(NO)(CO)_2,C_{12}H_8N_2$. $Co(CO)_3(NO)$ dissolved in C_5H_5N forms with *o*-phenanthroline the compound $Co(NO)(CO),C_{12}H_8N_2$. $Fe(CO)_2(NO)_2$ and I form $Fe(NO)_2I$. The thermal decomp. of $Fe(NO)_2(CO)_2$ at 50—100° yields CO, CO_2, N_2O, and N_2 by intramol. oxidation. H. J. E.

Substituted complex cobalticyanides. I. Disulphitotetracyanocobaltiates and the influence of substitution on the properties of complex ions. P. R. Ray and S. C. Chackrabarty (Z. anorg. Chem., 1933, **211**, 173—184; cf. this vol., 40).—Aq. Co acetate, saturated with SO_2, added to NaCN at 0° gave the *compound* $Na_5[Co(SO_3)_2(CN)_4],12H_2O$. The Na, K, NH_4, Li, Rb, Cs, Tl^I, Ag, Ba^{II}, and Ca^{II} *salts* and the *compounds* $PbO,Pb_5[Co(SO_3)_2(CN)_4]_2,12H_2O$, $Ag_4Na[Co(SO_3)_2(CN)_4],4H_2O$, and $Sr_2Na[Co(SO_3)_2(CN)_4],12H_2O$ are described. The basicity of the Na salt from conductivity measurements and its coagulating efficiency for $Fe(OH)_3$ sols was 4. $Na_4[Co(SO_3)(SO_3Na)(CN)_4],12H_2O$ is suggested as an alternative formula. From mobility determinations the relative ionic radii of $[Co(CN)_6]'''$, $[Co(SO_3)(CN)_5]''''$ and $[Co(SO_3)_2(CN)_4]$ are calc. H. J. E.

Fluorides of bivalent metals. I. Normal and acid fluorides. A. Kurtenacker, W. Finger, and F. Hey (Z. anorg. Chem., 1933, **211**, 83—97).—The compounds $NiF_2,4H_2O$, $CoF_2,4H_2O$, $ZnF_2,4H_2O$, CuF_2,H_2O, MnF_2, and CdF_2 have been prepared from the metal carbonate and excess of 40% HF, and their solubilities in H_2O and HF determined. Acid fluorides previously reported are shown to have been fluosilicates (cf. A., 1905, ii, 249; 1921, ii, 116). H. J. E.

Isomerism of the dichlorodiamminoplatinums. F. Rosenblatt and A. Schleede (Ber., 1933, **66**, [*B*], 472—477).—The third isomeride (I) $Pt[NH_3]_2Cl_2$ of Drew and others (A., 1932, 1101) is readily prepared from the *trans*-compound (II) by treatment with Ag_2O or NaOH followed by HCl. Repeated crystallisation of (I) from H_2O gives a product identical with (II) in solubility. The Röntgen diagram of (I) differs from that of (II) but is identical with that given by the product obtained by crystallisation of a mixture of (II) and the *cis*-compound (III). (I) is regarded as (II) in which the cryst. structure is altered by admixture with (III). The recent hypotheses of the complex chemistry of Pt'' hence lose their sole support, and Werner's theory of *cis-trans*-isomerism explains the relationship of the simple diammine and mixed tetrammine salts. H. W.

New type of complex platinum compounds. Ter- and quinque-valent platinum. V. P. C. Ray and S. C. S. Gupta (Z. anorg. Chem., 1933, **211**, 62—64; cf. A., 1932, 353).—The *compounds* $Pt_2Cl_5,3Me_2S_2$, $Pt_2Cl_4,3Me_2S_2$ and $Pt_2Cl_4,3Et_2S_2$ were prepared by the reaction of Me_2S_2 and Et_2S_2 with H_2PtCl_6. The mol. wt. of $PtBr_4,Et_2S_2$ in $CHCl_3$ solution by the b.-p. method indicates the simple formula. H. J. E.

Fluoremetric formula. K. S. G. Doss (J. Indian Chem. Soc., 1932, **9**, 601—607).—Theoretical. The

formula derived for the relation between fluorescence and concn. is not in good agreement with the experimental data available. E. S. H.

Spectrum analysis. B. KAMIENSKI, J. INGLOT, and E. KAMIEŃSKI (Rocz. Chem., 1933, **13**, 85—104).—The conditions for determination of the content of a given element in a mixture by means of emission spectrum analysis are discussed. The height of individual lines is not exactly proportional to duration of illumination, which should be as short as possible, in view of change in composition of the electrode during discharge. The electrodes should be symmetrical. Under optimal conditions, Fe can be determined in Fe–Al alloys with a mean error of 6—11%. R. T.

Rapid micro-determination of chlorides in fluids. L. T. FAIRHALL and J. W. HEIM (J. Amer. Chem. Soc., 1933, **55**, 968—970).—The whole determination is performed with 0·1 c.c. of (biological) fluid in a 15-c.c. centrifuge tube. The liquid is centrifuged after the addition of (1) tungstic acid, (2) 1·5 c.c. of 0·03*N*-$AgNO_3$, (3) almost sufficient KI, and then nitrite–citrate buffer and starch. The titration is completed with KI. 0·3 mg. of Cl is determined to within 2%. J. G. A. G.

Micro-determination of bromine in presence of a large excess of chlorine. F. HARTNER (Z. physiol. Chem., 1933, **214**, 179—183).—Br' is selectively oxidised to Br by $KMnO_4$. The oxidation of Cl' is repressed in weak acid solution in presence of $MnSO_4$, and if the Br is liberated in conc. Na_2SO_4 solution it is readily driven out by a current of CO_2. J. H. B.

Determination of small amounts of iodide in presence of much chloride and bromide. B. A. SKOPINTZEV (Z. anal. Chem., 1933, **92**, 175—184).—I' is oxidised to IO_3' by $KMnO_4$ in alkaline solution (cf. Reith, A., 1930, 386, 1628). The solution is brought to p_H 2·5—3, and the $KMnO_4$ destroyed by $H_2C_2O_4$. By addition of 0·1 c.c. of *N*-NaOAc (for 5 c.c. sample) the p_H is raised to 4·5, KI is added, and the I titrated with 0·001*N*-$Na_2S_2O_3$. 2—10 microg. I may be determined in presence of 500,000 pts. Cl and 25,000 pts. Br. J. S. A.

Determination and occurrence of fluorides in sea-water. T. G. THOMPSON and H. J. TAYLOR (Ind. Eng. Chem. [Anal.], 1933, **5**, 87—89).—The $Zr(NO_3)_4$–Na alizarin sulphate method is satisfactory when the interference due to Cl' and SO_4'' is eliminated by preparing comparison standards containing the same quantity of these ions as are present in the sea-H_2O, and when hot solutions are used. The max. error is about 5% in samples containing 1 mg. F' per litre. In ocean-H_2O the ratio $F' : Cl'$ has a const. val. $7·0 \times 10^{-5}$, but the ratio is somewhat higher in coastal H_2O. E. S. H.

Determination of sulphuric acid in the presence of ferric and aluminium sulphates. E. ERDHEIM (Przemysł Chem., 1933, **17**, 38—39).—10 g. of NaCl and 5 g. of NaF are added to 50 c.c. of solution containing H_2SO_4, $Fe_2(SO_4)_3$, and $Al_2(SO_4)_3$, and the colourless solution, together with the ppt. of Na_3AlF_6 and Na_3FeF_6, is titrated with standard NaOH in the presence of phenolphthalein. R. T.

Titration of sulphate ions by the visual conductivity method. O. PFUNDT (Angew. Chem., 1933, **46**, 200—202).—A sharp end-point is obtained in the conductometric titration of SO_4'' with $Ba(OAc)_2$. The results are better with sulphates of alkali metals than with those of Mg or Zn, and are very slightly lower than those obtained by the gravimetric method. E. S. H.

Acidimetric and alkalimetric titration of sodium thiosulphate solutions. A. SCONZO (L'Ind. Chimica, 1933, **8**, 297—298).—$Na_2S_2O_3$ solutions (approx. 0·1*N*) may be accurately titrated with 0·04—0·1*N*-HCl to which an excess of KIO_3 and KI has been added; the burette should contain the $Na_2S_2O_3$. For alkalimetric titration, approx. 0·1*N*-$AgNO_3$ solution is added dropwise to the $Na_2S_2O_3$ solution and the mixture is boiled for 2—4 min. to convert the $Ag_2S_2O_3$ ppt. into Ag_2S; NaCl solution is added to ppt. the excess of Ag, and the filtered solution is titrated with 0·1*N*-NaOH. H. F. G.

Analysis of naturally occurring selenides. IV. Separation of selenium from metals. Loss of selenium during analysis. W. GEILMANN and F. W. WRIGGE (Z. anal. Chem., 1933, **210**, 357—372).—Se may be separated from Cu, Bi, Hg, Ag, Au, and the Pt metals, but not from Pb, by reduction in alkaline solution by means of *p*-$C_6H_4(OH)_2$ and Na_2SO_3. The metal is pptd. (Cu as Cu_2O, Bi as an org. derivative, the others as metal), and the Se remains in solution as Na_2SeO_3. For Pb, the reduced solution should be strongly acidified with HCl and the Se pptd. by means of SO_2, the Pb remaining in solution. Ca, Mg, and Fe do not interfere with any of these separations. Lenher and Smith's method (A., 1924, ii, 698; 1931, 186) may be used for separating Se from metals, but Te tends to distil over with the Se. Evaporation of solutions of SeO_2 in H_2O, HNO_3, or dil. HCl below 120° does not lead to appreciable loss of Se, but with conc. HCl considerable loss occurs. D. R. D.

Micro-Dumas method [for determination of nitrogen]. M. L. NICHOLS (Ind. Eng. Chem. [Anal.], 1933, **5**, 149).—The adherence of N_2 bubbles at the Hg–aq. KOH interface can be obviated by adding a small amount of Hg_2O. E. S. H.

Volumetric determination of nitrites. R. D. COOL and J. H. YOE (Ind. Eng. Chem. [Anal.], 1933, **5**, 112—114).—A crit. comparison of 31 recognised methods showed 10 to be satisfactory. Of these, 8 are $KMnO_4$ oxidation methods, and the remaining 2, listed as iodometric procedures, involve oxidation by acid $KMnO_4$. The NH_2OH,HCl method is satisfactory when $>$ 50 mg. $NaNO_2$ are present. E. S. H.

Determination of nitric oxide in coke-oven gas. H. TRAMM and W. GRIMME.—See B., 1933, 257.

Separation of phosphoric, arsenic, and vanadic acids from alumina. A. TRAVERS and LU (Compt. rend., 1933, **196**, 703—704).—The method (cf. A., 1890, 1343) of separating VO_4 and PO_4 by reducing

V^{V} to V^{IV} and then pptg. PO_4 in HNO_3 solution as NH_4 phosphomolybdate is inaccurate, as V^{IV} is oxidised in the cold by HNO_3. V is accurately separated from P as $VOCl_3$ by heating in HCl at 400°; As is similarly removed at 450°. Al and P are separated as previously described (cf. A., 1924, ii, 699). C. A. S.

Colorimetric and gravimetric determination of arsenic, especially in water and filter-mud. H. Schröder and W. Lühr.—See B., 1933, 334.

Detection and recording of small amounts of carbon monoxide, particularly in purified contact hydrogen. O. Pfundt.—See B., 1933, 265.

Detection of small amounts of carbon monoxide in air. W. Ackermann.—See B., 1933, 334.

Determination of carbon dioxide in air. Y. Kauko.—See B., 1933, 305.

Determination of carbon dioxide in continuous gas streams. W. McK. Martin and J. R. Green (Ind. Eng. Chem. [Anal.], 1933, **5**, 114—118).—Apparatus for absorption of the CO_2 in $Ba(OH)_2$ and subsequent determination by titration is described. The efficiency of absorption depends on the design of the vessel, the concn. of the absorbing solution, and the rate of flow of gas, and is influenced more by the length of path of the bubbles through the absorbing liquid than by the surface of liquid exposed. Addition of $BaCl_2$ increases the absorbing efficiency of aq. $Ba(OH)_2$. The acid used for titrating solutions containing suspended $BaCO_3$ should not be more conc. than 0·07*N*. E. S. H.

Determination of small amounts of hydrocyanic acid. N. Gales and A. J. Pensa (Ind. Eng. Chem. [Anal.], 1933, **5**, 80—81).—HCN is distilled from a solution acidified with tartaric acid, collected in 0·1*N*-NaOH, and hydrolysed by HCl in an autoclave at 140—150°. After removal of excess of HCl by evaporation, H_2O is added and the NH_4Cl determined by Nessler's reagent. E. S. H.

Determination of hydrocyanic acid in coke-oven and similar gases. W. Klempt and W. Riese.—See B., 1933, 257.

Determination of silicon, aluminium, fluorine, and orthophosphoric acid in presence of one another. II. Determination of fluorine and orthophosphoric acid in presence of silicon and aluminium in aqueous solutions or water-soluble mixtures containing alkali fluorides or fluosilicates, cryolite, orthophosphoric acid or its alkali salts. T. Millner and F. Kunos (Z. anal. Chem., 1933, **92**, 255—264).—The Zr-alizarin method (A., 1926, 590) has been modified in order to render it suitable for the determination of a few mg. of F. Woy's method (F. P. Treadwell, "Kurzes Lehrbuch der anal. Chem.," II, 7 Aufl., 1917, 371) is suitable for the determinations of similar quantities of PO_4''' in mixtures such as the above. D. R. D.

Washing potassium cobaltinitrite precipitate. W. E. Thrun (Ind. Eng. Chem. [Anal.], 1933, **5**, 79).—The ppt. is more flocculent if washed with 1% aq. $Al_2(SO_4)_3$ in preference to H_2O. E. S. H.

Separation of potassium and sodium chlorides by means of aniline hydrogen tartrate. J. Kunz (Helv. Chim. Acta, 1933, **16**, 259—261).—The method depends on the formation of a ppt. of K H tartrate in 48% aq. EtOH, the reagent being a solution of NH_2Ph H tartrate in the same medium. For quant. purposes 77% EtOH is used. F. L.½U.

Micro-determination of calcium in sea-water. P. L. Kirk and E. G. Moberg (Ind. Eng. Chem. [Anal.], 1933, **5**, 95—98).—The procedure is a modification of the $(NH_4)_2C_2O_4$ pptn. method followed by titration with $KMnO_4$. The error is about ±0·5%. The average $Ca^{\cdot\cdot}$ content of sea-water along the coast of southern California is 0·405 g. per kg.; it increases very slightly with the depth, but there is a const. $Ca^{\cdot\cdot}$: Cl' ratio of 0·02154. E. S. H.

Calcium electrodes of the third order. J. Vešišek (Chem. Listy, 1933, **27**, 3—8).—Ca cannot be determined electrometrically in the presence of other ions, using any of the known electrodes of the third order. R. T.

Explosion hazard in analysis of calcium carbide. H. Moll.—See B., 1933, 265.

Gravimetric determination of beryllium and thorium [zirconium ?] using selenious acid, and its application to their separation from certain elements. J. Kot'a (Chem. Listy, 1933, **27**, 79—84, 100—105).—Be^{II} (≮ 0·5 mg.-% of BeO) is quantitatively pptd. from alkaline solution as basic selenite by H_2SeO_3; $NH_4^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, and $Li^{\cdot}$ do not interfere with the reaction. The BeO obtained by ignition of the ppt. is readily sol. in HCl or HNO_3. Zr^{IV} and Bi are quantitatively pptd. by H_2SeO_3 from acid solution (0·2*N*-HCl and 0·4*N*-HNO_3, respectively); should Be also be present, it is pptd. from the alkalised filtrate as above. Al, Mn, U, Mg, Ca, Ce^{III}, La, and Y do not interfere with the determination of Zr by the above method. R. T.

Determination and separation of zinc from the metals of the ammonium sulphide group as sulphide by application of the chloroacetic acid-sodium acetate buffer. C. Mayr (Z. anal. Chem., 1933, **92**, 166—174).—Pptn. is effected in solution of p_H 2·6—2·7. The neutral solution is treated with 10 c.c. of 2*N*-$CH_2Cl{\cdot}CO_2H$ and 10 c.c. of NaOAc, diluted to 150 c.c., and treated with H_2S. ZnS is pptd. in granular form. In presence of other metals, the ppt. is washed with 150 c.c. of buffered solution; one pptn. suffices for the separation except in presence of > 6% Co. J. S. A.

Quantitative emission-spectral analysis. IV. Determination of zinc in aluminium and aluminium alloys. J. Clermont.—See B., 1933, 310.

Determination of copper by the salicylaldoxime method. S. Astin and H. L. Riley (J.C.S., 1933, 314—315; cf. A., 1930, 1393).—Isolation of the salicylaldoxime is unnecessary. The reagent may be prepared by dilution of an alcoholic solution of equiv. amounts of salicylaldehyde and NH_2OH,HCl. J. S. A.

Application of the authors' rapid method for the determination of mercury to the separation

and determination of mercury in presence of elements of the hydrogen sulphide and ammonium sulphide groups. G. Spacu and G. Suciu (Z. anal. Chem., 1933, **92**, 247—253; cf. A., 1929, 901).—Hg may be pptd. quantitatively as $[Cu\ en_2][HgI_4]$ (I) by means of KI and $[Cu\ en_2][NO_3]_2,2H_2O$ (II). K, Na, Ca, Sr, Ba, and Mg do not interfere. If NH_3 and Na K tartrate or tartaric acid are added, quant. pptn. of pure (I) occurs even in presence of Cu, Bi, Pb, Sn$^{\cdot\cdot}$, Al, Fe$^{\cdot\cdot\cdot}$, Mn, Zn, Ni, and Co. For the prep. of (II) there is no need to use an excess of $C_2H_4(NH_2)_2$. D. R. D.

Analytical chemistry of rhenium. VIII. Volumetric determination of rhenium oxides. W. Geilmann and L. C. Hurd (Z. anorg. Chem., 1933, **210**, 350—356).—Re_2O_7 may be titrated directly against alkali. ReO_3 and ReO_2 cannot be so determined. They may be oxidised to $HReO_4$ by warming with acidified aq. $Fe_2(SO_4)_3$, adding H_3PO_4, and titrating the Fe$^{\cdot\cdot}$ salt formed with $KMnO_4$. $Ce(SO_4)_2$ may be used instead of $Fe_2(SO_4)_3$. Alternatively, ReO_3 may be oxidised by means of H_2O_2 to $HReO_4$, which is titrated against alkali. With ReO_2 this method is less accurate. Finely-divided Re is oxidised to $HReO_4$ by aq. H_2O_2, $Fe_2(SO_4)_3$, and $Ce(SO_4)_2$. $KBrO_3$ and Na_3AsO_4 do not oxidise ReO_3 and ReO_2 to $HReO_4$. D. R. D.

Qualitative separation of the iron group in the presence of phosphate. T. B. Smith (J.C.S., 1933, 253—257).—The method is designed to obviate loss of certain metals and to retain the metals in their original relative proportions. All insol. phosphates are pptd. by addition of $(NH_4)_2HPO_4$ after removal of group II. Mn in the ppt. is tested for with $NaBiO_3$, the main portion dissolved in dil. HCl, and Fe, Al, and Cr phosphates are pptd. at p_H 3 by addition of a formate buffer (57 g. HCO_2Na + 85 c.c. HCO_2H, d 1·200, per litre); Ba and Sr are pptd. with the phosphates by addition of $(NH_4)_2SO_4$ and subsequently converted into carbonates. Zn is pptd. from the filtrate as ZnS, and Ca as CaC_2O_4. Separate portions of the filtrate are tested for Co by 1-nitroso-β-naphthol, for Ni with dimethylglyoxime, and for Mg with Titan-yellow. J. S. A.

Detection and determination of iron in drinking water. L. W. Winkler.—See B., 1933, 334.

Volumetric determination of potassium dichromate and potassium permanganate in a mixture. B. L. Vaish and M. Prasad (Analyst, 1933, **58**, 148—149).—Mn and Cr may be separated by oxidising to $KMnO_4$ and $K_2Cr_2O_7$. The $KMnO_4$ is then reduced by H_2O_2, and, after filtration of $Mn(OH)_4$, $K_2Cr_2O_7$ is titrated in the usual manner. T. McL.

Potentiometric determination of chromic acid and iron in chromium-plating baths. E. Muller and G. Haase.—See B., 1933, 271.

5 : 7-Dibromo-3-hydroxyquinoline as specific reagent for vanadium. G. Gutzeit and R. Monnier (Helv. Chim. Acta, 1933, **16**, 239—240; cf. following abstract).—The reagent gives a dark brown ppt. with V$^{\cdot\cdot\cdot}$, 3×10^{-5} g. of which can be detected. Fe$^{\cdot\cdot\cdot}$, which gives a dark green ppt., must be separated previously. F. L. U.

Azo-derivatives of hydroxyquinoline in inorganic chemical analysis. I. G. Gutzeit and R. Monnier (Helv. Chim. Acta, 1933, **16**, 233—238).—4′-Sulphonaphthalene-1′-azo-5-8-hydroxyquinoline can be used to detect 2×10^{-6} g. Pd$^{\cdot\cdot}$ in 20% aq. HNO_3. The limit of dilution is 1 : 10,000, and the reaction is sp. The corresponding benzenesulphonic acid derivative gives a red colour with Hg$^{\cdot\cdot}$, Cu$^{\cdot\cdot}$, Pd$^{\cdot\cdot}$, and Ni$^{\cdot\cdot}$. The reagent can be used to detect 5×10^{-5} g. Hg$^{\cdot\cdot}$ by addition of tartaric acid, which suppresses the reaction with the other ions. F. L. U.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXV. Separation of uranium from tantalum, niobium, and titanium. W. R. Schoeller and H. W. Webb (Analyst, 1933, **58**, 143—147; cf. A., 1930, 184; 1931, 57; this vol., 139).—U is not pptd. by H_2S in the presence of tartrate, but may be pptd. by tannin from a neutral tartrate solution in the presence of NH_4OAc and NH_4Cl, so that it must be grouped with Zr, Th, and Al. U interferes with the pptn. of Nb from tartrate solution, but not with that of Ta or of mixed oxides in which there is an excess of Ta_2O_5. T. McL.

System of thermostats for a series of temperatures below room temperature. C. J. Dippel (Chem. Weekblad, 1933, **30**, 193—196).—An installation of thermostats operating between 5° and 20° is described. Each chamber is cooled by copper tubes through which H_2O at 2—3° circulates, and heated by a thermo-regulated electric lamp. The temp. is const. to within ±0·003°. H. F. G.

Reference tables for platinum to platinum-rhodium thermocouples. W. F. Roeser and H. T. Wensel (Bur. Stand. J. Res., 1933, **10**, 275—287).—The tables have been prepared for Pt|Pt–10% Rh and for Pt|Pt–13% Rh couples. The deviation curves obtained from these for individual couples are with few exceptions linear and give results above the Au point which agree with those of an optical pyrometer. A. R. P.

Determination and calculation of the flame temperatures of complex mixtures of combustible gases. B. Lewis, H. Seaman, and G. W. Jones.—See B., 1933, 291.

Laboratory cooling unit. D. H. Cook (Ind. Eng. Chem. [Anal.], 1933, **5**, 147—148).—A modification of a "Frigidaire" unit is described. E. S. H.

Improvements in psychrometry. D. B. Brooks and H. H. Allen (J. Washington Acad. Sci., 1933, **23**, 121—134).—The H_2O supply is maintained at or near the wet-bulb temp. C. W. G.

Electrically-driven psychrometer. J. F. Townsend (Science, 1933, **131**, 241—242). L. S. T.

Sublimation and solid condensation of vapours. O. Dony (Bull. Acad. roy. Belg., 1932, [v], **18**, 1138—1153).—An apparatus for carrying out sublimation experiments with definite heat control is described.

The sublimation of phthalic anhydride and of $C_{10}H_8$ was studied. The orientation of the crystals produced is governed by convection and the temp. of the moving air currents. A definite temp. is required to produce good crystals by sublimation. A. J. M.

Production of low temperatures. F. Simon (Physikal. Z., 1933, **34**, 232—233).—A simple method of liquefying He is described. A. J. M.

Pyrometer for temperatures up to 1000°. W. C. Stadie and S. L. Wright, jun. (Science, 1933, **77**, 172).—A chromel-alumel thermocouple is described. L. S. T.

Recording infra-red quartz spectrograph. J. W. Ellis (Rev. Sci. Instr., 1933, [ii], **4**, 123—127).—Detailed constructional details are given. C. W. G.

Grazing-incidence vacuum spectrograph. P. G. Kruger (Rev. Sci. Instr., 1933, [ii], **4**, 128—130).—The angle of incidence is 79° and the focal length of the grating is 21 ft. C. W. G.

Valves as a means of producing sparks for the spectroscopic analysis of very small quantities of metals. Goroncy and Urban (Z. anorg. Chem., 1933, **211**, 28—32).—A circuit giving suitable sparks is described. 10^{-8} g. of Pb or Hg could be detected in 1 drop of solution. H. J. E.

Universal camera for *X*-ray crystal structure investigations. E. Sauter (Z. Krist., 1933, **85**, 156—159; cf. A., 1932, 449). C. A. S.

Thermel technique. W. P. White (Rev. Sci. Instr., 1933, [ii], **4**, 142—146).—The following sources of error in resistance thermometers are discussed: insufficient depth of immersion, auxiliary resistance coils, reference temp., inhomogeneity, imperfect insulation, and stray e.m.f. C. W. G.

Resistance of glass towards acid in relation to its composition and weathering. A. Weberbauer.—See B., 1933, 267.

Extraction apparatus. E. Noyons (Chem. Weekblad, 1933, **30**, 228).—The apparatus is particularly suitable for clinical work, and in general for the extraction of small quantities of liquid with a solvent of $d > 1$. H. F. G.

Extraction apparatus for small quantities of substances. R. Gagarin (Chem.-Ztg., 1933, **57**, 204).—The apparatus resembles a Soxhlet extractor, but the extraction tube is of small diam., not jacketed, and connected to a reflux condenser. C. I.

Steam-distillation apparatus. J. A. Radley (Analyst, 1933, **58**, 153).—A steam-distillation flask fitted with a release for air and a Hg control valve is described. The substance is contained in an inner vessel, fitted with an internal tube connecting with the steam flask and a side tube connecting to a condenser. T. McL.

Capillary tubes for use in vacuum distillation. W. Franke (Chem.-Ztg., 1933, **57**, 204).—To prevent bumping in vac. distillation air is drawn through a capillary channel produced by fusing the end of an ordinary glass tube. C. I.

Automatic pressure-regulating unit for vacuum distillation. E. H. Huntress and E. B. Hershberg (Ind. Eng. Chem. [Anal.], 1933, **5**, 144—146).—The apparatus will maintain to $\pm 0{\cdot}15$ mm. any pressure within the range 2—30 mm. E. S. H.

Apparatus and methods for precise fractional-distillation analysis. II. Laboratory columns for precise and rapid fractionation of gaseous and liquid samples. III. Apparatus for precise high-temperature fractionation of complex liquid mixtures. W. J. Podbielniak (Ind. Eng. Chem. [Anal.], 1933, **5**, 119—135, 135—142).—II. An extensive theoretical and experimental study of the general design and construction of fractionating columns, their efficiency, and the influence of time and rate of distillation, reflux ratio, and distillation pressure is given. The columns described have a separate sleeve-like metal reflector type vac. jacket for thermal insulation over the range −190° to 300°, within which various distilling tubes may be inserted for the fractionation of gaseous or liquid samples ranging from < 1 c.c. to 20 litres. Effective spiral, continuous, wire-coil packings are described.

III. The apparatus is suitable for fractionating motor fuels, lubricating oils, crude petroleum, commercial solvents, etc., at reflux temp. between −190° and 300° and at 1—1000 mm. Methods are described for measurement of reflux temp., collection and measurement of distillate, changing receivers in vac. distillation, and vac. control. By changing the distilling tubes, one apparatus serves for the fractionation of liquid samples varying from a few c.c. to 3000 c.c. E. S. H.

Laboratory esterifying and fractionating apparatus. C. A. Doran (Ind. Eng. Chem. [Anal.], 1933, **5**, 101—102).—The apparatus is designed to simulate the conditions of large plant stills used in the chemical industries. E. S. H.

Automatic pipette for the accurate delivery of variable quantities of liquids. P. L. Varney and D. M. Hetler (J. Lab. Clin. Med., 1932, **18**, 70—74). Ch. Abs.

Ebulliometer for determining the dew point and b.p. of mixtures of volatile liquids. L. Gay and J. Soulié (Compt. rend., 1933, **196**, 776—777).—The heating is effected electrically and within a double-walled vac. vessel. C. A. S.

Rapid filtration device. H. Tramm (Chem.-Ztg., 1933, **57**, 225).—A porcelain cone is placed in an ordinary conical filter of similar angle and held at a little distance from it by bottom supports and a shoulder carrying a rubber joint ring near the top. Filter-paper is used and filtration can be made very rapid with a filter-pump. The device is suitable for quant. work. C. I.

Suction funnel for rapid filtration. S. Seuthe (Chem. Fabr., 1933, **6**, 148).—The funnel has a perforated cone in place of the plate of the ordinary Buchner funnel, thus allowing a relatively bigger surface to be exposed to suction. The perforated cone may be either detachable or made continuous with the rest of the funnel. M. S. B.

Measurements of gas currents by means of capillary flow-meters. R. Sips (Ann. Chim. Analyt., 1933, [ii], **15**, 97—110).—The rate of flow of gas is measured by means of a U-shaped capillary manometer with a capillary tube joining its ends. If the relation between manometer reading and rate of flow is determined experimentally using air, the calibration curve for any other gas of known density and viscosity may be calc. therefrom. D. R. D.

Mechanical device to agitate analytical solutions by swirling. A. F. Scott and E. F. Reid, jun. (Ind. Eng. Chem. [Anal.], 1933, **5**, 92). E. S. H.

Stirrer drive for laboratory use. M. H. Hubacher (Ind. Eng. Chem. [Anal.], 1933, **5**, 149). E. S. H.

Muencke blower. R. F. Robey (Ind. Eng. Chem. [Anal.], 1933, 5, 148). E. S. H.

Relation between volume of respiration chamber and concentration of carbon dioxide in end sample and in composite sample of air. M. Kleiber (Ind. Eng. Chem. [Anal.], 1933, **5**, 98—100).—Mathematical. E. S. H.

Apparatus for measuring radioactivity of substances irrespective of the exact position of the substance. A. Piccard and L. Meylan (J. Phys. Radium, 1933, [vii], **4**, 105—108).—On the upper of two large parallel plates forming the ionisation chamber is a Pb screen of const. thickness. N. M. B.

The kampometer, a new instrument of extreme sensitiveness for measuring radiation. C. G. Abbot (Smithson. Misc. Coll., 1933, **89**, No. 3, 1—5).—A system of two groups of magnets and two curled bimetallic strips (brass and invar coated with lampblack, or Mo plated with Cd) hangs in vac. between two electromagnets, and is astatic. Incidence of radiation on one metal strip causes a rotation of the system, which is measured with an attached mirror. H. J. E.

Andreae's methods for the accurate determination of the density of solids. E. Cohen and W. A. T. Cohen-de Meester (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1255—1266).—Andreae's methods (A., 1885, 332; 1911, ii, 469; 1913, ii, 188), with certain slight alterations, are the most accurate methods for the determination of the sp. gr. of solids. D. R. D.

Ångstrom's total immersion hydrometer. P. F. Gaehr (Rev. Sci. Instr., 1933, [ii], **4**, 138—141).—Permalloy is recommended for the core of the instrument. To obtain high sensitivity the solenoid should be as long as possible. C. W. G.

Micro-sublimation and micro-m.p. determination. J. Deininger (Pharm.-Ztg., 1933, **78**, 362).—The apparatus and procedure described are designed for the examination of soporifics of the barbituric acid series, and for other pharmaceutical preps. E. S. H.

Mathematical determination of p_H. O. Mayer (Gas- u. Wasserfach, 1933, **76**, 251).—A table is given, relating p_H to x, where x=free $CO_2 \times 100$/bound CO_2. E. S. H.

Determination of the specific gravity of hydrophilic and hydrophobic powders. M. V. Tschapek (Kolloid-Z., 1933, **63**, 34—36).—The liquid should not be adsorbed by the powder. H_2O is permissible for hydrophobic substances, but a non-polar liquid should be used for hydrophilic powders. E. S. H.

Apparatus for measuring the absorption of liquid by porous substances capable of swelling, and for the characterisation of wetting power. O. Enslin (Chem. Fabr., 1933, **6**, 147—148).—Swelling velocity and swelling max., pore space of non-swelling substances, and readiness of wetting of powders in connexion with flotation processes can be determined with the above apparatus. M. S. B.

Constant-volume differential manometer. F. Dickens and G. D. Greville (Biochem. J., 1933, **27**, 213—219).—An apparatus which combines the advantages of compensation and simplicity of reading and calculation is described. H. G. R.

Apparatus for accurate measurement of viscosity. P. Woog and J. Givaudon (Compt. rend. Congr. Graissage, 1931, 196—205; Chem. Zentr., 1932, ii, 2576).—A modification of the Baume–Vigneron viscosimeter is described. A. A. E.

Continuous viscosimeter. C. D. Miller (Instruments, 1933, **6**, 2—3).—The "vismeter" consists of a vertical conical journal revolving at const. speed in a bearing containing a channel extending about 0·8 of the distance around its face. The oil, flowing in the direction of revolution, enters at one end of the channel; at the other end is a pressure gauge, and about midway between is the oil outlet. Ch. Abs.

Controllable oil-less valve. A. Stock (Z. Elektrochem., 1933, **39**, 256).—The valve is similar to that of Wolf and von Reichel (this vol., 367). D. R. D.

Geochemistry.

Chemico-stratigraphical investigation of the sediment metamorphosis of a forest lake. W. Ohle (Biochem. Z., 1933, **258**, 420—428).—The org. and inorg. constituents of the sediment at different depths of a forest lake and of the shore soil have been determined. With increasing depth, a decrease in OMe and an increase of lignin are detected. The OMe content of the lake-H_2O suggests that humic acids or their salts can be dissolved. The bearing of the results on the history of the lake is discussed. P. W. C.

Age of meteor crater. F. M. Brown (Science, 1933, **77**, 239—240).—Critical (cf. this vol., 140). L. S. T.

X-Ray study of the transformation of marcasite into pyrite. H. V. ANDERSON and K. G. CHESLEY (Amer. J. Sci., 1933, [v], **25**, 315—324).—Marcasite, on grinding, gives rise to interplanar distances identical with those of pyrite. C. W. G.

Composition of nosean and hauyne. T. F. W. BARTH (Amer. Min., 1932, **17**, 466—471).—The nosean formula $6NaAlSiO_4,Na_2SO_4$ of Morozewicz (A., 1899, ii, 762) is substantiated, but is written in the form $Na_8Al_6Si_6O_{24},SO_4$. By fusing together $NaAlSiO_4$ and Na_2SO_4 in the ratios 6 : 1 and 3 : 1 a homogeneous product was obtained only with the 6 : 1 ratio. This is optically isotropic with n 1·492 and a unit cube of edge a 9·04 Å. Hauyne has the same space-group T_d^1 with a 9·11 Å., but it differs from nosean in having part of the Na replaced by Ca and in the presence of extra SO_4 groups. From structure considerations the formula is written as $(Na,Ca)_{4-8}Al_6Si_6O_{24}(SO_4)_{1-2}$. L. J. S.

Constitution of Devonian phosphates of Tennessee. L. CAYEUX (Compt. rend., 1933, **196**, 822—826).—These phosphates consist partly of fragments derived from shells, chiefly of echinoderms, and partly of a conglomerate of submicroscopic unidentifiable particles. In all the phosphate has replaced original $CaCO_3$, whether of org. or mineral origin. C. A. S.

Crystallography of allactite. C. PALACHE and H. BERMAN (Kungl. Svenska Vetensk. Handl., 1933, [iii], **11**, No. 4, 32—40).—Measurement of crystals from Langban, Sweden, gave, in a new orientation, $a : b : c = 0·9008 : 1 : 0·4494$, $\beta = 65°\ 56'$. Analysis of crystals by F. A. GONYER gave As_2O_5 28·10, MnO 60·12, MgO 1·92, CaO 0·57, $H_2O + 9·08 = 99·83$. L. J. S.

Adelite and its relation to tilasite. G. AMINOFF [with R. BLIX] (Kungl. Svenska Vetensk. Handl., 1933, [iii], **11**, No. 4, 24—31).—The "adelite" crystals measured by Sjogren (1893) are pyroxene. Crystals since found at Langban, Sweden, are orthorhombic with $a : b : c = 1·2057 : 1 : 0·8108$ and unit-cell dimensions a 8·85, b 7·43, c 5·88 Å. with 4 mols. $3RO,R(OH,F),As_2O_5$ in the cell. Analysis gave As_2O_5 47·40, P_2O_5 3·01, CaO 23·43, MgO 17·10, MnO 4·38, PbO 0·17, Cl 0·31, F 1·44, H_2O 3·33 = 100·57, d 3·696. Tilasite, also from Langban, has the same general formula, but is monoclinic, a 6·62, b 8·93, c 7·57 Å. (β 59°); in another orientation these vals. are close to those of adelite. L. J. S.

Lattice dimensions of thaumasite. G. AMINOFF (Kungl. Svenska Vetensk. Handl., 1933, [iii], **11**, No. 4, 21—23).—*X*-Ray rotation photographs of thaumasite crystals, d 1·914, from Långban, Sweden, gave a hexagonal cell, a 10·90, c 10·29 Å. (c/a—0·944), containing 2 mols. $CaCO_3,CaSO_4,CaSiO_3,15H_2O$. The space-group is probably or L. J. S.

Lattice dimensions of armangite. G. AMINOFF (Kungl. Svenska Vetensk. Handl., 1933, [iii], **11**, No. 4, 19—20).—Rotation *X*-ray photographs of armangite (A., 1921, ii, 269) from Langban, Sweden, gave a 13·44, c 8·72 Å. ($c/a = 0·6596$). The hexagonal cell contains 9 mols. $Mn_3As_2O_6$. The space-group is C_{3v}^5, D_3^5, or D_{3d}^5. L. J. S.

"Weslienite" and atopite. G. AMINOFF [with R. BLIX] (Kungl. Svenska Vetensk. Handl., 1933, [iii], **11**, No. 4, 14—18).—*X*-Ray data for weslienite (G. Flink, 1923) not being in agreement with the formula as originally given, a new analysis proves the identity of the mineral with atopite: Sb_2O_5 72·17, TiO_2 0·30, PbO 0·51, FeO 2·92, MnO 0·43, MgO 0·35, CaO 19·01, Na_2O 2·03, K_2O 0·17, F 3·50, H_2O 0·46, H_2O (hygr.) 0·20 = 102·05, corresponding with $2(R^{II},R^I_2)[O,F_2,(OH)_2],Sb_2O_5$. *X*-Ray powder photographs give a 10·285, and rotation photographs 10·23, agreeing with 10·31 Å. for atopite. L. J. S.

Structure and composition of swedenborgite. G. AMINOFF [with R. BLIX] (Kungl. Svenska Vetensk. Handl., 1933, [iii], **11**, No. 4, 3—13).—In the original description of swedenborgite (Aminoff, 1924) the agreement between the *X*-ray data and the composition was not satisfactory, and a new analysis now shows the presence of Be (not Al): Sb_2O_5 55·41, P_2O_5 0·63, BeO 34·92, MgO 0·65, CaO 0·90, Na_2O [8·49] = 100·00, corresponding with $4BeO,NaSbO_3$. New *X*-ray measurements gave a 5·42, c 8·80 Å. ($c/a = 1·624$) with 2 mols. in the unit cell. The space-group is C_{3v}^1, but the structure is hemimorphic only as regards the Sb ions, and the crystals do not show any marked hemimorphic morphological development. L. J. S.

Microscopical investigation of the Cambro-silurian bitumen-bearing strata at Billingen in South Sweden. R. SCHREITER (Petroleum, 1933, **29**, No. 8, 1—4).—Microscopical examination of the bituminous limestone shows the presence of concretions containing pyrites and irregular glauconitic bodies which are probably the remains of trilobites, mussel shells, etc. It is concluded that the bitumen has originated from animal remains embedded in the strata. A. B. M.

Occurrence, nature, and origin of asphaltites in limestone and oil-shale deposits in Estonia. P. N. KOGERMAN (J. Inst. Petroleum Tech., 1933, **19**, 215—222).—The properties and analysis of a solid bitumen and its resemblance to various other specimens found in Estonian oil shale establish it as an asphaltite. A theory of its origin by formation *in situ* from org. sediments by biochemical changes in parallel (synchronically) to the oil-shale formation is advanced. H. S. G.

Water content of tremolite of Monte Spinoza, Campiglia. F. RODOLICO (Atti R. Accad. Lincei, 1932, [vi], **16**, 645—647; cf. A., 1931, 1391).—Debye–Scherrer diagrams of the mineral before and after dehydration at 1000° show marked differences. This supports the view that the H_2O in tremolite is H_2O of constitution. O. J. W.

Mineral deposits from Monte Rosso di Verra (Monte Rosa group). T. CARPANESE (Atti R. Accad. Lincei, 1932, [vi], **16**, 641—645; cf. A., 1932, 1106).—The genesis of these deposits is discussed. O. J. W.

Microscopical analysis of phosphorite from the neighbourhood of Grodno (Poland). J. TOKARSKI (Bull. Acad. Polonaise, 1932, **A**, 300—317).—Samples examined include both high- and low-%

ores, the former appearing black and polished, the latter brown and dull. The structures and physical properties of the samples are discussed in relation to their chemical compositions. J. W. S.

Tertiary deposits of the Grozni district. V. A. Selski (Neft. Izdat., 1932, 199 pp.).—Mineral, clay, and oil deposits are described. Ch. Abs.

Group of typical spinels. C. W. Parmelee, A. E. Badger, and G. A. Ballam (Univ. Illinois Bull., 1932, No. 248, 54 pp.).—Mg, Zn, Fe, and Mn aluminates, chromites, and ferrites were prepared and their hardness and coeff. of thermal expansion determined. An attempt is made to correlate the physical properties with the relations in a group of isomorphous compounds. Ch. Abs.

Auriferous deposits in the neighbourhood of Saint-Yrieix. C. H. Wakker (Arch. Sci. phys. nat., 1933, [v], **15**, 23—46).—A petrological description is given. C. W. G.

Unusual double sulphate of copper and iron in the copper minerals of Katanga: orange bornite or chalmersite (?). M. Legraye (Bull. Acad. roy. Belg., 1933, [v], **19**, 262—268).—Microchemical tests are described. C. W. G.

Katapleite from the Chibinsky tundra. E. E. Kostyleva (Bull. Acad. Sci. U.S.S.R., 1932, [vii], 1109—1125).—This mineral occurs in pegmatite veins in various zones throughout the tundra. Its composition is $(Na_2O,CaO),ZrO_2,3SiO_2,2H_2O$; d 2·38, hardness 5—6. The distribution throughout the world is discussed. T. H. P.

Lievrite [ilvaite] from Seriphos. A. Schiener (Z. Krist., 1933, **85**, 89—118; cf. A., 1916, ii, 43).—The ilvaite occurs mainly in geodes in augitiferous metamorphic rock as black nearly opaque zoned rhombic crystals containing unusually little Mn; analysis: SiO_2 29·60, Al_2O_3 1·75, Fe_2O_3 17·57, FeO 35·12, MnO 0·27, CaO 13·75, MgO 0·25, H_2O 2·00, F 0·01%, corresponding with $(CaFe^{II}Mn^{II})_2[(Fe^{III},Al)OH](SiO_4)_2$; d^{18} 4·0397, $a:b:c$ = 0·6690 : 1 : 0·4452, n_β 1·89, $n_\beta - n_\gamma$ = 0·012. The zoning is attributed to irregular distribution of Al_2O_3. The formation of the mineral may have resulted from the action of $FeCl_3$ and H_2O on augite: $2CaFeSi_2O_6 + FeCl_3 + H_2O = CaFe^{II}_2(Fe^{III}OH)Si_2O_8 + CaCl_2 + HCl + 2SiO_2$. C. A. S.

Minor constituents of thermoluminescent calcite. S. Hata (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 163—169).—In the specimens examined the heavy metal content is $< 0·1\%$, and the mol. ratio of heavy-metal to rare-earth oxides is < 20. Pr and Nd are present. C. W. G.

Average recovery of copper from cupriferous minerals. F. Blondel (Compt. rend., 1933, **196**, 712—713).—The average yield of any Cu deposit, as soon as the first rich portion is exhausted, tends to a const. val., almost irrespective of price of the metal, but in accordance with current views on the formation of metallic deposits. C. A. S.

Structure of troostite. A. Glazunov (Coll. Czech. Chem. Comm., 1933, **5**, 76—83).—A discussion. H. J. E.

X-Ray analysis of idocrase from Miho, Japan, and the formula of the mineral. K. Takane (Proc. Imp. Acad. Tokyo, 1933, **9**, 9—12).—The unit-cell dimensions are a 15·65, c 11·93, giving an axial ratio c/a 0·7627. From published analyses of idocrase a formula is deduced as $Ca_8Al_4(Si,Al)_9(Fe,Mg,Ca,Al\cdots)_4(O,OH,F)_{38}$, of which there are 4 mols. in the unit cell. L. J. S.

Optical and thermal properties of cancrinite from Korea. S. Kôzu, J. Ueda, and S. Tsurumi (Proc. Imp. Acad. Tokyo, 1933, **9**, 13—16).—Refractive indices are ω 1·5238, ε 1·5015 (Na). The linear thermal expansion is about twice as great along the c axis as in a direction perpendicular thereto. The expansion curves show irregularities at about 900°, corresponding with the decomp. of the mineral. The heating curve shows only one distinct break at 920°. The curve plotting changes in wt. on heating shows breaks at 300°, 460°, 800°, and 910°, corresponding with the loss of H_2O and CO_2 and the decomp. of the mineral. L. J. S.

Inclusions of basalt-jasper in the basalt of Ság Mtn., Hungary. L. Jugovics (Tsch. Min. Petr. Mitt., 1933, **44**, 68—82).—The fragments of "basalt-jasper" ("porcelain-jasper") are bluish-grey and compact and consist of minute crystals of cordierite with some magnetite and fibrolite in a glassy groundmass. They represent fragments of clay caught up and baked in the basalt lava. Surrounding the fragments is a narrow zone consisting largely of felspar due to a reaction between the lava and the clay. Analyses are given for the "jasper," basalt, intermediate zone, and clay. L. J. S.

Occurrence of arsenic in the Eastern Alps. F. Czermak and J. Schadler (Tsch. Min. Petr. Mitt., 1933 **44**, 1—67).—Details are given of the occurrence of 27 As-bearing minerals at 120 localities. They occur in ore-veins which are connected with the intrusion of acid and intermediate eruptive rocks. L. J. S.

Fluorspar deposits in Western United States. E. F. Burchard (Amer. Inst. Min. Met. Eng., Tech. Publ. No. 500, 1933, 26 pp.).—The distribution of fluorspar in the Western States is briefly described and tables of production and estimates of reserves are given. A. R. P.

Portuguese uranium–radium minerals. C. Lepierre (Bull. Soc. chim., 1933, [iv], **53**, 72—80).—The only U minerals found in Portugal are black mineral, a product of alteration of UO_2 and U_3O_8 and always accompanied by PO_4''', S'', and SO_4'', and the products of alteration of this mineral, autunite and chalcolite. Analyses of two samples of black mineral from 15 m. and two from 95 m. depth are given. All except one of the latter have the normal Ra/U ratio, $3·2—3·3\times10^{-7}$. For the exception it is $2·80\times10^{-7}$, a fall in the val. being characteristic of an altered mineral. There is no const. ratio between Pb and U. The alteration process is discussed and the view advanced that H_2SO_4 formed by the oxidation of pyrites is an important factor. M. S. B.

Physico-chemical properties of Japanese acid clay. VII. Solubility in alkaline solutions and

essential constituents of acid clay. I. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1933, **36**, 38—42B).—Analyses are given of Japanese and other clays. D. R. D.

Formation of kaolin. E. DITTLER (Z. anorg. Chem., 1933, **211**, 33—40).—The prep. of sols of $Al(OH)_3$ and H_2SiO_3 is described. Mixed under controlled conditions they ppt. solids resembling kaolin, a chemical reaction, and not a reciprocal flocculation, taking place. H. J. E.

Cellulose as source of coal and mineral oil. E. BERL (Papier-Fabr., 1933, **31**, 141—149).—It is suggested that cellulose is the source of hard coal and of mineral oil and that the former does not pass through a lignite stage. Hard coals were formed in the carboniferous age from plants poor in lignin and wax, whereas the lignites were formed later from higher plants richer in lignin and wax. Coal produced artificially from cellulose yields a black but non-caking coke, whereas if the coal is produced in presence of alkali it yields a coke indistinguishable from that given by true coking coals. In presence of more alkali a proto-substance is formed which yields mineral oils by hydrogenation or by high-temp. cracking. A. G.

Occurrence of hydrocarbons in Ruhr coal. P. KUKUK (Petroleum, 1933, **29**, No. 8, 5—8).—A considerable quantity of a clear, yellow oil appeared in the Ewald mine in 1913. On distillation it gave 0·5% to 100°, 32·5% to 220°, and 98·5% to 280° (cf. B., 1920, 223A); it consisted principally of saturated hydrocarbons of the *iso*cyclic series (naphthenes). In 1922 a quantity of wax was found in the Rheinpreussen mine in the form of platelets of m.p. 66·5°; it consisted mainly of hydrocarbons of the paraffin series. The possible origin of these hydrocarbons is discussed. A. B. M.

Radioactivity of the soil air in soils of the podsol zone. A. A. KRASIUK and B. A. KRASIUK (Pedology, 1932, **27**, 437—451).—Radioactivity varies with soil type, being greatest in alluvial and least in swampy soils. The Rn content increases with increase in soil fertility, depends on the H_2O content, and is max. under dry conditions. It increases with depth, but after rain the upper layers are richer than the lower. A. M.

Distribution of soil acidity in Viennese forests. H. SCHWARZ (Z. Pflanz. Düng., 1933, **28**, **A**, 248—256).—Conditions influencing acidity in forest soils are examined. Differences between p_H (KCl) and p_H (H_2O) are greater in the more acid soils. Only in slightly acid or slightly alkaline soils is p_H (KCl) > p_H (H_2O). The acid gradient in profiles of very acid soils is > that of less acid types. A. G. P.

Descriptive soil map. A. TILL (Z. Pflanz. Dung., 1933, **28**, **A**, 241—248; cf. this vol., 369).—Use of the soil map is further developed. A. G. P.

Classification of mineral soils with respect to particle-size distribution and the content of alumina soluble in hydrochloric acid. K. UTESCHER (Z. Pflanz. Düng., 1933, **28**, **A**, 224—241).—The proportion of HCl-sol. Al in soils serves as an index of their mechanical composition. The following basis is adopted: < 0·7% Al_2O_3, sands; 0·7—1, slightly loamy sand; 1·0—1·3, loamy sand; 1·3—2·0, sandy loam; 2·0—3·0, slightly sandy loam; 3·0—4·0, loam; > 4·0, clay. A. G. P.

Fossil soils in Armenia. K. MIRIMANOV (Pedology, 1932, **27**, 578—586).—These soils are found under basaltic lavas, and their properties suggest that they were formed under much drier conditions than the present soil. A. M.

Genetic classification of soils of the turfy podsolised zone. J. N. AFANASIEV (Pedology, 1932, **27**, 534—554).—The soils are classified according to their situation and degree of development. The degree of saturation is found useful in further subdivision. A. M.

Principles of soil classification. V. A. KOVDA (Pedology, 1932, **27**, 555—577).—A crit. review of previous Russian classifications, with suggestions for their improvement. A. M.

Organic Chemistry.

Oxidation of hydrocarbons. (MLLE.) ESTRADERE (Compt. rend., 1933, **196**, 674—676).—When mixtures of hexane, *cyclo*-hexane or -hexene (4 pts.) with O_2 (1 pt.) are passed at the rate of 9·25 litres per hr. through a furnace for 0·5 hr., the amounts of CO formed increase rapidly, and of peroxides reach a max. at 330°, 340°, and 410° for the three hydrocarbons, respectively; peroxides disappear at higher temp. Explosions occur before the appearance of substantial amounts of CO. C. A. S.

Hydrogenolysis of alcohols to hydrocarbons. B. WOJCIK and H. ADKINS (J. Amer. Chem. Soc., 1933, **55**, 1293—1294).—*n*-Dodecyl, *n*-tetradecyl, *n*-octadecyl, and *γ-cyclo*hexylpropyl alcohols are converted by H_2 (100—200 atm.) at 250° over a Ni catalyst (A., 1932, 1213) into *n*-undecane, *n*-tridecane, *n*-heptadecane, and ethyl*cyclo*hexane, respectively, in almost quant. yields: $CH_2R{\cdot}OH+2H_2 \longrightarrow RH+CH_4+H_2O$. *cyclo*Hexanol and octan-8-ol are similarly converted into *cyclo*hexane and *n*-octane, respectively: $CHR_2{\cdot}OH+H_2 \longrightarrow CH_2R_2+H_2O$. Decane-αK-diol gives *n*-octane, whilst octadecane-αμ-diol affords *n*-heptadecane. H. B.

Preparation of pure *n*-Δα-hexene. H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1933, **52**, 251—256).—Pure *n*-Δα-hexene (I), b.p. 63·8—63·9°/774·1 mm., f.p. −138°, is prepared by the sequence $MeCHO+EtOH+HCl \longrightarrow CHMeCl{\cdot}OEt \xrightarrow{Br} CH_2Br{\cdot}CHBr{\cdot}OEt \xrightarrow{MgBu^{\alpha}Br} CH_2Br{\cdot}CHBu^{\alpha}{\cdot}OEt \xrightarrow{Zn}$ (I), and subsequent distillation over Na. The vals. of its physical consts. are tabulated and compared with those in the lit. J. W. B.

Preparation of pure *n*-Δ^{α}-heptene. H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1933, **52**, 298—302).—*n*-Δ^{α}-Heptene, b.p. 93·7—93·8°/771 mm., is prepared by the action of CH_2:CH·CH_2Br on $MgBu^{n}Br$ and repeated fractionation over Na. Its physical consts. are tabulated and compared with those in the lit. J. W. B.

Carotene. I. Preparation, detection, determination. N. T. DELEANO and J. DICK (Biochem. Z., 1933, **259**, 110—133).—Carotene (I) is quantitatively extracted from finely-shredded carrots, dehydrated with 95% EtOH, with light petroleum or CS_2 and from leaves by a modification of Willstatter's method. For the detection of (I), at dilutions down to 1 : 10^6, H_2O is added to a solution of it in light petroleum (II) after addition of CCl_3·CO_2H in (II). (I) passes quantitatively into (II) with a yellow colour. For the determination of (I) it is oxidised with excess of $K_2Cr_2O_7$ in presence of HCl, KI is then added, and the liberated I determined by titration with $Na_2S_2O_3$. One mol. of (I) consumes 32·5 mols. of O. Other pigments and other org. substances must be absent. The method can be used for ordinary (max. error ±2·3%) and micro-analysis (max. error ±4%). W. McC.

Polymerisation of unsaturated hydrocarbons. Catalytic action of aluminium chloride. W. H. HUNTER and R. V. YOHE (J. Amer. Chem. Soc., 1933, **55**, 1248—1252).—Little reaction occurs with C_2H_2 and $AlCl_3$ at room temp.; reaction is rapid at 100° (NMe_3 completely inhibits), but no liquid products are formed. When C_2H_2 is passed through Et_2O and then over $AlCl_3$, an exothermic reaction occurs; a liquid product of the approx. composition $2AlCl_3$,Et_2O,C_2H_2, which is decomposed by H_2O to HCl and cuprene-like material, is formed. C_2H_2 does not react with the *complex* (I), $AlCl_3$,Et_2O, even at 100°; the *complex* (II), $AlCl_3$,$NPhMe_2$, does not catalyse the polymerisation of C_2H_2 at 100°. C_2H_4 is adsorbed slowly by $AlCl_3$ and the gas is regenerated by heating; a little red oil is formed. Reaction is not accelerated by heat or Et_2O vapour and there is no reaction between C_2H_4 and (I) or (II) either at room temp. or 100°. *iso*Butene (III) and $AlCl_3$ give colourless (*M* 200) and dark red oils; the latter contains about 11·5% Al and reacts further with (III). (III) containing Et_2O vapour and $AlCl_3$ give a red oil containing 11·8—12·3% Al; the Al content of this decreases to 10·3—10·45% when Et_2O-free (III) is passed through it. (III) does not react with (II), but does so with the *complex*, $2AlCl_3$,$NPhMe_2$, to give a product of the approx. composition $2AlCl_3$,$NPhMe_2$,$2C_4H_8$. A theory of polymerisation based on the electronic structures of $AlCl_3$ and olefines is given. H. B.

Acetylene polymerides and their derivatives. VI. Magnesium vinylethinyl bromide and its reactions. W. H. CAROTHERS and G. J. BERCHET. **VII. Sodium vinylacetylide and vinylethinylcarbinols.** W. H. CAROTHERS and R. A. JACOBSON (J. Amer. Chem. Soc., 1933, **55**, 1094—1096, 1097—1101).—VI. Vinylacetylene (I) and MgEtBr give CH_2:CH·C:C·MgBr (II), which with $COMe_2$ affords *dimethyl(vinylethinyl)carbinol*, b.p. 67°/24 mm., which polymerises when kept and is reduced (H_2, PtO_2, EtOH) to CMe_2Bu·OH. (II) and CO_2 at 0° give *vinylpropiolic acid*, b.p. 64—71°/2 mm. [*α-naphthylamide*, m.p. (block) 125—126°, from (II) and α-$C_{10}H_7$·NCO]; with CPh_3Cl, *triphenyl(vinylethinyl)methane*, m.p. (block) 134—135°, results.

VII. CH_2:CH·C:CNa, prepared from (I) and $NaNH_2$ in liquid NH_3, often ignites spontaneously in moist air. Dialkyl(vinylethinyl)carbinols are prepared from (I), $COAlk_2$, and $NaNH_2$ in cold Et_2O; monoalkyl(vinylethinyl)carbinols are obtained similarly using Alk·CHO. The following are described: *methyl-* (III), b.p. 65°/22 mm. (3 : 5-*dinitrobenzoate*, m.p. 106—106·2°), n-*propyl-*, b.p. 74—76°/10 mm., dimethyl-, b.p. 68°/24 mm. (cf. above), *methylethyl-*, b.p. 75°/20 mm., *diethyl-*, b.p. 62°/4 mm., *di*-n-*propyl-* (IV), b.p. 98—99°/22 mm., methyloctyl- (V), b.p. 98—100°/5 mm., cyclo*pentyl-*, b.p. 104—105°/7 mm., cyclo*hexyl-*, b.p. 84—85°/2 mm., and *phenylmethyl-* (VI), b.p. 125—126°/4 mm., m.p. 40—41°, *-(vinylethinyl)carbinols*. *Methyl*-n-*butyloctyl-*, b.p. 94°/3 mm., and *phenylmethyl*-n-*butyl-*, b.p. 107—109°/6 mm., *-carbinols* are obtained by reduction (H_2, PtO_2, EtOH) of (V) and (VI), respectively. Vac. distillation of (IV) through a long column gives ε-n-*propyl*-$\Delta^{\alpha\epsilon}$-*octadien*-Δ^{γ}-*ine*, b.p. 57—58°/6 mm., whilst (III) is dehydrated by *p*-C_6H_4Me·SO_3H to divinylacetylene. The above unsaturated carbinols polymerise (during 6 weeks) to hard, translucent masses. H. B.

Vapour-pressure curve of diacetylene [butadiinene]. H. TANNEBERGER (Ber., 1933, **66**, [*B*], 484—486).—Diacetylene (I), prepared by pyrogenic fission of CH_4 and purified by fractionation in a Stock high-vac. apparatus, has m.p. −34·8° to −35·1°. Comparison of the v.-p. curve with that of synthetic (I) between −84·8° and 10·2° indicates the presence of amounts of allylene, allene, and butadiene too small to influence the m.p. appreciably. H. W.

Two hydrocarbons which form colloidal polymerides. R. LESPIEAU, GUILLEMONAT, and URION (Kolloid-Z., 1933, **63**, 84—87).—Et αβ-dibromoethyl ether and (:C·MgBr)$_2$ yield *δ-bromo-γ-ethoxy-*Δ^{α}-*butinine*, b.p. 47—48°/14 mm., and *αζ-dibromo-*βε-*diethoxy-*Δ^{γ}-*hexinine*, b.p. 158—162°/14 mm., giving two Br_4-compounds, m.p. 113—114° and 70—71°, respectively, converted by Zn dust in BuOH into *divinylacetylene*, b.p. 84·5—85°/760 mm., which polymerises to an explosive gel. $\Delta^{\beta\zeta}$-Hexadiene-δε-diol is transformed into the $\Delta^{\beta\zeta}$-*hexatrienes* (trans-cis-trans, b.p. 137—143°, and trans-trans-trans, b.p. 147—148°/764 mm., m.p. 52·5°); the latter passes into a plastic mass in presence of O_2. E. S. H.

Hydrolysis and rearrangement of olefine dibromides containing a tertiary bromine. W. R. EVERS, H. S. ROTHROCK, H. M. WOODBURN, E. E. STAHLY, and F. C. WHITMORE (J. Amer. Chem. Soc., 1933, **55**, 1136—1140).—CMe_2Br·CH_2Br (from $Bu^{\gamma}OH$ and Br at 60—70°) and CMe_2Br·CHMeBr (from *tert.*-amyl alcohol and Br at 60—65°) are hydrolysed by boiling H_2O to $Pr^{\beta}CHO$ (75% yield) and $COMePr^{\beta}$ (55% yield), respectively. Similarly, βγ-dibromo-β-methylpentane gives 25% of $COEtPr^{\beta}$, βγ-dibromo-β-methylhexane affords 33% of $COPrPr^{\beta}$, βγ-dibromo-

γ-methylpentane yields 20% of Me *sec.*-Bu ketone, βγ-dibromo-γ-ethylpentane furnishes 10% of γ-ethylpentan-β-one (and 30% of γ-ethyl-$\Delta^{\alpha\gamma}$-pentadiene), and βγ-dibromo-βγ-dimethylpentane gives 10% of Me *tert.*-amyl ketone. Products were not isolated from βγ-dibromo-β-methyltridecane, -βδ-dimethylpentane, -βγ-dimethylheptane, and -βγ-dimethyloctane, δε-dibromo-ε-methylnonane, and αβ-dibromo-βγγ-trimethylbutane. H. B.

Preparation of vinyl iodide. J. SPENCE (J. Amer. Chem. Soc., 1933, **55**, 1290—1291).—CH_2:CHI is obtained in 35% yield from *s*-$C_2H_4I_2$ and 3*N*-NaOEt. H. B.

Action of bromine and butadiene. G. B. HEISIG (J. Amer. Chem. Soc., 1933, **55**, 1297).—Reaction between butadiene and Br in N_2 (15—20 vols.) occurs on the surface of glass vessels; αδ-dibromo-Δ^{β}-butene is formed. The rate of reaction is markedly reduced when the glass surface is coated with paraffin wax. H. B.

α-Iodo-Δ^{α}-pentinene. T. H. VAUGHN (J. Amer. Chem. Soc., 1933, **55**, 1293).—Various physical data (cf. Grignard and Perrichon, A., 1926, 381) are reported. H. B.

Determination of the volume percentage of alcohol in water–alcohol mixtures at 4°. J. DE GRAAF (Pharm. Weekblad, 1933, **70**, 338—339).—Vals. of d^4 for EtOH–H_2O mixtures are calc. from recorded data. S. C.

***n*-Aliphatic long-chain alcohols.** J. W. C. PHILLIPS and S. A. MUMFORD (J.C.S., 1933, 235—236).—Fractionation of the acetates of "pure" commercial *n*-tetradecyl alcohol gives a 60% yield of the β-form, m.p. 13·85° (hydrolysed to the β-alcohol, f.p. 37·7°; dimorphous), from which the α-acetate, f.p. 3·2°, is obtained on cooling the liquid ester. The α-, f.p. 30·3°, and β-, m.p. 32·8° (40% yield), -acetates of *n*-octadecyl alcohol, f.p. 57·95° (dimorphous), are similarly prepared. J. W. B.

Rearrangement of methyl*tert.*-butylcarbinol (pinacolyl alcohol). I. F. C. WHITMORE and H. S. ROTHROCK (J. Amer. Chem. Soc., 1933, **55**, 1106—1109).—CHMeBu$^{\gamma}$·OH (I) is little affected by heating at 200° for 48 hr. in CO_2. Distillation of its acetate over porous earthenware in a PYREX tube at 300° gives about 35% of CH_2:CHBu$^{\gamma}$. (I) could not be dehydrated by boiling with traces of I or $PhSO_3H$; dehydration with $H_2C_2O_4$ gives CMe_2:CMe_2 (II) and CH_2:CMePr$^{\beta}$ (III) in the ratio 5 : 2. When CHMeBu$^{\gamma}$·OMgBr [from (I) and MgEtBr] is heated to 340°, a 3 : 2 mixture of (II) and (III) is produced. The chloride from (I) and fuming HCl (conc. HCl saturated with HCl at −10°) and moist Ag_2O give CMe_2Pr^{β}·OH; the bromide from (I) and dry HBr contains about 90% of $CMe_2Pr^{\beta}Br$. H. B.

Dehydration of ββ-dimethylhexyl alcohol and related *tert.*-alcohols. F. C. WHITMORE and J. M. CHURCH (J. Amer. Chem. Soc., 1933, **55**, 1119—1124).—Dehydration of ββ-dimethylhexyl alcohol (from CMe_2Bu·MgCl and CH_2O) with 6% of conc. H_2SO_4 and 4% of *p*-C_6H_4Me·SO_3H gives a 63% yield of a mixture of CMe_2:CHBu (I), β-methyl-Δ^{α}-heptene (II), CHPr:CMeEt (III), and CHMe:CMeBu (IV); the ratios (I) : (II) and (III) : (IV) are 12 : 1 and 2 : 1, respectively. Dehydration of CMeEtBu·OH with 50% H_2SO_4 gives (III) and (IV) (ratio 1 : 1·6) and 6% of CH_2:CEtBu, whilst dimethyl-*n*-amylcarbinol is similarly dehydrated to (I) and (II) (ratio 1·4 : 1). The olefine formed during the distillation of CMe_2BuCl contains β-methyl-Δ^{α}- and -Δ^{β}-hexenes (the former predominates slightly). The structures of the above olefines are determined by ozonolysis. H. B.

Oxidation of true acetylenic hydrocarbons by selenium dioxide: preparation of α-acetylenic alcohols. R. TRUCHET (Compt. rend., 1933, **196**, 706—709).—*n*-Δ^{α}-Heptinene (2 mols.) boiled with 1 mol. of SeO_2 in EtOH gives a 27% yield of *n*-Δ^{α}-*heptinen-γ-ol*, b.p. 67°/18 mm. [*Bz* derivative, b.p. 154—156°/18 mm.; *Ag* derivative: two active H atoms (Zerevitinov)], oxidised by $KMnO_4$ to *n*-valeric acid. Similarly, *n*-Δ^{α}-octinene affords *n*-Δ^{α}-*octinen-γ-ol*, b.p. 83°/19 mm. CPh·CH is unattacked by SeO_2. J. W. B.

Action of periodic acid on polyhydroxy-compounds. I. Technique. P. FLEURY and J. LANGE (J. Pharm. Chim., 1933, [viii], **17**, 196—208; cf. A., 1928, 269).—HIO_4 is determined iodometrically, or better with As_2O_3 and I. CH_2O is determined with Nessler's reagent (A., 1922, ii, 666), or with dimethyldihydroresorcinol after removal of HIO_4. CH_2O and HCO_2H are determined together with $KMnO_4$ after removal of HIO_4 with $MnSO_4$. A. A. L.

Isomeric θι-dihydroxyoctadecyl alcohols produced by oxidation of *cis*- and *trans*-Δ^{θ}-octadecenyl (oleyl and elaidyl) alcohols. G. COLLIN and T. P. HILDITCH (J.C.S., 1933, 246—248).—Oxidation of oleyl (*cis*-) alcohol or its acetate with H_2O_2 in AcOH, or of elaidyl (*trans*-) H phthalate with dil. alkaline $KMnO_4$ at 0° affords a θι-*dihydroxyoctadecyl alcohol*, m.p. 82—82·5°. Conversely, elaidyl alcohol with H_2O_2 or oleyl H phthalate with $KMnO_4$ gives an isomeric θι-*dihydroxyoctadecyl alcohol*, m.p. 126—127°, the behaviour of these unsaturated alcohols being parallel to that of the corresponding oleic and elaidic acids, the nature of the salt-forming group being without influence on the form of the $(OH)_2$-compound produced. J. W. B.

Synthesis of pentaerythritol. A. CORBELLINI and A. LANGINI (Giorn. Chim. Ind. Appl., 1933, **15**, 53—56).—Condensation of CH_2O and MeCHO to pentaerythritol in presence of $Ca(OH)_2$, $Ba(OH)_2$, $Mg(OH)_2$, NaOH, and Na_2CO_3 has been studied. The reaction proceeds quickest and at the lowest temp. (40°) with $Ca(OH)_2$, a 69% yield on the MeCHO being obtained. Syrupy saccharine products are formed as by-products in all cases. T. H. P.

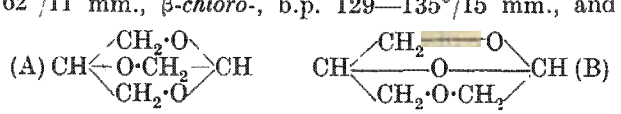
Reaction between acid chlorides and ethers in presence of zinc chloride. L. P. KYRIDES (J. Amer. Chem. Soc., 1933, **55**, 1209—1212; cf. Underwood *et al.*, A., 1930, 320).—Slow addition of Et_2O (1·21 g.-mol.) to BzCl (1·06 g.-mol.) and $ZnCl_2$ (0·5 g.) at 150—170° gives 78% of EtCl and 91·5% of BzOEt; $BzCl+Et_2O \longrightarrow BzOEt+EtCl$. Lauryl chloride reacts similarly but very slowly with Et_2O at its b.p. Phthalyl chloride (1·18 g.-mol.), Et_2O (1·48 g.-mol.),

and $ZnCl_2$ (0·4 g.) at 110—170° similarly give EtCl (80% yield) and o-$C_6H_4(CO)_2O$; o-$C_6H_4(COCl)_2$+ Et_2O ⟶ o-$C_6H_4(CO)_2O$+2EtCl. Phthalyl chloride and Pr^β_2O react similarly, but C_3H_6 is also produced. H. B.

Danger of explosions. (Sir) R. Robertson (Chem. and Ind., 1933, 274).—An explosion occurred during the distillation of Pr^β_2O. E. S. H.

Reaction of mono-substituted ethylene oxides (epoxides) with organic magnesium compounds. Mechanism of reaction, and the constitution of the Grignard reagent. I. Ribas and E. Tapia (Anal. Fís. Quím., 1932, **30**, 944—970).—A detailed study of the interaction of $(\cdot CH_2)_2O$ and MgEtBr in various proportions in Et_2O shows that the mechanism proposed by Grignard (A., 1903, i, 552) is incorrect. The addition of C_2H_4O to MgEtBr yields a ppt. of $CH_2Br\cdot CH_2\cdot OMgBr$ and $(CH_2Br\cdot CH_2\cdot O)_2Mg$ (cf. this vol., 48) by reaction with $MgBr_2$ resulting from the equilibrium $2MgEtBr \rightleftharpoons MgBr_2+MgEt_2$. Hydrolysis of the ppt. yields $CH_2Br\cdot CH_2\cdot OH$. If C_2H_4O is added in excess (2 mols. or more) $MgEt_2$ reacts with it, yielding $Mg(OBu)_2$, and hydrolysis of the mixture yields BuOH in addition to $CH_2Br\cdot CH_2\cdot OH$. If, however, MgEtBr is present in excess, the following reactions occur on heating (Grignard's "second phase"): $2CH_2Br\cdot CH_2\cdot OMgBr+MgEt_2 \longrightarrow 2Bu\cdot OMgBr+MgBr_2$, and $(CH_2Br\cdot CH_2\cdot O)_2Mg+MgEt_2 \longrightarrow Mg(OBu)_2+MgBr_2$, and hydrolysis yields BuOH. In the cases of epichlorohydrin and αβ-oxido-γ-methoxypropane, the reactivities with $MgBr_2$ and $MgEt_2$ or $MgPh_2$ are of the same order, and the composition of the products is correspondingly modified. R. K. C.

Reactions relating to carbohydrates and polysaccharides. XLIV. Synthesis of isomeric dicyclic acetal ethers. E. G. Hallonquist and H. Hibbert (Canad. J. Res., 1933, **8**, 129—136).—αγ-Bromoethylideneglyceryl β-benzoate with KOH gives the *compound* A, m.p. 99° (yield 95%), hydrolysed to glycollaldehyde and glycerol. Glyceryl α-benzoate (improved prep.) with tribromoparacetaldehyde (improved prep.) and a little H_2SO_4 gives (52% yield) αβ-bromoethylideneglyceryl γ-benzoate, b.p. 169—171°/1 mm., which with KOH gives *B*, m.p. 56—57°, b.p. 68—70°/12 mm. (cf. A., 1923, i, 439), hydrolysed to glycollaldehyde and glycerol. The reaction with KOH is slower in the latter case, and may be used to separate αβ-bromoethylideneglycerol from its isomeride. Anhyd. glycerol with chloroacetal at 115° gives *chloroethylideneglycerol*, b.p. 130—134°/13 mm. (yield 80%). *Chloroethylideneglycol*, b.p. 57°/13 mm., *chloroethylidenetrimethyleneglycol*, b.p. 60—62°/11 mm., *β-chloro-*, b.p. 129—135°/15 mm., and



(A) (B)

β-bromo-propylideneglycerol, b.p. 136—140°/18 mm., are similarly prepared (yields 40, 60, 56, and 65%, respectively). A. A. L.

Ethyl orthosilicate. L. Solana and E. Moles (Anal. Fís. Quím., 1932, **30**, 886—917).—The physical consts. of pure Et_4SiO_4 prepared in a vac. apparatus from pure $SiCl_4$ and anhyd. EtOH in 90% yield are recorded. Et pyrosilicate, from Et_4SiO_4 by decomp. in presence of moisture, has b.p. 231—232°/703 mm. R. K. C.

Preparation of glucose monosulphate salts and their rotatory powers. T. Soda (Bull. Chem. Soc. Japan, 1933, **8**, 37—49).—Glucose (in C_5H_5N) is treated with $ClSO_3H$ (in $CHCl_3$) at < 10°, the resulting syrup dissolved in H_2O, freed from $CHCl_3$ by evaporation in vac., the solution treated with PbO (to remove SO_4) and again evaporated (until free from C_5H_5N), and finally with Ag_2SO_4 (to remove Cl). Decomp. of the resultant solution with H_2S gives glucose H sulphate, which can be neutralised with the appropriate oxide or carbonate, freed from residual glucose by fermentation, and the salt finally pptd. with EtOH; the *K*, $[\alpha]^{14}_{\ 1}$ +44°, *Na* (+H_2O), $[\alpha]_{5461}$ +43·7°, *Ba* (+EtOH), $[\alpha]^{17\cdot3}_{5461}$ +38·5°, and *Ca* (+2EtOH), $[\alpha]^{16}_{5461}$ +38·1°, salts are thus prepared. The above and brucine (A., 1923, i, 441) salts all exhibit mutarotation; the vals. quoted above are final. The sp. rotation of the free acid is calc. to be $[\alpha]_D$ +40·1° to +43·7°. The constitutions of the salts are discussed. H. B.

Organic compounds of sulphur. XXIII. Constitution of the photodimeric thiophosgene. A. Schönberg and A. Stephenson (Ber., 1933, **66**, [*B*], 567—571).—The properties of photodimeric thiocarbonyl chloride, m.p. 119°, are not in harmony with Rathke's conception that it is CCl_3 chlorodithioformate, but are explicable by the constitution $CCl_2<\begin{matrix}S\\S\end{matrix}>CCl_2$. With NH_2Ph (1 : 3) it yields the substance, $CCl_2<\begin{matrix}S\\S\end{matrix}>C{:}NPh$, m. p. 70°, decomposed when warmed into $CSCl_2$ and PhNCS (I) and transformed by hot NH_2Ph into (I), $CS(NHPh)_2$, triphenylguanidine, and HCl. With dil. AcOH it is partly hydrolysed to the *compound* $CCl_2<\begin{matrix}S\\S\end{matrix}>CO$. H. W.

Preparation of higher aliphatic sulphonic acids. C. R. Noller and J. J. Gordon (J. Amer. Chem. Soc., 1933, **55**, 1090—1094).—$(\cdot SAlk)_2$, prepared from alkyl bromides and Na_2S_2 in aq. MeOH, are reduced (Zn dust, dil. H_2SO_4) to SHAlk, the Pb salts of which are oxidised by 50% HNO_3 to Pb sulphonates. These are decomposed by dry HCl in $Pr^\beta OH$, the $Pr^\beta OH$ solution evaporated at 80—90°/3—4 mm., the residue mixed with Et_2O, and the $Alk\cdot SO_3H$ extracted with H_2O. The following are described: nonyl, b.p. 100—104°/20 mm., decyl, b.p. 125—127°/19 mm., *undecyl*, b.p. 138—141°/21 mm., *dodecyl*, b.p. 153—155°/24 mm., *tridecyl*, b.p. 162—166°/22 mm., and *tetradecyl*, b.p. 176—180°/22 mm., *mercaptans*; *nonane-*, m.p. 46° (*Pb* and *benzylaniline*, m.p. 90·5—91°, salts), *decane-*, m.p. 46·5° (*Pb* and *benzylaniline*, m.p. 84—84·5°, salts), *undecane-* (+H_2O), m.p. 40—41°, m.p. (anhyd.) 49° (*Pb* and *benzylaniline*, m.p. 84·6—84·7°, salts), *dodecane-* (+H_2O), m.p. 43—45°, m.p. (anhyd.) 52° (*Pb* and *benzylaniline*, m.p. 91—91·2°, salts), *tridecane-* (+H_2O), m.p. 48—49°, m.p. (anhyd.) 58° (*Pb* and *benzylaniline*, m.p. 87·5—88°, salts), and *tetradecane-* (+H_2O), m.p. 55—56°, m.p. (anhyd.) 65·5° (*Pb* and *benzylaniline*, m.p. 82·5—82·7°, salts), *-sulphonic acids*. H. B.

Preparation and properties of di-*n*-butanesulphonylmethane. R. E. STUTZ and R. L. SHRINER (J. Amer. Chem. Soc., 1933, **55**, 1242—1245).—$(\cdot SBu)_2$, prepared by successive treatment of BuBr with $Na_2S_2O_3$ and KOH in aq. EtOH, is reduced (Na, EtOH), and the resultant BuSNa treated with CH_2I_2, thus giving *di*-n-*butylthiolmethane*, b.p. 133—138°/30—35 mm., 250°/760 mm. This is oxidised (CrO_3, AcOH) to *di*-n-*butanesulphonylmethane* (I), m.p. 95—96° (*Br*$_2$-derivative, m.p. 80°) (cf. Whitner and Reid, A., 1921, i, 300), readily sol. in aq. 5% NaOH. (I) is methylated (MeI, EtOH–NaOEt) to ββ-*di*-n-*butanesulphonylpropane*, m.p. 67—68°. $(\cdot SBu)_2$ and $(\cdot SPh)_2$ are cleaved by Na or Na–K alloy in xylene to the metal mercaptides. H. B.

Mobility of groups containing a sulphur atom. II. D. W. COWIE and D. T. GIBSON (J.C.S., 1933, 306—309).—The reaction $RSO_2\cdot CH_2Ac + R'SO_2\cdot SMe \longrightarrow R'SO_2\cdot CHAc\cdot SMe$ (A., 1932, 837) occurs when R=alkyl and R′=aryl but not when R=aryl and R′=alkyl. Et sulphonylacetone, Et ethanethiolsulphonate (I) (best prepared by oxidation of Et_2S_2 with H_2O_2 in AcOH at 70°), and Na_2CO_3 afford a 75% yield of *ethylsulphonylethylthioacetone*, b.p. 102—109°/0·2 mm. [giving $CH_2(SO_2Et)_2$ on hydrolysis and oxidation], similar condensation using Me *p*-toluenethiolsulphonate (II) affording only a 6% yield of *p*-tolylsulphonyl-α-methylthioacetone (III), also obtained from (II) and cyclo*hexylsulphonylacetone*, m.p. 40°, b.p. 135°/0·2 mm. [prepared from CH_2ClAc and Na *cyclo*hexylsulphinate (IV)]: *p*-tolylsulphonylacetone (V) and (I) give *p*-tolylsulphonyl-α-ethylthioacetone, and (III) with (IV) gives *p*-tolylsulphonylmethylthiolmethane. Na *d*-camphorsulphinate and CH_2ClAc give *anhydro*-d-*camphorsulphonylacetone*, m.p. 178°, $[\alpha]^{20}_{\ 1}$ −115° in EtOH. Me *d*-camphorthiolsulphonate with (V) and with *p*-chlorobenzenesulphonylacetone gives, respectively, (III) and *p*-chlorobenzenesulphonylmethylthiolmethane; and *d*-dicamphoryldisulphoxide and *p*-chlorophenylsulphonylacetone with Na_2CO_3 afford a *substance*, m.p. 149—150°. (I) or Et *p*-toluenethiolsulphinate with $CH_2(SO_2Et)_2$ and Na_2CO_3 gives *bisethylsulphonylethylthiolmethane*, m.p. 71°, oxidised by H_2O_2 to the *trisulphone*, m.p. 212°, and with phenylsulphonylethylsulphonylmethane (I) gives *phenylsulphonylethylsulphonylethylthiolmethane*, m.p. 108°, oxidised by cold $KMnO_4$ or H_2O_2 to a *substance*, m.p. 135—139°. αα′-Bisphenylsulphonylethane, *αα′-bisphenylsulphonylpropane*, m.p. 97—98°, prepared by H_2O_2 oxidation of *αα′-bisphenylthiolpropane* (from EtCHO and PhSH), and the αγ-disulphone (VI) are not identical with the compound (VII), m.p. 101°, obtained by a modification of Otto's method (A., 1895, i, 229) from Ph dibromopropylsulphone, $PhSO_2Na$, and EtOH–NaOH, but on keeping (VII) changes into (VI), m.p. 123°, and is therefore regarded as $SO_2Ph\cdot[CH_2]_3\cdot O\cdot SOPh$. Similarly, the substance, m.p. 123°, obtained by Troger and Artmann (A., 1896, i, 569) is prepared either from αβ-dibromo-γ-(β-naphthylsulphonyl)-propane and $PhSO_2Na$, or from αβ-dibromo-γ-phenylsulphonylpropane and $2\text{-}C_{10}H_7\cdot SO_2Na$, and must therefore be the αγ-compound. With the analogous *p*-toluene and β-naphthyl derivatives the third isomeride [corresponding with (VII)] depresses the m.p. of the αβ-compound in the first series, and of the αγ-derivative in the second. J. W. B.

Oxidation of propionic acid and potassium propionate with persulphate. F. FICHTER and H. E. SUENDERHAUF (Helv. Chim. Acta, 1933, **16**, 338—345).—Oxidation of aq. $EtCO_2K$ in presence of K_2CO_3 or of $EtCO_2H$ in H_2O at 100° gives CO_2, C_2H_4, CO, C_2H_6, CH_4, meso- and *dl*-αα′-dimethylsuccinic acids (I), amorphous products, and, in the former case, some EtOH. The acid conditions diminish the formation of gaseous products and favour (I), giving also (?) an isomeride of these (Et_2 ester, b.p. 122—126°/3—3·5 mm.). Explosive decomp. of $EtCO_3H$ (initiated at 250°) gives CO_2, C_2H_4, CO, C_2H_6, CH_4, H_2, and O_2. H. A. P.

Maximum rotations in homologous series of α-bromo-acids. P. A. LEVENE (J. Amer. Chem. Soc., 1933, **55**, 1295—1296).—α-Bromobutyric, $[M]^{25}_D$ +59·62°, and α-bromohexoic, −71·45°, acids are obtained by resolution with brucine and strychnine, respectively. The vals. of $[M]$ for the acids (and Me esters) increase progressively in this homologous series. H. B.

Acid sodium salts of fatty acids of high mol. wt. P. EKWALL (Ber., 1933, **66**, [*B*], 546—547).—Examination of the cooling curves or application of Rheinboldt's method to molten mixtures of Na palmitate and palmitic acid shows the existence of the *salts*, NaP,2HP (I) [$P=C_{15}H_{31}\cdot CO_2$], m.p. 73·6—73·9° (decomp.), and 2NaP,HP (II), m.p. 91—92° (decomp.). NaP,HP is obtained from under-cooled mixtures of definite composition. The m.p. recorded by Ekwall and Mylius (A., 1929, 676) are amended as follows: (I) m.p. 73·6—73·9°, becoming clear at 83°; (II) m.p. 91—92°, becoming clear at 180°. H. W.

Mixed esters of orthoformic acid. P. P. T. SAH and T. S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 223—258; cf. A., 1932, 921).—The physical consts. of a no. of mixed esters of orthoformic acid, predicted on the assumption that the properties are additive, agree with those determined experimentally. A. A. L.

Determination of lactic acid. T. E. FRIEDEMANN and J. B. GRAESER (J. Biol. Chem., 1933, **100**, 291—308).—Under certain conditions the aeration method for the determination of lactic acid as MeCHO (A., 1927, 800; 1929, 677) becomes untrustworthy and a modified distillation technique giving a 99+0·5% recovery is described, *Li lactate* (prep. described) being used as a standard. This involves the previous removal of other HSO_3-binding substances, and the technique with various biological fluids is described. The presence of excess of the oxidising agent throughout is essential, and addition of 1% $MnSO_4$ ensures almost quant. yields, greater consistency of results, and permits a shorter oxidation period and wider limits of concn. of the oxidising agent. Aliquot portions containing 1—3 mg. of the sample are usually employed, but the max. size of the sample must be determined in each case, recovery being incomplete if the sample is too large. Strong acidity (>0·05*N*) causes the results to be untrustworthy and adjust-

ment to approx. neutrality (phenol-red) is then necessary. Efficient cooling is essential during the titration of the bound HSO_3. J. W. B.

***trans*-γ-Hydroxycrotonic acid.** R. RAMBAUD (Compt. rend., 1933, **196**, 487—488).—Hydrolysis of Me or Et γ-acetoxy-Δ^{α}-butenoate with aq. KOH gives trans-*γ-hydroxy-*Δ^{α}*-butenoic acid* (I), m.p. 108·5° [*acetate*, m.p. 94°, identical with that obtained from γ-bromo-Δ^{α}-butenoic acid and NaOAc; *dibromide*, m.p. 156° (block), decomp. 121° in capillary tube]. The *trans*-configuration is adopted, since (I) is oxidised by CrO_3 and $KHSO_4$ in AcOH to fumaric acid, and is hydrogenated to γ-butyrolactone, identified by oxidation to succinic acid. (I) cannot be dehydrated to form a lactone. A. C.

Constitutional factors controlling prototropic changes in carbonyl compounds. IV. Carbethoxyl and allied groups. H. B. WATSON and E. D. YATES.—See this vol., 470.

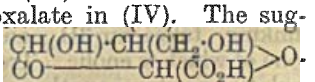
2 : 4-Dinitrophenylhydrazones of ketonic acids of biological importance. F. P. CLIFT and R. P. COOK (Biochem. J., 1932, **26**, 1800—1803).—The 2 : 4-*dinitrophenylhydrazones* of mesoxalic, m.p. 202° (uncorr.), acetoacetic, m.p. 125°, and oxaloacetic acids, m.p. 211° after softening at 208°, have been prepared. These derivatives may be titrated as acids and the data used for their identification. S. S. Z.

Cerebrosides. XIII. Cerebronic acid. E. KLENK and W. DIEBOLD (Z. physiol. Chem., 1933, **215**, 79—86; cf. A., 1931, 829).—Further evidence is afforded that the main product of the oxidative degradation of cerebronic acid is *n*-tricosoic acid. J. H. B.

Detection of oxalic acid as oxalatomanganate. G. LOCHMANN (Chem.-Ztg., 1933, **57**, 214—215).—The solution is buffered and its p_H is adjusted until a drop colours Me-orange paper brown. Mn_2O_3 is added and the mixture is shaken, when the characteristic red colour of the $Mn(C_2O_4)_3'''$ ion appears within 30 sec., even with very dil. (1 : 2500) solution; sunlight should be excluded. The limit is 0·2 mg. C_2O_4'' in 0·5 c.c., but the sensitivity is reduced by $Mn^{\cdot\cdot}$, WO_3, Al''', etc. Tartaric and lactic acids interfere. CaC_2O_4 should be treated with warm 10% H_2SO_4 and the test carried out with the centrifuged solution. Anhyd. or native Mn_2O_3 is almost inert. Suitable material may be prepared by adding 15 c.c. of 10% aq. NH_3 and then, in small portions, 30 c.c. of 3% H_2O_2, to a solution of 3 g. of $MnCl_2,4H_2O$ and 3 g. of NH_4Cl in 30 c.c. of H_2O; the ppt. is washed with hot H_2O and dried on the water-bath. Details are given of the prep. of $K_3Mn(C_2O_4)_3$. H. F. G.

Synthesis of α-alkyladipic acids. A. FRANKE, A. KROUPA, and S. HADZIDIMITRIU (Monatsh., 1933, **62**, 119—130).—Et *n*-hexylmalonate (A., 1924, i, 1037) (Na derivative) with $CH_2(CH_2Br)_2$ in boiling C_6H_6 during 1 hr. affords *γ-bromopropyl-*n*-hexylmalonic acid* (I), b.p. 142—145°/0·3 mm., with a tetracarboxylic acid. (I) with KCN in boiling EtOH–H_2O for 7 hr. affords the *nitrile*, b.p. 152—153°/0·2 mm., hydrolysed to *α-carboxy-α-*n*-hexyladipic acid*, m.p. 161° (decomp.), decarboxylated at 190° to *α-*n*-hexyladipic acid*, m.p. 65·4° (*diamide*, m.p. 187·5—188°, hydrolysed by alcoholic KOH to the *monoamide*, m.p. 149·5°), identical with the acid obtained from αε-oxidodecane (cf. A., 1931, 67). Et *n*-octylmalonate (prep. described) affords as above *Et γ-bromopropyl-*n*-octylmalonate*, b.p. 152—157°/0·2 mm., converted successively into the *nitrile*, b.p. 165—168°/0·2 mm., *tricarboxylic acid*, m.p. 160° (decomp.), and *α-*n*-octyladipic acid*, m.p. 75° (*diamide*, m.p. 186·7°; *monoamide*, m.p. 150°), identical with the acid obtained from αε-oxidododecane. J. L. D.

Reaction of hydroxymaleic anhydride with ammonia and aliphatic amines. Preparation of substituted maleimides. A. ROTHHAAS (Annalen, 1933, **501**, 295—304).—Hydroxymaleic anhydride (I) (simplified prep. given; cf. Wohl *et al.*, A., 1901, i, 365; 1907, i, 583) and Et_2O–CH_2N_2 give methoxymaleic anhydride (II), which with MeOH–NH_3 at 100° affords *methoxymaleamide* (III), m.p. 154°. (II) and cold MeOH–NH_3 give *methoxymaleamic acid*, m.p. 179·5°, which when heated rapidly affords *methoxymaleimide*, m.p. 169° (N-*Et* derivative, oil, prepared by the action of diazoethane). (III) and $KHSO_4$ at 85°/vac. give a *mixture*, m.p. 117—132°, of isomeric methoxymaleamic acids. (I) and Et_2O–diazoethane afford *ethoxymaleic anhydride* (+MeOH), m.p. 103·5°, which when heated at 80°/vac. over P_2O_5 gives some *Me H ethoxymaleate*, and is converted by cold conc. MeOH–NH_3 into *NH_4 H ethoxymaleate*, m.p. 158° (decomp.), which when heated passes into *ethoxymaleimide*, m.p. 138·5° (N-*Me* derivative, m.p. 75°). (II) and NH_2Me at 100° give *N-methyl-α-methylaminomaleimide*, m.p. 147°; *N-ethyl-α-ethylaminomaleimide*, m.p. 83·5° (1 : 1-*compound*, m.p. 204°, with $NHPh{\cdot}NH_2$), is similarly prepared. *Me methoxymaleate* has m.p. 41°. H. B.

Constitution of vitamin-*C*. F. MICHEEL and K. KRAFT (Z. physiol. Chem., 1933, **215**, 215—224).—With CH_2N_2, ascorbic acid (I) gives a Me_2 derivative (II), $[\alpha]_D^{17}$ +31·8° in EtOH, which forms a *di-p-nitrobenzoate* (III), m.p. 172°, $[\alpha]_D^{15}$ −78·7° in $CHCl_3$, unattacked by Br in AcOH or $KMnO_4$ in $COMe_2$. With NH_3 in MeOH, (II) gives a *product*, $C_8H_{15}O_6N$+0·5MeOH, m.p. 123° (decomp.), $[\alpha]_D^{20}$ −24·8° in MeOH. The $COMe_2$ derivative of (I) gives a *Me_2* derivative, m.p. 101°, $[\alpha]_D^{20}$ +16·2° in EtOH. Treatment of (III) with O_3 affords a *product* (IV), $C_{22}H_{18}O_{14}N_2$, m.p. 162°, $[\alpha]_D^{19}$ −41·8° in $CHCl_3$, which on hydrolysis with KOH in aq. dioxan uses five equivs. of alkali. The mixture contains $H_2C_2O_4$, p-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ (V), and trihydroxybutyric acid (VI). Two OH groups of (VI) are esterified with (V) and one with Me H oxalate in (IV). The suggested constitution for (I) is  . J. H. B.

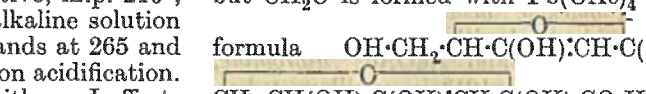
Structure of ascorbic acid. E. L. HIRST (Chem. and Ind., 1933, 221—222).—Ascorbic acid (I) (bisphenylhydrazone derivative, m.p. 187°, derived from $C_6H_8O_6$) is stereochemically related to *l*-sorbose, since oxidation (cf. this vol., 100) gives $H_2C_2O_4$ and *l*-threonic acid (II), further oxidised by HNO_3 to *d*-tartaric acid. (II) is also obtained by alkaline NaOCl oxidation of the product *A* obtained by the

action of aq. I on (I). At the moment of formation *A* shows no selective absorption, has a positive $[\alpha]_D$ val., gives a red *NHPh·NH*$_2$ derivative, m.p. 216°. (derived from $C_6H_6O_6$), and titrates as a lactone, but in aq. solution $[\alpha]_D$ gradually changes to −6° when a band at 295 mμ appears, and the product yields an isomeric *NHPh·NH*$_2$ derivative, m.p. 210°, but can still be reduced to (I). In alkaline solution the band at 295 mμ is replaced by bands at 265 and 340 mμ, displaced to 245 and 300 mμ on acidification. It is suggested that oxidation of (I) with aq. I effects the (reversible) removal of two H (*e.g.*, >CH·OH >CO), and that (I) may be 3-keto-*l*-sorbosone (the tautomeric furanose and pyranose forms of which are indicated), its acidic properties being due to an active OH group and not to a true CO_2H group. Such a structure is in harmony with *X*-ray data. J. W. B.

Constitution of vitamin-*C*. E. G. Cox and E. L. Hirst (Nature, 1933, **131**, 402).—The furancarboxylic acid structure for ascorbic acid (cf. this vol., 489) does not satisfy crystallographic requirements. L. S. T.

Antiscorbutic vitamin (vitamin-*C*). P. Karrer, H. Salomon, K. Schopp, and R. Morf (Helv. Chim. Acta, 1933, **16**, 181—183).—The hexuronic acid $C_6H_8O_6$ (I) of Szent-Gyorgyi (A., 1932, 548) is not a lactonic acid, since it gives a Na salt, $C_6H_7O_6Na$ (II). (I) contains a double linking [$C(NO_2)_4$; catalytic reduction], four active H atoms (Zerevitinov) (three of which are alcoholic or enolic), and two CO groups (formation of di-*p*-nitrophenylhydrazone), and with CH_2N_2 affords a Me ether Me ester [methylated further (Me_2SO_4) to a Me_4 derivative]. (II) gives a reddish-violet colour with $FeCl_3$, indicating its enolic character. Oxidation of (I) with $Cu(OAc)_2$ affords a dehydro-derivative which reduces Fehling's solution and is reduced by H_2S to (I). (I) consumes 2I in acid and 4I in alkaline solution (the resulting product does not reduce Fehling's solution). H. B.

Antiscorbutic vitamin (vitamin-*C*, ascorbic acid). P. Karrer, H. Salomon, R. Morf, and K. Schöpp (Biochem. Z., 1933, **258**, 4—15).—Ascorbic acid, $C_6H_8O_6$, m.p. 189—190°, is monobasic (Na salt, $C_6H_7O_6Na$, cryst. from EtOH). It yields a *dinitrophenylhydrazone*, a *Me*$_2$, $[\alpha]_D$ +43·66° (one Me removed by hydrolysis), and a *Me*$_4$ derivative (which yields a monocarboxylic acid containing 2OMe on oxidation with $KMnO_4$), a *compound* with $COMe_2$, m.p. 205° (*Me*$_2$ derivative, m.p. 100°), and a *dehydro*-derivative, $C_6H_6O_6$, on oxidation with $Cu(OAc)_2$. From this oxidation product the acid is easily regenerated by reduction (*e.g.*, with H_2S). It contains one double linking, takes up $3H_2$, and contains 4 OH groups, one of which is enolic. Treatment with 4I in alkaline solution produces another oxidation product. Spectroscopic examination of its solutions indicates that in addition to the keto and enol forms at least one other form exists. With CPh_3Cl it yields a *CPh*$_3$ derivative (presence of CH_2·OH), but its $COMe_2$ compound does not. Possibly its constitution is OH·CH_2·CH(OH)·CO·CH_2·CO·CO_2H. W. McC.

Vitamin-*C*. IV. P. Karrer, G. Schwarzenbach, and K. Schopp (Helv. Chim. Acta, 1933, **16**, 302—306).—The CPh_3 ester of vitamin-*C*, like vitamin-*C* (I), takes up 2I in H_2SO_4 and gives a blue coloration with $FeCl_3$; with CH_2N_2 it gives a *Me*$_2$ derivative (ether-ester). An alcoholic OH group in addition to an enolic OH group is therefore present in (I). Oxidation of (I) with H_2O_2 gives $H_2C_2O_4$, but CH_2O is formed with $Pb(OAc)_4$ in AcOH. The formula  or CH_2·CH(OH)·C(OH):CH·C(OH)·CO_2H is regarded as probable, and is supported by the dissociation const., but a furanoid structure based on a β-ketonic acid is not thereby excluded, although regarded as improbable on account of its stability. Study of the oxidation–reduction potential indicates the intermediate formation of a powerful reducing agent with $K_3Fe(CN)_6$ in alkaline solution. H. A. P.

Triphenylmethyl derivative of vitamin-*C*. L. Vargha (Nature, 1933, **131**, 363).—Treatment of ascorbic acid but not of its :CMe_2 derivative with CPh_3Cl yields triphenylmethylascorbic acid, $C_{25}H_{22}O_6$, m.p. 130 (decomp.), α +30° (*c* 3·0). The CO group of vitamin-*C* is ketonic. L. S. T.

C_4-Saccharic acids. VI. Further attempts to prepare ββ′-dihydroxy*iso*butyric acid. βγ-Dihydroxybutyrolactone from glycidol. Preparation of the two iodohydrins of glycerol. J. W. E. Glattfeld and R. Klaas (J. Amer. Chem. Soc., 1933, **55**, 1114—1119).—ββ′-Dihydroxy*iso*butyric acid could not be prepared by the following methods: (*a*) from glycerol β-chlorohydrin (I) (*dibenzoate*, b.p. 210—211°/1·5 mm.) and CuCN or $Hg(CN)_2$, (*b*) from the *diacetate*, b.p. 101—102°/4 mm., of (I), $ClCO_2Et$, and 4% Na–Hg, (*c*) oxidation ($KMnO_4$ or $BaMn_2O_8$) of $C(CH_2$·$OH)_4$. Hydrolysis [aq. $Ba(OH)_2$] of the product from glycidol and HCN (under various conditions) gives 25—50% of βγ-dihydroxybutyrolactone (II), thus confirming the hypothesis (A., 1931, 1148) that glycidol is an intermediate in the reaction between NaCN and glycerol α- or β-chlorohydrin. *Glycerol β-iodohydrin*, m.p. 52—53°, from (I) and NaI in $COMe_2$, and NaCN in EtOH give (after hydrolysis) some (II). Glycerol α-iodohydrin, m.p. 48—48·5°, is similarly prepared. H. B.

Action of alkalis on monobasic sugar acids. I. Conversion of gluconic into mannonic and of galactonic into talonic acid by the action of barium hydroxide. H. T. Bonnett and F. W. Upson (J. Amer. Chem. Soc., 1933, **55**, 1245—1248).—Ba gluconate (I) is treated with aq. $Ba(OH)_2$ at 95—97°/115 hr. or 140°/1 hr., the mixture neutralised (H_2SO_4), the resultant solution evaporated to remove much unchanged (I), the residual solution freed from Ba by H_2SO_4, evaporated in vac., and the residue dissolved in BuOH–EtOH; 17% of *d*-mannonolactone (II) is thereby obtained. (II) is similarly converted into 12% of (I), whilst *d*-γ-talonolactone is obtained in 13% yield from *d*-galactonolactone. The yields are comparable with those obtained using C_5H_5N and quinoline. A possible mechanism for the formation of isomeric hexonic acids during alkaline oxidation of hexoses is suggested. H. B.

Production of *d*-galacturonic acid from pectin. F. EHRLICH and R. GUTTMANN (Biochem. Z., 1933, **259**, 100—109; cf. A., 1932, 1063).—Commercial "citrus pectin" is submitted to rapid partial hydrolysis with 5% HCl. From the product pure *d*-galacturonic acid (Ba salt, $[\alpha]_D^{20}$ +29°) is obtained by heating for a short time under pressure with 1% H_2SO_4 (yield 30—35%) or by treatment with pectolase (yield 50%). W. McC.

Formation of furfuraldehyde and carbon dioxide from uronic acids. H. FRANKEN (Biochem. Z., 1933, **257**, 245—255).—Formation of furfuraldehyde (I) from uronic and boiling mineral acids proceeds at least in part by way of the related pentose (decarboxylation). By treatment of Ba galacturonate with steam under pressure, a substance is formed which gives succinic acid on oxidation and is probably γ-keto-δ-aldehydovaleric acid. Treatment with boiling acid also gives probably the same substance with CO_2 and (I). P. W. C.

Preparation of methyl esters of pectic acid. H. W. BUSTON and H. R. NANJI (Biochem. J., 1932, **26**, 2090—2096).—Me pectates (5—11·5% OMe) can be prepared by heating Ag pectate with MeI under slight pressure. The products resemble the natural sol. pectins in all respects. The Et esters of pectic acid undergo extensive decomp. in their prep. S. S. Z.

General method for the synthesis of aldehydes. G. DARZENS and M. MEYER (Compt. rend., 1933, **196**, 489—490).—Et sodioethoxymalonate and an alkyl halide RX afford a derivative $OEt{\cdot}CR(CO_2Et)_2$, converted successively into $OEt{\cdot}CR(CO_2H)$, $OEt{\cdot}CHR{\cdot}CO_2H$, and R·CHO (cf. this vol., 377). The following examples are given: lauryl bromide⟶ *Et* α-*ethoxy*-α-*laurylmalonate*, b.p. 196—197°/6 mm., ⟶α-*ethoxy*-α-*laurylmalonic acid*, m.p. 75°,⟶α-*ethoxymyristic acid*, b.p. 212°/14 mm.,⟶tridecaldehyde. CH_2PhCl⟶*Et* α-*ethoxy*-α-*benzylmalonate*, b.p. 162°/6 mm.,⟶α-*ethoxy*-α-*benzylmalonic acid*, m.p. 73°,⟶α-*ethoxy*-β-*phenylpropionic acid*, b.p. 174—175°/16 mm.,⟶$CH_2Ph{\cdot}CHO$. $CH_2Ph{\cdot}CH_2Br$⟶ *Et* α-*ethoxy*-α-(β′-*phenylethyl*)*malonate*, b.p. 178°/7 mm.,⟶α-*ethoxy*-α-(β′-*phenylethyl*)*malonic acid*, m.p. 79°,⟶α-*ethoxy*-γ-*phenylbutyric acid*, b.p. 180°/16 mm.,⟶γ-phenylpropaldehyde. *cyclo*Hexyl bromide⟶α-*ethoxy*-α-cyclo*hexylmalonic acid*, m.p. 146°, ⟶hexahydrobenzaldehyde. A. C.

Determination of formaldehyde with potassium bromate. L. SPITZER (Chem.-Ztg., 1933, **57**, 224).—2 g. of CH_2O are diluted to 100 c.c., 5 c.c. of the solution further diluted with 20 c.c. of H_2O, treated with 20 c.c. of $KBrO_3$–KBr solution, and acidified with 20% HCl. After separation of Br the solution is made alkaline with NaOH. After 30 min. at 20°, the solution is acidified, shaken, solid KI added, and the I liberated determined. C. I.

Primary stages in the conversion of formaldehyde into carbohydrates. L. ORTHNER and E. GERISCH (Biochem. Z., 1933, **259**, 30—52).—The primary products (I) of the action of $Pb(OH)_2$ on CH_2O yield glycol (16%), glycerol (23%), and meso- and *dl*-erythritol (46%) together with other polyhydric alcohols on catalytic hydrogenation (III) with Ni at 120°/100—120 atm. It follows that (I) include glycollaldehyde, dihydroxyacetone; *dl*-erythrose, *dl*-threose, and possibly glyceraldehyde. (I) reduce cold Fehling's solution and can be distinguished from and determined in presence of secondary condensation products (II) which do not. During (III) a max. in the amount of (I) is attained, after which the amount of (II) increases. (III) of AcCHO at 1 atm. gives $CH_2Ac{\cdot}OH$. The mechanism of the condensation processes is discussed. W. McC.

Ether-like compounds. IX. Rate of hydrolysis of ether- and hydroxyether-acetals. M. H. PALOMAA and V. AALTO (Ber., 1933, **66**, [*B*], 468—472; cf. this vol., 257).—The transition from $CHMe(OEt)_2$ to $OR{\cdot}CH_2{\cdot}CH(OEt)_2$ causes more marked depression of the rate of hydrolysis by acids than does that from $CH_2(O{\cdot}CH_2Me)_2$ to $CH_2(O{\cdot}CH_2{\cdot}CH_2{\cdot}OR)$. The influence of O in more distant positions is slight. The temp. coeff. retains the val. characteristic of acetal hydrolysis. The following Et_2 acetals are described: ethoxyacetaldehyde-, b.p. 167·2°/761 mm.; β-*hydroxyethoxyacetaldehyde*-, b.p. 234°/771 mm.; β-*methoxyethoxyacetaldehyde*-, b.p. 70·0°/1·2 mm.; acetaldehyde-, b.p. 103·2°/761 mm. H. W.

Determination of some biologically important aldehydes and ketones with special reference to pyruvic acid and methylglyoxal. F. P. CLIFT and R. P. COOK (Biochem. J., 1932, **26**, 1788—1799).—$AcCO_2H$ (I) and AcCHO (≮ 2 mg. in 5 c.c.) are determined as the H sulphite compounds. (I) and certain other ketones can be determined separately in the presence of some aldehydes and ketones by destroying the latter by heating the mixture in alkaline solution. (I) and the trioses can be recovered almost quantitatively when added to tissues. Compounds containing an ethylenic linking or SH do not affect the determination. S. S. Z.

Compounds of bivalent carbon. VI. Tri(carbon monoxide diethylacetal) ethyl alcoholate [heptaethoxypropane] and the course of the "carbon monoxide acetal fission" of ethyl diethoxyacetate. H. SCHEIBLER and A. SCHMIDT (Ber., 1933, **66**, [*B*], 501—506).—Et diethoxyacetate (I) is converted by $NaNH_2$ in Et_2O into $NAc(OEt)_2$, m.p. 81—82°. Addition of (I) to a boiling solution of $NEt_2{\cdot}MgBr$ in Et_2O gives ααααββγγ-*heptaethoxypropane*, b.p. 118°/14 mm., stable towards alkali, but readily transformed by successive treatment with dil. HCl and NaOH into tartronic acid. For fission of (I) the following schemes are postulated:
$CH(OEt)_2{\cdot}C(OEt)_2{\cdot}ONa \longrightarrow C(OEt)_2 + CH(OEt)_2{\cdot}ONa$.
$CH(OEt)_2{\cdot}C(OEt)(OMgBr){\cdot}NEt_2 \longrightarrow C(OEt)_2 +$ $OEt{\cdot}CH(OMgBr){\cdot}NEt_2$. Elimination of $C(OEt)_2$ is immediately followed by decomp. of the orthoformic derivative with production of EtOH, which reacts thus: $3C(OEt)_2 + EtOH = CH(OEt)_2{\cdot}C(OEt)_2{\cdot}C(OEt)_3$. H. W.

Condensation of butan-β-one with *n*-aliphatic aldehydes. S. G. POWELL, H. C. MURRAY, and M. M. BALDWIN (J. Amer. Chem. Soc., 1933, **55**, 1153—1154).—Condensation of COMeEt with PrCHO, *n*-valeraldehyde, and *n*-heptaldehyde under the con-

ditions previously described (A., 1925, i, 7) gives δ-*hydroxy-γ-methyl-hexan-β-one*, b.p. 94—96°/20 mm., *-octan-β-one*, b.p. 98°/16 mm., and *-decan-β-one*, b.p. 147°/23 mm., respectively. These are dehydrated, the products reduced to the saturated alcohols, and these oxidised to the ketones. *γ-Methyl-octan-β-ol* (I), b.p. 75°/15 mm., and *-decan-β-ol* (II), b.p. 125°/9 mm., and *-methyl-hexan-β-one*, b.p. 142—145°, *-octan-β-one*, .p. 64—65°/18 mm., and *-decan-β-one*, b.p. 121°/20 mm., are described. (I) and (II) are oxidised ($Na_2Cr_2O_7$, H_2SO_4) to *n*-valeric and *n*-heptoic acid, respectively. H. B.

Titrimetry of sugars. L. Bey, R. Bey, and G. Valensi (Compt. rend., 1933, **196**, 546—548).—An account of the influence of NH_3, time, and concn. on the titration of sugars with Cu solution. A. C.

Mechanism of the transformation of α- and β-forms of reducing sugars. T. Soda (Bull. Chem. Soc. Japan, 1933, **8**, 49—64).—A theoretical discussion of the intermediate forms in the transformation of α- and β-forms of reducing pentoses and hexoses and of the α- and β-forms of cryst. sugars. H. W.

Acetone [*iso*propylidene] derivatives of sugars and the products of their transformation. XVIII. *d*-Galactose 6-*p*-toluenesulphonate and 3 : 6-anhydro-*d*-galactose. H. Ohle and H. Thiel (Ber., 1933, **66**, [*B*], 525—532).—Di*iso*propylidenegalactose 6-*p*-toluenesulphonate (I) could not be partly hydrolysed, but is transformed by AcOH–H_2O at 100° into d-*galactose* 6-p-*toluenesulphonate* (II), *form* A (from H_2O), m.p. 127—129° (decomp.), $[\alpha]$, +14·53° to $[\alpha]_D^{18}$ +31·98° in C_5H_5N (*Ac*$_4$ derivative, m.p. 126—127°, $[\alpha]_D^{20}$ +9·31° in $CHCl_3$), *form* B (+EtOH) [from EtOH], m.p. 119—120° (decomp.), $[\alpha]_D^{19}$ +28·1° in C_5H_5N (=$[\alpha]_D$ +32·0° for the solvent-free material) (*Ac*$_4$ derivative, m.p. 117°, $[\alpha]_D^{20}$ +89·1° in $CHCl_3$). The vals. of $[M]_D$ suggest that both forms have the furanose structure and each when treated with cold AcOH–HBr gives the same 1-*bromo-α-galactose triacetate* 6-p-*toluenesulphonate* (III), m.p. 147°, $[\alpha]_D^{20}$ +157·3° in CHCl$_3$ (also obtained directly in poor yield from (I) and AcOH–HBr), transformed by AgOAc or $Pb(OAc)_4$ in AcOH into the β-tetra-acetate. Since, however, (III) with C_5H_5N and Ag_2SO_4 gives a non-cryst. product containing all the SO_4 in ester-like union, either the optical rules are not followed in this instance or the Bourjan reaction is not sp. for pyranoid acetohalogenoses. The (exceptional) isolation of a third *galactose tetra-acetate* 6-p-*toluenesulphonate*, m.p. 147°, $[\alpha]_D^{20}$ +16·1° in $CHCl_3$, appears contrary to the first assumption, since the compound corresponds closely with pyranoid galactose penta-acetate. It could not be prepared by acetylation of (II) in C_5H_5N according to Schlubach. Treatment of (II) with MeOH–HCl affords *α-methylgalacto-pyranoside* 6-p-*toluenesulphonate* (IV), m.p. 170°, $[\alpha]_D^{18}$ +103·5° in C_5H_5N (*Ac*$_3$ derivative, m.p. 128°, $[\alpha]_D$ +102·4° in $CHCl_3$), the structure of which follows from its ready conversion ($CuSO_4$–H_2SO_4–$COMe_2$) into 3 : 4-iso*propylidene-α-methyl*-d-*galactopyranoside* 6-p-*toluenesulphonate* (V), m.p. 129—130°, $[\alpha]_D^{18}$ +73·7° in $CHCl_3$. (IV) is readily hydrolysed by NaOH to 3 : 6-*anhydro-α-methyl-α-galactopyranoside*, m.p. 139°, $[\alpha]_D^{19}$ +83·9° in H_2O [probably identical with the product obtained by Valentin (A., 1932, 1237)]; converted by *N*-H_2SO_4 at 40° into 3 : 6-*anhydro-galactose* (VI) [phenylosazone, m.p. 213—214° (decomp.)]. (V) is stable towards KOH in EtOH–H_2O, but converted by distillation with NaOH–CaO into non-cryst. products. (II) is very sensitive towards NaOH, but (VI) cannot be isolated from the products of the change. 1-*Chloro*-α-d-*galactose triacetate* 6-p-*toluenesulphonate*, m.p. 120°, $[\alpha]_D^{19}$ +134·5° in $CHCl_3$, is described. H. W.

Sucrose and other disaccharides. Sir James Irvine's "correction." H. C. Carrington, W. N. Haworth, and E. L. Hirst (J. Amer. Chem. Soc., 1933, **55**, 1084—1090).—A criticism of the work of Irvine and McGlynn (A., 1932, 255) and a reply to Irvine (*ibid.*, 603, 835). Oxidation of 2 : 3 : 6-trimethylglucose (I) with Br-H_2O at 35° for 24 hr. gives 2 : 3 : 6-*trimethyl-γ-gluconolactone* (II), b.p. about 130°/0·05 mm., m.p. 29—30°, $[\alpha]_D^{18}$ (in H_2O) +55° (initial)⟶+37·5° (700 hr.) (the rate of mutarotation is greatly accelerated by aq. HBr), converted by $NHPh{\cdot}NH_2$ at 100° into 2 : 3 : 6-*trimethylgluconphenylhydrazide*, m.p. 145°, and methylated (Ag_2O, MeI) to 2 : 3 : 5 : 6-tetramethyl-γ-gluconolactone. Contrary to Irvine and McGlynn (*loc. cit.*), (II) is obtained by oxidation (Br-H_2O) of (I) in presence of HBr or $CaCO_3$; furthermore, Ca 2 : 3 : 6-trimethylgluconate (III) is produced in 66% yield in the latter case. (II) and $CaCO_3$ in H_2O at 0° give (after 5 hr.) 40% of (III). Oxidation of (I) by Isbell and Hudson's method (*ibid.*, 834) favours δ-lactone formation. The conditions governing the lactonisation of 2 : 3 : 6-trimethylgluconic acid, $[\alpha]_D^{20}$ (in H_2O) +28° (initial)⟶+32·5° (200 min.) are complex.

[With C. W. Long.] (I) and HNO_3 (*d* 1·42) at 95° give (after esterification with MeOH–HCl) Me *d*-dimethoxysuccinate. 2 : 3-Dimethyl-α-methylglucoside can be extracted from an aq. solution by $CHCl_3$ (cf. Irvine, *ibid.*, 603). H. B.

Osmometric investigation of dilute solutions of polymeric carbohydrates. III. Changes in state in solutions of cellobiose, maltose, and "cellotriose." M. Ulmann and K. Hess (Ber., 1933, **66**, [*B*], 493—501).—Determination of the mol. wt. of the octa-acetates of cellobiose (I) and maltose (II) in AcOH at 20° by the method of isothermal distillation shows the compounds to be present initially in the dimeric condition, which slowly passes into the monomeric form. The mean mol. wt.–time graphs of (I), (II), "hendecamethylcellotriose" in H_2O, and α-dextrin have similar S shape, indicating that the fundamental processes are similar. The conditions under which the dimeric forms of (I) and (II) are stable in AcOH are unknown. In camphor (III), (I) is bi- whereas (II) is uni-mol., indicating the influence of solvent. Determinations of mol. wt. of sugars in (III) are considered not to afford definite evidence in questions of constitution. The necessity is emphasised of using several solvents and using conditions which permit detection of the change in state of solution with time. H. W.

New substituted glucosides. (Miss) T. M. Reynolds (J.C.S., 1933, 223—226).—3 : 4 : 6-Triacetyl-β-glucosidyl chloride with p-$C_6H_4Me{\cdot}SO_2Cl$ and C_5H_5N in $CHCl_3$ affords, in addition to its 2-p-toluenesulphonyl derivative (I), 2-p-*toluenesulphonyl*-3 : 4 : 6-*triacetylglucosidopyridinium* p-*toluenesulphonate*, m.p. 218—219° (decomp. 222°), $[\alpha]_D$ +29·0° in 10% aq. glycerol. Hydrolysis of (I) with NaOMe in $CHCl_3$–MeOH at −15° gives β-*methylglucoside* 2-p-*toluenesulphonate*, m.p. 116—117°, −44·4° in H_2O. By heating a solution of 1 : 2-anhydroglucose 3 : 4 : 6-triacetate (Brigl, A., 1922, i, 1117) in $CH_2Ph{\cdot}OH$ at 100° is obtained β-*benzylglucoside* 3 : 4 : 6-*triacetate* (II), m.p. 115—116°, $[\alpha]^{24}$ −27·5° in $CHCl_3$ (converted by Ac_2O into β-benzylglucoside tetra-acetate), the 2-p-$C_6H_4Me{\cdot}SO_2$ derivative m.p. 105—106°, $[\alpha]_D^{24}$ −7·0° in $CHCl_3$, of which gives β-*benzylglucoside* 2-p-*toluenesulphonate*, m.p. 127—128°, $[\alpha]_D^{24}$ −34·3° in $CHCl_3$, on hydrolysis with NaOMe–MeOH. With $NHMe_2$ in MeOH at 100° (II) gives *methylglucosidodimethylammonium* p-*toluenesulphonate* (III), m.p. 68—69° (after prolonged drying over P_2O_5 in vac.), $[\alpha]_D^{18}$ −105·7° in MeOH, which by hydrolysis with 0·5N-HCl at 100° affords a mutarotatory *dimethylaminohexosephenylosazone*, shrinking at 120°, m.p. 130—132° (decomp. 188°), and a *substance*, m.p. 163—164° (decomp. 205°). The NMe_2 group in (III) appears to be in the 3-position.

J. W. B.

Hydrolysis of pentosans from corn cobs. F. E. Brown and E. R. Lewis (Iowa State Coll. J. Sci., 1932, **7**, 29—33).—The pentosans were conc. to 71% and hydrolysed with H_2O at various temp. (142—208°) for 5 hr. Furfuraldehyde was max. (5% of theoretical) at 173°. At > 150° the sum of the products determined represents < 50% of the original material. Ch. Abs.

Highly-polymerised compounds. LXXVII. Viscosity measurements on Zechmeister's oligosaccharide derivatives and constitution of cellulose. H. Staudinger and H. Freudenberger (Annalen, 1933, **501**, 162—174).—The sp. viscosity ($\eta_{sp.}$) of a 1·4% solution of cellotetraose acetate (I) (Zechmeister and Toth, A., 1931, 716) in m-cresol at 20° agrees fairly well with the val. calc. from the expression $(1{\cdot}4\%)=n\times14{\cdot}5\times10^{-3}+6{\cdot}5\times10^{-3}$ (n=no. of glucose residues in the mol.); the $\eta_{sp.}$ for glucose penta-acetate and cellobiose and cellotriose acetates deviate considerably from the calc. vals. The for one glucose residue is calc. to be $0{\cdot}0145\times10^{-3}$; the % deviation of the corresponding vals. (derived from the measurements on the above substances) for one glucose residue increases with diminished chain-length. The K_m const. for one glucose residue [from the measurements with (I)] is $11{\cdot}7\times10^{-4}$; this agrees well with vals. derived from other compounds. The validity of deductions from viscosity rules is discussed. H. B.

Decarboxylation of celluloses of natural composition. E. Schmidt, R. Schnegg, and M. Hecker (Naturwiss., 1933, **21**, 206).—The CO_2H content of natural cellulose (0·28%; cf. A., 1931, 934) is unaffected by treatment with ClO_2 and C_5H_5N at p_H 4, Na_2SO_3 at p_H 6·8, 10% aq. C_5H_5N at p_H 9·4, or by 5% aq. nicotine at p_H 10·35. Decarboxylation is effected by dil. $Ca(HCO_3)_2$, which probably has a more important role than enzymes in the natural degradation of natural cellulose. A. C.

Comparison of jute and cotton celluloses. J. K. Chowdhury and N. N. Basu (J. Indian Chem. Soc., 1932, **9**, 615—631).—Jute cellulose is best purified by delignification by ClO_2, boiling with H_2O, and repeated treatment with boiling 5% and cold 17·5% NaOH alternately in absence of O_2; it then has only 1·82% solubility in 17·5% NaOH and gives only 0·25% of furfuraldehyde. This (I) and cotton cellulose (II) (similarly purified) give almost identical yields of similar Ac derivative, pure methylglucoside (theoretical yield by a modified method), glucose (modified method), cellobiose octa-acetate, and Me derivative (modified method). (I) is less resistant to NaOH than (II), gives a viscose solution with higher γ and lower η, and solutions of acetate in $CHCl_3$ and cellulose nitrate in Et_2O–EtOH with lower η; (I) is more sol. in cuprammonium solution, and the resultant solution has a lower η. It is concluded that (I) and (II) consist solely of highly-polymerised anhydroglucose units, (II) being the more highly polymerised. R. S. C.

Preparation and isolation of quaternary bases. W. Keil (Biochem. Z., 1933, **259**, 138—139; cf. Gutbier and Wissmüller, A., 1915, i, 217).—The plumbichlorides (I) of quaternary ammonium bases (III) are sparingly, whereas those (II) of primary, *sec.*, and *tert.* bases (C_5H_5N and quinoline are exceptions) are easily, sol. in dil. HCl. (II) are also much more easily decomposed than are (I), which are stable when dry. The method of prep. and isolation of (III) from the corresponding amines takes advantage of these facts. (III) which are attacked by Cl_2 cannot be prepared thus.

W. McC.

Alkylamine and other organic alums [and chlorostannates]. K. Wendekamm [with F. Gille] (Z. Krist., 1933, **85**, 35—57).—The methods reputed to give S alums containing NH_2Me_2, NMe., NH_3Et, NH_2Et_2, $NHEt_3$, NEt_4, NH_3Bu, $NH_3C_5H_{11}$, and coniine (cf. A., 1928, 108) are shown by density and refractive index determinations and/or analyses of the supposed alums to yield only NH_4 alum, together with various easily sol. (apparently) double salts, whilst the supposed $NHMe_3$ and NH_3Pr alums are merely NH_3Me alum due to the presence of NH_2Me in the amines used. The only alkylammonium alums verified are those from NH_2Me and NH_2OH. Vals. of d and n are given for the chlorostannates, X_2SnCl_6 (cf. A., 1911, i, 953). C. A. S.

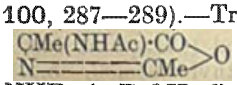
Reactions of ethylene oxide. I. Action of ethylene oxide on diethylamine. A. J. W. Headlee, A. R. Collett, and C. L. Lazzell (J. Amer. Chem. Soc., 1933, **55**, 1066—1069).—$NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [obtained in 81% yield from $(CH_2)_2O$ and $NHEt_2$ at 100°] and $(CH_2)_2O$ at 100° give β-(β′-diethylaminoethoxy)ethyl alcohol, b.p. 135°/46 mm. (p-*nitrobenzoate*, m.p. 128·5°), which with $(CH_2)_2O$ affords β-(β′β″-diethylaminoethoxyethoxy)ethyl alcohol, b.p. 163—165°/30 mm. Further treatment of this with $(CH_2)_2O$ gives the alcohol,

$NEt_2{\cdot}[CH_2{\cdot}CH_2{\cdot}O]_n{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (I, $n=3$), b.p. 185—188°/53 mm., which with $(CH_2)_2O$ affords the alcohol (I, $n=4$), b.p. 182—184°/9 mm. The physical data of the above compounds differ from those reported by Horne and Shriner (A., 1932, 935). The *alcohols* (I, $n=5$ and 6), b.p. 254—259°/36 mm. and 205—209°/4 mm., respectivelv, are prepared similarly. H. B.

Deamination of glucosamine. L. Zechmeister and G. Tóth (Ber., 1933, **66**, [*B*], 522—525).—Treatment of glucosamine hydrochloride with $AgNO_2$ or nitrous fumes in the cold and subsequent addition of $NHPh{\cdot}NH_2$ results in the separation of a small proportion of *d*-arabinosazone followed by *d*-glucosazone (I) (corresponding with about 70%) when the solution is boiled. The production of (I) from an anhydro-sugar is unlikely, since [α] of the solution is not affected by addition of AcOH to concn. of 10% and boiling for 3 hr., and mannose is an unlikely precursor, since the solution does not afford the corresponding sparingly sol. phenylhydrazone. Glucose (II) is regarded as the main product of deamination. The non-fermentability of the reaction mixture does not point to another direction, since under similar conditions the fermentability of (II) is very greatly restricted. The immediate possibility of a Walden inversion during deamination prevents the application of the result to the determination of the configuration of the amino-sugar. H. W.

Autoxidation of amino-acid derivatives on animal charcoal and hæmin. I. F. Bergel and K. Bolz (Z. physiol. Chem., 1933, **215**, 25—34).—In presence of active C, leucine is oxidised about 10 times as fast as alanine (I), the oxidation affording CO_2, NH_3, and the corresponding aldehyde. Leucylleucine, diketopiperazine, acetyl-leucine, and alanineamide are stable. *N*-Methylalanine is oxidised more readily than (I), giving NH_2Me. *N*-Dialkyl derivatives but not betaine are oxidised with extreme ease, affording $NHMe_2$ or $NHEt_2$, probably by way of a peroxide. The dialkylacid oxidation is catalysed by hæmin. The action differs from that of the kidney enzyme which produces α-keto-acids. *N-Dimethyl-leucine*, m.p. 187—187·5°, was obtained from α-bromo*iso*hexoic acid. J. H. B.

Action of sugar on amino-acids. II. Reaction in presence of oxidising agents. J. Watanabe (J. Biochem. Japan, 1933, **17**, 147—158).—Glucose, which normally accelerates the deamination of glycine or alanine (A., 1932, 1239), has an inhibitory action when in presence of alkaline $KMnO_4$, due to the formation of a gelatinous coagulum. In acid $KMnO_4$ or in alkaline solution in presence of H_2O_2 or mol. O_2, the deamination is markedly accelerated. F. O. H.

Preparation of esters of αα-bisacetamidopropionic acid. B. H. Nicolet (J. Biol. Chem., 1933, **100**, 287—289).—Treatment of the azlactone  (A., 1930, 585) with 2 equivs. of $NHEt_2$ in EtOH affords *Et αα-di(acetamido)propionate*, m.p. 156—157°, and with 1 equiv. of *p*-$C_6H_4Me{\cdot}SH$ and $NHEt_2$ in C_6H_6 is obtained *p*-C_6H_4Me *αα-di(acetamido)-thiopropionate*, m.p. 205—206° (decomp.), thus confirming the mechanism, involving the migration of an Ac group, proposed by Bergmann and Grafe (*loc. cit.*). J. W. B.

Determination of hydroxymethyl derivatives of amides and carbamides with Nessler's reagent. J. Bougault and J. Leboucq (J. Pharm. Chim., 1933, [viii], **17**, 193—196).—The method previously described (A., 1922, ii, 666) is applied to the CH_2O formed from the above derivatives with H_2O, or H_2SO_4 in the case of diamidomethylene derivatives. $NPh{:}CH_2$ and the derivative of *o*-tolylcarbamide could not be obtained pure. A. A. L.

Preparation of acetonitrile using Japanese acid clay as catalyst. K. Kobayashi and J. Abe (J. Soc. Chem. Ind. Japan, 1933, **36**, 42—43B).—MeCN is prepared in 90% yield from glacial AcOH and excess of NH_3 in contact with Japanese acid clay at 400—500°. The same yield is obtained with Ac_2O at 350°. The catalyst rapidly loses its activity > 500°. H. A. P.

Rule for the rotatory direction of the acetylated aldononitriles. V. Deulofeu (Nature, 1933, **131**, 548).—Tetra-acetyl-*d*-xylononitrile and -*l*-arabononitrile have $[\alpha]_D^{22}$ +50·3° and +4·2°, respectively, whilst penta-acetyl-*d*-galactononitrile has $[\alpha]_D^{22}$ +48·4°. From these and other data a rule for the sign of rotation is deduced. L. S. T.

Existence of optically active diazo-compounds. III. A. Weissberger (Ber., 1933, **66**, [*B*], 559—562; cf. A., 1932, 151, 372).—In reply to Noyes and Meitzner (A., 1932, 1140) it is maintained that a well-founded instance of the existence of optically active diazo-compounds has not been described. H. W.

Reactions of free ethyl radicals from the thermal decomposition of lead tetraethyl. R. N. Meinert (J. Amer. Chem. Soc., 1933, **55**, 979—989).—The products of the thermal decomp. of $PbEt_4$ at 150—500°/0·5—807 mm. by dynamic and static methods show that the reaction proceeds by the production of free Et radicals which can undergo four alternative reactions: (1) at low temp. with low [Et] and high [$PbEt_4$], the Et removes H from the latter forming C_2H_6 at the wall; (2) 2Et+X (or wall) $\longrightarrow C_4H_{10}$; (3) 2Et (at wall) $\longrightarrow H_2+2C_2H_4$, is favoured by high temp.; (4) 2Et (gas phase) $\longrightarrow C_2H_4+C_2H_6$, is favoured by high temp. and pressure, but is less prominent than (1), (2), and (3). Thermal decomp. of liquid $PbEt_4$ affords chiefly C_2H_4 and C_2H_6. J. G. A. G.

***cyclo*Decane.** W. Huckel, A. Gercke, and A. Gross (Ber., 1933, **66**, [*B*], 563—567).—The conditions under which $\Delta^{9:10}$-octahydronaphthalene is transformed through *cyclo*decane-1 : 6-dione and its dioxime into *cyclo*decane-1 : 6-diamine (I), m.p. 50° (*Ac*$_2$ derivatives, m.p. 296° and 242°, respectively), are more precisely defined (cf. A., 1930, 76). (I) is transformed by MeI, MeOH, and KOH into the quaternary *iodide*, converted by distillation after successive treatment with Ag_2SO_4, H_2S, $Ba(OH)_2$, and KOH followed by hydrogenation (PtO_2) into cyclo*decane* (II), b.p. 201°/760 mm. The structure of (II) is proved by its oxidation to sebacic acid. The ring

appears to be free from strain as judged by the heat of combustion. H. W.

_cyclo_Pentadiene and methyl_cyclo_pentadiene. N. D. ZELINSKI and R. LEVINA (Ber., 1933, **66**, [*B*], 477—478).—Reduction of *cyclo*pentanone (H_2 and Os) gives *cyclo*pentanol, converted by anhyd. $H_2C_2O_4$ into *cyclo*pentene, b.p. 45°. The corresponding *dibromide*, b.p. 76·5—77·5°/18·5 mm., is transformed by NaOAc and AcOH at 180° into *cyclo*pentadiene, b.p. 41°/757 mm., reduced by H_2 at 160° (Pt–C) to *cyclo*pentane and tri*cyclo*decane, m.p. 77°. Similarly 3-methyl*cyclo*pentanone is converted through the mixed methyl*cyclo*pentenes and *dibromomethyl*cyclo*pentane*, b.p. 73·5—74°/9 mm., into *methyl*cyclo*pentadiene*, b.p. 69—70°/736 mm. H. W.

Ergotetraenes. A. GUITERAS (Z. physiol. Chem., 1933, **215**, 196—198).—The so-called dihydroergotetraene *A* obtained by Rygl (cf. A., 1930, 203) is actually an ergotetraene *C* isomeric with *A* and *B* and is obtained by heating *A* in boiling amyl alcohol. *A*, *B*, and *C* all yield the same *hydrochloride*, m.p. 116°, $[\alpha]_D^{20}$ −137° in $CHCl_3$. J. H. B.

Sensitivity of the pernitric acid reaction in the detection of benzene. J. B. FICKLEN and W. A. COOK (Z. anorg. Chem., 1933, **211**, 141—144; cf. A., 1922, ii, 883).—The test gives a deep red colour with 0·05 c.c., and a slight colour with 0·005 c.c. of C_6H_6. PhMe and EtOH give a pale orange-red colour: $C_6H_4Me_2$, MeOH, and heptane (I) give none. 10% of C_6H_6 in PhMe, $C_6H_4Me_2$, MeOH, EtOH, or (I) may be detected. H. J. E.

Halogenation of *m*-diphenylbenzene. I. Mono-chloro- and -bromo-derivatives. W. A. COOK and K. H. COOK (J. Amer. Chem. Soc., 1933, **55**, 1212—1217).—*m*-$C_6H_4Ph_2$ (I) and Cl_2 in presence of Fe at 100° (bath) give 4-*chloro*-1 : 3-*diphenylbenzene*, b.p. 214—216°/4 mm. (84·2% yield), oxidised (CrO_3 or $KMnO_4$ in AcOH) to 2-*chlorodiphenyl*-*o*-*carboxylic acid*, m.p. 208—209° (*Aq* salt; *Me* and *benzyl*, m.p. 90°, esters), which is also prepared by oxidation ($KMnO_4$, AcOH) of 2-*chloro*-*o*-*methyldiphenyl*, b.p. 294—304°/735 mm. [obtained from 4-chloro-*m*-toluidine and C_6H_6 by Gomberg and Bachmann's method (A., 1924, i, 1295)]. Similar bromination of (I) gives 4-bromo-1 : 3-diphenylbenzene, b.p. 208—213°/1 mm. (cf. Olgiati, A., 1895, i, 149), oxidised to 2-bromodiphenyl-5-carboxylic acid, m.p. 242—243° (cf. *loc. cit.*), also prepared by oxidation of 2-*bromo*-*o*-*methyldiphenyl* (II), b.p. 304—308°/740 mm. 4-Bromo-*m*-toluidine, b.p. 129—130°/16 mm. [Ac, m.p. 120—121° (lit. 113·7—114·6° and 164°), and *Bz* derivatives, m.p. 107·5—108·5°], prepared by reduction of the NO_2-derivative with Fe and dil. H_2SO_4 (reduction with Sn and conc. HCl causes introduction of Cl), is converted (as above) into (II). 6-Bromo-*m*-toluidine is similarly converted into 4-*bromo*-3-*methyldiphenyl*, b.p. 318—323°/760 mm., which is completely destroyed by oxidation with CrO_3 or $KMnO_4$ in AcOH. H. B.

[Sulphonation of *m*-nitrotoluene.] A. F. HOLLEMAN (Helv. Chim. Acta, 1933, **16**, 245).—According to van Dorssen (A., 1911, i, 29) the sulphonation of *m*-$C_6H_4Me{\cdot}NO_2$ gives a little -5-sulphonic acid. In view of this result, and the known directing influence of the Me group the formation of 75% of -5-sulphonic acid as stated by Huber (this vol., 57) must be accepted with reserve. H. A. P.

Mechanism of reduction of sulphonyl halides by phosphorus tribromide. A. H. KOHLHASE (J. Amer. Chem. Soc., 1933, **55**, 1291—1292).—The author's mechanism (A., 1932, 940) for the reduction of Ph 3 : 5-dinitrobenzenethiosulphonate to 3 : 5-dinitrothiophenol is considered to be the only one applicable. Hunter and Sorenson's mechanism (*ibid.*, 1023) is applicable to most cases of reduction of RSO_2Hal. RSO_2Cl is reduced far less readily than RSO_2Br (cf. *loc. cit.*). H. B.

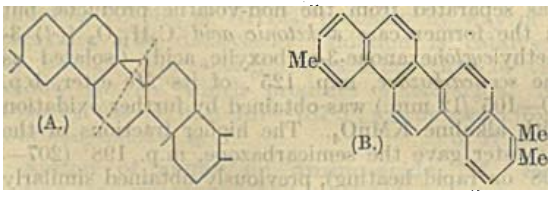
Polyterpenes and polyterpenoids. LXXX. Alantolactone. Synthesis of 1 : 4-dimethyl-6-*iso*propyl- and 1 : 5-dimethyl-7-*iso*propylnaphthalene. L. RUZICKA, P. PIETH, T. REICHSTEIN, and L. EHMANN [with P. MADERNI, F. VASS, and K. PFAHLER]. **LXXXI. Synthesis of 1 : 2 : 5 : 6-tetramethylnaphthalene and analogous hydrocarbons. Hydrocarbon skeletons of the triterpenes.** L. RUZICKA, L. EHMANN, and E. MORGELI [with O. ISLER, R. GEERING, L. WYSZEWIANSKI, C. SCHOLZ, and W. HAUSCHILD]. **LXXXII. Stereochemistry of ring-system of cholestan and *ψ*-cholestan.** L. RUZICKA, M. FURTER, and G. THOMANN [with M. W. GOLDBERG] (Helv. Chim. Acta, 1933, **16**, 268—275, 314—326, 327—336).—LXXX. Both alanto- (I) and *iso*alanto-lactone (II) are most probably mixtures, although the constituents to which the formulæ have been assigned (cf. A., 1931, 1301) preponderate. Exhaustive crystallisation of the lactone mixture gave dihydro*iso*alantolactone as sole homogeneous product. Further, ozonisation in CCl_4, and oxidation of the steam-volatile products with H_2CrO_4 gave only 20% of theory of AcOH with (II) and 4—7% with (I). No homogeneous substance was separated from the non-volatile products, but in the former case a *ketonic acid* $C_8H_{10}O_3$ [(?) 3-methyl*cyclo*hexanone-3-carboxylic acid] (isolated as the *semicarbazone*, m.p. 125°, of its *Me* ester, b.p. 90—105°/12 mm.) was obtained by further oxidation with alkaline $KMnO_4$. The higher fractions of the Me ester gave the semicarbazone, m.p. 198° (207—208° on rapid heating), previously obtained similarly from (I). The hydrocarbon $C_{15}H_{18}$, obtained as main product by reduction of tetrahydroalantolactone to the glycol, treatment with PBr_3, elimination of HBr, and dehydrogenation with Se (cf. A., 1931, 734), is proved by synthesis to be 1 : 5 : 7-$C_{10}H_5Me_2Pr^{\beta}$; a pinacolin rearrangement analogous to that of santonin into desmotroposantonin (cf. A., 1930, 919) is considered to occur during the bromination.

*p-iso*Propylacetophenone is converted by the Reformatsky reaction into a mixture of esters, b.p. 135—170°/13 mm., which on bromination (PBr_3) and heating with $NPhMe_2$ gives *Et* β-*methyl*-p-iso*propylcinnamate*, b.p. 172°/13 mm. This is reduced by Na and abs. EtOH to γ-p-*cumylbutyl alcohol*, b.p. 148—149°/12 mm., and β-p-iso*propylphenyl*-n-*butyric acid*, b.p. 176—177°/12 mm. The former is converted through the *bromide*, b.p. 147—148°/12 mm., into γ-p-*cumylvaleric acid*, b.p. 190—191°/10 mm., the

chloride, b.p. 160—161°, of which gives with $AlCl_3$ in CS_2 4-*keto*-1-*methyl*-6-iso*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 164—165°/10 mm. [*semicarbazone*, m.p. 175—176° (decomp.)], in 80% yield; this with MgMeI gives 1 : 4-*dimethyl*-6-iso*propyl*-1 : 2-*dihydronaphthalene*, b.p. 154—155°/12 mm. (direct), which, finally, with Se at 320° gives 1 : 4-*dimethyl*-6-iso*propylnaphthalene*, b.p. 155—157°/12 mm. [*picrate*, m.p. 102·5—103°; additive *compound* with $C_6H_3(NO_2)_3$, m.p. 144·5—145·5°].

β-o-*Tolyl*-α-iso*propylacraldehyde*, b.p. 82°/0·1 mm., prepared by condensation of CH_2Pr^{β}·CHO and *o*-C_6H_4Me·CHO in aq. EtOH in presence of NaOH at room temp., is reduced by H_2–PtO_2 to β-o-*methylbenzyl*-γ-*methyl*-n-*butanol*, b.p. 86—89°/0·07 mm., the *bromide*, b.p. 84—89°/0·1 mm. (HBr at 140°), of which gives with KCN the *nitrile*, b.p. 90—100°/0·1 mm., of β-o-*methylbenzyl*isovaleric *acid*, b.p. 125—130°/0·06 mm. (KOH in EtOH). The *chloride* ($SOCl_2$) of this acid is cyclised by $AlCl_3$ in CS_2 to 5-*keto*-1-*methyl*-7-iso*propyl*-ɔ : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 60—61°, b.p. 120°/0·3 mm., which with excess of MgMeI gives 1 : 5-*dimethyl*-7-iso*propyl*-7 : 8-*dihydronaphthalene*, b.p. 108°/0·8 mm., dehydrogenated by S (1 atom) at 180—240° to 1 : ɔ-*dimethyl*-7-iso*propylnaphthalene*, b.p. 110—112°/0·8 mm. [*picrate*, m.p. 115·5—116·5°; $C_6H_3(NO_2)_3$ *compound*, m.p. 145—147°]. The contentions of Barnett and Cook (this vol., 268) that cyclisation with $AlCl_3$ or dehydrogenation with Se may be accompanied by wandering of an alkyl group are refuted, so long as in the former case CS_2 or light petroleum is used as solvent.

LXXXI. The hydrocarbon $C_{14}H_{16}$ isolated by heating a number of triterpenes and triterpenoids with Se (cf. A., 1932, 517) is 1 : 2 : 5 : 6-$C_{10}H_4Me_4$, and is regarded as derived from the nucleus (A) by fission as indicated, whilst the structure of the hydrocarbon $C_{25}H_{20}$, m.p. 305° as trimethylpicene (B) is confirmed. Mixed m.p. of picrates are not trustworthy for the



identification of the alkylnaphthalenes, but the stvphnates give trustworthy results.

Interaction of Mg 3-*o*-xylyl bromide (prep. of *vic.*-bromo-*o*-xylene improved) and $(CH_2)_2O$ gives β-3-o-*xylylethyl alcohol*, b.p. 74—76°/0·05 mm., and 3 : 3'-di-*o*-xylyl. The former is converted by HBr at 100° into its *bromide*, b.p. 123—125°/10 mm., which with $CMeNa(CO_2Et)_2$ gives, after alkaline hydrolysis, γ-3-o-*xylyl*-α-*methylbutyric acid*, m.p. 63°, b.p. 130—135°/0·1 mm., whence the *chloride*, b.p. 150—151°/8 mm., and ɔ-*keto*-1 : 2 : 6-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 54—55°, b.p. 155—160°/10 mm. The condensation product, b.p. 145—150°/10 mm., of this ketone with MgMeI is dehydrogenated by Se to 1 : 2 : 5 : *tetramethylnaphthalene*, m.p. 116—116·5°, b.p. 150—155°/12 mm. [*picrate*, m.p. 154—154·5°; *styphnate*, m.p. 160—161°; $C_6H_3(NO_2)_3$ *compound*, m.p. 180—180·5°].

Condensation of 2 : 4-dimethylacetophenone with $CHMeBr·CO_2Et$ and Zn gives a mixture of the OH- and unsaturated esters, converted by heating at 130° in presence of I into *Et* β-4-m-*xylyl*-αβ-*dimethylacrylate*, b.p. 142—143°/12 mm. This is reduced by Na and EtOH to γ-4-m-*xylyl*-β-*methyl*-n-*butanol*, b.p. 143/12 mm., the *bromide*, b.p. 138—148°/12 mm., of which (HBr–AcOH at 100°) is converted through the nitrile into γ-4-m-*xylyl*-β-*methyl*-n-*valeric acid*, b.p. 187—188°/12 mm. The acid *chloride*, b.p. 158·5—159·5°/15 mm., is cyclised by $AlCl_3$ in CS_2 to 4-*keto*-1 : 2 : 6 : 8-*tetramethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I), b.p. 174—178°/15 mm. [*semicarbazone*, m.p. 173° (diffuse)], reduced by Na and abs. EtOH to the *carbinol*, b.p. 168—172°/15 mm., which on heating with Se gives 1 : 2 : 6 : 8-*tetramethylnaphthalene*, b.p. 166—168°/15 mm. (*picrate*, m.p. 133·5—134°; *styphnate*, m.p. 135—136°).

1 : 2 : 5 : 8-*Tetramethylnaphthalene*, b.p. 150°/9 mm. [*picrate*, m.p. 137—138°; $C_6H_3(NO_2)_3$ *compound*, m.p. 158—159°), is synthesised exactly as the preceding from 2 : 5-dimethylacetophenone. The following are described: *Et* β-2-p-*xylyl*-αβ-*dimethylacrylate*, b.p. 144—145°/12 mm.; γ-2-p-*xylyl*-β-*methyl*-n-*butanol*, b.p. 147—148°/12 mm. (*bromide*, b.p. 145°/12 mm.); γ-2-p-*xylyl*-β-*methyl*-n-*valeric acid*, b.p. 184—185°/10 mm. (*chloride*, b.p. 148°/10 mm.); 4-*keto*-1 : 2 : 5 : 8-*tetramethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (II), b.p. 153—154°/10 mm. (*carbinol*, b.p. 155—160°/12 mm.).

The Grignard compound from 4-bromo-*m*-xylene is condensed with $CH_2Cl·CH_2·OH$ and MgEtBr, and the resulting β-4-m-*xylylethanol* converted into its *bromide*. This is condensed with $CMeNa(CO_2Et)_2$ to *Et*$_2$ α-4-m-*xylyl*-n-*butane*-γγ-*dicarboxylate*, b.p. 199°/12 mm., which is hydrolysed by KOH in MeOH and the product decarboxylated. The resulting γ-4-m-*xylyl*-α-*methyl*-n-*butyric acid*, b.p. 192°/12 mm., is converted through its *chloride*, b.p. 153—155°/12 mm., into 5-*keto*-1 : 3 : 6-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b.p. 163—164°/12 mm. (*semicarbazone*, m.p. 203—204°), which with MgMeI gives a product, b.p. 140—156°/11 mm., dehydrogenated by Se at 300—310° to 1 : 2 : 5 : 7-*tetramethylnaphthalene*, b.p. 153—159°/10 mm. (*picrate*, m.p. 144—144·5°; *styphnate*, m.p. 143·7—144°).

1 : 2 : 4 : 8-*Tetramethylnaphthalene*, b.p. 150°/10 mm. (*picrate*, m.p. 145·5°), is obtained by condensing 4-keto-1 : 2 : 8-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (A., 1932, 278) with MgMeI (2 equivs.), and treating the product with Se. 2 : 7-*Dimethyl*-1-*ethylnaphthalene*, b.p. 140—142°/12 mm. (*picrate*, m.p. 119°), is obtained similarly, accompanied by a little 2 : 7-$C_{10}H_6Me_2$, from 1-keto-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (*loc. cit.*) and MgEtI (10 equivs.). 2 : ɔ-*Dimethyl*-1-*ethylnaphthalene* (*picrate*, m.p. 82°) is similarly prepared from 1-keto-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, as also are 1 : 2 : 4 : 5 : 8-*pentamethylnaphthalene*, b.p. 150°/10 mm. [*picrate*, m.p. 146—147°; $C_6H_3(NO_2)_3$-*compound*, m.p. 163·5—164°], from (II) and excess of MgMeI, and 1 : 2 : 4 : 6 : 8-*pentamethylnaphthalene*, m.p. 106—107°, b.p. 150°/10 mm. [*picrate*, m.p. 187—188°; $C_6H_3(NO_2)_3$ *compound*, m.p. 189°], from (I) and MgMeI.

LXXXII. Physical consts. (*d*, *M*[α], and m.p.) support the view that the isomerism of cholestane and ψ-cholestane is of the type of decahydronaphthalene. The vals. of d_4 and $M[\alpha]_D$ are determined at 87·7°, 117·6°, 172·2°, and 206·3°. Oxidation of cholestene at 15° with BzO_2H gives α-, m.p. 75—76°, and β-, m.p. 53° (impure ?) *-cholestene oxides* with absorption of 0·6—0·7 O. The former gives *cholestene*-5 : 6-*diol*, m.p. 125·5° (sinters at 110°), and a small amount of a *hydrocarbon* $C_{27}H_{46}$ (isomeric with cholestene), m.p. 82—83°, by heating at 50° in AcOH containing a little conc. H_2SO_4, and hydrolysing the oily product with 10% KOH in EtOH. The diol is not formed with H_2O or dil. HCl in a sealed tube. Under the same conditions the β-oxide gives more $C_{27}H_{46}$ and only a little diol, possibly derived from admixed α-oxide. The prep. of ψ-cholestane (cf. A., 1926, 1139) is modified by use of cholanic acid chloride and $ZnPr^{\beta}I$. H. A. P.

Ring-system of sterols and bile acids. III. O. Rosenheim and H. King (Chem. and Ind., 1933, 299—301; cf. A., 1932, 736; this vol., 62).—The ultra-violet absorption spectrum of the hydrocarbon $C_{18}H_{16}$ (I), obtained by Se-dehydrogenation of cholesterol (II) (Diels *et al.*, A., 1928, 169), ergosterol (III) (Diels and Karstens. A., 1930, 470), and cholic acid (IV) (Ruzicka and Thomann, this vol., 278), is very similar to that of retene; the curves for 1 : 2 : 7-trimethylphenanthrene and the hydrocarbon $C_{16}H_{14}$ (V), obtained by Jacobs and Fleck (A., 1932, 948) from strophanthidin, are also similar. (I), unlike (V), is not oxidised (CrO_3) to a quinone, indicating that it is not an alkylphenanthrene. Since spectroscopic analysis fails to distinguish 6 : 7-*cyclo*penteno- from 6 : 7-dimethyl-1 : 2-benzanthracene, (I) may be a methyl-1 : 2-*cyclo*pentenophenanthrene. It is improbable that a preformed methyl*cyclo*pentane ring exists in the cholane structure; a fluorene ring-system containing CH_2 is necessary to account for the properties of the pentacyclic hydrocarbon $C_{26}H_{22}$ ($C_{25}H_{24}$?) (formulated as 4-methyl-1-*iso*propyl-7 : 8-αβ-naphthofluorene), produced with (I) during dehydrogenation of the sterols. It is suggested that when the side-chain at C_{17} is removed from (II), (III), or (IV) during dehydrogenation, the C_{13}-Me group migrates to C_{17}. Accordingly, (I) may be 3-methyl-6 : 7-αβ-naphthohydrindene. H. B.

Photo-change of *N*-chloroacetanilide in various solvents. F. W. Hodges.—See this vol., 473.

Preparation of structurally related monoguanidines. C. E. Braun (J. Amer. Chem. Soc., 1933, **55**, 1280—1284).—*n*-Hexylamine and *S*-methyl-*iso*thiocarbamide sulphate in H_2O at 100° give n-*hexylguanidine sulphate*, m.p. 210—212°; m-*tolylguanidine sulphate*, m.p. 215—217°, and β-*phenylethylguanidine sulphate* (+EtOH), softens at 60—65°, decomp. 95°, re-solidifying with m.p. 168—173°, m.p. (EtOH-free) 175—177°, are similarly prepared. The following are prepared from the requisite RNH_2,HCl and $CN{\cdot}NH_2$ in EtOH : cyclo*hexyl*-, m.p. 224—226°, o-*tolyl*-, m.p. 133—135°, p-*tolyl*- (I), m.p. 136—137°, and α-*phenyl*-α-*methyl*-, m.p. 217—218°, *-guanidine hydrochlorides*. (I) is accompanied by a little *p*-tolyldiguanide hydrochloride, m.p. 245—247° (cf. Beutel, A., 1900, i, 367). H. B.

Reaction between *o*-toluidine and sulphur. H. H. Hodgson and H. V. France (J.C.S., 1933, 296—297).—*o*-$C_6H_4Me{\cdot}NH_2$ and S at the b.p. give, in addition to 2′-*amino*-1-*phenyl*-3-*methylbenzthiazole* (I), m.p. 125° (cf. A., 1889, 602) (*azo*-β-*naphthol* derivative, m.p. 165°; *hydrochloride*, m.p. 203°; *picrate*, m.p. 208°; *Ac*, m.p. 122°, and *Bz*, m.p. 127°, derivatives), 2 : 2′-*diamino*-3 : 3′- (II), m.p. 84° (*dihydrochloride*, m.p. 197°; *dipicrate*, m.p. 134°), and -5 : 5′-ditolyl disulphide (III), m.p. 112° (*dipicrate*, m.p. 179°; *di*-o-*nitrobenzoyl* derivative, m.p. 240°). The formation of (III) is favoured by addition of a little H_2O. Orientation of (I) is effected by its synthesis by reduction of the *di*-o-*nitrobenzoyl* derivative, m.p. 217—220°, of (II) with Fe and dil. HCl. 2 : 2′-*Diaminodiphenyl disulphide dipicrate* has m.p. 141°. (II) is converted into 2-*diazotoluene* 3-*sulphide* by HNO_2. H. A. P.

Nitration of chloral condensation products of alkylarylamines. A. H. Advani and T. S. Wheeler (Rec. trav. chim., 1933, **52**, 257—266).—5-βββ-trichloro-α-hydroxyethyl-*N*-methyl-*o*-toluidine (I), m.p. 100° (prep. to be published) is converted by HNO_3 (*d* 1·42) in a freezing mixture into its 3-NO_2-derivative, m.p. 110° (73% yield) (Ac_2 derivative, m.p. 139°). With boiling HNO_3 (*d* 1·42) either the *N*-Ac or Ac_2 derivative of (I) affords 5-βββ-*trichloro*-α-*hydroxyethyl*-o-*tolylmethylnitroamine* (II), m.p. 184° (*Ac* derivative, m.p. 112°). With warm HNO_3 (*d* 1·42) (I) gives the 3-NO_2-derivative, m.p. 195° (*Ac* derivative, m.p. 104—105°), of (II) (79·8% yield), oxidised by 1·5% aq. $KMnO_4$ in KOH to 5-*nitro*-6-*methylnitroamino*-m-*toluic acid*, m.p. 188—190°, and by boiling conc. HNO_3 to 3 : 5-dinitro-*o*-tolylmethylnitroamine, m.p. 119° (A., 1905, i, 487), converted by conc. H_2SO_4 into the corresponding *nitrosoamine*, m.p. 94°. The corresponding 5-βββ-trichloro-α-hydroxyethyl-*N*-ethyl-*o*-toluidine, m.p. 107°, similarly affords its 3-NO_2-derivative, m.p. 105° (Ac_2 derivative, m.p. 137—138°), and 3-*nitro*-5-βββ-*trichloro*-α-*hydroxyethyl*-o-*tolylethylnitroamine*, m.p. 134° (85% yield) (*Ac* derivative, m.p. 131°). *p*-βββ-Trichloro-α-hydroxyethyl-*N*-dimethylaniline (III). m.p. 111°, with 45% HNO_3 in a freezing mixture gives 2 : 6-*dinitro*-4-(βββ-*trichloro*-α-*hydroxyethyl*)*nitromethylmethylaniline*, m.p. 178—179° (*Ac* derivative, m.p. 151°), but at room temp. the product is 2 : 6-*dinitro*-4-(βββ-*trichloro*-α-*hydroxyethyl*)*phenylmethylnitroamine*, m.p. 146—147° (*Ac* derivative, m.p. 145°). When boiled with conc. HNO_3 (III) affords 2 : 4 : 6-trinitrophenylmethylnitroamine. J. W. B.

Optical isomerism of the complex salts of bivalent platinum and palladium. A. Rosenheim and L. Gerb (Z. anorg. Chem., 1933, **210**, 289—302).—The prep. of the following compounds is described : *monotolylenediaminedichloroplatinum*, *ditolylenediamine platinous chloride*, *bromide*, *dithionate*, *tripyrocatecholarsenate*, and *bromocamphorsulphonate*, [α] +81·8°, *ditolylenediamine palladous chloride* and *bromocamphorsulphonate*, and *cinchoninium palladium salicylate*, [α] +65·4°. The calc. mol. rotations of ditolylenediamine cation and the complex

anion of palladiumsalicylic acid are $[M]$ −304·3° and −399·2°, respectively. The slight solubility of the compounds described precluded optical measurements in most cases. The resolution effected is discussed in relation to the *cis–trans* type of isomerism and it is concluded that the structure of these complex salts is best represented sterically as a tetragonal bisphenoid. E. S. H.

Perylene and its derivatives. XXXVII. Oxidation of dinitro- and diamino-perylenes. K. FUNKE (Monatsh., 1933, **62**, 13—27).—3 : 10-Dinitroperylene (I) in dil. H_2SO_4 with CrO_3 at 100° during several hr. affords 10-*nitroperylene*-3 : 9-*quinone* (II) [2-nitroanthraquinone-1 : 5-dicarboxylic acid is a by-product obtained by oxidation of (II)], which when heated with conc. H_2SO_4 at 150° for 6 hr. affords *perylene*-3 : 4 : 9 : 10-*diquinone* (cf. A., 1929, 568). (II) is reduced by $Na_2S_2O_4$ in NaOH at 100° to 10-*aminoperylene*-3 : 9-*quinone* [*Bz* derivative, reduced and benzoylated to 10-*benzamidoperylene*-3 : 9-*quinol dibenzoate*, m.p. 270° (decomp.); *Ac* derivative and *quinol dibenzoate*, m.p. 298—300° (decomp.)]. (I) with $Na_2S_2O_4$ and NaOH affords 3 : 10-diaminoperylene (III), m.p. 307° (cf. A., 1929, 550), which with MnO_2–H_2SO_4 or CrO_3 gives a product (*Bz* derivative) which is reduced ($Na_2S_2O_4$–NaOH) and converted into 3 : 10-*diamino*-9-*hydroxyperylene dibenzoate*, m.p. 330° (*Bz* derivative, m.p. 315°), and *di*-p-*bromobenzoate*, both hydrolysed by H_2SO_4 at room temp. to 10-*aminoperylene*-3 : 9-*quinonemonimine*, which dyes cotton reddish-violet from the vat, changing to brown in air. J. L. D.

Chemical changes involved in the formation of aminoazo-compounds. II. Aniline nitrite. J. C. EARL and N. F. HALL (J. Proc. Roy. Soc. New South Wales, 1932, **66**, 453—458).—The action of acids on solutions of NH_2Ph,HCl (I) (1 mol.) and $NaNO_2$ (1 mol.) in MeOH is studied by the dilatometric method (A., 1932, 1125); the irregularity in the vol.–temp. curve is less abrupt with AcOH than with HCl or C_5H_5N,HCl. When cold conc. aq. solutions of (I) and $NaNO_2$ are mixed in presence of Et_2O, *aniline nitrite* (II) is pptd. and then dissolves in the Et_2O; (II) is obtained cryst. by evaporation of the Et_2O in vac. Aq. solutions of (II) rapidly deposit aminoazobenzene; solutions in MeOH undergo the characteristic vol. change under the influence of acids. H. B.

Hydrazines. I. *o*-Tolylhydrazine as reagent for aldehydes and ketones. P. P. T. SAH and T. S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 259—268).—*o*-Tolylhydrazine (improved prep.) gives the following *o-tolylhydrazones*: *p*-hydroxy-, m.p. 155—156°, and *m*-, m.p. 170—171°, and *p*-nitrobenzaldehyde, m.p. 163—164°, aceto-, m.p. 100—102°, *m*-nitroaceto-, m.p. 135—136°, and benzo-phenone, m.p. 103—104°, benzylidene-, m.p. 122—124°, *p*-nitrobenzylidene-, m.p. 180—181°, and furfurylideneacetone, m.p. 83—85°, and Et lævulate, m.p. 78—80° A. A. L.

Arylhydrazines and dithiocarboxylic acids. H. WUYTS and (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1933, **42**, 1—26).—Interaction of arylhydrazines with dithio-acids gives either the thiohydrazide of the acid or the arylhydrazone of the corresponding aldehyde: $R{\cdot}CS{\cdot}SH+NH_2{\cdot}NHAr \longrightarrow H_2S+R{\cdot}CS{\cdot}NH{\cdot}NHAr$ or $\longrightarrow H_2S+S+R{\cdot}CH{:}N{\cdot}NHAr$ (cf. A., 1929, 1176). Aliphatic dithio-acids and $NH_2{\cdot}NHPh$ or $NH_2{\cdot}NMePh$ give hydrazides; with aromatic dithio-acids $NH_2{\cdot}NHPh$ and its nuclear substitution products give both hydrazides and hydrazones, and $NH_2{\cdot}NMePh$ and $NH_2{\cdot}NPh_2$ give hydrazones only. In all the above cases the arylhydrazine is used in slight excess; if an equimol. amount be used the formation of hydrazide is slightly favoured. The dithio-acids are prepared by a slightly modified and improved method (cf. *loc. cit.*). The following appear to be new: dithiobenzoic acid (*phenyl-*, m.p. 88°, *diphenyl-*, m.p. 132—133°, p-*tolyl-*, m.p. 96°, p-*bromophenyl-*, m.p. 129·5°, and as-*phenylmethyl-hydrazide*, m.p. 95—95·5°); *dithio-o-toluic acid*; *dithio*-1-*naphthphenylhydrazide*, m.p. 158°; *dithio*-2-*naphthoic acid*, m.p. 48°; *dithiophenylacetphenylhydrazide*, m.p. 91·5—92°; *dithioacetphenylhydrazide*, m.p. 82°; *benzaldehyde-diphenyl-*, m.p. 122·5°, -p-*tolyl-*, m.p. 123°, -p-*bromophenyl-*, m.p. 124°, and -*phenylmethyl-hydrazone*, m.p. 103—104°; 1-*naphthaldehydephenylmethylhydrazone*, m.p. 91°. The *tetrazone*, $C_{28}H_{26}N_4$, m.p. 133°, is prepared from $CH_2Ph{\cdot}CH{:}N{\cdot}NHPh$ and amyl nitrite and also in a similar manner from an oily product from $NH_2{\cdot}NHPh$ and dithiophenylacetic acid. H. A. P.

Mechanism of catalytic hydrogenation of phenol under high pressure. III. S. ANDO (J. Soc. Chem. Ind. Japan, 1933, **36**, 33—38B).—In presence of Mo oxide at about 50—70 atm. hydrogenation of PhOH commences at 350°; it is almost complete at 450° and gives a hydrocarbon mixture consisting mainly of C_6H_6, *cyclo*hexane (I), and methyl*cyclo*pentane (II). Under these conditions C_6H_6 is not hydrogenated, but *cyclo*hexanol (III) is reduced below 330° to (I) and (II). *cyclo*Hexene (IV) also gives the same products and (I) is partly converted into (II) at 455°. The course of hydrogenation of PhOH is therefore regarded as $PhOH \longrightarrow C_6H_6+$ (III); (III) $\longrightarrow$ (IV) $\longrightarrow$ (I) and (II). H. A. P.

Condensation of phenols with dimethylamine and formaldehyde. J. DECOMBE (Compt. rend., 1933, **196**, 866—868).—Equimol. quantities of PhOH, CH_2O, and $NHMe_2$ in EtOH–H_2O at room temp. give mainly *o*-hydroxybenzyldimethylamine, b.p. 104°/13 mm. (*Bz* derivative, b.p. 171·5°/4 mm.) (giving salicylic acid on fusion with alkali), and no OMe derivative (cf. G.P. 89,979, 92,309). Deficiency of PhOH leads to formation also of 2 : 6-*di*(*dimethylaminomethyl*)*phenol*, b.p. 134—135°/3 mm., giving a poor yield of 2-hydroxy*iso*phthalic acid when fused with alkali. *o*-Cresol gives 3-*dimethylaminomethyl-o-cresol*, b.p. 110—112°/13 mm., *p*-cresol gives 3-*dimethylaminomethyl*-p-*cresol*, b.p. 117—120°/24 mm., and 2 : 6-*di*(*dimethylaminomethyl*)-p-*cresol*, b.p. 134°/3 mm., and 5-ethyl-*o*-cresol gives 3-*dimethylaminomethyl*-5-*ethyl*-o-*cresol*, b.p. 136—137°/15 mm. The above compounds give *Bz* derivatives (*hydrochlorides*, hygroscopic). 2-Methyl-6-ethylphenol reacts slowly to give *di*-(4-*hydroxy*-3-*methyl*-5-*ethylphenyl*)*methane*, m.p. 105°, and 2-*methyl*-6-*ethylphenyl dimethylaminomethyl ether*, b.p. 134—145°/0·2 mm. (decomp.) (*hydrochloride*). R. S. C.

Action of phosphorus pentachloride on neutral aryl sulphites. P. Carre and D. Libermann (Compt. rend., 1933, **196**, 864—866).—PCl_5 and Ph_2 sulphite react thus: at room temp., $SO(OPh)_2$ (I) + PCl_5 ⟶ $POCl_3$ + PhCl + PhO·SOCl (II); at 100°, 3(II) + $POCl_3$ ⟶ $3SOCl_2$ + $PO(OPh)_3$; at 120—130°, (I) + $SOCl_2$ ⟶ 2(II). Di-β-naphthyl sulphite reacts similarly (best in $CHCl_3$), but somewhat more violently; in absence of a solvent some dinaphthol, m.p. 215°, is also formed. R. S. C.

Formation of aromatic ethers from *p*-fluoronitrobenzene. M. J. Rarick, R. Q. Brewster, and F. B. Dains (J. Amer. Chem. Soc., 1933, **55**, 1289—1290).—*p*-$C_6H_4F·NO_2$ (I) reacts readily with AlkOH–KOH or KOAr to give the corresponding ethers. (I) is much better than *p*-$C_6H_4Cl·NO_2$ for the prep. of aromatic ethers; a catalyst is rarely necessary. The following appear to be new: p-*nitrophenyl* *Pr*$^{\beta}$, b.p. 276—277°/738 mm., *phenylethyl*, m.p. 56—57°, m-*tolyl*, m.p. 63°, o-*iodophenyl*, m.p. 105°, p-*diphenylyl*, m.p. 120°, p-tert.-*amylphenyl*, m.p. 60°, p-*acetamidophenyl*, m.p. 153°, and m-*nitrophenyl*, m.p. 123°, *ethers*; o-n′-*nitrophenoxybenzaldehyde*, m.p. 112°. H. B.

Nitration of *p*-cresol and *p*-tolyl carbonate in presence of sulphuric acid. H. J. Lucas and Y. P. Liu (J. Amer. Chem. Soc., 1933, **55**, 1271—1280).—Nitration of *p*-cresol (I) with HNO_3 (*d* 1·42) in AcOH in absence and presence of conc. H_2SO_4 [up to approx. 10 mols. per mol. of (I)] is studied. A trace of 2-nitro-*p*-cresol (II) is formed in AcOH alone, but with rise in concn. of H_2SO_4 (up to about 5 mols.) gradually increasing amounts of (II) result until the ratio (II) : 3-nitro-*p*-cresol=approx. 0·8 is reached. The change in directive power is ascribed to the salt-forming property of the O atom. Nitration of *p*-tolyl carbonate with fuming HNO_3 (approx. 2 mols.) in presence of varying amounts of oleum (5% SO_3) causes a change in the ratio 2-NO_2- : 3-NO_2-derivative from 0·1 (no oleum) to 2·4 (8·2—10·3 mols. of oleum); oxonium salt formation is considered to be responsible for the change. Small amounts of $(NO_2)_3$-derivatives are formed in the nitrations. H. B.

Preparation of β-naphthol-7-sulphonic acid. A. I. Kogan (J. Appl. Chem., Russia, 1931, **4**, 1060—1065).—2 : 7-$C_{10}H_6(SO_3Na)_2$ and 50% NaOH heated in an autoclave at 220—250° for 3—6 hr. afford 2 : 7-$C_{10}H_6(OH)·SO_3Na$ (73·2% of the disulphonate). Ch. Abs.

Nitration of α- and β-naphthols. F. Bell (J.C.S., 1933, 286—296).—1-Naphthyl *m*-nitrobenzenesulphonate with fuming HNO_3 in AcOH gives the 4- and 8-*nitro*-compounds, m.p. 166°, converted by further nitration (HNO_3 alone) into the 4 : 5-, m.p. 174°, and 4 : 8-*dinitro*-compound, m.p. 165°, respectively. Similarly, 2-naphthyl *m*-nitrobenzenesulphonate gives the 5- and 8-nitro-, and 1 : 5- (I), m.p. 153°, 4 : 5- (II), m.p. 212°, and 1 : 8-*dinitro*- (III), m.p. 201°, -compounds. Further nitration of 4-*nitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, m.p. 149°, gives (II) in 54% yield; 1-*nitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, m.p. 176°, gives (I) and (III). Identification is effected by direct comparison or by fission with piperidine to the nitronaphthols, of which 8-*nitro*-α-*naphthol*, m.p. 130°, 1 : 5-, m.p. 187° (decomp.), and 4 : 5-*dinitro*-β-*naphthol*, m.p. about 230°, are new. Nitration of β-naphthol sulphide gives, not 5 : 8- (cf. A., 1891, 320), but 1 : 8-dinitro-β-naphthyl Et ether. H. A. P.

Condensation products from triarylphosphine oxides and phenolic compounds. W. Lommel and H. Münzel, Assrs. to I. G. Farbenind. A.-G.—See B., 1933, 297.

New condensation reaction of thiophenols. G. Dougherty and W. H. Taylor (J. Amer. Chem. Soc., 1933, **55**, 1294—1295).—PhSH, $CH_2Ph·SH$, and many substituted thiophenols react with hexamethylenetetramine and hydrobenzamide in boiling dioxan as follows: $6PhSH + (CH_2)_6N_4 \longrightarrow 2N(CH_2·SPh)_3 + 2NH_3$; $3PhSH + 2(CHPh:N)_2CHPh \longrightarrow NH_3 + 3CHPh:N·CHPh·SPh$. H. B.

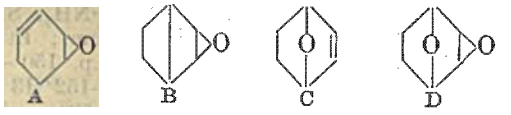
Influence of sulphur atom on reactivity of adjacent atoms or groups. VI. Aromatic side-chain and nuclear reactivity. G. Baddeley and G. M. Bennett (J.C.S., 1933, 261—268; cf. this vol., 268).—In a series of aryl α-chloroethyl sulphides, sulphoxides, and sulphones the velocity coeffs. for the replacement of Cl by I in $COMe_2$, a bimol. reaction (i), and by OH in 50% aq. $COMe_2$, a unimol. reaction in the case of the sulphides (ii), are determined at 55° and 75° (cf. A., 1927, 871), and the vals. of the activation energies calc. In the case of the sulphides the velocities are in the order *p*-anisyl < *p*-tolyl < Ph < *p*-halogenophenyl < *p*-$C_6H_4·NO_2$ < $C_6H_3(NO_2)_2$ for (i), and in the reverse order for (ii), in agreement with the general conclusions previously reached as to the nature of the reactions (*loc. cit.*) and with the polar natures of the substituents. The sulphoxides and sulphones (this vol., 268) are not hydrolysed under the conditions used. H. A. P.

Hydroxyphenyl alkyl sulphides. E. Miller and R. R. Read (J. Amer. Chem. Soc., 1933, **55**, 1224—1227).—The following *p*-hydroxyphenyl alkyl sulphides are prepared from *p*-OH·C_6H_4·SNa and the requisite alkyl halide in MeOH or by de-ethylation (20% HBr, AcOH) of *p*-OEt·C_6H_4·SAlk (which is obtained from diazotised *p*-OEt·C_6H_4·NH_2, SHAlk, and aq. NaOH): Me, b.p. 113°/6 mm.; Et, b.p. 153—155°/13 mm., m.p. 41°; *Pr*$^{\alpha}$, b.p. 150—153°/5—6 mm., m.p. 37°, and *Pr*$^{\beta}$, b.p. 150—152°/13 mm.; *Bu*$^{\alpha}$, b.p. 116—118°/7 mm., m.p. 49—50°, and *Bu*$^{\beta}$, b.p. 159—162°/10 mm.; *n*-amyl, b.p. 164—168°/3—4 mm. (lit. 123—130°/2—3 mm.), m.p. 59°; iso*amyl*, b.p. 150—152°/3 mm.; n-*hexyl*, b.p. 178—180°/5 mm., 194—196°/16 mm., m.p. 60°; *benzyl*, b.p. 220—225°/15 mm., m.p. 104°. o- and m-*Hydroxyphenyl* *Bu*$^{\alpha}$ *sulphides* have b.p. 110—112°/5 mm. and 127—140°/4 mm., respectively. The PhOH coeffs. (*S. aureus*) indicate that these sulphides are more powerful bactericides than the corresponding ethers. H. B.

Two methylamino*cyclo*hexanols and their resolution into optical antipodes. M. Godchot and M. Mousseron (Compt. rend., 1933, **196**, 621—622).—*dl*-3-Amino-1-methyl*cyclo*hexan-4-ol (I), m.p. 27°, b.p.

116—117°/15 mm. [*hydrochloride*, m.p. 130—131°; *picrate*, m.p. 180° (decomp.); *Ac* derivative, b.p. 198—200°/15 mm.], is obtained cryst. by Kotz and Merkel's method (A., 1926, 721), some *di*-(2-*hydroxy*-5-*methyl*-cyclo*hexyl*)*amine*, b.p. 205—206°/16 mm. [*hydrochloride*, m.p. 266—267°; *picrate*, m.p. 260° (decomp.); *NO*-derivative, m.p. 142—143°], being obtained as a by-product. Fractional crystallisation of the d-*H tartrate*, m.p. 130—131°, $[\alpha]_D$ +14·81°, of (I) from EtOH gives the less sol. d-*H tartrate*, m.p. 121—125°, $[\alpha]_D$ +25·27°, of the d-*amino-alcohol* (II), m.p. 24°, b.p. 110—111°/16 mm., $[\alpha]_D$ +16·60°, and the more readily sol. d-*H tartrate*, m.p. 154—155°, $[\alpha]_D$ +5·82°, of the l-*amino-alcohol* (III), $[\alpha]_D$ −16·60°. Similarly, the l-*H tartrate*, m.p. 130—131°, $[\alpha]_D$ −14·93°, of (I) affords the more sol. l-*H tartrate*, m.p. 154—155°, $[\alpha]_D$ +5·82°, of (II) and the l-*H tartrate*, m.p. 124—125°, $[\alpha]_D$ −25°, of (III). NH_2Me and *cyclo*hexene oxide at 110° afford dl-2-*methylamino*cyclo*hexanol*, m.p. 25°, b.p. 108—109°/17 mm. (*hydrochloride*, m.p. 114—115°), the d-*H tartrate*, m.p. 120—121°, $[\alpha]_D$ +13·05°, of which is resolved (EtOH–$COMe_2$) into the d-*H tartrate*, m.p. 146—147°, $[\alpha]_D$ +43·58° (less sol.), of the d-*base*, m.p. 23°, b.p. 106—107°/17 mm., $[\alpha]_D$ +82·82°, and the d-*H tartrate*, m.p. 137—138°, $[\alpha]_D$ −18·02°, of the l-*base*, m.p. 23°, $[\alpha]_D$ −82·82°. Nuclear substitution by Me decreases, and *N*-Me substitution increases, the rotatory power. The rotation–dispersion ratios are discussed. J. W. B.

Oxides and polyalcohols derived from $\Delta^{1:3}$-*cyclo*hexadiene. P. Bedos and A. Ruyer (Compt. rend., 1933, **196**, 625—627).—Partial hydration of the monoxide (I) of $\Delta^{1:3}$-*cyclo*hexadiene (this vol., 56) with H_2O at 0° affords (probably) Δ^3-cyclo*hexene*-1 : 2-*diol* (II), m.p. 77° (*dibromide*, m.p. 130—131°; Bz_2 derivative, m.p. 77°), giving only *cyclo*hexane-1 : 2-diol on reduction with H_2–Pt in MeOH. From the mother-liquor Δ^2-cyclo*hexene*-1 : 4-*diol* (III), m.p. 86° (*dibromide*, m.p. 157°; Bz_2 derivative, m.p. 96·5°), similarly reduced to *cyclo*hexane-1 : 4-diol, is obtained. (II) always predominates, but the proportion of (III) formed decreases with specimens of (I) prepared from the chlorohydrin, by oxidation of $\Delta^{1:3}$-*cyclo*hexadiene with BzO_2H, or from the iodohydrin, in this order, indicating that (I) is a non-separable mixture of



A (or B) and C. The dioxide (*loc. cit.*) is probably D, and by hydration with H_2O at 140° or H_2O–trace of H_2SO_4 at 95°, affords a mixture (2 : 1) of cyclo*hexane*-1 : 2 : 3 : 4-*tetraol*, m.p. 210° (Bz_4 derivative, m.p. 146°), and a *form*, m.p. 187° (Bz_4 derivative, m.p. 260°), separated as their Bz derivatives. J. W. B.

Ease of hydrolysis and solubility of sterol digitonides. R. Schonheimer and H. Dam (Z. physiol. Chem., 1933, **215**, 59—63).—Sterol digitonides (I) are hydrolysed in the cold by dissolution in C_5H_5N; the digitonin (II) may then be pptd. by Et_2O and the sterol (III) recovered. The amount of a (I) pptd. depends on the excess of (II), the previous treatment of the (II), and the nature of the (III), so that it appears impossible to correct for all the errors in a determination of (III) by this method. J. H. B.

Structural difference between sitosterol and cholesterol. B. E. Bengtsson (Z. physiol. Chem., 1933, **215**, 179—182).—Whereas cholesterol on oxidation (CrO_3–AcOH) gives $COMe_2$ and Me *iso*hexyl ketone, sitosterol gives $COMe_2$ and, in poor yield, another *ketone* $C_{11}H_{22}O$ (or $C_{10}H_{20}O$) (*semicarbazone*, m.p. 110—118°). J. H. B.

Photochemical changes of the irradiation products of ergosterol. P. Setz (Z. physiol. Chem., 1933, **215**, 183—192).—Irradiation of lumisterol (*allophanate*, m.p. 217—218°, $[\alpha]_D^{17}$ +75·4° in $CHCl_3$) for 50 hr. with ultra-violet light gave suprasterols I (*acetate*, m.p. 73—74°, $[\alpha]_D^{18}$ −71° in $CHCl_3$) and II, m.p. 109—110° (2 : 6-dinitro-4-toluate, m.p. 170°, $[\alpha]_D^{22}$ +108° in $COMe_2$). Prolonged irradiation of tachysteryl acetate and vitamin-D_2 also afforded suprasterols I and II. Ergosterol gave vitamin-D_2 (*allophanate*, m.p. 194—195°, $[\alpha]^{20}$ +50·4° in $CHCl_3$; *anisate*, m.p. 99·5—101°, $[\alpha]_D^{21}$ +120° in $CHCl_3$; *phenylurethane*, m.p. 122°). Irradiation of vitamin-D_2 gave no ergosterol, tachysterol, or lumisterol. J. H. B.

Sterol group. XVII. Unsaturated centres in ergosterol. I. M. Heilbron, A. L. Morrison, and J. C. E. Simpson (J.C.S., 1933, 302—306).—Since ozonisation of ergostadienetriol diacetate (A., 1930, 1178) gives $CHMePr^{\beta}$·CHO (I), the double linking in the side-chain is intact, and the OH groups must be in the nucleus. Ergostenetriol diacetate is isomerised by HCl in $CHCl_3$ to *ergostenetriol*-β *diacetate*, m.p. 209—210° (free *triol*, m.p. 191—193°), converted by H_2–PtO_2 into *ergostanetriol diacetate*, m.p. 191° (free *triol*, m.p. 246—247°). Methoxyergostatriene gives with BzO_2H in $CHCl_3$ *methoxyergostadienediol monobenzoate*, m.p. 158—159°, hydrolysed by KOH to the free *diol* (II), m.p. 174—175°, which with BzCl regenerates the original monobenzoate only. This suggests that one of the OH groups is *tert.*, which is confirmed by the oxidation of ergostadienetriol monobenzoate (III) (*loc. cit.*; prep. improved) by CrO_3 in aq. AcOH at 35—40° to *ergostadienediolone monobenzoate*, m.p. 217—218° [2 : 4-*dinitrophenylhydrazone*, m.p. 232° (decomp.)]. Ergostadienetriol (IV) under similar conditions gives *ergostadienoldione*, m.p. 249° (decomp.) [*oxime*, m.p. 232—233° (decomp.)]. The reactive double linking of ergosterol is therefore of the type :C:CH·, and it is suggested that the nuclear double linkings of ergosterol are at C_{9-11} (reactive) and C_{8-14} (inert); this is in conformity with its reactions with Na and EtOH and with maleic anhydride. Oxidation of (IV) with $Pb(OAc)_4$ in AcOH gives a *keto-aldehyde*, $C_{28}H_{44}O_3$, m.p. 155—156°; (III), however, is unaffected. Under the same conditions (II) gives a *substance*, $C_{29}H_{46}O_3$, m.p. 105—106°. Ozonisation of "β-dihydroergosterol" (V) (A., 1929, 2248) gives (I), which is not, however, formed under similar conditions from β- or dehydroergostenols. Hydrogenation of (V) (PtO_2 in AcOH) gives ergostanyl and α-ergostenyl acetates. It is therefore regarded as a eutectic mixture of α- and β-isomerides. H. A. P.

Hydroxyl group in ergosterol and cholesterol. I. M. HEILBRON and J. C. E. SIMPSON (Nature, 1933, **131**, 438).—Oxidation of ergostanyl chloride, $C_{28}H_{49}Cl$, with CrO_3 gives a chloronorcholanic acid, m.p. 213°, which is formed by scission of the ergostanyl side-chain: ·CHMe·[CH_2]$_2$·CHMe·$CHMe_2$ ⟶ ·CHMe·CH_2·CO_2H. L. S. T.

Dehydration of nuclear-halogenated β-phenylethyl alcohols with potash. L. PALFRAY, S. SABETAY, and (MLLE.) D. SONTAG (Compt. rend., 1933, **196**, 622—625).—$CH_2Ph·CH_2Br$ with Br (Fe catalyst) in the cold affords a mixture (mainly *o* and *p*), b.p. 143—144°/15 mm., of isomeric β-bromophenylethyl bromides, converted by KOAc into the mixed acetates, b.p. 148—149°/15 mm., which give a mixture, b.p. 144·5—145·5°/15 mm., of β-bromophenylethyl alcohols on hydrolysis. Fusion of this mixture with KOH effects dehydration to the mixed bromostyrenes, b.p. 88—90°/15 mm. (liquid and solid, m.p. 59·5°, dibromides). Similarly, Cl_2 acts on cold $CH_2Ph·CH_2·OH$ to give a mixture, b.p. 130—131°/11 mm., of *o*- and *p*-chlorophenylethyl alcohol, similarly dehydrated to mixed chlorostyrenes, b.p. 71·5—72·5°/15 mm. (liquid and solid, m.p. 53—54°, dibromides). J. W. B.

Preparation of unsymmetrical γ-glycols of the acetylene series and their catalytic hydrogenation. J. SALKIND and V. TETERIN [with, in part, A. IVANOV and A. ZACHAROV] (Ber., 1933, **66**, [*B*], 321—325).—Addition of a mixture of $COPh_2$ and $COMe_2$ in Et_2O to (:C·MgBr)$_2$ (I) in Et_2O at 0° affords tetramethylbutinediol, tetraphenylbutinediol (II), m.p. 191°, and as-*diphenyldimethylbutinediol* [αα-*diphenyl*-δ-*methyl*-Δ^{β}-*pentine*-αδ-*diol*], m.p. 114·5—115·5°, rapidly hydrogenated to αα-*diphenyl*-δ-*methyl*-Δ^{β}-*pentene*-αδ-*diol*, m.p. 91·5—92·5°. Similarly, a mixture of $COPh_2$ and MeCHO with (I) yields (II) and αα-*diphenyl*-Δ^{β}-*pentine*-αδ-*diol*, m.p. 110°, rapidly hydrogenated to non-cryst. αα-*diphenyl*-Δ^{β}-*pentene*-αδ-*diol* (converted by conc. H_2SO_4 in MeOH or AcOH into 5 : 5-*diphenyl*-2-*methyl*-3 : 4-*dihydrofuran*, m.p. 68°) and thence slowly to αα-*diphenylpentane*-αo-*diol*, m.p. 73°. $COPh_2$ and PhCHO likewise afford (II) and an inseparable mixture of crystals transformed by Br in $CHCl_3$ into the dibromide of the γ-oxide of (II), the dibromides, m.p. 180° and 172°, respectively, of the isomeric diphenylbutinediols, and 3 : 4-*dibromo*-2 : 2 : 5-*triphenyl*-2 : 5-*dihydrofuran*, m.p. 112°. $COPh_2$ and COPhMe or $COEt_2$ yield only the corresponding *s*-glycols, whereas with *cyclo*hexanone, γγ-*diphenyl*-α-1-*hydroxycyclohexyl*-Δ^{α}-*propin*-γ-*ol*, m.p. 110°, is obtained in very small yield. H. W.

Mechanism of reaction of sodium phenyl and lithium phenyl with phenylthiocarbimide. H. GILMAN and F. BREUER (J. Amer. Chem. Soc., 1933, **55**, 1262—1264).—Addition of LiPh or NaPh is considered to occur on the C:S of PhNCS, since treatment of the additive product with Me_2SO_4 gives *S*-methylthiobenzanilide and oily products (which afford no NHPhMe on hydrolysis). H. B.

Benzoyl peroxide and benzylamine. S. GAMBARIAN, O. CIALTICIAN, and A. BABAJAN (Bull. Inst. Sci. R.S.S. d'Armenie, 1931, 265—268).—$CH_2Ph·NH·OBz$ (I) is formed intermediately in the reaction between Bz_2O_2 and $CH_2Ph·NH_2$ in Et_2O. (I) reacts with $CH_2Ph·NH_2$ to give $CH_2Ph·NHBz$ (II). Direct formation of (II) may also occur simultaneously. CH. ABS.

Degradation of methyl and methylene ketones to acids. F. KRÖHNKE (Ber., 1933, **66**, [*B*], 604—610).—The pyridinium salts of monohalogenomethyl ketones are stable towards acid, but readily hydrolysed by alkali to the corresponding org. acid and methylpyridinium hydroxide or its ψ-base. The change is apparently preceded by changes in the C_5H_5N nucleus. C_5H_5N may less advantageously be replaced by quinoline or picoline. The presence of CO next the halogen-substituted Me or CH_2 group appears essential. The following changes are cited: phenacylpyridinium bromide (I) (corresponding *perchlorate*, m.p. 189°; *perbromide*; additive *compound* with Na nitroprusside) to BzOH [(I), PhCHO, and NaOH yield a *substance* $C_{13}H_{14}ONBr$, m.p. 222—230° (decomp.), also obtained from pyridine methobromide, NaOH, and PhCHO (*perchlorate*, m.p. 212—215°); analogously *m*-$NO_2·C_6H_4·CHO$ gives the *compound* $C_{12}H_{13}O_3NBr$, m.p. 210—212°]; acetonylpyridinium chloride, m.p. 201° (decomp.), to AcOH; α-*naphthacylpyridinium bromide*, m.p. 170°, to 1-naphthoic acid; β-*naphthacylpyridinium bromide*, m.p. 160° (decomp.), to 2-naphthoic acid; p-*phenylphenacylpyridinium bromide*, m.p. 233°, to *p*-phenylbenzoic acid, m.p. 221·5°; COPhEt to BzOH; p-*methylphenacyl*-2-*picolinium bromide*, m.p. 177—180°, becoming dark blue above 205°, to *p*-toluic acid, m.p. 179°; p-*chlorophenacylquinolinium bromide*, m.p. 220° (decomp.), to *p*-chlorobenzoic acid; p-*methylphenacylisoquinolinium bromide*, m.p. 219° after softening, to *p*-toluic acid; α-*acetyl*-β-*phenylethylpyridinium bromide* (corresponding *perchlorate*, m.p. 105°) to AcOH. *Phenylethylpyridinium perchlorate* has m.p. 140—141°. Phenacylpiperidinium bromide (corresponding *perchlorate*, m.p. 181°) is not affected by NaOH, whilst the behaviour of diphenacylpiperidinium bromide is doubtful. *Propiophenonylpyridinium chloride* has m.p. 271°. H. W.

Preparation of cyclic nitriles by catalytic degradation. II. Direct cyanogenation of cyclic hydrocarbons and phenolic ethers. J. HOUBEN and W. FISCHER (Ber., 1933, 66, [*B*], 339—349).—The following improvements of the method (A., 1930, 1584) are recorded. The cyclic compound (1 mol.), which must not contain an acidic radical, is condensed with $CCl_3·CN$ (1 mol.) in presence of $AlCl_3$ (2—2·5 mols. or 3 mols. in case of materials which react with difficulty) and PhCl (1—2·5 mols.). Excess of cyclic compound may replace the diluent in certain cases. Prolonged keeping is frequently advisable. Isolation of the ketimine (I) from the product is effected by NH_3 in Et_2O. Powdered NaOH, which need not be anhyd., is used for conversion of (I) into nitrile. With mixtures of the (I) and nitrile, the solution in Et_2O or light petroleum is treated with HCl, whereby the hydrochloride (II) of (I) is pptd. and the CCl_3-ketone is isolated from the filtrate; (II), suspended in Et_2O, is treated with NH_3 and the (I) obtained after removal of NH_4Cl. If only the isolation

of (I) is required, the solution in Et_2O is treated with NH_3, whereby ketone rapidly passes into acid amide. Details are given of the cyanogenation of 3 : 5-dimethylanisole, 2-methylindole, C_6H_6, PhMe, *o*-, *m*-, and *p*-$C_6H_4Me_2$, mesitylene, tetrahydronaphthalene, and *p*-$C_6H_4Me{\cdot}OMe$. The following compounds are described: 6-*methoxy*-2 : 4-*dimethylbenzamide*, m.p. 188—189°; 4-*acetoxy*-, m.p. 58—60°, and 4-*hydroxy*-, m.p. 174—176°, -2 : 6-*dimethylbenzonitrile*; *trichloroacetiminotoluene*, b.p. 128—130°/1—2 mm. H. W.

Hippurhydroxamic acid. J. V. Dubský and J. Trtilek (Coll. Czech. Chem. Comm., 1933, **5**, 103—111).—Hippuramide and NH_2OH in aq. EtOH give *hippurhydroxamic acids*, $NHBz{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}OH$, m.p. 141° (I) and 159—160° (II), according to the conditions used; (I) is converted into (II) when its aq. solution is boiled for several hr. (I) heated at 105—110°/10—20 mm. for 3 hr. loses 27·6% of its wt. (and undergoes decomp.), whilst (II) similarly loses only 5·22%, indicating that the OH groups are *cis* in (I) and *trans* in (II). (I) and (II) give the same *Cu* salt, $NHBz\,CH_2{\cdot}C{<}\begin{matrix}O\\N{\cdot}O\end{matrix}{>}Cu$ (also $+H_2O$), when treated with $Cu(OAc)_2$. (I), $CoCl_2$, NaOAc, and aq. NH_2 give a complex containing Co·· and Co···, whilst (II), $Hg(NO_3)_2$, and NaOAc afford an unstable *complex*, $[NHBz{\cdot}CH_2{\cdot}C(O{\cdot}){:}N{\cdot}O{\cdot}]Hg_2,3H_2O$. The *Fe* salt, $[NHBz{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}O{\cdot}]_2Fe{\cdot}OH,H_2O$, is described. H. B.

Steric series. XVIII. Configuration of the tertiary carbon atom. Atrolactic acid, mandelic acid, and related compounds. K. Freudenberg, J. Todd, and R. Seidler (Annalen, 1933, **501**, 199—219).—The rotatory powers of (—)-atrolactic acid (I) and its derivatives show that (I) is configuratively related to *d*-(—)-mandelic acid (II); the same conclusion is reached using Lutz's method (A., 1932, 720, 1246). If (I) is regarded as a phenyl-lactic acid, it should be related to *l*-(+)-lactic acid; this is, however, not the case. Introduction of Ph into the lactic acid mol. causes a rearrangement of optical properties; a possible explanation, based on Kuhn's theory (A., 1930, 276; this vol., 211), is given. The following are configuratively related: (II), *d*-(—)-chloro-, -amino-, and -azido-phenylacetic acids, (—)-phenylmethylcarbinol, (—)-phenylethylamine, *d*-(+)-mandelonitrile, and (+)-aminophenylacetonitrile (as salt). The possible inversions in the series $OH{\cdot}CHPh{\cdot}CO_2H$, $Cl{\cdot}CHPh{\cdot}CO_2H$, and $NH_2{\cdot}CHPh{\cdot}CO_2H$ are indicated.

*iso*Propylidene-*d*-mandelic acid (III), $[\alpha]_{5461}^{18}$ —99° in MeOH (Willstatter and Konigsberger, A., 1923, i, 1172), and EtOH–NH_3 give *d*-mandelamide, $[\alpha]_{5461}^{17}$ —75° in $COMe_2$ (iso*propylidene* derivative, m.p. 126°, $[\alpha]_{5780}$ —95° in $COMe_2$), whilst (III) and MeOH–$NHMe_2$ afford d-*mandeldimethylamide*, m.p. 151—152°, $[\alpha]_{5780}^{}$ —162° in $C_2H_2Cl_4$ (*Me ether*, b.p. 110°/0·6 mm., $[\alpha]_{5780}^{15}$ —14·33°, $[\alpha]_{5461}^{15}$ +5·3°). dl-*Mandeldimethylamide* (*Me ether*, m.p. 41°) has m.p. 158°. (II), MeI, and Ag_2O give Me *d*-(—)-mandelate Me ether, b.p. 123°/15 mm., $[\alpha]_{5461}^{20}$ —106°. *d*-(—)-Mandelic acid Me ether and PCl₅ in $CHCl_3$ afford *α-methoxy-α-phenylacetyl chloride*, b.p. 98°/11 mm., $[\alpha]_{5461}^{18}$ —72°. (—)-Atrolactic acid, $[\alpha]_{5791}^{18}$ —52° in H_2O [Me ester, b.p. 120—121°/13 mm., $[\alpha]_{5780}^{18}$ —30° (*Ac*, b.p. 108°/17 mm., $[\alpha]^{20}$ —24°, and *Bz*, b.p. 145°/0·2 mm., $[\alpha]_{5780}^{20}$ —24·8°, derivatives; *Me ether*, b.p. 80°/0·4 mm., $[\alpha]_{5780}^{20}$ +51·6°); *Et* ester, b.p. 82°/0·3 mm., $[\alpha]^{20}$ —30·4° (*Ac*, b.p. 86—87°/0·3 mm., $[\alpha]_{5461}^{20}$ —16·9°, and *Bz*, b.p. 153°/0·3 mm., $[\alpha]_{5780}^{20}$ —22·4°, derivatives); amide, m.p. 102°, $[\alpha]_{5780}^{20}$ +5·6° in $COMe_2$ (iso*propylidene* derivative, m.p. 182°, $[\alpha]_{5780}^{20}$ +50° in $COMe_2$); Me ether (*dimethylamide*, b.p. 100°/0·7 mm., $[\alpha]_{5461}^{20}$ +190°)], is reduced (Skita) to (—)-hexahydroatrolactic acid, $[\alpha]_{5780}$ about —13° in EtOH [*Me ether Me* ester, b.p. 77°/0·5 mm., which is dextrorotatory; (+)-*Me ether*, b.p. 113°/0·3 mm., prepared by similar reduction of the Me ether of (I)]. dl-*Hexahydroatrolactic acid* has m.p. 101·5°, whilst the iso*propylidene* derivative of *dl*-atrolactamide has m.p. 146°. (—)-Chlorophenylacetic acid, $[\alpha]_{5780}$ —163° in EtOH (chloride, b.p. 103°/11 mm., $[\alpha]_{5461}^{20}$ —250°; Me ester, $[\alpha]_{5780}$ —182°; *dimethylamide*, m.p. 47°, $[\alpha]_{5780}$ —165° in EtOH), is prepared by resolution of the *dl*-acid with (+)-$NH_2{\cdot}CHPhMe$. $CHBrPh{\cdot}CO_2Et$ and AgF at 40–60° give the *Et* ester, b.p. 108°/11 mm., of *fluorophenylacetic acid*, m.p. 78°, b.p. 115°/1 mm. H. B.

Unsaturated αδ-dicarbonyl compounds. VII. Unsaturated arylated αδ-diketones and ketonic acids derived from citraconic and mesaconic acids, with particular reference to the β-(*p*-bromobenzoyl)methylacrylic acids. R. E. Lutz and R. J. Taylor (J. Amer. Chem. Soc., 1933, **55**, 1168—1178).—The chloride from α-Me H mesaconate, PhBr, and $AlCl_3$ in CS_2 give *Me* trans-β-p-*bromobenzoylcrotonate*, m.p. 75·5° (all m.p. are corr.), hydrolysed by aq. MeOH–KOH to the free *acid* (I), m.p. 144·5—145°, and some α(?)-*hydroxy*-β-p-*bromobenzoylbutyric acid* (II), m.p. 85—86°, which is the sole product isolated when hydrolysis is effected with abs. MeOH–KOH. (II) passes into (I) when heated to 250°. Citraconic anhydride, PhBr, and $AlCl_3$ in CS_2 give cis-β-p-*bromobenzoylcrotonic acid* (III), m.p. 142·5° (*Me* ester, b.p. 156—158°/4 mm.), and a little (IV) (below); a smaller yield of (III) and a trace of (IV) are similarly obtained from citraconyl chloride. (III) is converted by PCl_5 into cis-*γ-chloro-γ-bromophenyl-β-methyl-γ-crotonolactone* [cis-*ψ*-β-p-*bromobenzoylcrotonyl chloride*], m.p. 82·5°, which with PhBr and $AlCl_3$ gives a *compound*, $C_{17}H_{12}O_2Br_2$, m.p. 208°. Reduction (Zn, AcOH) of (III) affords β-p-*bromobenzoylbutyric acid*, m.p. 95·5°. Mesaconyl chloride, PhBr, and $AlCl_3$ give trans-β-p-*bromobenzoyl-α-methylacrylic acid* (IV), m.p. 188° [*Me* ester, m.p. 86°; *acid chloride* (V), m.p. 66°], reduced (Zn, AcOH) to β-p-*bromobenzoyl*isobutyric *acid*, m.p. 124°. The production of (IV) from citraconic anhydride (above) shows that inversion of configuration occurs when H is α to the reacting CO group; when Me is α (main reaction) no inversion takes place. Citraconic anhydride, mesitylene, and $AlCl_3$ in CS_2 give trans-β-2 : 4 : 6-*trimethylbenzoyl-*(?)-*methylacrylic acid*, m.p. 142° [*Me* ester, b.p. 144·5° (corr.)/5 mm.], the unstable chloride of which with mesitylene and $AlCl_3$ affords a little αβ-di-2 : 4 : 6-trimethylbenzoyl-Δ^{α}-propene.

Mesaconyl chloride (VI), C_6H_6, and $AlCl_3$ in CS_2 yield trans-αβ-*dibenzoyl-*Δ^{α}-*propene*, m.p. 52°, convertible into the cis-*form*, m.p. 68·5°, by exposure of a solution in EtOH to sunlight; both forms are reduced

(Zn, AcOH) to αβ-*dibenzoylpropane*, m.p. 105°. (VI), mesitylene, $AlCl_3$, and CS_2 give trans-αβ-*dl*-2 : 4 : 6-*trimethylbenzoyl*-Δ^{α}-*propene*, m.p. 96°; the *cis*-form could not be prepared. The chloride of (I) and C_6H_6 similarly afford trans-α-*benzoyl*-β-p-*bromobenzoyl*-Δ^{α}-*propene*, m.p. 73—74°, whilst trans-β-*benzoyl*-α-p-*bromobenzoyl*-Δ^{α}-*propene*, m.p. 56°, is obtained similarly from (V). H. B.

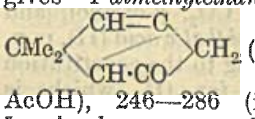
Constitution of oil-soluble basic bismuth salts. A. P. T. Easson and F. L. Pyman (J.S.C.I., 1933, 52, 97—99T).—The prep. of the basic Bi salts of several types of org. ester-acids is described, and their solubilities in olive oil and stabilities of the solutions are compared. The most sol. and stable salts are those of acids containing a saturated homocyclic residue, with a carbalkyloxy- or acyloxy-group in the α-position to the CO_2H group, *e.g.*, the α-*carbethoxy*cyclo*hexylacetate* ("Stabismol") and the 1-acetoxyhexahydrobenzoate. The corresponding dibasic acids and OH-acids do not give oil-sol. Bi salts. The presence of a C_6H_6 residue gives rise to sparingly sol. Bi salts. *cyclo*Hexylmalonic acid (Hope and Perkin, J.C.S., 1909, **95**, 1363) yields a *Me*$_2$ ester, b.p. 140°/12 mm.; *Pr*$^{\alpha}_2$ ester, b.p. 166°/12 mm.; *Bu*$^{\alpha}_2$ ester, b.p. 185°/12 mm.; *Me* ester, m.p. 74°; *Et* ester, m.p. 22°; *Pr*$^{\alpha}$ ester, m.p. 41°; *Bu*$^{\alpha}$ ester, m.p. 45°. 1-*Acetoxy*-, m.p. 108°, 1-*propionoxy*-, m.p. 58—59°, 2-*acetoxy*-, m.p. 96—101°, and 2-*propionoxy-hexahydrobenzoic acid*, a syrup; α-*carbethoxy*-α-*methyl*-β-*phenylpropionic acid*, m.p. 63°; α-*carbethoxy*-n-*hexoic acid*, α-*acetoxy*- and α-*butyroxy*-n-*heptoic acid*, syrups, are described.

Phenolic acids. II. Condensation of β-resorcylic acid with phthalic anhydride. P. P. T. Sah and J. Y. Yen (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 269—276).—The product is fluorescein. A. A. L.

Substituted βγ-diphenyladipic acids and derivatives of chrysene. A. I. Vogel (Nature, 1933, **131**, 402).—A statement of work in progress. L. S. T.

Bridge formation. I. Attempts to synthesise dicyclic terpene derivatives. P. P. Patel and P. C. Guha. **II. Formation and stability of a bridged *cyclo*hexenone, 1-dimethylethane-$^{1:2:2}$III$^{1:4:4}$-*cyclo*butan-2-one.** P. S. Mayuranathan and P. C. Guha (J. Indian Inst. Sci., 1932, **15**, A. 125—130, 131—137).—I. Me adipate added to $Me_2C_2O_4$ and NaOMe in Et_2O gives (after keeping at room temp. and then heating to 140°) *Me* 1 : 2-*diketo*cyclo*hexane*-3 : 6-*dicarboxylate*, m.p. 111—112° [*semicarbazone*, m.p. 170° (decomp.); *quinoxaline*, m.p. 175°, from *o*-$C_6H_4(NH_2)_2$], and some Me *cyclo*pentanone-2-carboxylate, b.p. 106—108°/17 mm. (*semicarbazone*, m.p. 176°). *Et* 1 : 2-*diketo*cyclo*hexane*-3 : 6-*dicarboxylate* (I), m.p. 56° (*quinoxaline*, m.p. 101°), is prepared similarly. Attempts to prepare bridged compounds by condensation of the *Na*$_2$ derivative of (I) with CMe_2Cl_2, *s*-$C_2H_4Cl_2$, $CHPhCl_2$, and CPh_2Cl_2 were unsuccessful; with I in EtOH, the *ester*, $[CO_2Et{\cdot}C<\begin{matrix}C(OH){\cdot}CO\\CH_2{-}CH_2\end{matrix}>C(CO_2Et){\cdot}]_2$, m.p. 90°, results.

II. $CH_2Ac{\cdot}CO_2Et$ and $CMe_2{\cdot}C(CO_2Et)_2$ in 1% EtOH–NaOEt at 105—110° give *Et* α-*acetyl*-ββ-*dimethylpropane*-αγγ-*tricarboxylate* (II), b.p. 155—158°/5 mm.; more conc. NaOEt affords Et 1 : 3-diketo-5 : 5-dimethyl*cyclo*hexane-4 : 6-dicarboxylate (III), b.p. 190—195°/4—5 mm. [*semicarbazone*, m.p. 205° (decomp.)]. (II) is hydrolysed (conc. HCl) to the dilactone of α-acetyl-ββ-dimethylpropane-αγ-dicarboxylic acid and is converted by EtOH–NaOEt into (III). (II) is not convertible into (III) by distillation or treatment with semicarbazide acetate (cf. Scheiber and Meisel, A., 1915, i, 253). Hydrolysis (EtOH–KOH; 75% H_2SO_4; conc. HCl) of (III) gives 1-*dimethylethane*-$^{1:2:4}$III$^{1:4:4}$-cyclo*butan*-2-*one*,



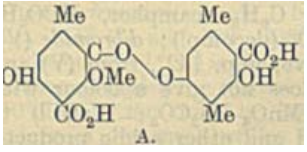
(IV), m.p. 176° (corr.), *M* 126 (in AcOH), 246—286 (in C_6H_6, camphor, HCO_2H) [*semicarbazone*, m.p. 220° (decomp.); *dibromide* (V), m.p. 196°; *Br*-derivative, m.p. 142°, from (V) and MeOH–KOH], which does not give a colour with $FeCl_3$, is oxidised ($KMnO_4$–Na_2CO_3; NaOCl) to ββ-dimethylglutaric acid and other acidic products, and is hydrolysed [aq. $Ba(OH)_2$] to 5 : 5-dimethyldihydroresorcinol (VI). The non-isolation of (IV) by Scheiber and Meisel (*loc. cit.*) is due to the use of $Ba(OH)_2$ for the hydrolysis of (III). Hydrolysis [EtOH–KOH or aq. $Ba(OH)_2$] of Et 1 : 3-diketo-5 : 5-dimethyl*cyclo*hexane-4-carboxylate gives (VI) only. Distillation of the product from (III), CH_2I_2, and EtOH–NaOEt affords (VI). H. B.

Synthesis [of compounds] related structurally to shellac and acaroid resins. W. Nagel and W. Hiller (Fettchem. Umschau, 1933, **40**, 49—51; cf. Diss., Berlin, 1932).—Certain condensation derivatives of OH-acids have been synthesised as models in the study of the reactions of these resins. *Et* α-*hydroxynaphthoyl-lactate* was prepared with difficulty by the method of Lassar-Cohn and Lowenstein (A., 1908, i, 984), and *Me* α-*hydroxynaphthoyl-aleuritate* rather more easily; attempts to remove the ester group, or to synthesise the acids directly, caused rupture of the depside linking. Only very mild methods of attack can therefore be expected to effect isolation of the components of shellac. On the other hand, the easy formation and relative stability of *salicoyl*-p-*hydroxybenzoic acid*, *salicoyl*-p-*coumaric acid*, and β-*hydroxynaphthoylcoumaric acid*, which were prepared as type models for acaroid resin, indicate that fairly drastic methods may safely be employed in attempts to isolate the OH-acid complexes existing in this resin. E. L.

Lichen constituents. III. Synthesis of hæmatommic acid. A. St. Pfau (Helv. Chim. Acta, 1933, **16**, 282—286).—Atranol is one of the products isolated by Simon (A., 1903, i, 98; 1906, i, 961) by reductive fission of cetraric acid with Zn and alkali. Et orsellinate is conveniently prepared from Et methyldihydroresorcylate by oxidation with $FeCl_3$ in 20% AcOH. It is converted by Gattermann's synthesis [$Zn(CN)_2$–HCl in Et_2O] into Et hæmatommate (Et 3 : 5-dihydroxy-4-aldehydo-*o*-toluate), m.p. 113—113·5°, identical with the natural product, and *Et* iso*hæmatommate* (*Et* 3 : 5-*dihydroxy*-6-*aldehydo*-*o*-*toluate*), m.p. 94—94·5°. Hæmatommic acid, m.p. 172—173° (decomp., block) (corr.), prepared by hydrolysis of the Et ester with cold conc. H_2SO_4,

is decarboxylated > 100—120° to atranol; *iso-hæmatommic acid*, m.p. 224—225° (decomp., block) (corr.), similarly prepared, gives orsellinaldehyde in presence of Cu at 250°. H. A. P.

Lichen substances. XVIII. *iso*Squamatic acid, a new depside from *Cladonia Boryi*, Tuck. Y. ASAHINA and M. YANAGITA (Ber., 1933, **66**, [*B*], 393—397).—Extraction of the thalli with hot $COMe_2$ affords *l*-usnic acid, m.p. 204°, $[\alpha]_D^{20}$ −503·5° in $CHCl_3$, a trace of zeorin, and *isosquamatic acid* (I), m.p. 226—227° (decomp.), hydrolysed to CO_2, β-orcinol, and 6-*hydroxy*-2-*methoxy*-4-*methyl*isophthalic acid (II), m.p. 202—203° (decomp.), thus leading to the constitution



A.

A for (I), which is supported by its exhaustive methylation to Me_2 squamatate Me_2 ether. (II) is prepared synthetically as follows: Et_2 2 : 6-dihydroxy-4-methyl*iso*phthalate is converted by $ClCO_2Et$ and KOH into *Et*$_2$ 2-*hydroxy*-6-*ethylcarbonato*-4-*methyl*iso*phthalate*, m.p. 97°, transformed by CH_2N_2 in Et_2O–$COMe_2$ into *Et*$_2$ 2-*methoxy*-6-*ethylcarbonato*-4-*methyl*-iso*phthalate*, b.p. 221—222°/5 mm., which is hydrolysed to (II) (*Me*$_2$ ester, m.p. 125°). H. W.

Bile acids. XLIX. Stereochemistry of bile acids and sterols. H. WIELAND, E. DANE, and C. MARTIUS (Z. physiol. Chem., 1933, **215**, 15—24; cf. this vol., 274).—The isolation of hyodeoxycholic acid from pig's bile is described. Catalytic hydrogenation (PtO_2) of 6-cholenic acid gives *allo*cholanic acid (I), m.p. 170° (cf. lit.), $[\alpha]_D$ +22·2° in $CHCl_3$, and a mol. *compound*, m.p. 162°, of (I) and cholanic acid (II). Reduction of the semicarbazone of 3-hydroxy-6-keto*allo*cholanic acid with Na in EtOH gives 3-hydroxy*allo*cholanic acid (III), m.p. 208—210° (Me ester, m.p. 164°), identical with Windaus' acid from cholesterol. Oxidation of (III) with CrO_3 in AcOH gives 3-*keto*allo*cholanic acid* (IV), m.p. 184° (*Me* ester, m.p. 114°). With HNO_3, (III) gives *isoallo*lithobilianic acid (stadenic acid) (V), m.p. 253—255° (Me_3 ester, m.p. 96°), identical with the product from cholesterol. The steric arrangement at C_5 probably governs the conditions of oxidative ring-fission, so that with the *allo*-configuration the derivatives O-substituted at C_3 open between C_2 and C_3, but with the normal configuration between C_3 and C_4.

Partial hydrogenation of 3 : 6-diketo*allo*cholanic acid gives β-3-*hydroxy*-6-*keto*allo*cholanic acid* (VI), m.p. 235° (decomp.). At 320° in vac. (VI) gives 6-keto*allo*cholenic acid (VII), m.p. 122—124°, which is hydrogenated to 6-hydroxy*allo*cholanic acid. (VI) by Kishner–Wolff reduction gives β-3-*hydroxy*allo-*cholanic acid* (VIII), m.p. 218° (*Me* ester, m.p. 151°), oxidised to ordinary 3-keto*allo*cholanic acid with CrO_3. The β- and ordinary forms are epistereoisomeric at C_3. (VIII) is oxidised by HNO_3 to (V). J. H. B.

Cannizzaro reaction. G. LOCK [with W. HOSAEUS, jun.] (Monatsh., 1933, **62**, 178—194).—Only those derivatives of *m*-OH·C_6H_4·CHO in which halogen occupies each of the positions *ortho* to ·CHO suffer removal of CHO under the influence of KOH. The corresponding halogenophenol and HCO_2H are obtained from all tri-derivatives in which the positions 2, 4, and 6 are occupied by halogen. The following observations appear new. 2-Chloro-3-hydroxybenzaldehyde is incompletely methylated by KOH and MeI, readily by Me_2SO_4 and $NaHCO_3$; 4 : 6-*dibromo*-3-*methoxybenzoic acid*, m.p. 202·5° (corr.); 2 : 4 : 6-*tribromo*-3-*methoxy*-*benzaldehyde*, m.p. 113° (corr.), and *-benzoic acid*, m.p. 154° (corr.); 2-*chloro*-4-*bromo*-3-*hydroxybenzaldehyde*, m.p. 139—140° (corr.) (from 2-chloro-3-hydroxybenzaldehyde and Br in $CHCl_3$) [*oxime*, m.p. 193° (corr.); *Me ether*, m.p. 80·5° (corr.)]; 2-*chloro*-4-*bromo*-3-*hydroxy*-*benzyl alcohol*, m.p. 135° (corr.) [*Me ether*, m.p. 101° (corr.)], and *-benzoic acid*, m.p. 206° (corr.); 2-*chloro*-4-*bromo*-3-*methoxybenzoic acid*, m.p. 154° (corr.); 2-*chloro*-4 : 6-*dibromo*-3-*hydroxybenzaldehyde*, m.p. 104—105° (corr.), from 2-chloro-3-hydroxy- or, preferably, 4 : 6-dibromo-3-hydroxybenzaldehyde, its *Me ether*, m.p. 100°, and *oxime*, m.p. 181—182° (corr.); 2 : 6-*dichloro*-4-*bromo*-3-*hydroxybenzaldehyde*, m.p. 104—105° (corr.), from 2 : 6-dichloro-3-hydroxy- or 2-chloro-4-bromo-3-hydroxybenzaldehyde, its *Me ether*, m.p. 82°, and *oxime*, m.p. 193° (corr.). H. W.

3 : 5-Dinitrobenzaldehyde. H. H. HODGSON and E. W. SMITH (J.C.S., 1933, 315).—Interaction of 4-bromo-3 : 5-dinitrobenzaldehyde with CuH in C_6H_6 at 65—70° gives 3 : 5-*dinitrobenzaldehyde*, m.p. 85° [*semicarbazone*, m.p. 256°; *oxime*, m.p. 159°; *phenylhydrazone*, m.p. 210°; p-*nitrophenylhydrazone*, m.p. 295° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 295°; p-*bromophenylhydrazone*, m.p. 250°; *azine*, m.p. 303°; *anil*, m.p. 123°; p-*tolil*, m.p. 160°; 3′ : 5′-*dinitro*-2-*styrylquinoline*, m.p. 270°]. Attempts to diazotise 3 : 5-dinitro-4-aminobenzaldehyde by several methods failed. H. A. P.

Thioaldehydes and thioketones. I. S. K. MITRA (J. Indian Chem. Soc., 1932, **9**, 633—637).—PhCHO (I), Et thioacetoacetate (II), and a little piperidine in EtOH give Et_2 benzylidenediacetoacetate and polymerised *thiobenzaldehyde* (III), $(PhCHS)_7$, m.p. 83—84°, also formed from (I), H_2S, and a little piperidine in EtOH. (III) gives benzaldehyde-phenylhydrazone and *-as*-phenylmethylhydrazone with the appropriate bases, with a little piperidine in hot $CHCl_3$ yields $CHPh{:}CH_2$ and H_2S, and with BzCl or AcCl and a little piperidine in cold $CHCl_3$ β-trithiobenzaldehyde, also obtained from (I), (II), and dry HCl in cold EtOH. *o*- and *m*-NO_2·C_6H_4·CHO, (II), and dry HCl in EtOH give o- and m-*nitrothiobenzaldehyde*, amorphous, m.p. 168—172° and 185—190° (after sintering at 110°), respectively; the former with NHPh·NH_2 and a trace of piperidine in C_5H_5N gives *o*-nitrobenzaldehyde-phenylhydrazone. Anisaldehyde and (II) in EtOH with piperidine or HCl give polymerised *thioanisaldehyde*, $(MeO{\cdot}C_6H_4{\cdot}CHS)_{11}$, m.p. 73—76°, giving anisaldehydephenylhydrazone. $COPhMe$ and $COPh_2$ with (II) and HCl in EtOH give *thioacetophenone*, b.p. 110°/20 mm., and unimol. *thiobenzophenone*, b.p. 175°/10 mm., respectively; the former gives the phenylhydrazone in the cold. R. S. C.

Colouring matters derived from triphenylmethane. II. A. GIACALONE (Gazzetta, 1933, **63**, 16—20; cf. A., 1932, 733).—4 : 4′-Dihydroxytri-

phenylmethane-3 : 3′-dialdehydebisphenylhydrazone (A., 1931, 957), dihydroxydibenzylidenehydrazino-, 4 : 4′-bis-*o*-hydroxybenzylidenedihydrazino-2″-hydroxy-, and 4 : 4′-bis-*p*-methoxybenzylidenedihydrazino-4″-methoxy-triphenylmethanes when dissolved in fuming H_2SO_4, either hot or cold, undergo pentasulphonation, shown by analysis of the *Ba* salts. Oxidation is absent or occurs only to a small extent; this is attributed to the "anti-oxygenic" effect of the OH and OMe groups. E. E. J. M.

Sulphonation of lignin from pine wood. II. E. Hagglund and G. E. Carlsson (Biochem. Z., 1933, **257**, 467—477).—In the exhaustive methylation of solid and sol. lignosulphonic acids, methylated acids are formed which have the same OMe content as the methylated original lignin. This can be explained only by assuming that during sulphonation an additional methylatable OH group per mol. of lignin is formed, and it is suggested that this most probably arises by the opening of an O-bridged ring. P. W. C.

Prototropic changes in carbonyl compounds. III. Prototropy of nuclear-substituted acetophenones. W. S. Nathan and H. B. Watson (J.C.S., 1933, 217—220).—Bromination of *p*-substituted acetophenones is powerfully catalysed by halogen acids, and is very slow in their absence. In the presence of a const. initial concn. of HCl the velocities of bromination at 25° are in the same order as the dipole moments of the starting materials, viz., $Me>H>I>Br>Cl>NO_2$. The results are in general agreement with a prototropic change initiated by co-ordination of the acid with the carbonyl group. H. A. P.

Products of the oxidation of benzophenone-oxime. K. von Auwers and H. Wunderling (Ber., 1933, **66**, [*B*], 538—545).—Oxidation of $CPh_2{:}N{\cdot}OH$ (I) by $K_3Fe(CN)_6$ at low temp. occurs without evolution of gas and with production of the unstable blue *compound* (II) (?) $CPh_2{:}N(\cdot O)\cdots$ or $CPh_2{:}N{\cdot}O\cdots$ which, when dil., may be preserved for a few hr. in hydrocarbons or Et_2O. In $C_6H_4Me_2$ at 70—80° it yields $COPh_2$ and N_2. Dil. HCl or, more slowly, dil. H_2SO_4 causes decomp. into $COPh_2$, $CPh_2{:}NH$, and HNO_2. At room temp., the production of (II) is accompanied by evolution of N_2 and formation of the stable, yellow *substance* (III), $CPh_2{:}N(:O){\cdot}N{:}CPh_2$, m.p. 157—157·5° (decomp.), obtained also, in poor yield, by the action of HCl on (II). With NH_2OH in alkaline solution (III) affords (I). Heated above its m.p., (III) affords N_2 and $COPh_2$ and diphenylketazine (IV) in approx. equal proportions. Since (IV) is not produced by the action of PCl_5 on (III), the constitution is assigned to it with reserve. Benzaldoxime and $K_3Fe(CN)_6$ afford the so-called benzaldoxime peroxide $CHPh.N(:O){\cdot}O{\cdot}N{:}CHPh$. H. W.

Relative reactivities of organo-lithium and -magnesium compounds. H. Gilman and R. H. Kirby (J. Amer. Chem. Soc., 1933, **55**, 1265—1270).—LiBu reacts more rapidly with various compounds than LiPh; both react more rapidly than MgBuBr or MgPhBr. LiPh and $CPh_2{:}NPh$ in Et_2O give 71% of $CPh_3{\cdot}NHPh$; LiMe and p-$NMe_2{\cdot}C_6H_4{\cdot}CN$ (which does not react with MgPhBr) in Et_2O afford 45% of p-$NMe_2{\cdot}C_6H_4{\cdot}COMe$; LiPh similarly gives 56% of p-$NMe_2{\cdot}C_6H_4{\cdot}COPh$. p-$OMe{\cdot}C_6H_4{\cdot}CN$ is similarly converted into p-$OMe{\cdot}C_6H_4{\cdot}COMe$ (75% yield) and p-$OMe{\cdot}C_6H_4{\cdot}COPh$ (85% yield). The differences in behaviour of LiR and MgRX are discussed. H. B.

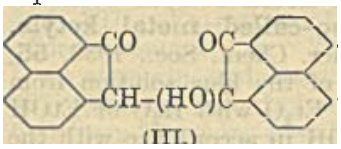
Reaction of aromatic ketones with sodium. I. Structure of the so-called metal ketyls. W. E. Bachmann (J. Amer. Chem. Soc., 1933, **55**, 1179—1188).—Hydrolysis of the blue solution from $COPh_2$ and 2% Na–Hg in Et_2O with H_2O or EtOH gives $COPh_2$ and $CHPh_2{\cdot}OH$ in accordance with the results of Schlenk *et al.* (A., 1913, i, 1205; 1914, i, 396); hydrolysis with 10% AcOH affords benzpinacol (I) in approx. 90% yield. (I) is undoubtedly formed during hydrolysis with H_2O or EtOH, but is converted by the liberated alkali (cf. this vol., 276, 391) into $COPh_2$ and $CHPh_2{\cdot}OH$. 9 : 10-Dihydroxy-9 : 10-dihydrophenanthrene, which is unaffected by alkali, is obtained in 100% yield by hydrolysis of the product from 2 : 2′-dibenzoyldiphenyl, 2% Na–Hg, and Et_2O. These results indicate that Na ketyls are not unimol. free radicals but are Na pinacolates or mixtures of $CR_2{\cdot}ONa$ and $(\cdot CR_2{\cdot}ONa)_2$ (II) in which the equilibrium is almost entirely in favour of (II). (I) is produced (as above) from $COPh_2$ and Li, K, Li–Hg, K–Hg, Rb–Hg, Cs–Hg, Ca–Hg, Mg–Hg, Mg+MgI_2, and Be+BeI_2. The corresponding pinacols are similarly obtained from Na–Hg and fluorenone and 4-phenyl- and 4 : 4′-diphenyl-benzophenones. H. B.

Preparation of ketones by carbonation of organolithium compounds. H. Gilman and P. R. van Ess (J. Amer. Chem. Soc., 1933, **55**, 1258—1261).—Carbonation of LiR (R=Bu, Ph, and *p*-tolyl) under ordinary conditions usually gives high yields of COR_2 and little RCO_2H; much higher yields of RCO_2H are obtained when the "spray method" (A., 1931, 1405) is used. A possible mechanism is discussed. LiPh and LiOBz in Et_2O give 70% of $COPh_2$; similarly, LiPh and $PrCO_2Li$ afford 62% of COPhPr, whilst LiBu and $PrCO_2Li$ in C_6H_6 give 10% of COPrBu. $CPh_3{\cdot}OH$ is obtained in 42% yield from LiPh and BzCl, whilst LiPh and BzOH afford 37% of $COPh_2$ and 14% of $CPh_3{\cdot}OH$. It is recommended that organolithium compounds be prepared in an atm. of H_2 or N_2. H. B.

Oxidation products of 5-acetoacenaphthene. K. Dziewoński and S. Piasecki (Bull. Acad. Polonaise, 1932, **A**, 287—292).—Oxidation of 5-acenaphthyl Me ketone with $Na_2Cr_2O_7$ in AcOH gives *5-acetoacenaphthenequinone*, m.p. 181—182° [*trioxime*, m.p. 242° (decomp.); *trisphenylhydrazone*, m.p. 222—224°], and *4-acetonaphthalic anhydride*, m.p. 191—192° (*dioxime*, m.p. 275—278°; *bisphenylhydrazone*, m.p. 241—242°; *Me*$_2$ *4-acetonaphthalate*, m.p. 112—114°; *4-acetonaphthalimide*, m.p. 270—272°). The former gives with 3-hydroxythionaphthen in alkaline EtOH solution the red vat dye, *2-thionaphthen-1-(5-acetoacenaphthene)-indigo*, m.p. 260—261°. H. A. P.

Acenaphthenone. III. Reactivity of its CH_2 group. A. C. Sircar and M. D. R. Gopalan (J. Indian Chem. Soc., 1932, **9**, 639—648; cf. A., 1932,

1041).—Acenaphthenone (I) is oxidised by nitrosophenol, -dimethylaniline, and -thymol in AcOH–NaOAc at 60—80° to bisacenaphthylidenediketone (II), but in EtOH with 10% KOH, piperidine, or $NPhMe_2$ at room temp. a *compound*, $(C_{12}H_8O)_x$, m.p. 289—290°, is also formed. (I) and acenaphthenequinone in AcOH–NaOAc at 60—70° give a 50% yield of 7-*hydroxy*-8 : 8′-*diketo*-7 : 7′-*diacenaphthenyl* (III), m.p. 168—169°, dehydrated by Ac_2O–NaOAc to (II).



(III.)

Phenanthraquinone gives a poor yield of a similar *derivative*, decomp. 185—187°, but with benzil no aldol product could be isolated. *Anisylidene-*, m.p. 126·5—127°, m- and p-*nitrobenzylidene-*, m.p. 177—178° and 239—240°, respectively, *cinnamylidene-*, m.p. 214—215° after sintering at 196°, *salicylidene-*, m.p. 186—187°, m-*hydroxybenzylidene-*, m.p. 191—192°, and p-*acetamidobenzylidene-acenaphthenone*, m.p. 255—256°, are prepared. (I) and amyl nitrite give acenaphthenequinonemonoxime.

R. S. C.

Synthesis of 2-propionyl- and 2 : 7-dipropionylfluorene. K. Dziewoński and J. Schweiger (Bull. Acad. Polonaise, 1932, A, 293—299).—Interaction of fluorene, EtCOCl, and $AlCl_3$ in CS_2 gives the 2-COEt and 2 : 7-$(COEt)_2$ derivatives, identified by Beckmann rearrangement of their oximes to 2-propionamido- and 2 : 7-dipropionamido-fluorenes and hydrolysis of these to the known amines. The following are described: 2-*fluorenyl Et ketone* (I), m.p. 120—121° (*oxime*, m.p. 185—186°; *phenylhydrazone*, m.p. 155—156°); 2 : 7-*dipropionylfluorene*, m.p. 216—217° (*dioxime*, m.p. 219—220°); 2-*propionamidofluorene*, m.p. 202—203°, and 2 : 7-*bispropionamidofluorene*, m.p. 286—287°. By oxidation of (I) with $Na_2Cr_2O_7$ and AcOH 2-*fluorenonyl Et ketone*, m.p. 169—170° (*bisphenylhydrazone*, m.p. 186—187°), and *fluorenone*-2-*carboxylic acid*, m.p. 340°, are formed. H. A. P.

Synthesis of 4 : 4′-diacenaphthylmethane and of 4 : 4′-diacenaphthyl ketone, and their oxidation reactions. K. Dziewoński, W. Kahl, W. Koczorowska, and A. Wulffsohn (Roczn. Chem., 1933, **13**, 154—165).—Acenaphthene (I) and methylal in $CHCl_3$ solution yield 4 : 4′-*diacenaphthylmethane*, m.p. 140—141° (*picrate*, m.p. 151°), together with a substance, $(C_{40}H_{29}O_2)_4$, m.p. 360°. (I) reacts with $COCl_2$ in PhMe solution in presence of $AlCl_3$ to yield 4 : 4′-*diacenaphthyl ketone* (II), m.p. 234—235°; (I) or (II) on oxidation with $Na_2Cr_2O_7$ gives *keto*-4 : 4′-*dinaphthalic anhydride*, $CO(C_{10}H_5\langle^{CO}_{CO}\rangle O)_2$, m.p. 348° (*di-imide*, m.p. 375°; *anilide*, m.p. 207—208°; *dianilide*, m.p. 354—356°; *dioxime*, m.p. 368—370°; *bisphenylhydrazone*, m.p. 385°; *trisphenylhydrazone*, m.p. 362°; *dinitro*-derivative, m.p. 230°), which on fusion with KOH yields 1 : 4 : 8-naphthalenetricarboxylic anhydride, m.p. 272—273° (*anilide*, m.p. 308°; *phenylhydrazone*, m.p. 318—320°; *oxime*, m.p. 302—303°; *imide*, m.p. 338°; *Et* ester, m.p. 182—183°).

R. T.

Heteropolarity. XX. Colour of arylated *cyclo*pentadienones. W. Dilthey and W. Schommer (J. pr. Chem., 1933, [ii], **136**, 293—298).—2 : 3 : 5-*Triphenyl*-$\Delta^{2:4}$-*cyclopentadienone* (I), colourless, m.p. 183—184° (becoming red; decomp.) [p-*dimethylaminoanil* (II), blue, m.p. 172—173°], prepared from 2 : 3 : 5-triphenyl-$\Delta^{2:4}$-*cyclo*pentadiene (III) by Ziegler and Schnell's method (A., 1926, 57) is bimol. (f.p. in C_6H_6). When a solution of (I) in C_6H_6 is kept, the violet-red unimol. form (IV) of (I) is produced (slowly in the cold; rapidly in the hot) to some extent. The deep red solution obtained when (I) is heated with $PhNO_2$ to 160° consists almost entirely of (IV) (f.-p. method); association of (IV) occurs fairly rapidly in the cold solution. (I) may result from (IV) by a "dien" synthesis; (IV) (and related *cyclo*pentadienones) react readily with maleic anhydride to give colourless products. (II) and (III) are unimol. in C_6H_6 (f.p.). H. B.

Antiseptics related to indan-1 : 3-dione. F. A. Robinson, A. J. Suthers, and T. K. Walker (Biochem. J., 1932, **26**, 1890—1901).—The following *derivatives* of 4-hydroxyindan-1 : 3-dione (I), all of which possess antiseptic power, have been prepared by condensing mono-*n*-alkylmalonyl chlorides (II) with *p*-*n*-alkyl derivatives of phenol (III) and with 3-*n*-amyl-*p*-cresol in presence of $AlCl_3$: dialkyl: -7-*ethyl*-, m.p. 110°, and -7-n-*propyl*-, m.p. 122—123°, -2-n-*butyl*-; -2 : 7-*di*-n-*butyl*-, m.p. 120°; -2-n-*butyl*-7-n-*amyl*-, m.p. 110°, -7-n-*hexyl*-, m.p. 118—119°, -7-n-*octyl*-, m.p. 115°; -2-*ethyl*-7-n-*butyl*-, m.p. 129°, and -7-n-*hexyl*-, m.p. 120°; -2 : 7-*di*-n-*amyl*-, m.p. 114—115°; -7-*ethyl*-2-n-*hexyl*-, m.p. 110°; -2-n-*amyl*-7-n-*hexyl*-, m.p. 100°; -7-n-*amyl*-2-n-*hexyl*-, m.p. 98—99°; -2 : 7-*di*-n-*hexyl*-, m.p. 95—96°; trialkyl: -7-*methyl*-2-n-*propyl*-5-n-*amyl*-, m.p. 149°, -2-n-*butyl*-5-n-*amyl*-, m.p. 119—120°, -5-n-*amyl*-2-n-*hexyl*-, m.p. 143—144°, and -2 : 5-*di*-n-*amyl*-, m.p. 90—92°. When a given (II) is condensed with the lower members of the homologous series of (III) the antiseptic powers of the members of the resulting homologous series of (I) increase progressively as the series is ascended. It is confirmed that the condensation of several consecutive lower members of the homologous series of (II) with an appropriate phenol results in the formation of an homologous series of (I), the members of which exhibit antiseptic power which increases progressively to a max. val. as the series is ascended. The antiseptic activity of these compounds is highly selective in character; it is depressed considerably by culture media which are slightly alkaline and suppressed entirely by ox-serum. S. S. Z.

Reaction between unsaturated ketones and organic magnesium compounds. Secondary products. E. P. Kohler and W. D. Peterson (J. Amer. Chem. Soc., 1933, **55**, 1073—1082).—$CHPh_2$·CH:CPh·OMgBr (I) [from $CHPh_2$·CHBr·COPh and MgPhBr in N_2 (cf. A., 1932, 616)] and Ph styryl ketone give $CHPh_2$·CHBz·CHPh·CH:CPh·OMgBr (II), which is hydrolysed to *αγ-dibenzoyl-βδδ-triphenylbutane* (III), m.p. 180°, the *monoxime* (α-Bz derivative), m.p. 165°, of which is converted by PCl_5 in Et_2O into the *anilide*, m.p. 198°, of *γ-benzoyl-βδδ-triphenylvaleric acid*, m.p. 156° (IV). (IV) and Br in $CHCl_3$ give $CHPh_2Br$ and *γ-bromo-γ-benzoyl-β-phenylbutyric acid*, m.p. 166°, readily hydrolysed to *γ-hydroxy-γ-*

benzoyl-β-phenylbutyric acid, m.p. 146° (*lactone*, m.p. 120°). (III) and Br similarly afford γ-bromo-αγ-dibenzoyl-β-phenylpropane. (II) does not react with Ph styryl ketone or PhCHO, but with BzCl gives (probably) *ααγ-tribenzoyl-ββδ-triphenylbutane*, m.p. 180°. Styryl Me ketone and (I) yield a little *γ-benzoyl-α-acetyl-ββδ-triphenylbutane*, m.p. 153°. *β-Benzoyl-αγγ-triphenylpropyl alcohol*, m.p. 133°, from (I) and PhCHO, is oxidised (CrO_3, AcOH) to $CHBz_2$·$CHPh_2$, whilst *γ-hydroxy-ββδ-dibenzoyl-ααεε-tetraphenylpentane*, m.p. 202°, from (I) and HCO_2Et, is similarly oxidised to *di-(α-benzoyl-ββ-diphenylethyl) ketone*, m.p. 232°, which with 10% EtOH–KOH gives $CHPh_2$·CH_2·COPh. (I) behaves like the enolate of a β-CO ester.

$CHPh_2$·CPh:CPh·OMgBr (from $CHPh_2$·CBrPh·COPh or CHPh:CPh·COPh and MgPhBr) does not react with Ph styryl ketone, PhCHO, or HCO_2Et; with BzCl, *αβγγ-tetraphenyl-Δ$^{\alpha}$-propenyl benzoate*, m.p. 110°, and a *stereoisomeride*, m.p. 131°, result. Both benzoates are hydrolysed (MeOH–KOH) to $CHPh_2$·CHPh·COPh. *p-Bromophenyl benzyl ketone*, m.p. 115° (from PhBr, CH_2Ph·COCl, and $AlCl_3$), PhCHO, and EtOH–HCl give *p-bromophenyl β-chloro-αβ-diphenylethyl ketone*, m.p. 171°, converted by MeOH–KOAc into *p-bromophenyl α-phenylstyryl ketone*, m.p. 105°. Successive treatment of this with MgPhBr and BzCl affords *βγγ-triphenyl-α-p-bromophenyl-Δ$^{\alpha}$-propenyl benzoate*, m.p. 144°, hydrolysed (MeOH–KOH) to *p-bromophenyl αββ-triphenylethyl ketone*, m.p. 200°. Successive treatment of deoxybenzoin with MgPhBr and *p*-C_6H_4Br·COCl gives *αβγγ-tetraphenyl-Δ$^{\alpha}$-propenyl p-bromobenzoate*, m.p. 183°, hydrolysed to $CHPh_2$·CHPh·COPh.

H. B.

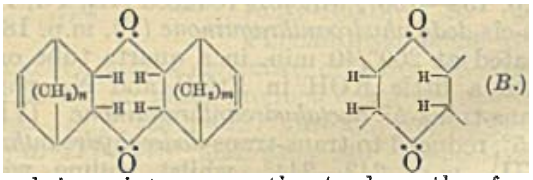
Action of hydroxylamine on β-naphthaquinone derivatives. H. Goldstein, P. Koetschet, and O. Duboux (Helv. Chim. Acta, 1933, **16**, 241—245).—Oximation of 4-amino- and 4-anilino-1 : 2-naphthaquinones gives the 1-oxime both in acid and alkaline solution; they behave, therefore, as 2-hydroxy-1 : 4-quinoneimines. In acid media, however, 4-acetamido-1 : 2-naphthaquinone behaves as a true 1 : 2-quinone and gives 2-nitroso-4-acetamido-α-naphthol; in alkaline solution indefinite products free from the 2-NO-compound are formed.

H. A. P.

Polymerisation of cyclic hydrocarbons. IV. Stereoisomeric forms of perhydrogenated naphtha- and anthra-quinones. K. Alder and G. Stein (Annalen, 1933, **501**, 247—294).—Δ$^{2:6}$-Tetrahydro-1 : 4-naphthaquinone (A., 1929, 1303) is reduced (Zn, dil. AcOH) to Δ^{6}-*hexahydro*-1 : 4-*naphthaquinone*, m.p. 108° (*dioxime*, m.p. 238—239°), which is further reduced (H_2, Pd, EtOH) to cis-1 : 4-*diketodecahydronaphthalene* (I), m.p. 49—50° (*dioxime*, m.p. 213—214°). (I) is converted by boiling with Ac_2O into the trans-*form* (II), m.p. 122° (*dioxime*, m.p. 283°), is oxidised (HNO_3–AcOH) to succinic and adipic acids [(II) is similarly oxidised to *trans*-hexahydrophthalic acid], and is converted [as is (II)] by Br in $CHCl_3$ into 1 : 4-dihydroxy-5 : 6 : 7 : 8-tetrahydronaphthalene. *cis*-5 : 8-Diketo-1 : 4-*endo*methylenedecahydronaphthalene (A., 1928, 1018) is oxidised (HNO_3–AcOH) to *cyclo*pentane-1 : 3-dicarboxylic acid, thus proving that 1 : 4-addition occurs with *cyclo*pentadiene and *p*-benzoquinone (III). 5 : 8-*endo*Ethylene-Δ$^{2:6}$-tetrahydro-1 : 4-naphthaquinone (A., 1929, 1303) is reduced (as above) to the *hexahydro*-derivative, m.p. 57—58°, and thence to 1 : 4-*diketo*-5 : 8-endo*ethylenedecahydronaphthalene*, m.p. 65°, which is oxidised to *cis*-hexahydroterephthalic acid. In the above oxidations (of *cis*-derivatives) none of the expected *cis*-hexahydrophthalic acid derivative is produced. Butadiene (2 mols.) and (III) (1 mol.) in C_6H_6 at 100° give cis-cis-Δ$^{2:6}$-*octahydroanthraquinone* (IV), m.p. 154—155°, which is reduced (H_2, Pd, EtOH) to cis-cis-*dodecahydroanthraquinone* (V), m.p. 181°. (IV) heated at 200°/40 min. in a quartz tube or treated with a little KOH in EtOH and N_2, passes into trans-trans-Δ$^{\sim:6}$-*octahydroanthraquinone* (VI), m.p. 245°, reduced to trans-trans-*dodecahydroanthraquinone* (VII), m.p. 243—244°, whilst boiling with Ac_2O converts (IV) into cis-trans-Δ$^{2:6}$-*octahydroanthraquinone* (VIII), m.p. 186°, which is reduced to cis-trans-*dodecahydroanthraquinone* (IX), m.p. 137°, and a smaller amount of (VII). (V) and (IX) are converted by EtOH–KOH in N_2 into (VII). (IV), (VI), and (VIII) are all oxidised by air in EtOH–KOH to anthraquinone, whilst (V), (VII), and (IX) are dehydrogenated by Br in $CHCl_3$ to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthraquinone and oxidised (HNO_3–AcOH) to adipic and *cis*-, *trans*-, and *trans*-hexahydrophthalic acid, respectively. *cis-cis*-2 : 6- and -2 : 7-Dimethyl-Δ$^{2:6}$-octahydroanthraquinones are similarly converted into the *cis-trans*-forms, m.p. 163° and 125°, respectively, and thence (by alkali) into the *trans-trans*-modifications (cf. A., 1929, 1303). 1 : 4 : 5 : 8-Di*endo*ethylene-Δ$^{2:6}$-octahydroanthraquinone (X) (*loc. cit.*) is unaffected by very dil. alkali or Ac_2O; with 5% EtOH–KOH in N_2, an *isomeride* (XI), m.p. 268° (decomp.), results. (XI) is reduced to a 1 : 4 : 5 : 8-*di*endo*ethylenedodecahydroanthraquinone* (XII), m.p. 292°, also obtained by fusion of the *tetrahydro*-derivative (XIII), m.p. 245°, re-solidifying at about 255° with m.p. 280—290°, of (X). (XII) and (XIII) are dehydrogenated by Br–$CHCl_3$ to 9 : 10-dihydroxy-1 : 4 : 5 : 8-di*endo*ethylene-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene, m.p. 334° (*diacetate*, m.p. 293°), and oxidised (HNO_3–AcOH) to 1 : 4 : 5 : 8-*di*endo*ethylene*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthraquinone*, m.p. 342°. Δ$^{2:6}$-Tetrahydro-1 : 4-naphthaquinone and Δ$^{1:3}$-*cyclo*hexadiene give 1 : 4-endo*ethylene*-Δ$^{2:6}$-*octahydroanthraquinone* (XIV), m.p. 136°, reduced to cis-cis-1 : 4-endo*ethylenedodecahydroanthraquinone* (XV), m.p. 157°. (XIV) is unaffected by boiling with Ac_2O, but (XV) is similarly converted into the cis-trans-*isomeride* (XVI), m.p. 184°, which is unaffected by EtOH–KOH. (XV) is oxidised (HNO_3–AcOH) to adipic, *cis*-hexahydroterephthalic (XVII), and 3 : 6-*endo*ethylene-Δ^{1}-tetrahydrophthalic acid, whilst (XVI) similarly gives (XVII) and *trans*-hexahydrophthalic acid. 1 : 4 : 5 : 8-Di*endo*methylene-Δ$^{2:6}$-octahydroanthraquinone (XVIII) (Albrecht, A., 1906, i, 674) is also converted by 10% EtOH–KOH in N_2 into an *isomeride* (XIX), m.p. 187° [*adduct*, m.p. 214° (decomp.), with 2 mols. of PhN_3], the *tetrahydro*-derivative, m.p. 225°, of which is obtained by catalytic reduction of (XIX) or by rearrangement of the tetrahydro-derivative of (XVIII), and is

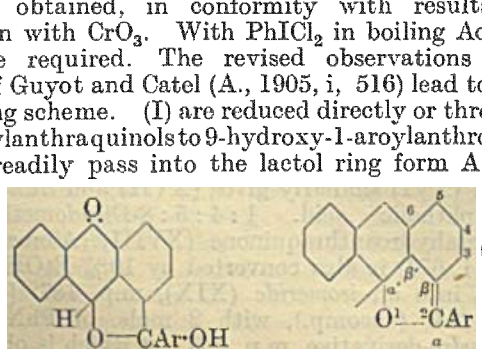
dehydrogenated (Br–$CHCl_3$) to 9 : 10-dihydroxy-1 : 4 : 5 : 8-di*endo*methylene-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene (A., 1929, 1303). 1 : 4-endo-*Methylene*-5 : 8-endo*ethylene*-$\Delta^{2:6}$-*octahydroanthraquinone* (XX), m.p. 163°, from 5 : 8-*endo*methylene-$\Delta^{2:6}$-tetrahydro-1 : 4-naphthaquinone and $\Delta^{1:3}$-*cyclo*hexadiene, is also rearranged by EtOH–KOH to an *isomeride* (XXI), m.p. 225° (decomp.).

Compounds such as (X), (XVIII), and (XX), which are isomerised only by EtOH–KOH, are considered to be *cis-cis*-derivatives of type (*A*) having

(*A*.)  (*B*.)

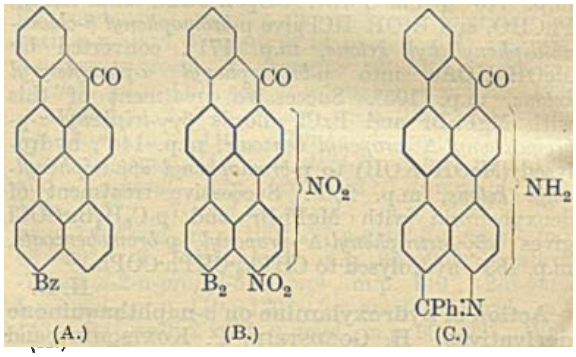
the lateral rings *cis* to one another (and are, therefore, designated *an-cis*). (XI), (XIX), and (XXI) are also *cis-cis*-derivatives [type (*B*)], but the lateral rings are *trans* (designated *an-trans*). The $\Delta^{2:6}$-octahydroanthraquinones isomerised by Ac_2O are those containing no *endo*-groups [*i.e.*, (*A*), where $m=n-0$); isomerisation occurs with the dodecahydroanthraquinones when n or $m=0$. In both cases, the *cis*-H atoms rearrange to *trans*; in the latter case, however, *cis–trans* isomerism involves only the two H atoms attached to the ring containing no *endo*-group. H. B.

Supposed aryloxy*peri*hydrofuranoanthroxyls as derivatives of benzoylene-ββ′-benzofuran. R. Scholl and J. Donat (Ber., 1933, **66**, [*B*], 514—522).—New analyses of "aryloxy*peri*hydrofuranoanthroxyls," $C_{15}H_8O_3Ar$ (Schaarschmidt, A., 1915, i, 696; 1916, i, 408; Scholl and others, A., 1923, i, 807; 1931, 845), shows them to have the formula $C_{15}H_7O_2Ar$; in freezing $PhNO_2$ and boiling C_6H_6 they are unimol. and hence the necessity for regarding them as anthroxyls with O^I is excluded. Under the conditions previously outlined (*loc. cit.*) the absorption of 3Br per mol. is confirmed, but in more dil. solution 4Br may be absorbed, whilst at higher temp. only 2Br reacts. At room temp. several reactions appear to occur simultaneously. Titration with $KMnO_4$ in heterogeneous system readily leads to apparent addition of 3O, whereas in homogeneous system (AcOH and 20% H_2SO_4) only 2O are required and aroylanthraquinones (I) are almost quantitatively obtained, in conformity with results of titration with CrO_3. With $PhICl_2$ in boiling AcOH, 2Cl are required. The revised observations and those of Guyot and Catel (A., 1905, i, 516) lead to the following scheme. (I) are reduced directly or through the aroylanthraquinols to 9-hydroxy-1-aroylanthrones, which readily pass into the lactol ring form A and

(A.)  (B.)

thence under the influence of conc. acid into 6 : 7-benzoylene-2-aryl-ββ′-benzofurans (B). The new formulation embraces all compounds described hitherto as aryloxy*peri*hydrofuranoanthroxyls and their sulphonic acids known only in solution. The chemistry of free org. radicals with O^I is in the position reached by the work of Pummerer and Goldschmidt. The following revised data are recorded: 6 : 7-benzoylene-2-phenyl-ββ′-benzofuran (B; Ar=Ph), m.p. 200° [prepared from 9-hydroxy-1-benzoylanthrone and conc. H_2SO_4 or AcOH–HCl or from 1-*benzoylanthraquinol diacetate*, m.p. 256° (decomp.), and H_2SO_4 in MeOH–H_2O]; 6 : 7-benzoylene-2-*m*-xylyl-ββ′-benzofuran, m.p. 178° (prepared from hydroxyxyloylanthrone and conc. H_2SO_4 or from 1-*m*-*xyloylanthraquinol diacetate*, m.p. 185—187°); 6 : 7-benzoylene-2-*p*-chlorophenyl-ββ′-benzofuran, m.p. 150° (prepared from 9-hydroxy-1-*p*-chlorobenzoylanthrone). H. W.

Perylene and its derivatives. XXXIX. A. Pongratz and A. Zinke [with E. Gesell and G. Hauswirth] (Monatsh., 1933, **62**, 172—177).—3 : 9-Dibenzoylperylene is converted into 9-*benzoyl*-3(CO)-4-*benzoyleneperylene* (I) (A) by treatment with



MnO_2 in conc. H_2SO_4 at −8°, with a little $FeSO_4$ and HNO_3 (*d* 1·39) in H_2SO_4 at room temp. or by $PhNO_2$ and conc. H_2SO_4 at room temp. It gives a blue vat with $Na_2S_2O_4$ which has only slight affinity for cotton. It is readily transformed into *iso*violanthrone by $AlCl_3$. When treated with HNO_3 (*d* 1·39) in boiling AcOH (I) yields a $(NO_2)_2$-compound (B) reduced by $Na_2S_2O_4$ and NaOH to the *substance* C. H. W.

Glabratic acid. G. Koller and G. Pfeiffer (Monatsh., 1933, **62**, 169—171).—Extraction of *Parmelia glabra* with Et_2O followed by dissolution of the extracted acid in $COMe_2$ and fractional pptn. with H_2O affords Zopf's glabratic acid (I), $C_{16}H_{14}O_7$, decomp. 179° (vac.), which, however, gives a violet-red colour with $FeCl_3$. (I) is transformed by Ac_2O and C_5H_5N into an Ac_3 derivative, decomp. 197° (vac.) (Me ester, m.p. 156—157°), identical with the corresponding compounds of lecanoric acid (II). "Glabratic acid" therefore is probably (II) contaminated with a material which gives a blue colour with $FeCl_3$. H. W.

Constitution of pinastric acid. G. Koller and G. Pfeiffer (Monatsh., 1933, **62**, 160—168).—Extraction of *Cetraria pinastri* or *juniperina* with Et_2O affords usnic acid and pinastric acid (I), $C_{20}H_{16}O_6$, m.p. 203—204° (vac., slight decomp.), which, contrary to Hesse, has 1 OH (Zerevitinov) and 2 OMe

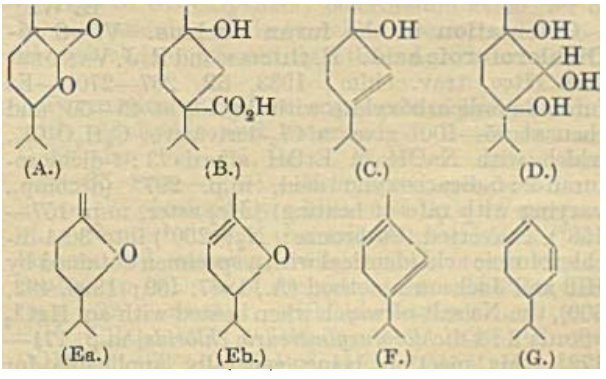
groups. (I) is transformed by CH_2N_2 into the *Me ether* (II), m.p. 153° (analogously, vulpic acid affords a *Me ether*, m.p. 143—144°), oxidised by $KMnO_4$ in alkaline solution to BzOH and *p*-OMe·C_6H_4·CO_2H, also obtained by oxidation of (I). Treatment of (I) with conc. aq. $Ba(OH)_2$ leads to $H_2C_2O_4$, $CH_2Ph·CO_2H$, and *p*-OMe·C_6H_4·CH_2·CO_2H, from which a small amount of *p*-OH·C_6H_4·CH_2·CO_2H is derived. The structure *p*-OMe·C_6H_4·C(CO_2Me):C<O——C / C(OH):CPh> or *p*-OMe·C_6H_4·C<CO O / C(OH)>C:CPh·CO_2Me is assigned to (I). H. W.

Pigments of the lobster [*Astacus gammarus*, L.] and their parent substance, astacin. R. Kuhn and E. Lederer (Ber., 1933, **66**, [*B*], 488—495).—The shell of the Norwegian lobster contains a brownish-black chromoprotein from which a red epiphasic astacin ester is obtained by treatment with HCl and $COMe_2$, from which *astacin* (I), (?) $C_{27}H_{32}O_3$, m.p. 240—243° when slowly heated in vac. or m.p. 265—267° on object glass, is derived by treatment with NaOH. The hypodermis contains a red lipochrome, insol. in H_2O, and giving when extracted with $COMe_2$ a red, epiphasic astacin ester from which (I) is obtained. The green chromoprotein of the eggs is sol. in H_2O and when treated with $COMe_2$ affords a red, hypophasic ovo-ester hydrolysed to (I). Very little carotene is present. (I) absorbs 10·3 H_2, and hence is mainly a highly unsaturated, aliphatic acid. When pure, it is very stable towards atm. O_2. The absorption spectrum shows a single, apparently homogeneous band with a max. at 500 mμ. H. W.

α-Amyrin. II. H. Dieterle, A. Salomon, and W. Rosenfelder (Arch. Pharm., 1933, **271**, 177—189; cf. A., 1931, 624).—α-Amyrin (I) with O_3 in AcOH gives *amyranone* (II), $C_{27}H_{42}O$, m.p. 94—96°, $[\alpha]_D^{15}$ +75·14° (all rotations in $CHCl_3$) (*dinitrophenylhydrazone*, m.p. 250°), and in $CHCl_3$ a dibasic keto-acid, *amyranonic acid*, m.p. 248—249°, $[\alpha]_D^{15}$ +38·4° (*anhydride*, m.p. 212—213°, $[\alpha]_D$ +17·82°; *phenylhydrazone*, m.p. 143°; *Me*$_2$ ester, m.p. 190—191°), also obtained from (I) by CrO_3–AcOH. (II) with $K_3Fe(CN)_6$ yields a *perhydrophenanthrenedicarboxylic acid*, $C_{16}H_{24}O_4$, m.p. 124°, +20·11° (gives a phthalein with resorcinol), giving phenanthrene when distilled with Zn dust. (II) with HI (*d* 1·7) and red P at 200—220° gives *amyranene* (III), $C_{27}H_{44}$, m.p. 282—283°. α-Amyrin benzoate and Se give (III) and $C_{15}H_{20}$; the latter with active Zn dust affords 2-methylanthracene (IV). α-Amyrone (*dinitrophenylhydrazone*, m.p. 217·5°) and MgMeI in Et_2O give the *tert.*-alcohol, *amyranol*, $C_{31}H_{51}$·OH, m.p. 234—235° (*Ac* derivative, m.p. 217—218°), oxidised by hot CrO_3–AcOH to a 2-*methylperhydroanthracenedicarboxylic acid*, m.p. 130—131° after decomp. from 128°, $[\alpha]_D^{15}$ +15·8° (*Me*$_2$ ester, m.p. 197°), giving (IV) with Zn dust. (I) is thus probably a derivative of benzanthrene or 1 : 2-benzanthracene, containing a Pr^β group, a *sec.*-OH group in a fifth ring, and an ethylenic linking probably in a sixth ring. The Me group of (IV) is considered to be formed by a secondary reaction, since it does not give rise to a CO_2H group on oxidation of (I). R. S. C.

Menthoglycol and its dehydration. J. Dœuvre (Bull. Soc. chim., 1933, [ii], **53**, 27—33).—Citronellal and 5% H_2SO_4 give 12% of *iso*pulegol (I) and mainly *p*-menthane-3 : 8-diol (menthoglycol) (II). (I) is not hydrated to (II) under these conditions, and hence is not an intermediate product in the reaction (cf. A., 1908, i, 429). However, (II), particularly with more conc. acid, gives (I), It is considered that cyclisation is probably preceded by hydration of the CHO group. (II) with PBr_3 in $CHCl_3$ gives mainly a mixture of $\Delta^{2:4(8)}$- and $\Delta^{3:8}$-*p*-menthadienes, oxidised incompletely by O_3 to CH_2O (2%), HCO_2H (62%), and $COMe_2$ (18%), and by $KMnO_4$ in AcOH to $COMe_2$ (28%). With I (II) gives a mixture of menthadienes and (I) [p-*xenylcarbamate*, m.p. 172° (block)] (giving with O_3 only 2% of $COMe_2$); with Ac_2O mainly *iso*pulegol acetate (giving < 1% of $COMe_2$ with O_3) is formed. R. S. C.

Autoxidation of αβ-unsaturated ketones. VI. Course and products of the autoxidation of piperitone. W. Treibs (Ber., 1933, **66**, [*B*], 610—620; cf. A., 1931, 94).—Piperitone (I) is slowly transformed by 30% H_2O_2 and MeOH at 15—20° into *piperitone peroxide*, $C_{10}H_{16}O_2$. (1), 30% H_2O_2, and 30% KOH–MeOH afford *piperitone oxide* (II, A), b.p. 108—109°/15 mm., 225—228°/atm. pressure, +22° (*l*=1) [*semicarbazone*, m.p. 213° (decomp.), converted by dil. H_2SO_4 into diosphenol (III)]. Addition of (II) in MeOH to boiling KOH–MeOH leads to the OH-acid (B, *loc. cit.*), whereas treatment of (II) in cold MeOH with KOH–MeOH or, preferably, NaOMe–MeOH affords the *Me* ester of B, m.p. 79—80°, $[\alpha]_D$ −5·8° in MeOH, demethylated by HCl–AcOH to the lactone. Addition of 30% KOH–MeOH to a boiling mixture of (II) and MeOH affords a fraction, b.p.



105—110°/15 mm., demethylated to carvacrol and *diosphenol Me ether*, b.p. 115—117°/15 mm., demethylated to (III), m.p. 84°. Alternate addition of MeOH–KOH and H_2O_2 to a well-cooled mixture of (I) and MeOH gives the tert.-*alcohol* (C; IV), b.p. 79—81°/15 mm., also obtained from (II), which is oxidised by $KMnO_4$ to the trihydric *alcohol* (D), b.p. 160—163°/15 mm., converted by boiling dil. H_2SO_4 into the unsaturated *ketone*, $C_9H_{14}O$ (Ea or b), b.p. 192—193° (*semicarbazone*, m.p. 177—178°). Repeated distillation of (IV) under atm. pressure yields the stable *hydrocarbon* C_9H_{14} (F), b.p. 147—149°, unchanged by Na and EtOH, but hydrogenated (Skita) to pulegane, b.p. 141—142°, also obtained directly from (IV). Dehydration of (IV) by dil. acid or Ac_2O

gives an unstable hydrocarbon (G), b.p. 165—167°, probably identical with that obtained by Wallach from *iso*propyl*cyclo*pentanone and hydrogenated (Skita) to a tetrahydride, b.p. 145—147°, probably hexahydrocumene. Boiling 10% H_2SO_4 transforms (II) into (III) and a ketone (semicarbazone, m.p. 196°). Similar treatment of carvone oxide (V) yields a *phenol*, $C_{20}H_{24}O_2$, m.p. (indef.) 174—178°, also obtained by treatment of the product from (V) and MeOH with hot HCl–AcOH.

Analysis and determination of mol. wt. lead to the formula $C_{20}H_{26}O_5$ for the resin (VI) obtained by autoxidation of (I). When heated at 150°/vac. it loses H_2O and gives the *compound* $C_{20}H_{24}O_4$, thus establishing the presence of a *tert.*-OH. When treated with Me_2SO_4 it loses H_2O and forms the *substance* $C_{22}H_{28}O_4$, showing in all 3OH. The dark brown solution of (VI) is almost completely decolorised by Zn dust, and the absorption of 1O restores the colour to the solution.

H. W.

***tert.*-Propylbornyl alcohol and its transformations.** S. S. Nametkin and A. I. Schavrigin (Ber., 1933, **66**, [*B*], 511—514).—*tert.*-Allylbornyl alcohol, from *d*-camphor and Mg allyl bromide, is reduced (H_2 and Pt black) to tert.-*propylbornyl alcohol*, $C_9H_{16}Pr{\cdot}OH$, b.p. 133°/24 mm., m.p. 34—36°, transformed by $NaHSO_4$ at 120—125° into a *hydrocarbon* (I), $C_{13}H_{22}$, b.p. 100—101°/22 mm., which is oxidised to camphoric acid. (I) is converted by AcOH and H_2SO_4 into an acetate, hydrolysed to 4-*propyliso*borneol (II), m.p. 57—58°. Oxidation of (II) with nitric acid (*d* 1·4) affords 4-*propylcamphor*, m.p. 62—63° (*semicarbazone*, m.p. 203—204°), oxidised by $KMnO_4$ to 1 : 2 : 2-trimethyl-3-propyl*cyclo*pentane-1 : 3-dicarboxylic acid, m.p. 189·5—190° (anhydride, m.p. 94—95°).

H. W.

Orientation in the furan nucleus. V. 3 : 4-Dichlorofuroic acid. H. Gilman and R. J. Vanderwal (Rec. trav. chim., 1933, **52**, 267—270).—Et furan-2 : 5-dicarboxylate with dry Cl_2 at 45—50° and then at 95—100° gives a Cl_5-derivative, $C_6H_9O_5Cl_5$, which with NaOH in EtOH affords 3 : 4-dichlorofuran-2 : 5-dicarboxylic acid, m.p. 297° (decomp., varying with rate of heating) (Me_2 ester, m.p. 157—158°), converted (Cu-bronze; N_2; 250°) into 3 : 4-dichlorofuroic acid identical with a specimen obtained by Hill and Jackson's method (A., 1887, 469; 1890, 482, 600), the Na salt of which when heated with aq. $HgCl_2$ affords 3 : 4-*dichlorofurylmercuric chloride*, m.p. 171—172°, this reaction being generally applicable for decarboxylating furan-α-carboxylic acids.

J. W. B.

Furan reactions. IV. Furoic acid from furfuraldehyde. C. D. Hurd, J. W. Garrett, and E. N. Osborne (J. Amer. Chem. Soc., 1933, **55**, 1082—1084).—An improved method (cf. Org. Synth., 1926, **6**, 44) of prep. of furoic acid (I) [$Mn^{\cdot\cdot}$ salt ($+3H_2O$), decomp. (anhyd.) about 290°] and furfuryl alcohol from furfuraldehyde (II) is given. Oxidation ($K_2Cr_2O_7$, H_2SO_4) of (II) affords a 75% yield of (I).

H. B.

Furan reactions. VI. [Attempted preparation of] *cyclo*propene. C. D. Hurd and F. D. Pilgrim (J. Amer. Chem. Soc., 1933, **55**, 1195—1197).—*cyclo*Propene is not obtained when Ba, Ca, and Na furoates are heated with or without soda-lime (cf. Freundler, A., 1897, i, 506); furan and a little CH:CMe are isolated. Epibromohydrin and Mg–Cu alloy give allyl alcohol. *ββ′-Dibromoisopropyl benzoate*, from *αγ*-dibromohydrin and BzCl, has b.p. 185°/16 mm.

H. B.

Furan polycarboxylic acids. T. Reichstein, A. Grussner, K. Schindler, and E. Hardmeier (Helv. Chim. Acta, 1933, **16**, 276—281).—Cyclisation of Et bis-αα′-dioxalosuccinate (I) (Sutter, A., 1932, 1234) with conc. H_2SO_4 at 50° gives *Et*$_4$ *furantetracarboxylate*, m.p. 34·5°, b.p. about 175°/0·2 mm. (free *acid* (II), m.p. 247° (decomp.); *K* H_3 salt; *Me*$_4$ ester, m.p. 107—108° (corr.), b.p. 175°/0·2 mm.]. (II) is also formed in addition to (III) (below) by action of hot HCl on (I). Successive decarboxylation of (II) at 270° gives *furan*-2 : 3 : 4-*tricarboxylic acid* (III), m.p. 107·5—108·5° (corr.) (*Et*$_3$ ester, m.p. 37°, b.p. about 140°/0·3 mm.), *furan*-3 : 4-*dicarboxylic acid* (IV), m.p. 217—218° (corr.) (*Me*$_2$ ester, m.p. 46°), and furan-2-carboxylic acid. The structure of (III) follows from the non-identity of (IV) with the remaining known furandicarboxylic acids and the final formation of furan-2-carboxylic acid. It is identical with Sutter's "2 : 3 : 5-tricarboxylic acid" (*loc. cit.*), whence it is concluded that (I) must be $CO_2Et{\cdot}CO{\cdot}CH(CO_2Et){\cdot}O{\cdot}C(CO_2Et){:}CH{\cdot}CO_2Et$, and that the ester from which (III) was prepared by Sutter is similarly constituted.

H. A. P.

Preparation of furil. W. W. Hartman and J. B. Dickey (J. Amer. Chem., Soc., 1933, **55**, 1228—1229).—Furil is obtained in 63% yield by oxidation of furoin (improved prep. given) with $CuSO_4$ in aq. C_5H_5N.

H. B.

Anthoxanthins. XIII. Synthesis of a colouring matter of *Robinia pseudacacia*. E. H. Charlesworth and R. Robinson (J.C.S., 1933, 268—270; cf. A., 1930, 785).—The anhydride and Na salt of *O*-trimethylgallic acid with ω-methoxyresacetophenone at 180—185° give a product, which with hot KOH–aq. EtOH yields 7-*hydroxy*-3 : 3′ : 4′ : 5′-*tetramethoxyflavone*, m.p. 250—251° (*Ac* derivative, m.p. 149—150°), which with hot HI in CO_2 gives 3 : 7 : 3′ : 4′ : 5′-*pentahydroxyflavone* (*robinetin*), a powerful mordant dye, identical with the natural product.

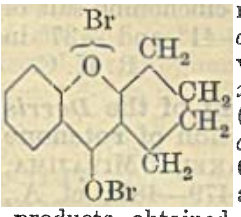
R. S. C.

Synthetical experiments in the *iso*flavone group. VII. Synthesis of daidzein. W. Baker, R. Robinson, and N. M. Simpson (J.C.S., 1933, 274—275; cf. A., 1932, 859).—7-Acetoxy-4′-methoxy-2-methyl*iso*flavone, m.p. 193°, with hot KOH–aq. EtOH gives the 7-OH-compound, m.p. 281° after sintering at 277°, converted by Me_2SO_4 into 7 : 4′-dimethoxy-2-methyl*iso*flavone, m.p. 167°, sublimes at 110°/vac., which with PhCHO and NaOEt in hot EtOH gives 7 : 4′-*dimethoxy*-2-*styryl*iso*flavone*, m.p. 197—198° after sintering at 194°. This with aq. $KMnO_4$ at 25—40° gives BzOH and 7 : 4′-*dimethoxy*iso*flavone*-2-*carboxylic acid*, m.p. 243° (decomp.), which at 250° gives CO_2 and 7 : 4′-dimethoxy*iso*flavone. demethylated by HI to 7 : 4′-dihydroxy*iso*flavone (Ac_2 derivative, m.p. 181°), identical with *O*-dimethyldaidzein and natural daidzein, respectively.

R. S. C.

Synthesis of cyanomaclurin and its derivatives. I. 3 : 5 : 7 : 2′ : 4′-Pentamethoxyflavan. A. L. Bhalla and J. N. Rây (J.C.S., 1933, 288—290).—Resorcinol, β-*o*-methoxyphenylpropionic acid, and $ZnCl_2$ at 100—110° in H_2 yield 2 : 4-*dihydroxy*-2′-*methoxy*-β-*phenylpropiophenone* (I), m.p. 138°, giving with Ac_2O the *Ac*$_2$ derivative, m.p. 81—82°, or with more Ac_2O 7-*acetoxy*-2′-*methoxy*-3-*benzyl*-2-*methylchromone*, m.p. 141—142°. β-*o*-Methoxyphenylpropionyl chloride, resorcinol Me_2 ether, and $AlCl_3$ in hot CS_2 give 2 : 4 : 2′-*trimethoxy*-β-*phenylpropiophenone*, m.p. 78°. Neither this nor (I) could be converted into a flavan. 2-Hydroxy-4 : 6-dimethoxy- (II) and 2-hydroxy-4-methoxy-benzaldehyde (from resorcylaldehyde, Me_2SO_4, and 20% KOH at 70—80°) with the required ketone give 2′-*hydroxy*-3 : 4 : 4′ : 6′-*tetramethoxy*-, m.p. 165—166°, and 2′-*hydroxy*-2 : 4 : 4′-*trimethoxy-benzylideneacetophenone*, m.p. 156°. Neither (II) nor β-resorcylaldehyde condenses with resacetophenone Me_2 ether. Catalytic hydrogenation (Pd–$BaSO_4$ in EtOH) of the appropriate chalkone affords 2′-*hydroxy*-2 : 4-*dimethoxy*-, m.p. 95°, -2 : 4 : 4′-*trimethoxy*-, m.p. 110°, and -3 : 4 : 4′ : 6′-*tetramethoxy*-β-*phenylpropiophenone*, m.p. 135°, reduced by Na–Hg to α-2 : 4-*dimethoxyphenyl*-γ-*o*-*hydroxy*-, m.p. 106—107°, and α-3 : 4-*dimethoxyphenyl*-γ-2-*hydroxy*-4 : 6-*dimethoxy-phenyl*-n-*propyl alcohol*, m.p. 118—119°. ω-Chloro-2-hydroxy-4-methoxyacetophenone, 2-hydroxy-4-methoxybenzaldehyde, and HCl in EtOAc at 0° give 3-*chloro*-2′-*hydroxy*-7 : 4′-*dimethoxyflavylium chloride*, m.p. > 250°, which could not be reduced catalytically. Catalytic reduction (Pd–$BaSO_4$) of 3 : 5 : 7 : 2′ : 4′-pentamethoxyflavylium chloride in EtOH gives 3 : 5 : 7 : 2′ : 4′-*pentamethoxyflavan* (? *dihydrocyanomaclurin*), m.p. 42°. (II), ω-methoxyresacetophenone, and HCl in dry Et_2O give *morinidin* 3 : 5 : 7-*Me*$_3$ *ether*, —1·5H_2O, m.p. 160°, which resisted catalytic hydrogenation. Veratraldehyde, ω-chloro-2-hydroxy-4-methoxyacetophenone, and HCl in EtOAc give 3-chloro-7 : 3′ : 4′-trimethoxyflavanone, which resisted replacement of Cl by OH and reduction by Clemmensen's method. R. S. C.

1 : 2 : 3 : 4-Tetrahydroxanthone. H. I. Hall and S. G. P. Plant (J.C.S., 1933, 232—235).—Et *cyclo*hexanone-2-carboxylate, PhOH, and P_2O_5 give 1 : 2 : 3 : 4-tetrahydroxanthone (I), m.p. 104°, b.p. 195—212°/9 mm., which with hot KOH–aq. EtOH gives *cyclo*hexanone, salicylic acid, and ε-*o*-*hydroxybenzoylhexoic acid*, m.p. 97—99° (*Me* ester, m.p. 40—42°) [whereby the constitution of (I) is confirmed], and a small amount of a neutral *substance*, m.p. 130° (also obtained from 7-methyltetrahydroxanthone under similar conditions and therefore probably a secondary product formed by intermol. condensation of *cyclo*hexanone). (I) with HNO_3 (*d* 1·5) at 0° gives the 7-*NO*$_2$-derivative, m.p. 203°, reduced by Zn dust and AcOH at 40° to the 7-*NH*$_2$-derivative, m.p. 179°, whence the 7-*Cl*-compound (II), m.p. 151—153°, was prepared. The constitution of these compounds is proved by the preparation of (II) from *p*-C_6H_4Cl·OH by the Simonis reaction. *p*-C_6H_4Br·OH and *p*-cresol yield similarly 7-*bromo*- (III), m.p. 151°, and 7-methyl- (IV) 1 : 2 : 3 : 4-*tetrahydroxanthone*, m.p. 102—103° (lit. 113°). (II) with KOH–aq. EtOH gives *cyclo*hexanone, ω-chloro-2-hydroxybenzoic acid, and ε-5-*chloro*-2-*hydroxybenzoylhexoic acid*, m.p. 122°; (III) and (IV) yield similarly 5-bromo- and 5-methylsalicylic acid and ε-ω-*bromo*-2-*hydroxy*-, m.p. 120°, and ε-2-*hydroxy*-5-*methyl-benzoylhexoic acid*, m.p. 87°, respectively. (I) with Br (1 mol.) in AcOH or CS_2 at



room temp. gives the annexed *dibromide*, yellow, m.p. 115°, but, when boiled, ??-*dibromotetrahydroxanthone*, colourless, m.p. 147°. (I) with Cl_2 in CCl_4 gives 10 : 11-*dichlorohexahydroxanthone*, m.p. 64—65° (does not liberate I from aq. KI), degraded by alkali to the products obtained from (I). Chlorination of (IV) gives 10 : 11-*dichloro*-7-*methylhexahydroxanthone*, m.p. 87°, similarly degraded. Et *cyclo*pentanone-2-carboxylate, PhOH, and P_2O_5 give 2 : 3-*dihydropentachromone*, m.p. 120—121°, b.p. 185—195°/20 mm., degraded by alkali to δ-*o*-hydroxybenzoylvaleric acid only, and yielding the 6-*NO*$_2$-, m.p. 184°, and 6-*NH*$_2$-, m.p. 240°, -derivatives. R. S. C.

Derivatives of dioxan. J. Boeseken, F. Tellegen, and P. C. Henriquez (J. Amer. Chem. Soc., 1933, **55**, 1284—1288; cf. this vol., 73).—2 : 3-Dichlorodioxan (I) and *o*-$C_6H_4(OH)_2$ in boiling xylene give 2 : 3-*o*-*phenylenedioxydioxan*, m.p. 74—76°. 2 : 3-*Dibenzyloxydioxan*, m.p. 66—68°, an *Et naphtho*-1 : 4 : 5 : 8-*dioxan*-2 : 3-*dicarboxylate*, m.p. 93·3—94·7°, $[\alpha]_D$ —0·3° in EtOH, and 2 : 3-*diacetoxydioxan*, m.p. 104—105·5°, are prepared from (I) and CH_2Ph·OH, Et *d*-tartrate, and KOAc–AcOH, respectively. Chlorination of (I) at 130—150° gives an *as*-tetrachlorodioxan, b.p. < 102°/15 mm., hydrolysed by H_2O to OH·CH_2·CHO; chlorination at 60° for 50 hr. also affords a little *hexachlorodioxan*, m.p. 89·5—91°, which is unaffected by EtOH–$AgNO_3$ or –KOH. H. B.

Formation of cyclic compounds of pyrocatechol with aldehydes and ketones. J. Boeseken and G. Slooff (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1250—1255).—*Methylenedioxybenzene* derivatives are obtained by addition of P_2O_5 to mixtures of pyrocatechol and the following aldehydes and ketones and warming until reaction occurs (figures denote b.p./20 mm. of the compound): MeCHO, 118° (m.p. 32°; reaction with paraldehyde at —5°); C_6H_{13}·CHO, 155°; COMeEt, 94°; COMePr, 94°; COMePr$^\beta$, 102°; COMeBu$^\beta$, 115°; COMe·C_9H_{19}, 188°; $COEt_2$, 105°; $COPr^\beta_2$, 132°; *cyclo*pentanone, 124°; *cyclo*hexanone, 140° (m.p. 45°); Et acetoacetate, 155° (I). The following *iso*propylidenedioxybenzenes are obtained from $COMe_2$ and the corresponding pyrocatechol derivative: 3-, m.p. 83°, and 4-*NO*$_2$-, m.p. 93° (II); 4-*Cl*-, b.p. 224°/750 mm.; 4 : 5-*Cl*$_2$-, m.p. 88° (III). *iso*Propylidenedioxybenzene (IV) (A., 1932, 860) and HNO_3 yield (II), reduced by Sn and HCl in Et_2O to the 4-*NH*$_2$-compound, m.p. 35°, b.p. 134—136°/11 mm. (Sn and aq. HCl yield 4-aminopyrocatechol). (IV) with Cl_2 yields (III), and with Br a *Br*-compound, m.p. 92°.

Et *iso*propylidenedioxybenzene-ω-carboxylate (I), *o*-C_6H_4<O>O>CMe·CH_2·CO_2Et, and HNO_3 yield the

4-NO_2-compound, m.p. 72°, which cannot be hydrolysed to the acid, but with KOH–EtOH gives a *compound*, $C_{12}H_{14}O_7NK$, yielding two *acids*, $C_{12}H_{13}O_6N$, m.p. 125° and 137°. Hydrolysis of (I) yields the *acid*, m.p. 61°, yielding with HNO_3 the 4-NO_2-derivative (V), m.p. 125°, decomposed by distillation to give (II). Fractionation of the cinchonine salt of (V) yields the d- and l-*acids*, $[\alpha]_D^{16}$ +41° and −37° in EtOH. R. K. C.

Rotenone, the active component of the *Derris* root. X. Oxidation and reduction of rotenone in feebly alkaline solution. S. Takei, S. Miyajima, and M. Ono (Ber., 1933, **66**, [*B*], 479—483; cf. A., 1932, 860).—Rotenone is rapidly oxidised by atm. O_2 at room temp. in very feebly alkaline EtOH to a mixture of varying proportions of *rotenolone* A (I), m.p. 138° (*oxime*, m.p. 175°), and *rotenolone* B (II), m.p. 137—138°, which do not afford tubaic acid when boiled with 5% KOH–EtOH. (I) and (II) are quantitatively converted by boiling 5% H_2SO_4 containing EtOH into dehydrorotenone. Catalytic hydrogenation of rotenone (Pd–$BaSO_4$) in feebly alkaline solution yields dihydrorotenone (III), m.p. 214°, and *dl-iso*dihydrorotenone (IV), m.p. 206°. (IV), but not (III), is further hydrogenated to tetrahydrorotenone, m.p. 210°. The behaviour of rotenone in an alkaline medium explains the comparatively rapid loss of physiological activity of *Derris* extract in aq. and, particularly, aq. alkaline suspension. H. W.

Thiophen series. XXIV. Nitrothiophens and thiophensulphonyl chlorides. W. Steinkopf and T. Hopner. **XXV. Thioaldehydes and thioketones of thiophen.** W. Steinkopf and H. Jacob (Annalen, 1933, **501**, 174—188, 188—191).—XXIV. Thiophen-2-sulphonyl chloride (I), b.p. 123—125°/14 mm., m.p. 31·5—33° (lit. 28°) (convenient prep. given), and fuming HNO_3 at 30—40° give a *mixture*, b.p. 147—152°/2 mm., of NO_2-derivatives, which when hydrolysed and desulphonated (superheated steam) affords 3 pts. of 2- (II) and 8 pts. of 3- (III), b.p. 225° (corr.), m.p. 75—77° (lit. 67—69°), -nitrothiophens. Reduction ($SnCl_2$, conc. HCl) of (III) gives the *hydrochloride chlorostannite* of 3-aminothiophen [3-thiophenin] (*Ac*, m.p. 145—148°, and *Bz*, m.p. 153—155°, derivatives); (III) and fuming HNO_3 at 35—60° afford 2 : 4-*dinitrothiophen*, m.p. 56° (*compound* with thionaphthen). The dinitrothiophen prepared from (II) contains some 2 : 5-*dinitrothiophen* (IV), m.p. 78—82° [*compound*, m.p. 56—58° (previous sintering), with $C_{10}H_8$; *compound*, m.p. 41—43°, with thionaphthen], separable by treatment of the original product with fuming HNO_3 and oleum (33% SO_3) at 70—80° [whereby (IV) is unaffected]. Thiophen-3-sulphonyl chloride (V) and fuming HNO_3 at 30—60° give o-*nitrothiophen-2-sulphonyl chloride*, b.p. 153°/2 mm., m.p. 45—47° (sinters at 40°); when this is hydrolysed and desulphonated, (II) results. (I) and 7% oleum at 20—30° give (after hydrolysis and treatment of the Na salt with PCl_5) thiophen-2 : 4-disulphonyl chloride, m.p. 75—78° (2-NO_2-derivative, m.p. 148—149°) [also prepared (as above) from (V) and 50% oleum], and *thiophen*-2 : 5-*disulphonyl chloride*, m.p. 44—46°, separable by fractional crystallisation from petroleum. Thiophen, FSO_3H, and $SOCl_2$ give a *compound*, $C_{24}H_{12}S_8$, blackens at 180—190° without melting. Thiophen-2-sulphonamide, m.p. 146—147° (lit. 141—142°), -2-*sulphonmethylamide*, m.p. 71—72°, -2-*sulphonyl fluoride*, b.p. 94—96°/20 mm., m.p. −1° to 0° [from (I) and aq. NH_4F], -2 : 4-disulphonamide, m.p. 218° (previous sintering) (lit. 211·5°), and -2 : 5-*disulphonamide*, m.p. about 240°, are described.

XXV. Thiophen-2-aldehyde, H_2S, and HCl in EtOH give α-, m.p. 179°, and β-, m.p. 221°, *-trithiophen-2-thioaldehydes* $(C_4H_3S{\cdot}CHS)_3$, separable through their differing solubilities in C_6H_6. A trace of s-2 : 2′-*dithienylethylene*, m.p. 132·5°, is obtained when the β-form is heated with Cu powder. *Ph* 2-*thienyl thioketone*, b.p. 150—153°/high vac., is prepared from Ph 2-thienyl ketone, H_2S, and HCl in EtOH. H. B.

Reaction of organic halides with piperidine. III. *cyclo*Hexyl bromide and butyl bromides. W. V. Drake and S. M. McElvain (J. Amer. Chem. Soc., 1933, **55**, 1155—1158).—Piperidine (I) and the appropriate BuBr at 150—155° give [after removal of the hydrobromide of (I) and unchanged (I) (with CS_2) and subsequent treatment with HCl] N-n-, m.p. 239—240°, -sec.-, m.p. 208—209°, -iso-, m.p. 257—258° (decomp.), and -tert.-, m.p. 268—269° (decomp.), *-butylpiperidine hydrochlorides*, showing that rearrangement of the bromides does not occur (cf. A., 1931, 494). The difference in reactivity of *sec.*-BuBr and *cyclo*hexyl bromide is one of degree; N-*cyclohexylpiperidine hydrochloride* has m.p. 292—293° (decomp.). N-sec.- and -iso-*Butylpiperidines* have b.p. 169—170° and 160—161°, respectively. H. B.

Electrolytic reduction of *N*-methylglutarimide. R. Lukeš and M. Smetačkova (Coll. Czech. Chem. Comm., 1933, **5**, 61—66).—Glutaric acid [*methylimide* (I), m.p. 33°, b.p. 240—241°/760 mm., 125°/13 mm.; bismethylamide, m.p. 127°] is separated from the products of oxidation of *cyclo*hexanone by means of its Ba salt. Electrolytic reduction of (I) gives according to the conditions mainly *N*-methylpiperidone or -piperidine. A *substance*, $C_{12}H_{22}N_2$, is also obtained. A. A. L.

Cyclisation of methyl-ωω′-dicarbethoxydialkylamines through the acetoacetic ester condensation. E. A. Prill and S. M. McElvain (J. Amer. Chem. Soc., 1933, **55**, 1233—1241).—The cyclisation of esters of the type $CO_2Et{\cdot}[CH_2]_m{\cdot}NMe{\cdot}[CH_2]_n{\cdot}CO_2Et$ (*m* and *n*=1—4) by NaOEt in absence and presence of C_6H_6 and xylene is studied. NaOEt (alone or, better, in C_6H_6) is a better condensing agent than Na in the conversion of methyldi-β-carbethoxyethylamine (I) into Et 1-methyl-4-piperidone-3-carboxylate (A., 1924, i, 985), which is hydrolysed (dil. HCl) to 1-*methyl*-4-*piperidone*, b.p. 56—58°/11 mm. *Methyl*(*carbethoxymethyl*)-*γ-carbethoxypropylamine*, b.p. 134—135°/10 mm. (from $NHMe{\cdot}CH_2{\cdot}CO_2Et$ and $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$), condenses (no solvent) more readily than (I) to give (probably) Et 1-methyl-3-piperidone-4-carboxylate [*hydrochloride*, m.p. 171—173° (decomp.)], which is hydrolysed (dil. HCl) to 1-*methyl*-3-*piperidone*, b.p. 63—64°/13 mm. (*hydrochloride*, m.p. 110—111°); this is readily oxidised by air, ammoniacal Ag_2O, or Fehling's solution. *Methyl-*

(*carbethoxymethyl*)-β-*carbethoxyethylamine*, b.p. 124—125°/10 mm., is converted (best in C_6H_6) into (probably) Et 1-methyl-3-pyrrolidone-4-carboxylate (*hydrochloride*, m.p. 132—133°), hydrolysed to 1-*methyl*-3-*pyrrolidone*, b.p. 46—47°/18 mm. (*hydrochloride*, m.p. 62—63°), which is also readily oxidised. Condensation (in xylene) of *methyl*(*carbethoxymethyl*)-δ-*carbethoxybutylamine*, b.p. 146—147°/9 mm., from $NHMe\cdot[CH_2]_4\cdot CO_2Et$ (II) and $CH_2Br\cdot CO_2Et$, gives about 20% of a product hydrolysed to 1-methyl-1-aza*cyclo*heptan-3-one [3-keto-1-methylhexamethyleneimine] (*hydrochloride*, m.p. 195—196°). Cyclic condensation products were not obtained from *methyldi*(*carbethoxymethyl*)*amine*, b.p. 114—115°/11 mm. (from $NHMe\cdot CH_2\cdot CO_2Et$ and $CH_2Br\cdot CO_2Et$), *methyl*-β-*carbethoxyethyl*-δ-*carbethoxybutylamine*, b.p. 159—160°/9 mm. [from (II) and $CH_2Br\cdot CH_2\cdot CO_2Et$], *methyl*-γ-*carbethoxypropyl*-δ-*carbethoxybutylamine*, b.p. 166—167°/9 mm., and *methyldi*-(δ-*carbethoxybutyl*)-*amine*, b.p. 177—178°/9 mm. In most of these cases, condensation (as determined by the EtOH produced) is slow and intermol. products result.

Et δ-*methylaminovalerate hydrochloride*, m.p. 108—109°, is prepared by hydrolysis (aq. NaOH) of 1-methyl-2-piperidone, b.p. 97—98°/11 mm. (hydrochloride, m.p. 104—105°) [obtained by reduction (Ni) of 1-methyl-2-pyridone], and subsequent esterification (EtOH–HCl). *Et* β-*methylaminopropionate hydrochloride* has m.p. 59—60°. *Methyldi*-(γ-*carbethoxypropyl*)*amine*, b.p. 159—160°/9 mm., obtained together with 1-methyl-2-pyrrolidone, b.p. 84—85°/14 mm. (*hydrochloride*, m.p. 79—81°), from NH_2Me and $CH_2Br\cdot CH_2\cdot CH_2\cdot CO_2Et$, does not give a cyclic condensation product. H. B.

Action of ultra-violet rays on pyridine. III. Photopyridine formation in the spectrum. H. Freytag and F. Hlucka (J. pr. Chem., 1933, [ii], **136**, 288—292; cf. A., 1932, 1149).—Light of λ = 254 and 266 mμ is almost entirely responsible for the production of photopyridine (absorption curve given) during irradiation of C_5H_5N. H. B.

Additive compounds of pyridine. S. S. Joshi (J.C.S., 1933, 313).—The following are described: 2-*bromo*-4 : 6-*dinitro*-, m.p. 224°, 2-*iodo*-4 : 6-*dinitro*-, m.p. 219°, 4-*iodo*-2 : 6-*dinitro*-, m.p. 213° (decomp.), 4-*bromo*-2 : 6-*dinitro*-, m.p. 212° (decomp.) [corresponding *bromide*, m.p. 193° (decomp.)], and 4-*chloro*-2 : 6-*dinitro*-*phenylpyridinium chloride*, m.p. 197°. The presence of a Me group in the *m*-position in 2 : 4- and 2 : 6-dinitrohalogenobenzenes prevents formation of such additive compounds. R. S. C.

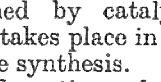
Stereochemistry of *N*-phenylpyrroles. XXIX. Preparation and properties of *o*-*N*-carbazolyl- and *o*-*N*-3-nitrocarbazolyl-benzoic acid. W. I. Patterson and R. Adams (J. Amer. Chem. Soc., 1933, **55**, 1069—1072).—*o*-*N*-Carbazolylbenzoic acid (Eckert *et al.*, A., 1922, i, 952) (*brucine*, *strychnine*, *morphine*, *quinine*, and *cinchonine* salts) could not be resolved. *o*-*N*-3-Nitrocarbazolylbenzoic acid, m.p. 226—227° (lit. 230°), from $o\text{-}C_6H_4I\cdot CO_2H$ and 3-nitrocarbazole, is partly resolved by brucine into d-, m.p. 224—225°, $[\alpha]_D^{20}$ +40·57° (variable) in $CHCl_3$ (*brucine* salt, decomp. 160—180°), and l-*forms*, m.p. 225—226°, $[\alpha]_D^{20}$ −56° to −62° in $CHCl_3$ (*brucine* salt, m.p. 246—247°), which racemise slowly in cold $CHCl_3$ and readily in warm $CHCl_3$, EtOH, or 0·1*N*-NaOH. H. B.

Resolution of *dl*-tryptophan. C. P. Berg (J. Biol. Chem., 1933, **100**, 79—83).—Fractionation of the *quinine* salt of acetyl-*dl*-tryptophan (A., 1930, 243) from MeOH affords the *quinine* salt, $[\alpha]^{20}$ −125·4°, of acetyl-*d*-, and the *quinine* salt, $[\alpha]^{20}$ −91·6°, of acetyl-*l*-tryptophan, from which are obtained acetyl-*d*-, m.p. 189—190° (corr.), $[\alpha]_D^{20}$ −26·2°, and acetyl-*l*-, m.p. 189—190°, $[\alpha]^{20}$ +26·1°, hydrolysed by 2*N*-H_2SO_4 to *d*-, m.p. 281—282° (corr.), $[\alpha]^{25}$ +32·45°, and *l*-, m.p. 281—282° (corr.), $[\alpha]_D^{20}$ −32·1°, -tryptophan, respectively (cf. du Vigneaud and Scalock, A., 1932, 753). All vals. of $[\alpha]_D$ are in MeOH. J. W. B.

Action of halogens on polycyclic indole derivatives. III. S. G. P. Plant and (Miss) M. L. Tomlinson (J.C.S., 1933, 298—300; cf. A., 1932, 1039).—Treatment of tetrahydrocarbazole successively with Br (1 mol.) in AcOH at room temp., H_2O, and aq. NH_3 gives 10-*hydroxy*-1 : 2 : 3 : 10-*tetrahydrocarbazole* (I), m.p. 153°, giving with hot Ac_2O 2 : 3-dihydrocarbazole (also obtained with a small amount of a *substance*, m.p. 196—198°, by hot abs. EtOH), with aq. EtOH or, better, KOH–aq. EtOH 11-hydroxytetrahydrocarbazolenine (II), and by diazotisation and coupling with β-naphthol the *azo-dye*, $C_{22}H_{18}O_2N_2$, m.p. 143°. In the last reaction (I) reacts as 2-*o*-*aminophenyl*-Δ^2-cyclo*hexenone*. Similar chlorination of 9-acetyl-, 9-carbethoxy-, and 9-cinnamoyl-tetrahydrocarbazole gives 10 : 11-dihydroxy-9-acetylhexahydrocarbazole, Et 10 : 11-dihydroxyhexahydrocarbazole-9-carboxylate, and 10 : 11-dihydroxy-9-cinnamoylhexahydrocarbazole, respectively; the last compound with hot KOH–aq. EtOH gives (II) and with hot Ac_2O 6-*cinnamoyl*-ψ-*indoxyl*spirocyclo*pentane*, m.p. 165°, also obtained by cinnamoylation of ψ-indoxyl*spirocyclo*pentane. 9-Benzoyltetrahydrocarbazole with Cl_2 in AcOH yields a little 11-hydroxy-9-benzoyl-2 : 3 : 4 : 11-tetrahydrocarbazole and in CCl_4 a little 10 : 11-dihydroxy-9-benzoylhexahydrocarbazole. Dihydropentindole and Br (1 mol.) in AcOH give a 10% yield of 9 : 10-*dihydroxytetrahydropentindole*, m.p. 140°, which after diazotisation couples with β-naphthol, and with Ac_2O gives the 8-*Ac* derivative, m.p. 152°, also obtained in 50% yield by chlorination of 8-acetyldihydropentindole. Chlorination of 8-benzoyldihydropentindole gives a 5% yield of 9 : 10-dihydroxy-8-benzoyltetrahydropentindole. R. S. C.

Attempts to extend the Mannich reaction to derivatives of 4-methylquinoline and 2 : 4-dinitrotoluene. W. O. Kermack and W. Muir (J.C.S., 1933, 300—302).—The Mannich reaction succeeds with 2 : 4-dinitrotoluene, but not with 2 : 6-*dimethoxy*- (I) or 8-*chloro*-2-*methoxy*-4-*methylquinoline* (II). 2-Chloro-6-methoxy-4-methylquinoline with NaOAlk gives (I), m.p. 56° [*hydrochloride*, m.p. 237° (decomp.)], and 6-*methoxy*-2-*ethoxy*-4-*methylquinoline* (III), m.p. 81°, with piperidine or piperazine 6-*methoxy*-2-*piperidino*-, m.p. 97° (*hydrochloride*, hygroscopic; *picrate*, m.p. 135°), and -2-*piperazino*-4-*methylquinoline*, m.p. 92°. *o*-Chloroacetoacetanilide in paraffin oil at 250° or, better, with conc. H_2SO_4 at 65° gives (II),

m.p. 230°, whence 2 : 8-*dichloro-* (by PCl_5 and $POCl_3$), m.p. 87—88°, 8-*chloro*-2-*methoxy-*, m.p. 122°, 8-*chloro*-2-*piperidino-*, m.p. 125—126° (*picrate*, m.p. 159°), and 8-*chloro*-2-*piperazino*-4-*methylquinoline*, m.p. 135°, are obtained. (I) with hot aq. CH_2O and a little piperidine hydrochloride, or (I) or (III) with hot *N*-HCl gives a *substance*, $C_{11}H_{11}O_2N$, m.p. 271° (*picrate*, m.p. 165—166°), not 2-hydroxy-6-methylquinoline (*picrate*, m.p. 191°); it may be the ketamic form of the latter, although this is improbable, since interconversion is impossible. 2 : 4-Dinitrotoluene with aq. CH_2O (1 mol.) and piperidine (1 mol.) in hot EtOH gives α-*piperidino*-β-(2 : 4-*dinitrophenyl*)*ethane*, an oil (*picrate*, m.p. 175°), and with 2 mols. of base αγ-*dipiperidino*-β-(2 : 4-*dinitrophenyl*)*propane*, m.p. 134°. α-*Diethylamino*-β-(2 : 4-*dinitrophenyl*)*ethane* (*picrate*, m.p. 129—130°) was similarly prepared. R. S. C.

Attempts to prepare derivatives of 1 : 2-dihydroisoquinoline. New interpretation of J. S. Buck's experiments on the synthesis of so-called 1 : 2-dihydropapaverine. P. C. Young and R. Robinson (J.C.S., 1933, 275—280).—Ring-closure of suitably substituted compounds of the types $CH_2Ar{\cdot}NMe{\cdot}CH_2Bz$ and $CH_2Ar{\cdot}NMe{\cdot}CH_2{\cdot}CH(OEt)_2$ gives complex mixtures containing little, if any, dihydroisoquinoline derivative. On this account and because of its feebly basic nature Buck's 4-hydroxy-6 : 7 : 3′ : 4′-tetramethoxy-1 : 2 : 3 : 4-tetrahydroprotopapaverine (A., 1930, 1455) is considered to be 5-*veratryl*-2-*homoveratryloxazole* (I),  [R= 3 : 4-$(MeO)_2C_6H_3{\cdot}CH_2$·] (cf. J.C.S., 1913, **103**, 1768). Buck's 1 : 2-dihydropapaverine, m.p. 97—98°, is really 3 : 4-dihydropapaverine [previously (A., 1924, i, 1336) known as an oil], obtained by way of homoveratro-6-veratrylethylamide [formed by catalytic reduction of (I)]; ring-closure thus takes place in the last, and not in the first, stage of the synthesis.

[With J. C. Resuggan.] Condensation of the appropriate aldehyde with NH_2Et or NH_2Me in cold MeOH, followed by electrolytic reduction, affords benzyl-, piperonyl- (*p-toluenesulphonyl* derivative, m.p. 108°), *vanillyl-* (*di-p-toluenesulphonyl* derivative, m.p. 108°), and o-*vanillyl-ethylamine*, m.p. 76°, and anisyl- (*p-toluenesulphonyl* derivative, m.p. 85°), o-*vanillyl-*, m.p. 89° (*p-toluenesulphonyl* derivative, m.p. 115°), and benzyl-*methylamine* (also prepared from aq. CH_2O and $NH_2{\cdot}CH_2Ph$), in 70—85% yield.

Homopiperonylmethylamine (I), similarly prepared (b.p. 95—126°/0·1 mm.) [*hydrobromide*, m.p. 186—186·5°; *hydrochloride*, m.p. 188·5°; *H oxalate*, m.p. 177°; *oxalate*, m.p. 202·5° (decomp.); *picrate*, m.p. 153·5°; quaternary *methiodide*, m.p. 226° (decomp.) after darkening at 223°], and phenacyl bromide in Et_2O give *phenacylpiperonylmethylamine*, an oil (*picrate*, m.p. about 146—147°; *hydrobromide*, m.p. 194°; *oxalate*, m.p. 138·5—141°; *methiodide*, m.p. 166°), which with P_2O_5 or $POCl_3$ gives inseparable mixtures, and with 80% H_2SO_4 saturated with HCl affords a little 6 : 7-*methylenedioxy*-4-*phenyl*-2-*methyl*-1 : 2-*dihydroisoquinoline* (*picrate*, m.p. 186—187°) (also obtained with much amorphous *solid* by conc. HCl at 100°) or a *base*, $C_{16}H_{15}O_3N$ (? phenacylhomopiperonylamine), m.p. 146° [*picrate*, m.p. 182° (decomp.)]. (I) and bromoacetal in a little hot EtOAc give *homopiperonylmethylaminodiethylacetal* (II), b.p. about 141°/0·1 mm. (*methiodide*, m.p. 153°; *methochloride*, m.p. 171—172°); the corresponding *dimethylacetal* (III) has b.p. 138°/0·1 mm. (II) with AcOH–HCl at 40° or with conc. HCl gives a *base*, $C_{11}H_{13}O_3N$ [either NN-*piperonylmethylaminoacetaldehyde* or the related 4-*hydroxytetrahydroisoquinoline* (*methiodide*, m.p. 216—218°)], and a substance (possibly the preceding base) which gives a p-*nitrophenylhydrazone*, m.p. 191—196° (decomp.); with $POCl_3$ in hot CS_2 it affords a mixture containing (?)6 : 7-*methylenedioxy*-4-*ethoxy*-2-*methyltetrahydroisoquinoline* (*picrate*, m.p. 153—155°) and (?) 4-*hydroxy*-6 : 7-*methylenedioxy*-2-*methyltetrahydroisoquinoline* [*picrate*, m.p. 185—186° (decomp.)]. (III) with 10% HCl at 100° gives a *hydrochloride*, $C_{11}H_{13}O_3N$,HCl, m.p. 256° (decomp.) after sintering and decomp. from 235°. Other attempts at ring-closure gave very low yields of unidentified products. R. S. C.

Ethylene-*NN*′-bis-5 : 5-diethylbarbituric acid, a bimolecular barbital with hypnotic properties. A. W. Dox (J. Amer. Chem. Soc., 1933, **55**, 1230—1232).—$(\cdot CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$ (I), $CEt_2(CO_2Et)_2$ (2 mols.), and 10% EtOH–NaOEt at 100—106° give *ethylene-NN′-bis-5 : 5-diethylbarbituric acid*, m.p. 189°, which has about 75% of the hypnotic activity of 5 : 5-diethylbarbituric acid. *Ethylene-NN′-bis-5-ethyl-5-hexylbarbituric acid*, not obtained cryst., possesses only slight activity. (I) and $CPhEt(CO_2Et)_2$ give $CHPhEt{\cdot}CO_2Et$ and the *allophanate*, $(\cdot CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO_2Et)_2$, m.p. 219° (decomp.) [also prepared from (I), Et_2CO_3, and EtOH–NaOEt], converted by 25% aq. NH_3 at 100° into the *biuret*, $(\cdot CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, m.p. 245° (decomp.). H. B.

Rearrangement of phenylhydrazones of unsymmetrically substituted distyryl ketones. L. C. Raiford and J. B. Entrikin (J. Amer. Chem. Soc., 1933, **55**, 1125—1128).—The *phenylhydrazone*, m.p. 165—166°, of styryl *p*-chlorostyryl ketone is rearranged by boiling AcOH to 1 : 5-*diphenyl*-3-*p-chlorostyrylpyrazoline*, m.p. 184—185°. Similarly, the *phenylhydrazone*, m.p. 100—101°, of *p*-chlorophenyl styryl ketone gives 1 : 5-*diphenyl*-3-*p-chlorophenylpyrazoline* (I), m.p. 149—150°. 1 : 5-*Diphenyl*-3-*m-chloro-*, m.p. 153—154°, -*m-nitro-*, m.p. 182—183°, and -*p-nitro-*, m.p. 191—192° (also + AcOH, decomp. 130—131° and gives a clear liquid at 192°), -*styrylpyrazolines* are obtained directly from the requisite ketone and $NHPh{\cdot}NH_2$. Oxidation ($KMnO_4$, aq. Na_2CO_3) of the above pyrazolines [except (I)] gives small amounts of 1 : 5-diphenylpyrazole-3-carboxylic acid. *Styryl p-nitrostyryl ketone* has m.p. 178—179°. H. B.

β-Phenylethylpyrazolones. E. Votoček and F. Valentin (Coll. Czech. Chem. Comm., 1933, **5**, 84—90).—$CH_2Ac{\cdot}CO_2Et$ with β-phenylethylhydrazine (A., 1932, 942) gives 1-β-*phenylethyl*-3-*methylpyrazolone*, m.p. 139—141·5° (2-*Me* derivative, m.p. 102—103°), the *oximino*-derivative, m.p. 120°, of which is reduced to 4-amino-1-β-phenylethyl-3-methylpyrazolone (I), isolated as the *benzylidene* derivative, m.p. 166—168°. This with HCl gives the unstable *dihydrochloride* of (I). Action of air on (I) gives "*homorub-*

azonic acid," $C_{24}H_{25}N_5O_2$, m.p. 95—96°. 1-β-*Phenylethyl*-3 : 4-*dimethylpyrazolone*, m.p. 176°, is similarly obtained. A. A. L.

Pyrimidines. CXXXI. Reduction of 1 : 2 : 3 : 4-tetrahydropyrimidines. K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1933, **55**, 1140—1147).—Reduction (H_2, PtO_2, AcOH) of *Et* 2-*keto*-6-*phenyl*-4-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 165—166·5° [from $CO(NH_2)_2$, MeCHO, $CH_2Bz{\cdot}CO_2Et$, and AcOH–conc. HCl], gives the *Et* ester, m.p. 179—181°, of 2-*keto*-6-cyclo*hexyl*-4-*methylhexahydropyrimidine*-5-*carboxylic acid*, m.p. 290—291° (decomp.). Similar reduction of the following does not affect the 5 : 6-double linking: Et 2-keto-4-phenyl- (I), -4-β-phenylethyl- (II), and -4-styryl- (III), -6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate. (I) gives *Et* 2-*keto*-4-cyclo*hexyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 237·5—238·5°, which could not be reduced further; (II) affords *Et* 2-*keto*-4-β-cyclo*hexylethyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate* (IV), m.p. 192·5—193·5°, whilst (III) gives (IV) or *Et* 2-*keto*-4-β-*dihydrophenylethyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 170·5—171·5° [reducible to (IV)], according to the amount of catalyst used. (I) could not be reduced by 2·5% Na–Hg and AcOH, HI, or H_2, PtO_2, and EtOH. H. B.

Quinazolines. V. Partial hydrolysis of 2 : 4-dialkoxyquinazolines with the formation of 4-keto-2-alkoxydihydroquinazolines. N. A. LANGE and F. E. SHEIBLEY (J. Amer. Chem. Soc., 1933, **55**, 1188—1194).—2 : 4-Dicthoxyquinazoline (I) and EtOH–NaOEt give (after acidification with AcOH) 4-keto-2-ethoxydihydroquinazoline (II), m.p. 179°, methylated (Me_2SO_4, *N*-NaOH) to its 3-Me derivative, m.p. 75—76°. In one case only, (I) and abs. MeOH–NaOMe gave a second *form*, m.p. 202—205°, of (II). 2 : 4-Dimethoxyquinazoline and MeOH–NaOMe afford 4-keto-2-methoxydihydroquinazoline, m.p. 218° (3-*Me* derivative, m.p. 93°), also prepared (with m.p. 226°) from *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$, $NH{:}C(CN){\cdot}OEt$, and CuCl at 80°. 2-Chloro-4-ethoxyquinazoline and EtOH–KOH give 2-chloro-4-ketodihydroquinazoline, m.p. 212°, also formed from 2 : 4-dichloroquinazoline and *N*-NaOH. 4-*Keto*-2-*phenoxydihydroquinazoline*, m.p. 272°, is prepared from 2 : 4-diphenoxyquinazoline and EtOH–KOH. H. B.

Acid derivatives of aminotetrazole. R. STOLLÉ and O. ROSER (J. pr. Chem., 1933, [ii], **136**, 314—320).—ɔ-α-*Ethylbutyramido*- (I), m.p. 238° (decomp.) [*Na* salt, m.p. 285° (decomp.)], 5-α-*bromo*-α-*ethylbutyramido*- (II) [*Na* salt, m.p. 191° (not sharp)], and ɔ-α-*bromoisovaleramido*-, m.p. 205° (decomp.) [*Na* salt, m.p. 100° (not sharp)], -*tetrazoles* are prepared from 5-aminotetrazole (III) and the appropriate acid halide. (II) and $NPhMe_2$ at 140° give 5-α-*ethylcrotonamidotetrazole*, m.p. 240° (decomp.), also formed when the Na salt of (II) is heated at 150° for some time. $CEt_2(COCl)_2$ (1 mol.) and (III) (2 mols.) in cold C_5H_5N afford *diethylmalon*-5-*tetrazolylamic acid*, m.p. 188°, re-solidifying with m.p. 225°, which passes into (I) when heated; equimol. quantities in hot C_5H_5N give *diethylmalon*-5-*tetrazoylamide*, m.p. 287°. 5 : 5-Diethyl-2-thiobarbituric acid, NaN_3, and PbO in CO_2 afford (I); 2-thiohydantoin similarly gives (III). H. B

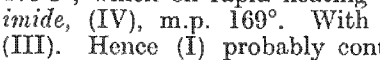
Glyoxaline derivatives of barbituric acid. M. S. TAGGART and G. H. RICHTER (J. Amer. Chem. Soc., 1933, **55**, 1110—1111).—The products from 4(5)-chloromethylglyoxaline and $CHBu(CO_2Et)_2$ and Et *iso*amylmalonate condense with $CO(NH_2)_2$ to give 5-n-*butyl*-, decomp. about 290°, and 5-iso*amyl*-, decomp. and chars when heated, -5-4′(5′)-*glyoxalinylmethylbarbituric acid*, respectively. H. B.

Decomposition of cyclic nitrogen compounds by light from the quartz lamp. F. LIEBEN and V. GETREUER.—See this vol., 473.

Porphyrin syntheses. XLVII. Synthesis of 1 : 3 : 5 : 8-tetramethyl-6 : 7-di-β-carboxyethyl-2 : 4-dipropenylhæmin. H. FISCHER and M. DURR (Annalen, 1933, **501**, 107—131).—Deuterohæmin, $(EtCO)_2O$, and $SnCl_4$ give (after removal of Fe with HBr–AcOH) dipropionyldeuteroporphyrin [2 : 4-dipropionyl-1 : 3 : 5 : 8-tetramethyl-6 : 7-di-β-carboxyethylporphin] {*Me*$_2$ ester, m.p. 185° (corr.) [*dioxime*, m.p. 231°; *phyllin*, m.p. 280—288° (corr.)]}, reduced by EtOH–KOH to *dimethylhæmatoporphyrin* [1 : 3 : 5 : 8-*tetramethyl*-2 : 4-*di*-α-*hydroxypropyl*-6 : 7-*di*-β-*carboxyethylporphin*], which when heated at 145°/0·4 mm. loses 2 mols. of H_2O and passes into dimethylprotoporphyrin (I). Exposure of a solution of the *Me*$_2$ ester, m.p. 265° (corr.), of (I) in $CHCl_3$ to (electric) light in air causes oxidation; hydrolysis (conc. HCl) of the resultant product and esterification (MeOH–HCl) of the porphyrin fraction give an *ester*, m.p. 248° (corr.). The *hæmin* of (I) is reconvertible into (I) by HBr–AcOH and when fused with *m*-$C_6H_4(OH)_2$ at 190—200° affords deuterohæmin; similar fusion of (I) gives deuteroporphyrin. (I) is reduced (Na, *iso*amyl alcohol) to dimethylmesoporphyrin, the *Me*$_2$ ester, m.p. 246° (corr.), of which also undergoes a change when exposed to light (as above). Protoporphyrin Me_2 ester [prep. from tetramethylhæmatoporphyrin (II) (*phyllin*, m.p. 188°) described] is similarly converted into a *substance*, m.p. 212°, which probably contains a CO group; (II) and hæmatoporphyrin undergo slow changes on irradiation. Reduction of hæmin (from blood) with 25% PrOH–KOH gives (after removal of Fe with HBr–AcOH) mesoporphyrin. The *phyllin* from deuteroporphyrin Me_2 ester has m.p. 255—263° (corr.); the *phyllin* of diacetyldeuteroporphyrin ester is prepared. H. B.

Chlorophyll. IV. Optical activity. A. STOLL and E. WIEDEMANN (Helv. Chim. Acta, 1933, **16**, 307—314).—Optical activity is shown both by chlorophyll and its phytol-free derivatives. Vals. of $[\alpha]_{-20}$ are measured on account of lack of transparency to light of shorter wave-length. Observations are both visual and by photography on infra-red plates. The following vals. of were observed: chlorophyll-*a* ($+1H_2O$), −262° in $COMe_2$; chlorophyll-*b* ($+1H_2O$), −267° in 90MeOH : 10$COMe_2$ (by vol.); phæophytin-*a* ($+0{\cdot}5H_2O$), −126° in 95MeOH : 5C_5H_5N (by vol.) (I); phæophytin-*b*, −133° in (I); methylphæophorbide-*a*, −131° in (I); methylphæophorbide-*b*, −184° in (I); phæophorbide-*a* ($+0{\cdot}5H_2O$), −342°

in (I); phæophorbide-*b*, −316° in (I). These vals. are for freshly-prepared solutions; on keeping, the optical activity is rapidly lost, although the phase-test remains good. Reduced activity or none at all is also shown by some old solid preps., although otherwise apparently normal. H. A. P.

Prodigiosin, the red pigment of *Bacillus prodigiosus*. III. F. Wrede and A. Rothhaas (Z. physiol. Chem., 1933, **215**, 67—78: cf. A., 1932, 1043).—Distillation of prodigiosin (I) with soda-lime or Zn dust, or reduction with HI–AcOH affords a *pyrrole* (II), $C_{10}H_{17}N$, b.p. 105°/5 mm. (*diazobenzenesulphonyl* derivative). Catalytic hydrogenation (PtO_2) of (II) gives a pyrrolidine, $C_{10}H_{21}N$ [*chloroaurate*, m.p. 105°; *chloroplatinate*, m.p. 212° (decomp.)]. With Me_2SO_4 (II) yields a substance giving a *chloroaurate*, $C_{10}H_{20}NMe_2AuCl_4$, sinters about 75°. Oxidation of (I) with H_2O_2 gives a neutral substance A, which with CH_2N_2 gives N-*methylmethoxymaleimide* (III), m.p. 127°, and acidic products B and C yielding on methylation an *oil*, $C_4H_8O_3$, b.p. 70°/high vac., and Me oxamate, respectively. Treatment of hydroxymaleic anhydride with CH_2N_2 and then with NH_3 in MeOH gives *methoxymaleic acid monoamide*, m.p. 179·5°, which on rapid heating affords *methoxymaleimide*, (IV), m.p. 169°. With CH_2N_2, (IV) yields (III). Hence (I) probably contains the grouping:  (R+R′+R″=C_6H_{12}).

J. H. B.

Derivatives of methylene-blue. H. D. K. Drew and F. S. H. Head (J.C.S., 1933, 248—253).—A derivative of the *o*-quinonoid form of methylene-blue (I) is prepared. Methylene-blue chloride with aq. KI gives the *iodide* (II), $+0·5H_2O$ (not lost over P_2O_5 at room temp. or at 110° in vac.), with KCNS the *thiocyanate*, two forms, and with Ag_2O the *base*, $+2H_2O$ (lost at 80° in vac.). (II) with NH_2·NHPh gives the leuco-base (III), cryst., yellow, and with hot EtOH and EtI or with HI and EtOH yields *leucomethylene-blue dihydriodide* (IV), HI,$Me_2N·C_6H_3<^{NH}_{S}>C_6H_3$·$NMe_2$,HI, m.p. 247°, oxidised by H_2O_2, $FeCl_3$, dil. HNO_3, or I, and giving (III) with NaOH, $NaHCO_3$, or C_5H_5N. (III) with hot, or slowly with cold, MeOH and MeI gives *leucomethylene-blue dimethiodide* (V), $+2H_2O$ (lost at 105° in N_2), m.p. 229° (decomp.) [N-*Ac* derivative, $+2H_2O$, m.p. 234° (decomp.); *picrate*]; at 120° a mixture containing probably mostly (V) is obtained (cf. A., 1886, 54). (II) with hot MeOH and MeI gives (V), but with much MeI also *methylene-blue iodide monohydriodide* (VI), HI,$Me_2N·C_6H_3<^{N}_{S}>C_6H_3$·$NMe_2$I or HI,$Me_2N·C_6H_3<^{N}_{SI}>C_6H_3$·$NMe_2$, m.p. 217° (decomp.) (rapid heating) or decomp. 250° (slow heating). (VI) is also formed from (II), EtOH, and EtI, or (III) and I in MeCN. (VI) with (*a*) hot MeOH, (*b*) hot H_2O, or (*c*) HI in AcOH, or (II) with HI (1 or 2 mols.) in AcOH, gives *methylene-blue iodide dihydriodide* (VII), HI,$Me_2N·C_6H_3<^{N}_{SI}>C_6H_3$·$NMe_2$,HI or, much less probably, HI,$Me_2N·C_6H_3<^{NHI}_{S}>C_6H_3$·$NMe_2$I, copper-bronze, m.p. 200° (decomp.), or black form, m.p. 150°, from MeOH, and golden-bronze or purplish-red form, +0·5MeCN. (VII) with aq. $K_2S_2O_8$, with quinoline at 100°, or by long boiling with H_2O, gives (II), and with (II) in MeCN forms (VI). Bindschedler's-green iodide with hot MeOH and MeI, or leuco-Bindschedler's-green (prepared by $Na_2S_2O_4$) and MeOH–I give *Bindschedler's-green iodide monohydriodide*, m. p. 152—153° (decomp.). This and (II), but not (VI) or (VII), can be determined by reduction to the leuco-compound by $TiCl_3$ in aq. EtOH. In many of the above reactions MeI acts as a source of HI. R. S. C.

Oxidation of ethyl carbamate. J. V. Dubsky and J. Trtílek (Coll. Czech. Chem. Comm., 1933, **5**, 49—60; cf. A., 1930, 199).—Oxidation of Et carbamate with I, H_2O_2 (acid or neutral), or $CuCl_2$ gives 3 : 5-diethoxy-1 : 2 : 4-thiodiazole and S. A. A. L.

Absorption spectra of 2 : 2′-dimethyl- and 2 : 2′-diethyl-selenocarbocyanine iodides and of *p*-dimethylaminostyrylbenzthiazole methiodide. L. M. Clark (J.C.S., 1933, 216).—A correction (cf. this vol., 405). J. L. D.

Constitution of *ψ*-conhydrine. E. Späth, F. Kuffner, and L. Ensfellner (Ber., 1933, **66**, [*B*], 591—601).—*ψ*-Conhydrine hydrochloride (isolation described from the technical product, which contains much coniine hydrochloride) has m.p. 213—214° and the base (I) has m.p. 105—106°. (I) is transformed by P_2O_5 in PhMe at 130° followed by hydrogenation into *d*-coniine (2 : 4-*dinitrobenzoyl* derivative, m.p. 139—140°; 3 : 5-*dinitrobenzoyl* compound, m.p. 108—109°; 2 : 4-*dinitrobenzoyl* derivative of *dl*-coniine, m.p. 115—116°). (I) is converted by successive treatment with MeI and Ag_2O followed by distillation into *ψ-conhydrinemethine*, $C_{10}H_{21}ON$, b.p. 101·5—103·5°/14 mm., $[\alpha]_D^{15}$ +18·7°, hydrogenated (Pd–C) to *dihydro-ψ-conhydrinemethine* (II), $C_{10}H_{23}ON$, b.p. 99—100·5°/11 mm., $[\alpha]_D^{15}$ +12·2°, which is oxidised by $KMnO_4$ in dil. H_2SO_4 to *n*-heptoic acid (phenylhydrazide, m.p. 102·5—103°). Hofmann degradation of (II) leads to *octylene-αβ-oxide* (III), b.p. 60—70° (bath)/17 mm., $[\alpha]_D^{17}$ −12·2°, and *octane-αβ-diol*, m.p. 35—37° after softening at 33°, $[\alpha]_D^{17}$ −4·7° in EtOH, also obtained from (III) and H_2O at 180°; in one instance, octan-β-one was isolated as the semicarbazone. *Benzoyl-ψ-conhydrine*, m.p. 132—133°, $[\alpha]_D^{15}$ +23·4° in EtOH [from (I) and BzCl in Et_2O], is is oxidised by $KMnO_4$ in faintly alkaline solution, the product is heated with fuming HCl at 150°, treated with Ag_2CO_3, and distilled. Thus are obtained the *lactam* of *γ-aminoheptoic acid* (IV), m.p. 45—47° (converted by treatment with HCl at 150° followed by BzCl into *γ-benzamido*-n-*heptoic acid*, m.p. 130—131°), and β-*amino*-n-*hexoic acid* (V), m.p. 205—207° [β-*benzamido*-n-*hexoic acid*, m.p. 150—152° (vac.)]. The constitution of (IV) is established by treatment with $NaNO_2$ followed by oxidation to *γ-ketoheptoic acid*, m.p. 50—51° [*semicarbazone*, m.p. 149—150° (decomp.)], prepared synthetically from ZnPr^{n}I and methosuccinyl chloride. Oxidation of (I) with CrO_3 leads to (IV) and (V). (I) is therefore 5-hydroxy-2-*n*-propylpiperidine. H. W.

Alkaloids of *Anabasis aphylla*. VI. Hydrogenation of anabasine. A. Orekhov and D. Brodski (Ber., 1933, **66**, [*B*], 466—468; cf. A., 1932, 952).—Anabasine is converted by reduction (PtO_2) or by Na and EtOH into a mixture of bases from which 1-2 : 3-*dipiperidyl hydrochloride*, $C_{10}H_{20}N_2$,2HCl, not molten below 300°, is isolated. The very hygroscopic *base* has m.p. 66—68°, b.p. 113—114°/5 mm., $[\alpha]^{20}$ −5° in EtOH, gives a *picrate*, m.p. 214—215° (decomp.), *chloroaurate*, m.p. 211—212° (decomp.), *chloroplatinate*, m.p. 231—232° (decomp.), $(NO)_2$-, m.p. 112—113°, and Bz_2, m.p. 149—150°, $[\alpha]^{20}$ −180° in EtOH, derivative. H. W.

Dehydrometanicotine. J. P. Wibaut and J. W. P. L. Gitsels (Rec. trav. chim., 1933, **52**, 303—304).—The dipicrate, m.p. 161—162°, of dihydrometanicotine (I) (Wibaut and Hackmann, this vol., 77) after crystallisation from H_2O has m.p. 166·5—167° (corr.), not depressed by admixture with a specimen, m.p. 167·8—168·4° (corr.), obtained from (I) prepared by catalytic reduction of metanicotine (Pinner, A., 1894, i, 388). J. W. B.

Alkaloids of *Convolvulus pseudocantabricus*, Schrenk. I. A. Orekhov and R. Konovalova (Arch. Pharm., 1933, **271**, 145—148).—The seeds contain 0·5% of mixed alkaloids, whence was isolated *convolvuline*, $C_{15}H_{21}O_4N$, m.p. 114—115°, [α] 0 in EtOH [*hydrochloride*, m.p. 260—261°; *oxalate*, m.p. 265—266° (decomp.); *picrate*, m.p. 261—263°; *chloroplatinate*, m.p. 240—241° (decomp.); *chloroaurate*, m.p. 217° (decomp.)]. This is a *tert.*-base (*methiodide*, m.p. 230—231°), contains 2OMe, but not OH or CH_2O_2. R. S. C.

Synthesis of physostigmine (eserine). VII. F. E. King and R. Robinson (J.C.S., 1933, 270—173; cf. A., 1932, 759).—*l*-Esermethole gives a *d*-bromocamphorsulphonate and *d*-camphorsulphonate, gums, and *d*-tartrate, m.p. 160—161°, hygroscopic. Spontaneous resolution is not effected by crystallisation of *dl*-esermethole methopicrate from EtOH. *l*-Esermethole methochloride at 160—200° in vac. gives 5-methoxy-1 : 3-dimethylindole (I). Nitrosomethyl-*p*-anisidine, m.p. 45—46° (lit. an oil) (modified prep.), gives *p*-methoxyphenylmethylhydrazine, which with EtCHO gives the hydrazone, converted by hot EtOH–H_2SO_4 into (I), m.p. 60°, b.p. 120—122°/1 mm.; this does not condense with ethyleneimine (modified prep.) at 120°. The prep. of β-phenoxyethylamine, m.p. 192—193° after sintering [*picrate*, m.p. 167—169°; *picrolonate*, m.p. 216—217° (decomp.)], is modified. *p*-Methoxyphenylmethylhydrazine and γ-phenoxypropyl Me ketone in hot EtOH give the hydrazone, which with H_2SO_4–EtOH forms *5-methoxy-1 : 2-dimethyl-3-β-phenoxyethylindole*, m.p. 67°, b.p. 215—225°/1 mm., unchanged by MeI in hot EtOAc, but giving with MeOH and MeI at 100—105° 5-methoxy-1 : 2 : 3-trimethyl-3-β-phenoxyethylindoleninium iodide. (I) is, however, not methylated by either method. β-Phenoxyethyl bromide (II) and Et α-acetopropionate with (*a*) NaOEt–EtOH, or (*b*) KOEt–EtOH and a little KI give *Et γ-phenoxy-α-methylbutyrate*, b.p. 147°/13 mm., and by method (*b*) a little ethylene Ph_2 ether [sole product from (II) and KCN in hot aq. EtOH]. The corresponding acid was converted successively into the *acid chloride*, b.p. 150—152°/15 mm. (unchanged by H_2 and Pd–$BaSO_4$ in boiling xylene), *amide*, m.p. 102—103·5°, *nitrile*, b.p. 165°/18—20 mm., and by Stephen's method into *γ-phenoxy-α-methylbutaldehyde* (cannot be distilled) (*$NaHSO_3$* compound), the phenylhydrazone of which with EtOH–HCl affords *3-methyl-3-β-phenoxyethylindolenine*, amorphous (*picrate*, m.p. 152—153°). R. S. C.

α-*iso*Quinidine. T. Domański and J. Suszko (Rocz. Chem., 1933, **13**, 140—153).—Quinidine, on treatment successively with HCl or HBr and boiling aq. NaOH, yields α-*iso*quinidine (I) (+1H_2O), m.p. 80°, $[\alpha]_D$ +111° [*H tartrate* (II), decomp. 161°; *methiodide*, m.p. 220°; *dimethiodide*, decomp. 222°; N-*oxide*, m.p. 100—125°; *perbromide*, m.p. 218°], a stereoisomeride of β-*iso*quinidine (A., 1930, 97), into which it is converted by heating at 80° with H_2SO_4. *α-Ketodihydroquinotoxine*, m.p. 95°, $[\alpha]_D$ −22·5° [N-*NO*-derivative, an oil (*hydrochloride*, decomp. 155°); p-*nitrophenylhydrazone*, m.p. 95—100°; N-*Me* derivative, an oil (*methiodide*, m.p. 205—206°; p-*nitrophenylhydrazone*, m.p. 90°; its *sulphate*, m.p. 170°)], is prepared by heating (I) with H_3PO_4 at 100°, or similarly from α-*iso*quinicine, m.p. 125—130° [N-*NO*-, m.p. 70°, *Br*-, m.p. 73°, N-*Ac*, m.p. 90°, and N-*Me* derivatives, m.p. 126° (*hydrobromide*, m.p. 224—226°; *methiodide*, decomp. 261—262°)], prepared by heating (II) at 150° during 30 min. Hydrobromo*apo*quinidine dihydrobromide is obtained by heating α- or β-*iso*quinidine at 100° with 64% HBr in a sealed tube. R. T.

***Strychnos* alkaloids. LXXII. Derivatives of tetra- and hexa-hydrobrucine.** H. Leuchs and H. W. Sattler (Ber., 1933, **66**, [*B*], 532—537).—Tetrahydrobrucine (I) yields a *mono-* (II), $[\alpha]_D$ −66·7°/*d*, and a *di-*, $[\alpha]^{20}$ −45°/*d*, *-perchlorate*. Warm AcOH containing 10% of HCl transforms (I) into *O-acetyltetrahydrobrucine*, m.p. 219—221° [*perchlorate*. *methiodide*, m.p. 240—242° (decomp.)]. (II) and Bz_2O at 100—110° yield the non-cryst. *dibenzoyltetrahydrobrucine* (III) (*benzoate*, m.p. 166—168°, $[\alpha]^{20}$ +63·7°/*d* in EtOH; *perchlorate*; *methiodide*, m.p. 255—257°), hydrolysed to N-*benzoyltetrahydrobrucine*, m.p. 266—268° (decomp.), $[\alpha]_D^{20}$ +71·5°/*d* in EtOH (*benzoate*, m.p. 187° after foaming at 147°; *perchlorate*; *methiodide*, not molten below 300°). (III) in $COMe_2$ is oxidised by $KMnO_4$ at −5° to 0° to ON-*dibenzoyltetrahydrobrucinonic acid*, $C_{37}H_{36}O_{10}N_2,H_2O$, m.p. indef.

The acid, $C_{19}H_{22}O_5N_2$, obtained as by-product of the oxidation of (I) with CrO_3 (A., 1931, 1312) is reduced (PtO_2) to 2-ketodihydronucidine-3-acetic acid isolated as the perchlorate (cf. A., 1931, 1433).

(I) in dil. AcOH is hydrogenated (PtO_2) to hexahydrobrucine (IV) (*mono-* (V), $[\alpha]_D^{20}$ −69·3°/*d*, and *di-*, $[\alpha]_D^{20}$ −38°/*d*, *-perchlorate*) oxidised by CrO_3 to a *base* $C_{17}H_{22}O_4N_2$, m.p. 245—247°. (V) and Bz_2O at 100—110° afford *dibenzoylhexahydrobrucine*, m.p. about 135° (decomp.) after softening at 120°, $[\alpha]^{20}$ +62°/*d* in EtOH (*benzoate*, m.p. 223—224°, $[\alpha]^{20}$ +67·8° in EtOH; *perchlorate*; *methiodide*, decomp. 190° after softening at 175°), hydrolysed to N-*benzoylhexahydrobrucine*, decomp. 135° after softening at 128°, $[\alpha]^{20}$ +83°/*d* in EtOH [*methiodide*, m.p. 300° (decomp.);

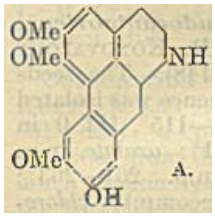
benzoate, m.p. 233—235°; *perchlorate*]. *Diacetylhexahydrobrucine* (VI), m.p. about 135° after softening at 120°, $[\alpha]_D^{20}$ +66·5°/*d* in H_2O, +39·9°/*d* in EtOH, is obtained by hydrogenating the tetrahydro-compound (PtO_2) or from (V), Ac_2O, and NaOAc at 100°; the *methiodide* has m.p. 176—180°, $[\alpha]_D^{20}$ +64·6°/*d* in H_2O. Partial hydrolysis of (VI) or hydrogenation of the Ac derivative of $C_{23}H_{30}O_4N_2$ affords N-*acetylhexahydrobrucine*, m.p. 185—186°, $[\alpha]_D^{20}$ +70°/*d* in H_2O, +44·6°/*d* in EtOH (*perchlorate*; *methiodide*, decomp. above 200° after softening above 180°, $[\alpha]_D^{20}$ +78·4°/*d* in H_2O). H. W.

Identity of narceine with ψ-narceine, its dehydration and structure. C. R. Addinall and R. T. Major (J. Amer. Chem. Soc., 1933, **55**, 1202—1209).—Narceine (I), $C_{23}H_{27}O_8N,3H_2O$, m.p. 176—177° (decomp.), m.p. (anhyd.) 137—138°, isolated from opium is identical (physical data; comparison of derivatives) with that prepared from narcotine by the methods of Roser (A., 1888, 1316) and Hope and Robinson (J.C.S., 1914, **105**, 2100); (I) gives a *methoxime*, m.p. 190°, when treated with NH_2·OMe in MeOH at 118°. Narceonic acid (*Me*, m.p. 155°, and *Et*, m.p. 139—140°, esters), prepared by a modification of Freund's method (A., 1894, i, 58), is reduced (H_2, Pt, MeOH–dioxan) to dihydronarceonic acid, $C_{21}H_{22}O_8$, m.p. 197—198°, the *Me* ester, m.p. 155° (*Br*-derivative, m.p. 189°), of which contains no active H (Zerevitinov in *iso*amyl ether). The formulation of (I) as a substituted deoxybenzoin is favoured by the above results. H. B.

Preliminary synthetic experiments in the morphine group. V. Completion of the synthesis of a laudanosoline dimethyl ether related to sinomenine. R. Robinson and S. Sugasawa (J.C.S., 1933, 280—281; cf. A., 1932, 527).—The prep. of ω-nitro-3 benzyloxy-4′-methoxystyrene is improved. *O*-Benzylhomo*iso*vanillo-6-(3-benzyloxy-4-methoxyphenyl)ethylamide and PCl_5 in $CHCl_3$ give 6-*benzyloxy*-7-*methoxy*-1-(3′-*benzyloxy*-4′-*methoxybenzyl*)-3:4-*dihydro*isoquinoline, +0·5H_2O, m.p. 105—110° (*hydrochloride*, m.p. 148—150°; *methiodide*, m.p. 198—200° after sintering at 163—164°), the methochloride of which with PtO_2 and H_2 in EtOH affords impure 6-*benzyloxy*-7-*methoxy*-1-(3′-*benzyloxy*-4′-*methoxybenzyl*)-2-*methyl*-1:2:3:4-*tetrahydro*isoquinoline (O-*dibenzyl*-O-*dimethyl*-*laudanosoline*), m.p. 96—97°, giving with HCl–AcOH at 100° 6-*hydroxy*-7-*methoxy* (4′-*methoxy*-3′-*hydroxybenzyl*)-2-*methyl*-1:2:3:4-*tetrahydro*isoquinoline (*protosinomenine*) (I), amorphous [*picrolonate*, m.p. 177—178° (sinters at 170—171°); *perchlorate*, m.p. 107—108° (decomp.) after sintering at 97—98°]. 6-*Hydroxy*-7-*methoxy*-1-(3′-*benzyloxy*-4′-*methoxybenzyl*)-2-*methyl*isoquinolinium *chloride*, m.p. 241—242° (sinters at 238°), obtained from the related phenol-betaine (modified prep.) by EtOH–HCl, with H_2–PtO_2 in 90% EtOH affords the -*benzyloxy*-derivative, m.p. 52—54°, of (I). hydrolysed to (I) by hot HCl–AcOH. R. S. C.

Constitution of laurotetanine. E. Späth and K. Tharrer (Ber., 1933, **66**, [*B*], 583—591).—Laurotetanine, from *Litsea citrata*, Bl, is converted into the resinous Et ether and thence by NaOMe and MeI into the quaternary *iodide* $C_{23}H_{30}O_4NI$, m.p. 225—226° (vac.); the corresponding base is decomposed to the amorphous methine base giving a *methiodide* $C_{24}H_{32}O_4NI$, m.p. 272—273° (vac.), the base from which yields *trimethoxyethoxyvinylphenanthrene* (I), m.p. 136—138°. (I) is oxidised by $KMnO_4$ in anhyd. $COMe_2$ to trimethoxyethoxyphenanthrenecarboxylic acid (II), m.p. 222—223°, decarboxylated by Cu powder and quinoline to *trimethoxyethoxyphenanthrene* (III), m.p. 114—116°.

*iso*Vanillin Et ether is converted by hippuric acid, Ac_2O, and NaOAc into the *azlactone* of 4-*methoxy*-3-*ethoxybenzaldehyde*, m.p. 177—178° (vac.), oxidised by H_2O_2 to 4-*methoxy*-3-*ethoxyphenylacetic acid*, m.p. 69—69·5°, the *Na* salt of which is transformed by 2-nitroveratraldehyde into 2-*nitro*-3:4:4′-*trimethoxy*-3′-*ethoxystilbene*-7′-*carboxylic acid*, m.p. 169—170° (NH_4 salt), reduced by $FeSO_4$ and NH_3 to the corresponding *aminostilbenecarboxylic acid*, m.p. 140—141°. Ring-closure is effected by treatment with $NaNO_2$ and H_2SO_4 in MeOH–H_2O and subsequently with Cu powder to a mixture of 3:4:6-*trimethoxy*-7-*ethoxyphenanthrene*-9-*carboxylic acid* (IV), m.p. 223—224°, and 3:4:6-*trimethoxy*-5-*ethoxyphenanthrene*-9-*carboxylic acid* (V), m.p. 203—206°. (IV) is decarboxylated to 3:4:6-*trimethoxy*-7-*ethoxyphenanthrene*, m.p. 114—116°, identical with (III); the position of the substituents follows from the production of the compound from the two sources. The structure A is assigned to laurotetanine. 3:4:6-*Trimethoxy*-5-*ethoxyphenanthrene*, m.p. 130—132°, is obtained by decarboxylation of (V).



A.

Vanillin Et ether, hippuric acid, NaOAc, and Ac_2O give the *azlactone* $C_{19}H_{17}O_4N$, m.p. 159—160°, transformed into 5-methoxy-4-ethoxyphenylacetic acid (VI), m.p. 118·5—119° (Barger, m.p. 183—185°). (VI) and 2-nitroveratraldehyde give the *nitrostilbenecarboxylic acid*, m.p. 187—188°. The corresponding *aminostilbenecarboxylic acid*, m.p. 122—124°, is converted into 3:4:7-*trimethoxy*-6-*ethoxyphenanthrene*-9-*carboxylic acid*, m.p. 164—165° (vac.) (whence 3:4:7-*trimethoxy*-6-*ethoxyphenanthrene*, m.p. 120—120·5°), and 3:4:5-*trimethoxy*-6-*ethoxyphenanthrene*-9-*carboxylic acid*, m.p. 218—219°. H. W.

Phenyl- and diphenyl-arsine. F. F. Blicke and L. D. Powers (J. Amer. Chem. Soc., 1933, **55**, 1161—1167).—AsH_2Ph (I) (in PhBr) absorbs (rapidly at first and then more slowly) approx. 1 mol. equiv. of O_2. (I) and S in C_6H_6 give PhAsS and H_2S. (I) (2 mol. equivs.) and I (4 mol. equivs.) in Et_2O react instantly to give a quant. yield of AsI_2Ph; with 2 mol. equivs. of I, $(\cdot AsPh)_n$ results, whilst 3 mol. equivs. affords $(\cdot AsIPh)_2$. Equimol. amounts of (I) and $AsCl_2Ph_3$ react thus: $2AsH_2Ph+2AsCl_2Ph_3 \longrightarrow 2AsPh_3+(\cdot AsPh)_2+4HCl$. $AsHPh_2$ (II) (in PhBr) absorbs O_2 (approx. 2 mol. equivs.) as rapidly as CPh_3 or $(\cdot AsPh_2)_2$; Ph_2AsO_2H is isolated in 93% yield. (II) (1 mol.) and I (1 mol.) give $AsIPh_2$, but with 0·5 mol. of I, $(\cdot AsPh_2)_2$ results. Tetraphenylarsyl oxide or sulphide and (II) in EtOH afford $(\cdot AsPh_2)_2$, whilst (II) and OEt·AsClPh give $AsClPh_2$, $(\cdot AsPh)_2$, and EtOH. CPh_3Br and (II) yield $AsBrPh_2$ and

$CHPh_3$, whilst $(\cdot AsPh_2)_2$ and $CHPh_3$ are obtained from (II) and CPh_3. (II) and $AsCl_2Ph_3$ react thus: (*a*) $2AsHPh_2 + AsCl_2Ph_3 \longrightarrow AsPh_3 + (\cdot AsPh_2)_2 + 2HCl$; (*b*) $AsHPh_2 + AsCl_2Ph_3 \longrightarrow AsPh_3 + AsClPh_2 + HCl$. The following reactions occur between (II) and $OH\cdot AsClPh_3$: $4AsHPh_2 + 4OH\cdot AsClPh_3 \longrightarrow 4AsPh_3 + (\cdot AsPh_2)_2O + 2AsClPh_2 + 3H_2O + 2HCl$; $4AsHPh_2 + 2OH\cdot AsClPh_3 \longrightarrow 2AsPh_3 + 2(\cdot AsPh_2)_2 + 2HCl + 2H_2O$. H. B.

Diarsyls. V. Reactions of tetraphenyldiarsyl. F. F. Blicke, R. A. Patelski, and L. D. Powers (J. Amer. Chem. Soc., 1933, **55**, 1158—1161).—$(\cdot AsPh_2)_2$ (I) and S in CS_2–C_6H_6 (all experiments are carried out in N_2) give tetraphenylarsyl sulphide; with sulphur chloride or $SOCl_2$ in C_6H_6, $AsClPh_2$ results. (I) is converted by CNBr and MgPhBr into $AsBrPh_2$ and $AsPh_3$, respectively, and by PCl_3 into $AsClPh_2$. (I) and $AsCl_3$ give $AsClPh_2$ and As in almost quant. yield, whilst (I) and AsPhCl·OH afford $AsClPh_2$ and AsPhO. Successive treatment of (I) with liquid Na–K alloy and PhBr gives $AsPh_3$. (I) does not react with $(CH_2)_2O$ or with AcCl, BzCl, CCl_2Ph_2, 2 : 4-dinitrobromobenzene, or dichlorotetraphenylethane in cold C_6H_6. (I) is unaffected by cold HHal or alkali. H. B.

Intensely coloured products of the reduction of dihydrophenarsazine derivatives. G. A. Razuvaiev and V. S. Malinovski (Ber., 1933, **66**, [*B*], 463—466).—Reduction of dihydrophenarsazine oxide (I) by HCO_2H at 25°, 35°, and 50° is a reaction of the first order during the initial 50—60% of its course. Treatment of the resulting solution with H_2O or KOH yields a yellow *oxide*, $C_{24}H_{20}ON_2As_2$, moderately stable in air when dry, sol. in acid to coloured solutions which absorb O and immediately add halogen. The very ready oxidation of (I) with I (6 equivs.) and H_2O to phenarsazinic acid is not in harmony with the constitution $(NHPh\cdot C_6H_4As)_2O$. H. W.

Interconversion of arylmercuric halides and mercury diaryls. I. F. C. Whitmore and R. J. Sobatzki (J. Amer. Chem. Soc., 1933, **55**, 1128—1135).—The following aryl-mercuric iodides are converted into Hg diaryls by boiling with an excess of EtOH–NaI: *o*-, *m*-, and *p*-tolyl-, *m*-xylyl-, mesityl-, and α- and β-naphthyl-. HgPhI is unaffected (probably owing to its relative insolubility in EtOH), benzyl- and *cyclo*hexyl-mercuric iodides are decomposed, p-$C_6H_4Et\cdot HgI$ gives some $Hg(C_6H_4Et)_2$, and *p*-cymylmercuric chloride is converted into Hg di-*p*-cymyl. The effects of solubility of the halides in EtOH, relative concn. of NaI, amount of EtOH, and time of heating are studied. An iodometric method for the determination of mixtures of HgArI and $HgAr_2$ is described. The following appear to be new: *Hg* o-*tolyl bromide*, m.p. 169·5°, and *iodide*, m.p. 176°; *Hg* p-*ethylphenyl chloride*, m.p. 221°, *bromide*, m.p. 227—228°, and *iodide*, m.p. 229°; *Hg phenylethyl iodide*, m.p. 154°; *Hg di*-p-*ethylphenyl*, m.p. 136·5°. H. B.

Yields of organolithium compounds by the improved procedure. H. Gilman, E. A. Zoellner, and W. M. Selby (J. Amer. Chem. Soc., 1933, **55**, 1252—1257).—The yields of organolithium compounds from 20 alkyl and aryl halides, using conditions (cf. A., 1932, 728) essentially those for the prep. of Grignard reagents, are determined. Various factors are discussed. H. B.

Distibyls. II. Tetra-*p*-bromophenyl- and -*p*-tolyl-distibyls. Di-α-naphthyliodostibine. F. F. Blicke and U. O. Oakdale (J. Amer. Chem. Soc., 1933, **55**, 1198—1201).—p-*Bromophenyldichlorostibine*, m.p. 90—92° (from p-$C_6H_4Br\cdot SbO_3H_2$, aq. HCl, and SO_2), is converted into p-$C_6H_4Br\cdot SbO$ (I) and thence into p-*bromophenyldi-iodostibine*, m.p. 124—125°. (I) heated at 145° in N_2 gives tetra-*p*-bromophenylstibyl oxide, converted by AcOH into the corresponding acetate, m.p. 134—135°, and thence (by HI–AcOH) into *di*-p-*bromophenyliodostibine*, m.p. 73—74°. This is reduced (NaH_2PO_2) to *tetra*-p-*bromophenyldistibyl* (II), m.p. 211—213° (sealed tube; in N_2). *p*-Tolyldichlorostibine is similarly converted by way of p-$C_6H_4Me\cdot SbO$, *tetra*-p-*tolylstibyl oxide*, m.p. 101°, *di*-p-*tolylstibyl acetate*, m.p. 122—123°, and *di*-p-*tolyliodostibine*, m.p. 76—78°, into *tetra*-p-*tolyldistibyl* (III), m.p. 155—157° (sealed tube; in N_2). (II) and (III) possess properties similar to those of $(\cdot SbPh_2)_2$ (A., 1931, 637) and the corresponding diarsyls. *Di*-α-*naphthyliodostibine*, m.p. 136—137°, is prepared in small yield from α-*naphthyldichlorostibine*, m.p. 105—106°. A method for the determination of Sb is described. H. B.

Reactions of tin tetra-*p*-tolyl. R. W. Bost and H. R. Baker (J. Amer. Chem. Soc., 1933, **55**, 1112—1113).—Sn tetra-*p*-tolyl (I) reacts with $Cl(Br,I)$ in $CHCl_3$ to give p-$C_6H_4MeCl(Br,I)$, with conc. HNO_3 to form p-$C_6H_4Me\cdot NO_2$, and with conc. H_2SO_4 to give PhMe. (I) and S (3 equivs.) at 170° give di-*p*-tolyl disulphide; with 5 equivs. at 190°, 3 : 7-dimethylthianthrene results. (I) does not react with EtBr or Pr^sBr; with $Bu^\gamma Br$, HBr, *iso*butene, and a little PhMe are formed. (I) and BzCl afford 5% of p-$C_6H_4Me\cdot COPh$; with $PhSO_2Cl$ at 200°, 84·3% of p-$C_6H_4Me\cdot SO_2Ph$ results. H. B.

Theory of the polymerisation of caseinogen. M. Beau (Lait, 1933, **13**, 325—330).—A further discussion of a theory concerning the change: caseinogen ⟶ paracaseinogen. The work of Palmer and Richardson (A., 1926, 905) is discussed. E. B. H.

Fractionation of caseinogen by ammonium chloride. E. Cherbuliez and M. L. Schneider (Lait, 1933, **13**, 264—277).—By treatment with aq. NH_4Cl, caseinogen gave two fractions, α (80—90%; insol.) and β (sol. in the salt solution). α had approx. the properties of caseinogen; β differed from caseinogen in S and P content, and in coagulability by rennin. E. B. H.

Chemistry of integument. V. Colour reaction for hydroxyproline and its use in distinguishing the scleroproteins. W. Morse (J. Biol. Chem., 1933, **100**, 373—377).—A colour test for hydroxyproline (I) consists in heating the sample [containing approx. 1 mg. of (I)] with 3 drops of a *sec.*-alcohol (*e.g.*, methylhexylcarbinol), a few drops of H_2O, and 0·5 g. of Na_2O_2 (free from Na_2CO_3), nearly to dryness, cooling, adding 2 c.c. of 5*N*-HCl, and heating to 100°, when an amber-rose colour

develops. Owing to the high content of (I) in collagen this test serves to distinguish the latter from associated scleroproteins. The results obtained using various alcohols and substrate materials are recorded. J. W. B.

Modification of the Backlin–Kirk combustion chamber for micro-determination of carbon and lipins. W. L. DOYLE (Science, 1933, 77, 173). L. S. T.

Kjeldahl method. I. Mercuric oxide as a catalyst when block tin condensers are used. II. Comparison of selenium with mercury and with copper catalysts. R. A. OSBORN and A. KRASNITZ (J. Assoc. Offic. Agric. Chem., 1933, 16, 107—110; 110—113).—I. The high vals. obtained when HgO is used as catalyst with block Sn condensers are due, not to Hg amalgam in the condensers, but to the acid requirements of 200—250 c.c. H_2O to shift the p_H to that responded to by Na alizarinsulphonate.

II. Se and $SeOCl_2$ have slight advantages over $CuSO_4$ as a catalyst but not over HgO. Pptd. Se is better than $SeOCl_2$. A mixture of Se with HgO or $CuSO_4$ has advantages over any of these catalysts used alone, Se with HgO being the best combination. J. W. S.

Thompson–Oakdale method for determination of halogen in organic compounds. J. J. THOMPSON and U. O. OAKDALE (J. Amer. Chem. Soc., 1933, 55, 1292).—The alkaline solution obtained in the original method (A., 1930, 799) should be oxidised with H_2O_2 (to convert Na_2SO_3 into Na_2SO_4). $K_2S_2O_8$ free from $KClO_4$ must be used. H. B.

Determination of minute amounts of mercury in organic material. A. STOCK, F. CUCUEL, and H. KOHLE (Angew. Chem., 1933, 46, 187—191).—Pre-treatment of the material with HNO_3 in bomb, Cl_2, $KClO_3$–HCl, NaOCl followed by $KClO_3$–HCl, H_2SO_4–$K_2S_2O_8$, H_2SO_4–$KMnO_4$, H_2SO_4–HNO_3, or HNO_3–H_2O_2 is examined. Use of $KClO_3$–HCl usually permits the determination of minute amounts of Hg within a few %. If higher accuracy is desired, HNO_3–H_2O_2 is used; allowance must be made for Hg in the reagents and for that volatilised with N oxides. Fats are burnt in a lamp, the volatile products being condensed by liquid air and Hg determined in condensate after treatment with Cl_2-H_2O. The examination of urine and fæces is described in detail. H. W.

Detection of organic compounds. X. L. ROSENTHALER (Pharm. Ztg., 1933, 78, 229—231).—The physical and chemical properties of *p*-chloro-*m*-cresol, chloroxylenol, chlorothymol, "pyridium," "isacene" [di-(*p*-acetoxyphenyl)isatin], "sedormide" (CH_2:CH·CH_2·$CHPr^{\beta}$·CO·NH·CO·NH_2), "avertine" (CBr_3·CH_2·OH), Na "arsylene" (CH_2:CH·CH_2·AsO_3Na_2), "sulpho-mesarca" (Na 3:3′-diamino-4:4′-dihydroxyarsenobenzene-*N*-methylene-sulphonate), thyroxine, 3:5-di-iodo-*l*-tyrosine, and acetylcholine are summarised. J. W. B.

Volumetric determination of cholesterol. I. In pure solution. F. RAPPAPORT and R. KLAPHOLZ (Biochem. Z., 1933, 258, 467—470).—The cholesterol is pptd. by a known excess of digitonin and the excess in the filtrate determined from the content of hexose after hydrolysis with dil. H_2SO_4. P. W. C.

New method of dye analysis. A. GOLD and A. E. STEARN (Stain Tech., 1933, 8, 53—59).—Positive and negative dye ions are titrated with one another conductometrically; the vals. obtained are reproducible to approx. 1%. H. W. D.

Biochemistry.

(*a*) **Parallel determination of the respiratory quotient and alveolar air of man in the post-adsorptive condition.** (*b*) **Effect of glucose and of fructose on the human respiratory quotient and alveolar air.** T. M. CARPENTER and R. C. LEE (J. Nutrition, 1933, 6, 37—53, 55—82).—(*a*) Suitable apparatus is described.

(*b*) Observations on two subjects are recorded. A. G. P.

Effect of cyanide and of variation in alkalinity on the oxidation-reduction potential of the hæmoglobin–methæmoglobin system. R. D. BARNARD (J. Gen. Physiol., 1933, 16, 657—675).—Both CN′ and OH′ reduce the oxidation activity of methæmoglobin (I), combination occurring with the Fe of (I) leading to the formation of undissociated $Fe^{'''}$ compounds, cyanomethæmoglobin, and alkaline (I). Electronic formulæ for the prosthetic nucleus of derivatives of (I) are suggested. F. O. H.

Bicolorimetric determination of methæmoglobin. B. B. CLARK and R. B. GIBSON (J. Biol. Chem., 1933, 100, 205—208).—An accurate bicolorimetric method depending on the comparison of the sample saturated with CO with a methæmoglobin standard prepared from the dil. blood with $K_3Fe(CN)_6$, both in the presence of a carboxy-hæmoglobin standard prepared from the dil. blood with NaHS and CO, is described. A. L.

Hæmoglobin concentration of normal English males and females. C. E. JENKINS and C. S. D. DON (J. Hyg., 1933, 33, 36—41).—The mean val. for males was about 115% and for females 100% (Haldane's scale). NUTR. ABS.

Solubility coefficient of ethyl chloride and hæmatoporphyrin. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1932, 108, 1201—1203; Chem. Zentr., 1932, ii, 3575).—The solubility of $CHCl_3$, Et_2O, and EtCl in liquids which contain hæmoglobin, hæmochromogen, or hæmatin, but not in those containing hæmatoporphyrin, is > in the absence of these substances. A. A. E.

Blood analyses of normal Bronze turkeys. H. M. SCOTT, P. J. SERFONTEIN, and D. H. SIELING (Poultry Sci., 1933, 12, 17—19).—Individual variation within a sex was slight. The male turkey blood differed from the female only in having higher uric acid and hæmoglobin. Turkey blood resembled

chicken blood, but contained more urea-N. In chickens the sex difference in uric acid was absent, but the sex difference in hæmoglobin was more marked. NUTR. ABS.

Determination of blood-catalase. H. J. JUSATZ (Klin. Woch., 1932, **11**, 1188—1190; Chem. Zentr., 1932, ii, 2475).—Blood (0·05 c.c.) is added to H_2O (50 c.c.) and of this 5 c.c. is treated with 15 c.c. of 1% H_2O_2 in a suitable apparatus (described), the vol. of gas liberated in 2 hr. being determined. This catalase val. divided by the no. of erythrocytes gives the catalase index. A. A. E.

Alleged transformation of serum-albumin into serum-globulins. S. B. HOOKER and W. C. BOYD (J. Biol. Chem., 1933, **100**, 187—194; cf. this vol., 175).—Heparin–serum-albumin compounds behave immunologically like unaltered albumin and not like globulin. A. L.

Dependence of the structure of blood-serum-proteins on metabolic processes. E. G. SCHENCK and H. K. KUNSTMANN (Z. physiol. Chem., 1933, **215**, 87—92).—The constitution of the blood-serum-proteins varied in the individual even when an attempt was made to standardise the metabolic changes in the tissue. J. H. B.

Carotene in horse serum. R. NETTER (Compt. rend. Soc. Biol., 1933, **112**, 165—167).—The yellow pigment of horse serum is probably bilirubin, and not carotene. NUTR. ABS.

Relation between sugar and cholesterol in the blood. Influence of insulin, adrenaline, pituitrin, thyroid gland, male genital glands, ovarian function, bile acid salts, glucose, phloridzin, and cholesterol on the amounts of sugar and cholesterol in the blood. S. KUSAKA (Japan. J. Gastroenterol., 1932, **4**, 132—138, 139—147, 148—152, 190—195, 196—201, 202—208).—Normal rabbit's blood contained sugar (Hagedorn–Jensen) 0·089—0·107 g., total cholesterol (Bloor) 0·114—0·182 g. and free cholesterol (I) 0·089—0·169 g. per 100 c.c. Injection of insulin decreases (I) > the cholesteryl esters (II). Adrenaline and pituitrin increase (I) and decrease (II). Thyroid extract decreases blood-sugar (III) and (I)+(II), but increases (II); it diminishes only the cholesterol in thyroidectomised rabbits. Normally after thyroidectomy (II) increases; (I) is low at first and gradually increases. A saline extract of ox testes diminishes (I)+(II) by 16—34% in rabbits, but (I) by 19—36%. Castration does not alter (III), but temporarily increases (II). A saline extract of ovarian interstitium decreases (III) and (I)+(II) in normal and castrated rabbits. In normal animals (II) increases and (I) is diminished; in castrates (II) is unchanged. An extract of the lutein bodies increases (III) without affecting the cholesterol. Ovariectomy increases (I)+(II) but decreases (II); (III) is unchanged. 1% Na glycocholate, taurocholate, cholate, or dihydroxycholate (40 c.c., ingested) lowers (III) by 10—19% and (I)+(II) by 18—30%; change in (II) is slight. 25% glucose solution (0·5 c.c., intravenous) diminishes (I)+(II) of rabbits by 11—31%, and (II) by 25%. Phloridzin diabetes does not change the blood-cholesterol. Feeding cholesterol may produce hyperglycæmia some days after max. hypercholesterolæmia. CH. ABS.

Saccharoid fraction of human blood. G. J. FASHENA (J. Biol. Chem., 1933, **100**, 357—363).—The glutathione (I) and saccharoid contents of deproteinised blood filtrates were determined, showing that only 37% of the total reducing power of the blood filtrate can be accounted for by (I). The latter may be pptd. by concentrating a portion of the fermented blood filtrate, adding an equal vol. of 7% $HgCl_2$, and centrifuging. H. D.

Nature of blood-sugar. I. I. NITZESCU and E. MACOVSKI (J. Physiol. Path. gen., 1932, **30**, 873—879).—Creatinine did not alter the rotatory power of glucose in aq. solution. No change in rotation took place when glucose was added to serum *in vitro* even in presence of insulin. It is suggested that insulin reacts with living tissues yielding a substance which forms a complex with glucose *in vivo*. NUTR. ABS.

Apparent and true sugar of the blood of lactating cows fed on rations of varying fat content. K. L. TURK and S. H. WORK (J. Dairy Sci., 1933, **16**, 33—39).—Substitution of part or approx. all of the fat of a grain ration by an isodynamic quantity of starch did not affect the apparent or true sugar contents of the whole blood or plasma. A. G. P.

Determination of blood-sugar. H. BIERRY, B. GOUZON, and C. MAGNAN (Compt. rend., 1933, **196**, 862—864).—Aldoses in blood are determined by deproteinising with $Hg(NO_3)_2$ and Na_2CO_3 (to p_H 6·5), removing excess Hg by Cu, adding excess of Na_2CO_3 and I, and titrating the excess I. The results agree with those obtained by the Cu method. R. S. C.

Characteristics of ultra-filtrates of plasma. R. C. INGRAHAM, C. LOMBARD, and M. B. VISSCHER (J. Gen. Physiol., 1933, **16**, 637—655).—Plasma (I) ultra-filtered through collodion membranes gives a filtrate (II) such that $[Cl']_{II} > [Cl']_I$ and $[Na^*]_{II} < [Na^*]_I$. Increase of protein-bound base by reducing $[HCO_3']_I$ increases the difference in ionic distribution. These differences, which are probably due to the influence of protein in lowering the activity coeff. of cations when on the alkaline side of the isoelectric point, agree in magnitude with vals. calc. from the Donnan equation. F. O. H.

Regulation of blood-calcium in the dog. A. BAUDOUIN, J. LEWIN, and AZERAD (Compt. rend. Soc. Biol., 1933, **112**, 367—369).—Intravenous injection of 2 c.c. per kg. body-wt. of 25% aq. $Na_2C_2O_4$ was followed by an immediate decrease of blood-Ca, with later recovery towards normal. The blood-P curve did not follow that of the Ca. This fact does not support the view that the recovery of the blood-Ca level is due to mobilisation of bone-Ca, unless the Ca reaches the blood in some form other than phosphate. NUTR. ABS.

Forms of the calcium and inorganic phosphorus in human and animal sera. I. Normal, rachitic, hypercalcæmic, and other conditions. II. Nature and

significance of the filterable, adsorbable calcium–phosphorus complex. H. R. BENJAMIN (J. Biol. Chem., 1933, **100**, 27—55, 57—78).—I. In normal serum, 2/3 of the diffusible Ca consists of an adsorbable Ca–P complex (I) and the remainder contains $Ca^{\cdot\cdot}$ (II); ¼ of non-diffusible Ca is regarded as a second adsorbable complex (III), the remainder being bound to protein (IV). In low-P rickets, there is no change in total Ca, but a diminution in (I) and (III), associated with a diminution in total and adsorbable P, and an increase in (II) and (IV). Other conditions of Ca–P disturbance were examined.

II. Epiphyseal cartilage adsorbs (I) from artificial solutions as well as from serum; this occurs only in the region of calcification and not in resting or non-calcifying cartilage. When (I) is removed, practically no adsorption takes place. In rickets a low concn. of (I) retards adsorption and calcification. H. G. R.

Magnesium content of the plasma and the red corpuscles in human blood. D. M. GREENBERG, S. P. LUCIA, M. A. MACKEY, and E. V. TUFTS (J. Biol. Chem., 1933, **100**, 139—148).—The Mg in the blood of 58 healthy young adults, determined by the 8-hydroxyquinoline method, was as follows: plasma-Mg 2·74±0·30, whole blood-Mg 4·55±0·38, red blood-corpuscle-Mg 6·61±0·53 mg. per 100 c.c. Evidence is given indicating that the Mg content of the corpuscles and that of the plasma are independent. Essentially similar results are obtained using the $MgNH_4PO_4$ method for Mg determination. A. L.

Blood-iodine. I. Determination. C. B. DAVIS and G. M. CURTIS (J. Lab. Clin. Med., 1932, **18**, 24—29).—Blood (10 c.c.) is ashed with KOH, the KI is extracted with EtOH, which is then acidified, and the I is oxidised to HIO_3 with Br. KI is added and the I liberated is titrated with $Na_2S_2O_3$. Blood normally contains 0·012 mg. I per 100 c.c. CH. ABS.

Effect of cations and anions on coagulation of blood. A. FISCHER and A. SCHMITZ (Biochem. Z., 1933, **259**, 61—66).—$Ag^{\cdot}$ cannot replace $Cu^{\cdot\cdot}$ as a coagulant for blood, but it and the ions of other metals, especially heavy metals, counteract the inhibition of coagulation produced by heparin ($Hg^{\cdot\cdot}$ > $Ag^{\cdot}$ > $Cu^{\cdot\cdot}$ > $Cd^{\cdot\cdot}$ > $Mg^{\cdot\cdot}$ > $Pt^{\cdot\cdot}$ > $Zn^{\cdot\cdot}$ > $Co^{\cdot\cdot}$ > $Ca^{\cdot\cdot}$ > $Ba^{\cdot\cdot}$ > $Fe^{\cdot\cdot}$ > $Fe^{\cdot\cdot\cdot}$, Al, Mn). Acid ions (lactate, citrate, tartrate, salicylate, OAc, antimonate, S_2O_3'') react with the groups of thrombin with which heparin also reacts and likewise counteract its effect. W. McC.

Blood coagulation. A. FISCHER and A. SCHMITZ (Biochem. Z., 1933, **259**, 67—75).—The rate (I) of coagulation of blood is directly proportional to the concn. of thrombin (II), and when heparin (III) is present the logarithm of (I) is inversely proportional to the concn. of (III), (I) depending on the free electric charge on the ion of (II). W. McC.

Action of heparin on serum-albumin. A. SCHMITZ and A. FISCHER (Biochem. Z., 1933, **259**, 53—60; cf. A., 1932, 413, 870).—Heparin (I) does not affect the pptn. of serum-albumin (II) by $(NH_4)_2SO_4$, but displaces the isoelectric point to the acid side and causes flocculation at this point. When (I) is added to solutions of (II) a membrane potential is developed. W. McC.

Blood-coagulation. I. Inhibitory substance from kidney. O. KASHIWAMURA (J. Biochem. Japan, 1933, **17**, 117—130).—Animal and yeast nucleic acids have a slight inhibitory action on blood-coagulation (I). The extraction of $COMe_2$-dried kidney powder by 1% aq. NaCl in presence of NH_3, followed by pptn. of the extract by HCl and treatment of the ppt. with MeOH, $COMe_2$, etc., yields a substance (II) which strongly inhibits (I). (II) is free from nucleic acid, but, like heparin (A., 1928, 318), contains glycuronic acid, the content of which, however, is not proportional to the activity of the prep. in inhibiting (I). F. O. H.

Physico-chemical properties of isohæmo-agglutinogens. V. SCHRÖDER (Z. Immunität., 1932, **75**, 77—99; Chem. Zentr., 1932, ii, 3573).—The group-sp. receptors A, B, AB, and O are thermostable and undecomposed by ultra-violet light. They are of lipin–lecithin nature, with isoelectric point at p_H 2·7. They are differentiated by the I vals. of the fatty acids in the lipin mol. The group-sp. receptors A and B are differently adsorbed by C. A. A. E.

Analyses of egg-shell keratin. H. O. CALVERY (J. Biol. Chem., 1933, **100**, 183—186).—Egg-shell keratin obtained by treatment of the shells with HCl and pepsin contained ash 0·05, H_2O 8·60, N 16·57, S 3·78, tyrosine 2·54, proline 3·83, glutamic acid 10·11, aspartic acid 3·38, tryptophan 2·61, cystine 12·67, arginine 8·88, histidine 0·86, lysine 3·66%. A. L.

Ovoflavin, the pigment of white of egg. R. KUHN, P. GYÖRGY, and T. WAGNER-JAUREGG (Ber., 1933, **66**, [*B*], 576—580).—Dry ovalbumin is extracted with MeOH and, after acidification, the pigment is adsorbed by fuller's earth which is eluted with dil. C_5H_5N. Adsorption is repeated in neutral solution. The pigment is purified through the *Ag* salt, which is decomposed by H_2S. *Ovoflavin*, crystallised from 2*N*-AcOH, decomposes at 265° (Berl) after darkening at 240°. The composition is not certainly established. In presence of Pd it absorbs $1H_2$ per $C_{16}H_{20}O_6N_4$, but $3H_2$ in presence of PtO_2. In absorption spectrum it resembles closely the pigment obtained by Warburg and Christian from yeast. It does not contain a free CO_2H or a readily-eliminated NH_2. It is very sensitive to alkali, stable towards conc. HNO_3, H_2O_2, or $NaNO_2$+AcOH. The colour of alkaline solutions is discharged by Zn dust or $Na_2S_2O_4$, but is restored by air. Purified ovoflavin solutions contain a component of vitamin-B_2 which is not homogeneous. H. W.

Osmotic relationships in the hen's egg. J. M. JOHLIN (J. Gen. Physiol., 1933, **16**, 605—613).—A method for the accurate determination of the f.p. of a viscous fluid such as egg-yolk (I) is described. F.-p. vals. for (I) markedly differ from those for the white (II) of both fertile and unfertile eggs (cf. A., 1932, 1153). On mixing (I) and (II), osmotic equilibrium is but slowly attained. Hence the postulation of a vital activity at the yolk membrane appears unnecessary. F. O. H.

F.p. of yolk and white of egg. H. P. HALE and W. HARDY (Proc. Roy. Soc., 1933, **B**, **112**, 473—479).—The f.p. of yolk is −0·57°, and of thin and thick white −0·42°. The cause of lag in freezing the intact yolk is discussed. A. C.

Ultra-filtration. II. "Bound" water (hydration) of biological colloids. D. M. GREENBERG and M. M. GREENBERG (J. Gen. Physiol., 1933, **16**, 559—569).—Various crystalloid substances (I) were added to aq. colloidal systems (gelatin, caseinogen, serum, starch, pectin, glycogen), the mixture was ultra-filtered, and the concn. of (I) in the ultra-filtrate determined. Assuming that "bound" H_2O has lost its normal solvent properties, the results indicated that only a small part of the H_2O was present in this form. F. O. H.

Oil from the glands of the musk-rat. W. H. SIMMONS and C. A. HILLS (Analyst, 1933, **58**, 154).—The glands contain 50—54% of oil, acid val. 80·6, sap. val. 145·9, I val. 136·9, unsaponifiable matter (I) 22·8%, and insol. fatty acids 70·0%. (I) gave 44·5% sol. and 55·5% insol. in 90% EtOH (I vals. 122 and 333, respectively). Other consts. are given. T. McL.

Fœtal fat. I. Influence of high- and low-fat diets on the quality of fat formed in the rat's fœtus. I. L. CHAIKOFF and A. ROBINSON (J. Biol. Chem., 1933, **100**, 13—26).—Fœtal fat is dependent on the degree of unsaturation of the food or maternal fat for I val. between 36·3 and 145. From mothers on low-fat diets, I val. averaged 73·3, variation in protein and carbohydrate having no effect. H. G. R.

Unsaponifiable lipins of ox liver. I. Methods of separation; crystalline fractions. II. Vitamins-*A* and -*E*; anti-oxygens. F. C. FREYTAG and H. G. SMITH (J. Biol. Chem., 1933, **100**, 309—317, 319—322).—I. The unsaponifiable lipins were fractionated by recrystallisation from MeOH, light petroleum (I), $COMe_2$, and EtOAc. Sterols constituted 62% of the total lipins. All the sterol fractions contained traces of ergosterol. Bromination and pptn. by digitonin of the later fractions gave a compound, m.p. 141·5° (dihydrocholesterol?). From the non-sterol fraction lignocerylsphingosine was obtained by recrystallising from (I).

II. The liquid fractions contain vitamin-*A* and one of them vitamin-*E*; the former may be conc. by extraction with MeOH. By vac. distillation vitamin-*A* is conc. in the lower-boiling fractions, but with destruction of as much as 4/5 of the active material. Traces of anti-oxygen material were present which were not conc. by vac. distillation. H. D.

Relationship between liver lyochrome and catalase. K. G. STERN (Ber., 1933, **66**, [*B*], 555—559).—Lyochrome and catalase of liver are different substances. H. W.

Lipin substances of the adrenals. I. Method of treatment of the adrenals and elucidation of the fatty portion. C. COESTER (Z. physiol. Chem., 1933, **215**, 207—214).—The Et_2O extract of the dried adrenal contains a tristearate in larger amounts than other organs. Lecithin, kephalin, and mixtures of cerebroside- and sphingomyelin-like substances are present. J. H. B.

Phosphatide content of skin. B. REWALD and A. SCHWIEGER (Biochem. Z., 1933, **259**, 180—181; cf. Nerking, A., 1908, ii, 608).—The phosphatide content (I) of the skin of freshly-killed animals (calf, cow, pig, sheep) does not differ appreciably from that of other organs. In the calf (I) is about double what it is in the cow. W. McC.

Glutathione of tissue. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1933, **215**, 151—163).—Oxidised glutathione was absent from all normal body tissues examined (except blood). Glutathione therefore does not participate in the reversible oxido-reduction processes. Since the higher I val. obtained after deproteinisation with tungstic or sulphosalicylic acid is not due to reduction of ·S·S·, the method is untrustworthy, and a colorimetric method using the nitroprusside reaction is more accurate. The hypothesis of Waldschmidt-Leitz that the increase of cathepsin activation of isolated tissue on keeping is due to increase of ·SH content of the tissue, and that the increased activation in tumours is related to a glutathione increase, could not be confirmed. J. H. B.

Reaction of tissues with alloxan. F. LIEBEN and E. EDEL (Biochem. Z., 1933, **259**, 8—10; cf. A., 1932, 410).—Air acts without oxidising on the SH group (glutathione) of tissue, eventually inhibiting the reaction with alloxan, but the reaction between the latter and NH_2-acids is not so affected. The content of reduced glutathione of lung is ≮ that of other organs. W. McC.

Total carbohydrate and glycogen content of mammalian muscle. C. F. CORI and G. T. CORI (J. Biol. Chem., 1933, **100**, 323—332).—The gastrocnemii of rats and rabbits were hydrolysed in *N*-H_2SO_4 and the total fermentable carbohydrate (I) was determined by pptn. of proteins with $HgSO_4$, and analysis of the reducing powers of the filtrate before and after fermentation. Glycogen (II) was determined as glucose after hydrolysis for 3 hr. in *N*-H_2SO_4 by the Shaffer-Hartmann method. In contrast to the findings of Bischoff and Long (A., 1932, 546) no difference between the contents in (I) or (II) was found. H. D.

Occurrence of labile phosphorus in fish-muscle. J. C. KERNOT and N. E. SPEER (Z. physiol. Chem., 1933, **215**, 1—7).—Labile P compounds are present in the muscle tissue of *Teleostei*. The presence of a labile P compound only slowly hydrolysed by the Mo reagent of Fiske and Subbarow is indicated. J. H. B.

Distribution of iodine in central nervous system of men and animals. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1933, **86**, 290—293).—The I contents of various portions of the nervous system of man, various mammals, and birds are recorded. Where the thyroid gland was functioning normally the I content was highest in the mid-brain. NUTR. ABS.

Distribution of iodine in central nervous system of thyroidless animals. A. SCHITTENHELM

and B. EISLER (Z. ges. exp. Med., 1933, **86**, 294—298).—Removal of the thyroid in dogs and rabbits reduced the I content of the mid-brain to very small amounts. Administration of thyroxine to thyroidectomised animals led to an increase in the I of mid-brain to a normal, and, if excessive doses of thyroid were given, to a supernormal, val. NUTR. ABS.

Potassium, its micro-determination, fixation, and distribution [in tissues etc.]. A. LEULIER (Bull. Soc. Chim. biol., 1933, **15**, 158—202).—A lecture.

Determination of connective tissue substance (collagen) in organs. G. HOPPE-SEYLER and K. LANG (Z. physiol. Chem., 1933, **215**, 193—195).—An improved method is described. J. H. B.

Digestive enzymes of the silk-worm (*Bombyx mori*, L.). K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1932, **8**, 156—159).—There is no difference in the protease activity of the digestive juice of different species at p_H 10·74 and 30°. China-7-*D* had the highest amylase content of those investigated. The invertase of all species exhibits optimal activity at p_H 9·5 and 45°; it is destroyed by heating at 70° for 1 hr. P. G. M.

Experimental studies on ticks. R. HOEPPLI and L. C. FENG (Chinese Med. J., 1933, **47**, 29—43).—Emulsions of the salivary glands of male specimens of *Dermacentor sinicus* and *Hyalomma detritum peretrigatum* contain a powerful anticoagulin for rabbits' blood *in vitro*. Subcutaneous injection of emulsions of the eggs of three species of tick does not produce symptoms of tick paralysis in animals. P. G. M.

Fast-green [as a stain]. L. A. MARGOLENA (Stain Tech., 1933, **8**, 73).—Fast-green is a good counterstain for hæmatoxylin, for Feulgen's reaction, and for differentiating safranin, lignin, and chromatin. H. W. D.

Carbon and nitrogen in blood-filtrate and cerebrospinal fluid. J. CLAUDATUS (Z. physiol. Chem., 1933, **215**, 10—14).—The total C in cerebrospinal fluid in mental cases is 82·5—135 mg. per 100 c.c. (normal val. 102); the total N, 18·4—28·7 mg.; residual N, 11·6—18·6 mg. The residual N in the fluid increases with that of the blood; the ratio of blood/fluid residual N falls with increase in the fluid val. (2·46—1·63). J. H. B.

Protein content and normal flow of lymph from the foot of the dog. J. C. WHITE, M. E. FIELD, and C. K. DRINKER (Amer. J. Physiol., 1933, **103**, 34—44).—The protein content varied from 0·5% to 1·52% during exercise; during rest it increased to 2·12%. NUTR. ABS.

Potassium content of aqueous humour and plasma. C. E. RAIHÄ (Skand. Arch. Physiol., 1933, **65**, 276—286).—Intravenous injection of KCl increases the K content of both plasma (I) and aq. humour (II). In both (I) and (II) the K content is unaffected by acidosis. In acidosis, intravenous injection of KCl does not increase the K in (II). Acidosis therefore impedes passage of K from (I) to (II). In alkalosis the K of both (I) and (II) is diminished. With a decreasing acidosis K diminishes in (I) and increases in (II). The action of insulin resembles that of alkalosis, and of adrenaline that of acidosis. NUTR. ABS.

Appearance of cations in the stomach. S. KAYA (Japan. J. Gastroenterol., 1932, **4**, 128—131).—The rabbit's stomach, flushed with glucose solution, contains Ca : Mg : K : Na=1·4 : 1 : 2·7 : 35. Intravenous injection of any one increases its concn. in the gastric juice. CH. ABS.

Fate of dehydrocholic acid in the dog. S. SHIBUYA (J. Biochem. Japan, 1933, **17**, 159—162).—In dogs with biliary fistulæ the feeding of 25 g. of Na dehydrocholate was followed by the appearance of approx. 20% of the acid in the bile. Taurocholic and palmitic acids were also isolated. F. O. H.

Affinity of bilirubin for erythrocytes. I—II. Inhibitory effects. III. Affinity for erythrocytes of various animals, and of jaundiced and normal subjects. K. SAKEI and T. MAEDA (Japan. J. Gastroenterol., 1932, **4**, 108—118, 119—127, 255—261).—I. Human erythrocytes absorb bilirubin with increase in vol., the effect being increased by acidity and by rise of temp.

II. The absorption is inhibited by human serum, ovalbumin, and cholates. The first two liberate bilirubin from erythrocytes.

III. The affinity is in the order: rabbit>hen>man>guinea-pig>goat; normal>jaundiced persons. CH. ABS.

Photodynamic hæmolytic action of bilirubin. I—IV. K. SAEKI (Japan. J. Gastroenterol., 1932, **4**, 153—165, 166—174, 231—243, 244—254).—I. Hæmolytic activity has been employed to measure the photodynamic action of bilirubin (I). The action is not due to a secondary decomp. product. Light rays passed through (I) lose their photodynamic action. (I) is active only when exposed to light in presence of erythrocytes (II), and the activity is proportional to the concn. of (I). Biliverdin also has photodynamic activity.

II. The resistance of (II) to hypotonic solutions is diminished when they are mixed with (I) and exposed to light. The photodynamic–hæmolytic action is inhibited as the osmotic pressure of the solution rises. The resistance of (II) diminishes in the order: guinea-pig, man, rabbit, hen, goat.

III. The action is inhibited by sera, serum-albumin, ovalbumin, hæmoglobin, tyrosine, glycine, alanine, and phenylalanine. Only NH_2-acids inhibit the "after-effect" (additional hæmolysis in the dark after exposure to light).

IV. The velocity curves do not resemble those for a unimol. reaction. A latent period is prolonged by sera. CH. ABS.

[Variations in milk composition.] BÜNGER (Landw. Versuchs-Stat., 1933, **115**, 63—72).—The I content of milk from different areas is examined. Vals. for colostrum were invariably high, especially when cows had been dry for relatively long periods. Standard analytical vals. for marketable milk are examined. A. G. P.

Effect of ingestion of glucose on composition of human milk and butter. M. POLONOVSKI

(Compt. rend. Soc. Biol., 1933, **112**, 191—192).—Addition of glucose to the diet of nursing women caused an increased fat content of the milk. The butter contained greatly increased amounts of the volatile fatty acids. NUTR. ABS.

Distribution of fat in milk. H. RAUER (Arch. Tierernahr. Tierzucht, 1932, **8**, 246—289).—With the advance of the lactation period there was an increase in the proportion of "small" fat globules ($< 2\ \mu$) and a decrease in "large" globules ($> 4\ \mu$). The influence on the size distribution of globules of the nature of the ration, the breed of the animal, and of variations in total fat content are recorded. A. G. P.

Butter-fat variations in cow's milk. J. W. G. MACEWAN and V. E. GRAHAM (Sci. Agric., 1933, **13**, 324—340).—Day-to-day variations in the % of fat in milk from individual cows were considerable. In general, the fat content increased during the fourth month of lactation and subsequently declined. There was also a slight decline with advancing age. The first-drawn milk had least fat and the strippings the greatest amount. The solids-not-fat val. was practically const. for the individual cow. Reduced supplies of drinking-H_2O restricted the total yield of milk, but not its fat content. A. G. P.

Ether-soluble urinary acids with varying nutrition. R. KAPELLER-ADLER and E. LAUDA (Biochem. Z., 1933, **258**, 429—448).—The urinary excretion of Et_2O-sol. acids by rabbits on a pure vegetable diet (cabbage, carrots, oats), by dogs on a pure fresh diet, and by normal men on a mixed diet is examined, the total acidity of the extract and its content of formic, oxalic, citric, and hippuric acids being determined. On a vegetable diet, greens increased whilst oats decreased the production of these acids. On a fresh diet, HCO_2H and $H_2C_2O_4$ were increased, hippuric acid was decreased, and only traces of citric acid were obtained. On a mixed diet, all the acids were readily obtained. In each extract an undetermined residual acidity was detected which, although usually small, was very considerable in urine of rabbits receiving carrots. P. W. C.

Detection of lactosuria by the bacterial method of Castellani and Taylor. T. STRANDRING (J. Trop. Med. Hyg., 1932, **35**, 375—377).—Urinary glucose and lactose are distinguished by fermentation reactions in presence of *E. coli* and *S. schotmuelleri*. CH. ABS.

Behaviour of small quantities of urinary sugar with Nylander's reagent. K. FEIST and R. HOFMANN (Pharm. Ztg., 1933, **78**, 312).—Small quantities of sugar in urine (limit 0·05%) may be detected by treatment of the urine with $Pb(OAc)_2$, filtration, pptn. of the Pb by addition of Na_2SO_4, and heating with a small quantity of Nylander's reagent (about 5 drops per 10 c.c.) at 100° for 5—10 min. W. O. K.

Detection and determination of strychnine in urine. O. NOETZEL (Pharm. Zentr., 1933, **74**, 205—211).—Details are given for the determination of 0·05 mg. by a colorimetric method depending on reduction by Zn and HCl and subsequent treatment with $NaNO_2$. P. G. M.

Detection of iodine in urine. H. MATTIS and E. MANDRYSCH (Arch. Pharm., 1933, **271**, 174—177).—I (free or as I′) can be detected in urine in concn. > 1 mg. per litre by addition of HCl, HNO_3, and CS_2, and centrifuging. R. S. C.

Changes in the carbohydrate and gas metabolism of muscle during acidosis. K. KODERA and K. ADACHI (Tohoku J. Exp. Med., 1932, **20**, 178—190).—Acids (0·4*N*-HCl) injected into dogs cause decreased CO_2-binding power in blood and muscle, hyperglycæmia, decreased consumption of sugar and O_2 by muscle, decreased lactic acid in blood and muscle, decreased blood flow, and increased blood pressure. CH. ABS.

Glutamic acid in the treatment of experimental anæmia. T. H. RIDER (J. Biol. Chem., 1933, **100**, 243—248).—A study of the hæmoglobin regeneration in anæmic rats fed on a milk diet with daily supplements free from and containing Na H glutamate, indicates that glutamate has a small accelerating effect only when administered with both Fe and Cu. The metals in this combination probably exist as complex glutamates. A. L.

Anæmia. IV. Colloid-osmotic pressure of the blood in anæmia. V. Thoracic lymph. H. SAITO (Tohoku J. Exp. Med., 1932, **19**, 445—461, 462—478).—IV. Blood-protein and the colloid-osmotic pressure per unit protein are slightly decreased in anæmia. The effects of large and small venesections, and of injection of $NH_2{\cdot}NH_2Ph$ are described.

V. Similar observations on the thoracic lymph of dogs are described. CH. ABS.

Colloid-osmotic pressure of the blood in normal and pathological conditions. VI. Blood and lymph. Effect of lymphagogues of the first and second order. VII. Experimental kidney damage. H. SAITO and F. NAKAZAWA (Tohoku J. Exp. Med., 1932, **19**, 233—251, 252—261).—VI. The colloid-osmotic pressure (I) of the thoracic lymph of normal dogs is (av.) 172 mm. H_2O and 35·2 mm. for 1% lymph protein; per unit protein it is approx. equal to that of blood. Peptone increases (I) of lymph per unit protein, whilst NaCl and glucose decrease it; all decrease that of blood per unit protein.

VII. Experimental kidney damage generally decreases (I) for lymph and blood per unit protein. CH. ABS.

Effect of trypan-blue, thionine, and pyronine on the agglutination titre of cows infected with Bang's disease. E. E. SLATTER and R. GRAHAM (J. Amer. Vet. Med. Assoc., 1933, **35**, 76—78).—No effect was observed. CH. ABS.

Hydrogen-ion concentration of blood in cancer. J. O. ELY (Amer. J. Cancer, 1933, **17**, 58—73).—There was a tendency for the blood-p_H to be above normal in patients with benign and malignant tumours and in 70% of miscellaneous diseases. NUTR. ABS.

Heliotropism of cholesterol in relation to skin cancer. A. H. ROFFO (Amer. J. Cancer, 1933, **17**, 42—57).—The cholesterol content of the skin was highest in those parts which were exposed to light. NUTR. ABS.

Glycolysis in and mitogenetic radiation from blood in experimental carcinoma. A. E. Braunstein and P. A. Heyfetz (Biochem. Z., 1933, **259**, 175—179).—The decrease in the mitogenetic power of blood which results from the development of malignant tumours is not accompanied by decrease in the glycolytic power of the blood. W. McC.

Blood-sugar curves in dry catarrh of the upper respiratory passages to diagnose latent disturbances of carbohydrate metabolism. K. Weinland (Arch. Ohren-, Nasen-, u. Kehlkopfheilk., 1932, **132**, 42—48).

Bronchial disinfection and immunisation. I. Effect in rabbits of intrabronchial injections of disinfectants. J. A. Kolmer (Arch. Int. Med., 1933, **51**, 346—366).—Many chemical disinfectants were studied for bactericidal and spirochæticidal activity, first *in vitro*, and later by intratracheal injection into rabbits. Their toxicities in rabbits are given. A no. of the disinfectants tested, including dyes, Ag-protein, chloramine-*T*, hexylresorcinol, and org. As and Hg compounds, are suggested for use, with suitable concns. R. N. C.

Non-glucose reducing substances in diabetic blood. R. J. Pickard and F. W. Godwin (J. Lab. Clin. Med., 1932, **18**, 3—6).—The concn. of substances which produce *Y*-reduction is increased in diabetes; sugar *X* is normal. Ch. Abs.

Consequences of total extirpation of the pancreas in dogs. H. Mischnat (Arch. exp. Path. Pharm., 1933, **170**, 94—110).—Following pancreatectomy (I) in 5 dogs, the body-wt. decreased steadily, but at a rate different with each dog. Polydipsia and polyuria were absent, whilst polyphagia occurred in one dog. Hyperlipæmia and fatty infiltration of the liver did not occur, whilst the degree of ketonuria was not significant. The liver-glycogen (II) decreased by only a relatively small amount, whilst a glycogen–fat antagonism was observable. A low (II) was associated with hyperglycæmia and glycosuria. Differences between the syndrome of (I) in dogs and that of diabetes mellitus in man are discussed. F. O. H.

Serum-proteins and glaucoma. A. C. Krause (J. Lab. Clin. Med., 1932, **18**, 1—3).—Serum-albumin, -globulin, and -total protein are normal. Ch. Abs.

Iodine and goitre problem in New Zealand. C. E. Hercus and H. A. A. Aitken (J. Hyg., 1933, **33**, 55—79).

Effect of iodine on the basal metabolism in exophthalmic goitre. E. Delcourt-Bernard (Compt. rend. Soc. Biol., 1932, **110**, 999—1001; Chem. Zentr., 1932, ii, 3732).

Iodine excretion in myxœdema after continued administration of thyroxine. A. Schittenhelm and B. Eisler (Z. ges. exp. Med., 1933, **86**, 299—308).

Lactic acid in bile. Lactic acid content of the urine of patients with liver disease and of rabbits with experimentally injured liver. Lactic acid content of blood and bile in lactic acid-loading in rabbits having injured livers. H. Mizuno (Japan. J. Gastroenterol., 1932, **4**, 75—83, 84—93, 94—99).—(1) Three normal rabbits excreted 6·23, 6·39, and 10·13 mg. of lactic acid (I) in the bile during the second 5 hr. period after operation. Comparable vals. after liver injury were: hepatotoxin 47, 76; P 37, 43, 99; CCl_4 50, 51, 60; *X*-ray 13, 20, 24, 30, 38, 53; Chinese ink 21, 25, 26. (2) In normal rabbits urinary (I) is 4·4—4·9 mg. per 100 c.c. The concn. increases 3—5 times after partial extirpation of the liver, $\geq$ 10 times after ligation of the bile duct, and 3—8 times after liver injury with P, $CHCl_3$, or CCl_4. Normal human urine contains 2·7—4·7 mg. of (I) per 100 c.c.; the val. increases 3—7 times in cancer and cirrhosis. As a rule urinary is $<$ blood-(I). (3) (I) injected into the blood of normal rabbits disappears in 5—10 min., but in 2—3 hr. after liver injury. Part of the injected (I) is excreted in the bile. After liver injury bile-(I) remains high. Ch. Abs.

Nephritic albuminuria. J. M. Hayman, jun., and J. A. Bender (Arch. Int. Med., 1933, **51**, 447—451).—The plasma of three nephritic patients who were excreting large quantities of protein in their urine, when injected intravenously into healthy recipients, produced no albuminuria (I). This does not support the conception that nephritic (I) is caused by foreign proteins in the blood-stream. R. N. C.

Colloidal gold test for poliomyelitis immune bodies in blood-serum. F. Eberson and W. G. Mossman (J. Lab. Clin. Med., 1932, **18**, 167—186).—The antibody content of poliomyelitis sera is determined from "curves" obtained by the action of the inactivated sera on a colloidal Au sol containing cholesterol. Ch. Abs.

Experimental rickets as a phosphorus-deficiency disease. H. D. Kay and B. L. Guyatt (Nature, 1933, **131**, 468—469).—Evidence that a serious defect of P uptake from the diet is the most important single factor in the production of rickets in rats, and probably in man, is summarised. $BeCO_3$, but not $Be_3(PO_4)_2$, added to a normal diet produces rickets in rats. L. S. T.

Colloidal carbon flocculation test [for syphilis] in cerebrospinal fluid. P. G. Schube and H. E. Harms (J. Lab. Clin. Med., 1932, **18**, 65—70).—Neurosyphilitic cerebrospinal fluid flocculates colloidal C; the test appears sp. Ch. Abs.

Action of double pneumothorax. H. Reichel (Arch. exp. Path. Pharm., 1933, **169**, 180—187).—Intrapulmonary injection of aq. KI–I in dogs with double pneumothorax results in a more prolonged excretion of I than that occurring in normal dogs. F. O. H.

Histochemical demonstration of gold. F. Timm (Deut. Z. ges. ger. Med., 1933, **20**, 211—214).—Au was detected by Timm's technique in the tissues of animals treated with Sanocrysin. The same technique was successfully applied after injection of the Ag analogue of Sanocrysin. Nutr. Abs.

Hyperglycæmia after lumbar puncture. H. Schonfeld (Jahrb. Kinderheilk., 1933, **138**, 174—178). Nutr. Abs.

Calcium balance: technique and pathological interpretation. M. Paget, Langeron, and Cor-

DONNIER (J. Pharm. Chim., 1933, [viii], **17**, 248—260). —The relationship between Ca ingested and that excreted gives valuable information about the influence of hormones on Ca metabolism, although it cannot replace the study of calcæmia in certain conditions. Paget's disease, cases of chronic rheumatism, fractures, etc. are reported and the effects of treatment on the Ca balance are given which lead to the above conclusions. P. G. M.

Physical nature of the nerve impulse. A. V. HILL (Nature, 1933, **131**, 501—508).—A lecture. L. S. T.

***In vitro* respiration of nerve.** T. H. CHANG, R. W. GERARD, and M. SHAFFER (Proc. Nat. Acad. Sci., 1933, **19**, 152—153).—At 37° nerves suspended in serum show higher initial O_2 consumption than when suspended in Ringer solution, but in the latter case a marked rise occurs after 6—7 hr. which is not observed when serum is used. This rise is due to bacterial growth, which is inhibited by some bacteristatic constituent (I) apparently protein in nature. The initial high level in serum is also traceable to a protein constituent which appears to be similar to, but not identical with, (I). W. O. K.

Differences of oxidation and reduction properties of tissues with sex. IV. Fowl embryonic tissue. S. KAGIYAMA (J. Biochem. Japan, 1933, **17**, 135—146; cf. A., 1932, 1281).—On the 12th—13th day of incubation the oxidation (I) and reduction activities (II) of the embryo increase more rapidly, but in the male the increase in (I) is $>$, and that in (II) $<$, in the female. In both sexes, (I) and (II) in heart- are $>$ in brain-tissue. These differences are probably connected with the development of the sexual organs. The body-wt of the embryo increases rapidly after 12 days' incubation, that of the male being slightly $>$ that of the female. F. O. H.

Isometric oxygen coefficient of normal muscle and muscle poisoned with iodoacetic acid. O. MEYERHOF, C. L. GEMMILL, and G. BENETATO (Biochem. Z., 1933, **258**, 371—388).—The isometric O_2 coeff., K_{mO_2}, for a single twitch of the normal sartorius, based on the total O_2 used during activity (unreduced val.), is 600×10^6, and based on the extra O_2 of stimulation and recovery phases (reduced val.) 730×10^6. With greater initial tension, the unreduced val. decreases considerably and the reduced val. increases, the mean val. being 690×10^6. A K_{mO_2} val. of 700×10^6 corresponds with an isometric heat coeff. in O_2 of K_{H_0} 4·7 (total) and of K_{H_i} (initial). Under resting conditions, poisoned muscle in *d*-lactate solution gave an unreduced val. of 300—500×10^6, and a reduced val. of $6{\cdot}68 \times 10^6$ (the same as for unpoisoned muscle). P. W. C.

Natural redox system catalysing cell respiration. E. A. H. FRIEDHEIM (Naturwiss., 1933, **21**, 177—178).—Dihydroindole-2-carboxylic acid 5 : 6-quinone, the red pigment formed by the action of tyrosinase on tyrosine, is reversibly reduced by cysteine, or H_2 in presence of Pd, to the colourless $(OH)_2$-derivative. Mixtures of the two form a redox system with E_2 +125 mv. at p_H 4·6 and 17°. The red pigment acts as an accessory respiratory enzyme, trebling the respiration of red blood-corpuscles (rabbit) at a concn. of $M/1180$. A. C.

Standards for predicting basal metabolism. I. Prediction for girls from 17 to 21. M. E. STARK (J. Nutrition, 1933, **6**, 11—35).—Statistical examination of data from a no. of observations and prediction tables are compared. A. G. P.

Effect of protracted exercise, intestinal fermentation, and modification of diet on attainment of abnormal respiratory quotients by rats on a fat-deficient diet. L. G. WESSON (J. Biol. Chem., 1933, **100**, 365—371).—Exercise does not increase carbohydrate assimilatory coeffs.; the effect of gastro-intestinal fermentation is negligible. The abnormally high respiratory coeffs. obtained by feeding rats on a fat-deficient diet are not due to deficiency in proteins, or vitamins-*A*, -*B*, and -*D*. H. D.

Metabolism of the pancreas. E. U. STILL (Proc. Nat. Acad. Sci., 1933, **19**, 155—157).—In the resting pancreas of the dog the metabolism rate fluctuates within narrow limits, whilst the R.Q. varies from 0·71 to 1·01 (average 0·87). When the gland is stimulated by administration of secretin, marked increase of O_2 consumption takes place, whilst the $NaHCO_3$ of the venous blood falls. When allowance is made for the extra $NaHCO_3$ which passes into the juice, the excess CO_2 formed is approx. equal to the extra O_2 consumption, so that the R.Q. of the stimulated gland is approx. 1·0. W. O. K.

Autosynthetic cells. Possible role of the nitro-group in the energy phenomena of protoplasm. G. CRILE, O. GLASSER, M. TELKES, and A. ROWLAND (Proc. Amer. Phil. Soc., 1932, **71**, 411—420).—The R.Q. of autosynthetic cells is 0·8—0·9; $CO_2 : NH_3$ produced was 33 : 1. Mitogenetic rays were observed when the lipin fraction was added to the protein fraction of the cells. The dynamic phenomena of living cells are attributed to the formation of NO_2-compounds. CH. ABS.

Food consumption of, and the digestibility of nutrients by, white rats under reduced air pressures. W. FREDRICH (Arch. Tierernahr. Tierzucht, 1932, **8**, 290—322).—At high altitudes (6000—8000 m.) food consumption was smaller, body-wt. decreased, and temp. fell. No difference in the digestibility of the nutrients was observed. Effects of sudden changes of pressure and of slow acclimatisation are compared. A. G. P.

Relation between liver function and liver-glycogen, -fat, and -nitrogen. I—VII. T. HAYASHI (Japan. J. Gastroenterol., 1932, **4**, 287—297).—Rabbit liver rich in glycogen excretes more, and that rich in fat less, glycogen. The tissue respiration of the liver is also related to its excretory power. CH. ABS.

Physical chemistry of resorption. IV. P. J. JURISIĆ (Biochem. Z., 1933, **258**, 449—459).—The permeability of sacs of surviving frog's skin from the outer to the inner surface and in the opposite direction is investigated by pressure filtration and osmotic methods and varying fluids in contact with the two surfaces. Closure of the skin from the outside is

especially well marked when distilled H_2O is employed as both outer and inner fluid. By means of osmotic experiments it is shown that the feebler diffusion of acid dyes through the skin from the inner to the outer surface than in the reverse direction is probably due to the contraction of the diffusion path when the inner surface comes in contact with the dve solution. P. W. C.

Rate of absorption of glucose from the gastro-intestinal tract of the dog. H. C. Trimble, B. W. Carey, jun., and S. J. Maddock (J. Biol. Chem., 1933, **100**, 125—138).—The average rate of absorption of *d*-glucose from the gastro-intestinal tract (I) of male dogs weighing 11—20 kg. is 0·99 g±0·17 g. per kg. per hr., viz., 2/3 of the accepted val. This val. becomes more const. with increase of absorption period. No definite relationships between the rate of absorption and variations in concn. and abs. wt. of glucose ingested, wt. of animals used, and excitement occasioned by experimentation are apparent. It appears that although in many cases the venous blood-sugar val. gives no indication of the course of the absorption, the rate of absorption of glucose from (I) is ≯ the max. rate of removal from the blood. A. L.

Relation between alimentary hypoglycæmia, "Staub effect," and various sugars. M. Sawada (J. Biochem. Japan, 1933, **17**, 91—109).—A single intravenous injection of glucose (I), fructose (II), or mannose (III) into rabbits produces a hyperglycæmia (IV) followed by a slight hypoglycæmia (V). With galactose (VI), maltose (VII), or lactose (VIII), (V) does not occur. If after 2 hr. a second intravenous or intraperitoneal injection is given, the second (IV) is equal to the first (negative "Staub effect") with (VI), (VII), and (VIII), and less (positive "Staub effect") with (I), (II), and (III). (V) is due to a decrease in the true blood-sugar. The difference between the two groups is explained by differences in the rate of assimilation. F. O. H.

Bile acids and carbohydrate metabolism. XXV. Production of glycogen in the liver of splenectomised rabbits following administration of bile acids. K. Fuziwara (Biochem. Z., 1933, **259**, 203—209).—In rabbits the production (I) of glycogen in the liver from injected glucose is reduced as a result of splenectomy, but the reduction is counteracted by administration of cholic acid (II) or of extract (III) of rabbit spleen, and (I) is increased far beyond normal by administration of both together. Administration of adrenaline (IV) together with (II) increases the reduction, which, however, is counteracted by giving (III). Thus there is antagonism between the hormone of the spleen and (IV), but synergism between it and (II). W. McC.

Intermediate products of carbohydrate metabolism in muscle extract. O. Meyerhof and W. Kiessling (Naturwiss., 1933, **21**, 223—224).—Aq. muscle extracts acting anaerobically on hexose diphosphate or glycogen yield glycerol, in the first case partly as the α-phosphoric acid. The total glycerol is equiv. to 70% or 50%, respectively, of the $AcCO_2H$ simultaneously formed. Glycolysis takes place by dismutation to glycerol and $AcCO_2H$ and not by way of AcCHO (cf. Embden, Deuticke, and Kraft, Klin. Woch., 1933, 213). R. K. C.

Fate of tartaric acid in human body. P. Finkle (J. Biol. Chem., 1933, **100**, 349—355).—Intramuscularly injected Na tartrate is totally excreted in the urine by man in about 8 hr. After administration by mouth only 20% is recovered in the urine, the remainder probably being destroyed in the intestine, as none is found in the fæces. H. D.

Tartrate metabolism. I. Grape tartrates and the acid-base balance. II. Mode of action of injected tartrates. O. B. Pratt and H. O. Swartout (J. Lab. Clin. Med., 1933, **18**, 354—366, 367—370).—All the tartrates tested had an alkalising action, although in differing degrees; the Na K salt was more potent than the K H salt. Tartrates, albumin, or casts were not found in the urines. Nutr. Abs.

Regulation of intracellular protein and carbohydrate metabolism by thiol. E. Waldschmidt-Leitz, L. Weil, and A. Purr (Z. physiol. Chem., 1933, **215**, 64—66).—Inhibition or acceleration of enzymic reactions by iodoacetic acid (which oxidises SH) is an indication of the sp. stimulant or inhibitory action of SH on the reaction examined. J. H. B.

Passage of polypeptides through the liver. N. Fiessinger, M. Herbain, and R. Lançon (Arch. int. Pharmacodyn., 1932, **43**, 216—236).—Ingestion of peptone by dogs caused a brief rise of the polypeptide content of the portal blood, and of the general circulation, which exceeded the increase of total non-protein-N. A certain amount of polypeptide is removed by the liver to be released gradually in order to maintain the level of these proteins in the blood. Nutr. Abs.

Fate of intravenously injected tyrosine. F. B. King and D. Rapport (Amer. J. Physiol., 1933, **103**, 288—297).—After intravenous injection of tyrosine (I) to dogs, the NH_2-acid disappeared almost completely from the blood within 5 min. No significant increase in blood- or urine-urea occurred. The total N of the urine was sometimes slightly increased and sometimes decreased; ≯5% of the injected (I) appeared in the urine as (I) or phenols. Similar experiments on thyroidectomised dogs gave the same results. No appreciable amount of tyrosine is taken up by the thyroid gland. Nutr. Abs.

Biological action of tyrosine. A. Risi (Arch. internat. Pharmacodyn., 1933, **44**, 131—155).—Tyrosine had no effect on blood-sugar. Nutr. Abs.

Biological value of proteins in the nutrition of growing pigs. H. Schiftan (Arch. Tierernahr. Tierzucht, 1932, **8**, 212—245).—The biological vals. (Thomas and Mitchell) of milk, caseinogen, fish meal, potatoes, and barley in a maintenance ration were < in a productive ration, the difference in the case of milk being small. The corresponding protein vals. (Mitchell) are calc. and their significance in the evaluation of rations is demonstrated. A. P. G.

Chemical composition and nutritive properties of milk as affected by the level of protein feeding.

I. Chemical composition. A. E. PERKINS. **II. Nutritive properties.** W. E. KRAUSS and C. C. HAYDEN (Ohio Agric. Exp. Sta. Bull., 1932, No. 515, 69 pp.).—I. Of the milk constituents examined the non-protein-N alone was significantly influenced by the level of protein feeding. Widest variations occurred in the proportions of urea-N. Similar but smaller changes occurred in the NH_2-N and the creatine–creatinine-N. The ratio protein : total solids was correspondingly increased. With a very high protein ration the increased non-protein-N was accompanied by a small increase in albumin. A slight reduction in fat content was caused by low-protein feeding.

II. Slight differences in the vitamin-*A* and -*D* contents of milk from cows receiving various levels of protein feed were traceable to small differences in the vitamin content of the rations. A direct relationship is indicated between the vitamin-*B* of the milk and the level of protein feeding. A. G. P.

Nutritive value of milk. II. Effect of pasteurisation on some nutrient properties of milk. W. E. KRAUSS, J. H. ERB, and R. G. WASHBURN (Ohio Agric. Exp. Sta. Bull., 1933, No. 518, 33 pp.).—Pasteurisation did not increase the rate of development of nutritional anæmia in rats receiving exclusive milk diets. No significant differences in total nutritive effect were observed between fresh and pasteurised milk supplemented with Fe and Cu. Pasteurisation did not reduce the Cu content of the milk, the availability of the Ca and P constituents, or the activity of vitamins-*A*, -B_2, or *D*, but destroyed approx. 25% of the vitamin-*B* content. A. G. P.

Distribution of the urinary representatives of nitrogen metabolism and its physiological significance. III. Minimum specific endogenous nitrogen excretion of various species of homeotherms. E. F. TERROINE, M. CHAMPAGNE, and G. MOUROT. IV. Influence of the predominance of sources of acid on the specific endogenous nitrogen excretion. E. F. TERROINE and M. CHAMPAGNE (Bull. Soc. Chim. biol., 1933, **15**, 203—234, 235—262).—III. In different species of mammals at a min. level of N metabolism and on identical diets, the distribution of urinary N varies considerably. The sum (S)=urea- +NH_3- +NH_2-N is taken as a measure of the true protein metabolism. The allantoin excretion, although not strictly proportional to this sum, varies in harmony with it, and appears to be proportional to the energy output of the animal, even in the case of species the energy outputs of which are in the ratio 1 : 10. The ratio of allantoin-N to total N of the urine is considerably > the ratio of purine-N to total N of the whole animal, although the latter remains const. even after a prolonged period of inanition resulting in a loss of 30—40% of wt. Creatinine appears to bear no relationship to the other constituents in fasting animals even of the same species, and it is not a satisfactory index of the endogenous N metabolism. In all species creatinine-N/total N much exceeds creatine-N/total N of the whole organism. The organism maintains const. the ratio creatine-N/total N even during a long period of N starvation. In the rat, dog, pig, and man at a min. N level, S represents about 60% of the total urinary N. The coeff. of protein oxidation urea-N/S or (urea- +NH_3-N)/S varies considerably according to the species, the former being for the rabbit 97%, for dog and pig 80%, and for rat 60%. The amount of NH_3 in the urine varies considerably for animals of different species even when all are on the same diet, being very small in the rabbit and high in the rat, dog, and pig. These differences are not explicable by variations of the p_H of the urine.

IV. In pigs at a min. level of N metabolism, the administration of acid (H_3PO_4 and HCl) in the place of basic salts altered the p_H of the urine from 8·0—8·8 to one markedly acid, and resulted in an increase in the total N excretion. No significant increase occurred in the excretion of creatinine, allantoin, or undetermined N. Urea-N decreased, but NH_3- and NH_2-N increased, the increase in the former exceeding the decrease in urea-N. Neither the total NH_3 excretion nor the ratio NH_3-N/(urea- +NH_3- +NH_2-N) is closely correlated with the p_H of the urine. Even strongly acidic urines are often quite free from creatine, although the latter may sometimes be present. W. O. K.

Nutritive value of cranberries. C. R. FELLERS (Amer. J. Pub. Health, 1933, **23**, 13—18).—The cranberry is high in vitamin-*C*, I, and energy val.; the ash contains significant amounts of K, P, Mn, and Fe. Fresh berries contain BzOH (0·035—0·095%) and quinic acid (0·6—0·9%). Vitamin-*A*, but not -B_1, -B_2, or -*D*, is also present. CH. ABS.

Inorganic salts in nutrition. VI. Mineral metabolism of rats receiving a diet low in inorganic constituents. R. O. BROOKE and A. H. SMITH (J. Biol. Chem., 1933, **100**, 105—124).—Utilisation of protein was unimpaired, the Cl in the diet being ample for secretion of gastric juice, as the renal threshold val. was not reached. There was increased excretion of P in the urine and production of NH_3 by the kidneys. There was also a loss of Ca. H. G. R.

Calcium and phosphorus requirements of dairy cows. II. Weekly balances through lactation and gestation periods. H. B. ELLENBERGER, J. A. NEWLANDER, and C. H. JONES (Vermont Agric. Exp. Sta. Bull., 1932, No. 342, 20 pp.).—The cumulative Ca and P balances over the whole period of lactation and gestation were positive, although losses are recorded in the first few weeks of the period. The feeding of mineral supplements (bone-meal and limestone) increased the storage of Ca, but slightly decreased that of P. A. G. P.

Effect of colloidal tricalcium phosphate on the calcium and phosphorus metabolism of the organism. M. GURSCHING (Biochem. Z., 1933, **259**, 140—155).—In white rats oral administration of "tricalcol" (cf. A., 1912, ii, 1069) has a favourable effect on the Ca and P balance, the P retention being increased five-fold, a negative Ca balance becoming positive, and the general growth being improved. The administration does not increase the average wt. of the skeleton, but produces an 8—10% increase in its $Ca_3(PO_4)_2$ content without altering the P : Ca

ratio. "Tricalcol" in Na_2CO_3 solution is negatively charged, the $Ca_3(PO_4)_2$ being associated with protein as protective colloid. Extensive tryptic digestion of the protein does not result in pptn. of the $Ca_3(PO_4)_2$. W. McC.

Phosphates in blood after strenuous muscular exercise. C. L. Gemmill and B. A. Ribeiro (Amer. J. Physiol., 1933, **103**, 367—373).—At rest inorg. P (man) was 2·78—2·9 mg. and the acid-sol. PO_4''' 21·86—23·42 mg. per 100 c.c. A slight fall in inorg. P was noted 30 sec. after exercise in six experiments. Org. P showed a slight rise in each case. In dogs under "phanodorm" anæsthesia, electrical stimulation of the muscles for 60 sec. caused increase of inorg. P from 4·07 to 4·88 mg. and of acid-sol. PO_4''' from 29·9 to 33·2 mg. per 100 c.c. Nutr. Abs.

Leg-bone deformities in growing chicks. I. Deformities produced by high mineral rations. M. C. Herner and A. D. Robinson (Poultry Sci., 1932, **11**, 283—288).—Rations containing $>4·7\%$ of ash generally caused non-rachitic abnormal leg-bone growth and digestive disturbances. The bone-ash was normal. Ch. Abs.

Influence of bile acids on phosphorus metabolism. III. Influence of cholic acid, adrenaline, and the sympathetic nervous system on blood-phosphate. T. Kuramoto and H. Yuuki (J. Biochem. Japan, 1933, **17**, 1—9).—The blood-PO_4 (I) level of fasting rabbits is higher in summer than in winter. It is decreased by splanchnicotomy (II) and increased by vagotomy (III). Administration of cholic acid increases (I), the effect being increased by (II) and decreased by (III). Large doses of adrenaline markedly increase whilst small doses decrease (I), both effects being diminished by (II) and (III). F. O. H.

Influence of bile acids on calcium metabolism. IV. Normal and thyroparathyroidectomised dogs. T. Hosizima (J. Biochem. Japan, 1933, **17**, 29—45).—Repeated removal of blood from dogs is followed by a transient hypocalcæmia during which the urinary excretion of Ca is diminished. Administration of cholic acid (I) produces an increased Ca level in the blood and urine of both normal and thyroparathyroidectomised dogs (II), the result being but slightly influenced by simultaneous administration of thyroxine. Administration of parathyroid extract to (II) produces a hypercalcæmia and increased excretion of Ca, but this result is neither synergised nor antagonised by the simultaneous administration of (I). F. O. H.

Effect of calcium carbonate and calcium sulphate on bone development. H. W. Titus, E. McNally, and F. C. Hilberg (Poultry Sci., 1933, **12**, 5—8).—The ash content of the bones of chicks fed with rations containing $CaCO_3$ decreased progressively from 51·1 to 40·5% as the Ca : P ratio increased. With $CaSO_4$ in place of $CaCO_3$ the ash content of the bones tended to increase slightly (from 52·0 to 53·5%). Nutr. Abs.

Effects of sulphur on Merino sheep. D. G. Steyn (18th Rept. Dir. Vet. Serv. Union S. Afr., 1932, 597—610).—S feeding resulted in a much greater increase in body-wt. and wool yield than in the controls. Nutr. Abs.

Mineral metabolism. XVIII. Phosphorus in nutrition of sheep. P. J. Du Toit, A. I. Malan, and J. W. Groenewald. **XIX. Influence of phosphorus and other minerals on wool growth.** J. E. Duerden, V. Bosman, and P. S. Botha. **XXI. Comparison of phosphatic supplements for prevention of aphosphorosis.** A. I. Malan and P. J. Du Toit. **XXII. Phosphorus, calcium, and protein.** J. S. Otto. **XXIII. Phosphorus and iodine supplements in field experiments with sheep.** J. G. Bekker. **XXV. Effect of calcium and magnesium supplements on growth of Merino sheep.** J. W. Groenewald (18th Rept. Dir. Vet. Serv., Union S. Afr., 1932, 611—630, 631—649, 677—702, 703—732, 733—750, 799—803).—XVIII. The trials reported illustrate the advantage of P supplements. Excess of P was not beneficial; deficiency was reflected in blood-inorg. I.

XIX. With P-sufficient sheep fleece wt. was 32% higher, staple length 16·6% greater, and fibre thickness 13·5% more than in the P-deficient sheep. Excess of P gave no advantage in wool growth.

XXI. The availability for cattle was in the order Na_2HPO_4 > pptd. $Ca_3(PO_4)_2$ > bone-meal and degelatinised bone-flour.

XXII. The P of Na_2HPO_4 (I) is practically 100% available to cattle and that of bone-meal about 70%. Ca eliminated through the kidneys increased when the ration was low in P. Addition of (I) to a ration low in P influenced absorption and retention of Ca favourably. Addition of $CaCO_3$ to a ration low in P reduced the absorption of P. Addition of (I) to a ration low in Ca resulted in a higher absorption of P, but in a very high elimination by way of the kidneys. Utilisation of proteins, carbohydrates, Et_2O extract, and fibre of the ration was apparently not affected by P and Ca deficiency or sufficiency.

XXIII. The beneficial effects of P (as bone-meal) on wt. gain are confirmed; I (as KI) had no effect.

XXV. $CaCO_3$ (7 g. daily) had an apparently beneficial effect; Mg supplement did not produce such rapid gains as Ca. Nutr. Abs.

Iodine balance in normal men. L. Scheffer (Biochem. Z., 1933, **259**, 11—18; cf. A., 1932, 641).—About half of the I excreted daily by healthy men is found in the urine and fæces. Of the remainder most is excreted through the skin, but some also escapes in the expired air. In experiments on I balance the I content of the food and drink as consumed, and the excretion in 24 hr., must be determined. The results contradict the view of von Fellenberg (A., 1924, i, 114). W. McC.

Poisonous secretions of twelve species of toads. K. K. Chen and A. L. Chen (J. Pharm. Exp. Ther., 1933, **47**, 281—293).—General description of 12 species of toads, of their parotid glands, and of their expressed secretions. The H_2O content of the fresh secretions varies from 51 to 61%. W. O. K.

Physiological action of the principles isolated from the secretion of the common European toad (*Bufo bufo bufo*). K. K. Chen, H. Jensen,

and A. L. CHEN (J. Pharm. Exp. Ther., 1933, **47**, 307—320).—From the secretion of the parotid gland of *B. bufo bufo* (*B. vulgaris*) there have been isolated *vulgarobufotoxin* (I), $C_{38}H_{60}O_{11}N_4$, m.p. 202°; *vulgarobufotenine* (II), isolated as *flavianate*, $C_{12}H_{18}O_2N_2 \cdot C_{10}H_6O_8N_2S$, m.p. 180—181°; and cholesterol admixed with 0·47% of ergosterol. (I), which gives a positive Sakaguchi reaction, has a digitalis-like action, stimulates the isolated intestine and uterus, and has a pressor action due to vasoconstriction. (II) stimulates the isolated intestine and uterus and has a marked pressor action. In neither the secretion nor the skin of *B. bufo bufo* could bufotalin be found (cf. Wieland, A., 1922, i, 784). W. O. K.

Chemistry and pharmacology of *Digitalis* glucosides. K. W. MERZ (Pharm. Ztg., 1933, **78**, 246—248, 262—265).—A lecture. P. G. M.

Toxicity of alkaloids; combination of nicotine with caseinogen. G. F. GAUSE (Protoplasma, 1933, **17**, 554—557).—Nicotine (I) combines with an equiv. of caseinogen (II), and the compound is innocuous to *Paramecium caudatum* for a considerable period. With excess of (I) or on addition of $NaHCO_3$ the solution becomes toxic. A similar prep. in which (II) was replaced by Na caseinogenate also exhibited toxicity of (I). A. G. P.

Intestinal motility. V. Analysis of atropine alkaloids. W. STRAUB and E. M. FERNANDEZ (Arch. exp. Path. Pharm., 1933, **170**, 26—38).—Atropine (I), hyoscyamine (II), scopolamine (III), and "bellafoline" (IV) have no action on the peristaltic movement of the small (V) or large intestine (VI), but increase the tonus, (I) and (II) affecting mainly (V), (III) mainly (VI), whilst (IV) acts on both (V) and (VI). The effective doses for the guinea-pig are proportional to the corresponding doses for man. *l*-(II) is > 15 times as active as *d*-(II). The action of (I) is inhibited by prostigmine. F. O. H.

Comparative physiological actions of *dl*-β-phenyl*iso*propylamines. I. Pressor effect and toxicity. G. A. ALLES (J. Pharm. Exp. Ther., 1933, **47**, 339—354).—On intravenous injection into dogs under barbital anæsthesia, the following order is found for pressor activity: β-phenylethylamine = β-phenyl*iso*propylamine < β-*p*-hydroxyphenylethylamine = β-*p*-hydroxyphenyl*iso*propylamine > β-3:4-dihydroxyphenylethylamine = β-3:4-dihydroxyphenyl-*iso*propylamine < adrenaline. The Pr^{β} compounds tend to act for a longer time than the corresponding ethylamines (I). The toxicity, determined by subcutaneous injection into guinea-pigs, of the NH_2Pr^{β} compounds is > that of (I), but in both series the toxicities are reduced by the introduction of OH groups into the Ph nucleus. W. O. K.

Blood-iodine and the effect on it of sympathomimetic drugs as influenced by the nervous system and thyroid. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1933, **86**, 309—330).

Effect of guanidine hydrochloride and synthalin on the blood-sugar of bilaterally adrenalectomised or splanchnicotomised rabbits. H. TADA (Tohoku J. Exp. Med., 1932, **19**, 584—602).—Splanchnicotomy inhibits guanidine hydrochloride hyperglycæmia in rabbits; bilateral adrenalectomy also inhibits synthalin hyperglycæmia. CH. ABS.

Toxicity of rotenone hydrochloride, acetylrotenone, and rotenolone using the goldfish as the test animal. W. A. GERSDORFF (J. Amer. Chem. Soc., 1933, **55**, 1147—1152).—Solutions of rotenone hydrochloride and acetylrotenone containing < 0·02 mg. per litre are definitely toxic (method, cf. A., 1930, 1316). The theoretical threshold of toxicity of rotenolone is 0·2 mg. per litre. H. B.

Toxicity of rotenone and its derivatives in fish. I. R. DANNEEL (Arch. exp. Path. Pharm., 1933, **170**, 59—71).—The respiration-paralysing action of rotenone and 14 of its derivatives was investigated in sticklebacks. A preliminary discussion of the correlation of paralysing action with constitution is given. F. O. H.

Cascara. J. H. HOCH.—See B., 1933, 365.

Chlorine metabolism. I. Experimental hypochloræmia and azotæmia. G. FERRO-LUZZI (Arch. Farm. sperim., 1933, **55**, 134—150).—Slight hypochloræmia and a simultaneous increase in blood-N is caused by administration of diuretics and, less markedly, purgatives to human patients. R. K. C.

Bones of growing mammals after injection of different porphyrins. R. FIKENTSCHER, H. FINK, and E. EMMINGER (Virchow's Archiv, 1933, **287**, 764—783).—Following daily injections of small amounts of *iso*uro- (I), hæmato- (II), copro-, and deuteroporphyrin into growing guinea-pigs, rabbits, and dogs (I) was richly deposited in the bones, (II) slightly deposited, and the others doubtfully or not at all. NUTR. ABS.

Influence of dyes on the functions of cells and organs. I. Vital dyes and surviving organs. II. Oxidative gaseous metabolism of surviving tissues. F. AXMACHER (Arch. exp. Path. Pharm., 1933, **170**, 39—50, 51—58).—I. The action of the following dyes on the beat of the isolated frog's heart and on the peristalsis of rabbit's small intestine was investigated: neutral-red, toluidine-blue (I), methylene-blue, Bordeaux-red, Nile-blue (II), carmine, acid-fuchsin (III), Congo-rubin, trypan-blue (IV). No distinction between acidic and basic dyes was detected.

II. The action on the O_2 consumption (V) of sections of rat's kidney by (I), (II), (III), (IV), Me-green and -violet, alizarin-blue (VI), and indigo-carmine (VII) was determined. (I), (VI), and (VII) increase (V) both when the last is normal and when it is partly inhibited by NaCN. F. O. H.

Effect of sensitisation with foreign protein and of anaphylactic shock on blood-iodine. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1933, **86**, 360—367).—Rabbits were injected intravenously with 1 c.c. of ox serum daily for 6 days [sensitisation (I)] and 18—20 days later with 0·2 c.c. [producing anaphylaxis (II)]. (I) produced no effect on the I concn. of the blood, but (II) led to a marked fall. In thyroidectomised animals in which the blood-I was low prior to (II), no further fall was caused. NUTR. ABS.

Taste of soya-bean. III. Change in the quantity of succinic acid during fermentation. IV. Chemical constituents and taste. S. UDO (J. Agric. Chem. Soc. Japan, 1932, **8**. 673—675, 675—684).—III. The production of succinic acid was max. at the 5th month of fermentation; an increase at the 10th month may be due to secondary production from glutamic acid.

IV. The p_H is 4—5. The tastes of various combinations of salts found in soya bean were examined. CH. ABS.

Acquisition of the antitoxic character of the liver. S. KIMURA and I. ISODA (Japan. J. Gastroenterol., 1932, **4**, 298—303).—Rabbit's liver poisoned with $CHCl_3$ (20% in olive oil, 0·1 c.c. per kg. subcutaneously) or P (0·015 g. per kg., perorally), after recovery (3 weeks) is less impaired after a second administration. Liver which has recovered from $CHCl_3$ poisoning has some antitoxic action against P. CH. ABS.

Effect of narcosis on blood-iodine. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1933, **86**, 368—382).—Barbituric acid derivatives (somnifen, pernocton) which have an action on the brain stem had no apparent effect on the blood-I of dogs, apart from a slight transient reduction. Of the other narcotics, Et_2O, $CHCl_3$, chloralose in the early stage, EtOH in the later stage, paraldehyde and morphine led to marked increase, whilst chloralose in the later and EtOH in the earlier stages led to a fall. When the thyroid was removed the action of these narcotics was greatly diminished or entirely prevented. NUTR. ABS.

Effect of sodium thiocyanate on the action of anæsthetic and narcotic drugs. T. M. BURKHOLDER (J. Lab. Clin. Med., 1932, **18**, 29—41).—Injection of NaSCN does not shorten the period of Et_2O anæsthesia in rabbits or counteract the action of morphine. CH. ABS.

Reversible coagulation in living tissue. XI. W. D. BANCROFT, R. S. GUTSELL, and J. E. RUTZLER (Proc. Nat. Acad. Sci., 1933, **19**, 85—91).—Chronic alcoholism may with advantage be treated by administration of NaCNS (cf. A., 1931, 1088, 1454; 1932, 425). W. O. K.

Agglomeration theory of sleep. W. D. BANCROFT and J. E. RUTZLER (Proc. Nat. Acad. Sci., 1933, **19**, 73—78).—Sleep is due to agglomeration of the colloids in the brain by the accumulation of an unknown substance *X*, but sensory stimulation may retard the action of *X* and therefore the onset of sleep. Small doses of NaCNS, by decreasing sensory stimulation, favour sleep, whilst larger doses, by acting on the central nervous system and preventing agglomeration, may tend to prevent sleep. W. O. K.

Colour reaction of *m*-dinitrobenzene in the forensic detection of benzene. J. PELTZER (Chem.-Ztg., 1933, **57**, 162—163).—C_6H_6 is removed from the organs by steam distillation and collection in CCl_4. The CCl_4 solution is shaken with HNO_3, and the solvent removed after neutralisation. Et_2O removes m-$C_6H_4(NO_2)_2$ (I) from the residue, and this can be detected by a variety of colour reactions. When 0·0005 mg. of (I) in 0·05 c.c. of EtOH is shaken with 10 drops of 30% aq. NaOH and 0·2 c.c. of $COMe_2$, the $COMe_2$ layer is coloured violet. P. G. M.

Mercury derivative of sodium thiolpropanolsulphonate. A. LEULIER and H. TÊTE (J. pharm. Chim., 1933, [viii], **17**, 154—160).—After subcutaneous injection of > a lethal dose (5—5·5 mg. per kg. body-wt.) of Na β-hydroxy-γ-mercurithiolpropanesulphonate into guinea-pigs the Hg is localised in the liver, kidneys, and mainly in the intestines, although the largest concn. is found in the kidneys. With sub-lethal doses Hg is found in the liver and kidneys, but is almost absent from the intestines. Elimination of Hg in the urine can be detected 1 hr. after injection. J. W. B.

Neuromuscular excitability in relation to the biochemistry of minerals. I. Influence of change of the Ca : P ratio in the diet. B. SJOLLEMA and L. SEEKLES (Biochem. Z., 1933, **258**, 471—479).—The effect of variation of the Ca : P ratio of the food on the neuromuscular excitability, using the flexor muscle of the normal rabbit's fore paw and stimulating by placing an electrode on the *N. medianus*, is examined. A direct relationship between the appearance of latent tetany and the Ca, inorg. P, and Mg contents of the blood-serum could not be established. P. W. C.

Stimulation by hydrochloric, sulphuric, and nitric acid in the sunfish, *Eupomotis*. W. H. COLE and J. B. ALLISON (J. Gen. Physiol., 1933, **16**, 677—684).—The stimulation of *E. gibbosus* by HCl, H_2SO_4, or HNO_3 is dependent on the $[H^+]$ produced in the animal's environment, the reaction time being a log. function of $[H^+]$ (cf. A., 1932, 963). F. O. H.

Blood-catalase in intoxication by phosphorus, lead, manganese, and nickel. L. DI PRISCO (Arch. Farm. sperim., 1933, **55**, 123—133).—Red P, $PbCO_3$, $MnCO_3$, and $NiCl_2$ were injected subcutaneously at intervals into rabbits and the immediate (*a*) and chronic (*b*) effects on blood-catalase measured. Blood-catalase is (*a*) lowered and (*b*) raised by P; it is raised (*a*) and (*b*) by Mn, raised (*a*) and lowered (*b*) by Pb, and lowered (*a*) and (*b*) by Ni. R. K. C.

Inherent sensitivity of the skin to nickel and cobalt. S. G. STEWART (Arch. Int. Med., 1933, **51**, 427—434).—A patient whose skin was sensitive to Ni and Co developed a non-sp. type of lesion in contact with the metals or their salts, but exhibited no reaction with Fe. The effects are attributed to a reaction between the metallic salts and a sp. complex mol. in the epidermal cells. R. N. C.

Hyperglycæmic action of β-dimethyltelluronium dichloride. T. KAIWA (Tôhoku J. Exp. Med., 1932, **20**, 163—177). CH. ABS.

Thallium poisoning. GORONCY and R. BERG (Deut. Z. ges. ger. Med., 1933, **20**, 215—236).—Account of a fatal case. NUTR. ABS.

Mitogenetic radiation. III. L. K. WOLFF and G. RAS (Biochem. Z., 1933, **259**, 210; cf. A., 1932, 1098).—Dissolution of electrolytes (NaCl) in H_2O

gives rise to mitogenetic radiation, but that of non-electrolytes in H_2O or EtOH does not. W. McC.

Effect of different kinds and quantities of light on metabolism in the pig. L. PINCUSSEN, V. BAYERL, E. BRÜCK, J. GÖRNE, and A. ROTHMANN (Strahlenther., 1932, **45**, 401—433).—The most marked changes in pigs subjected to irradiation by infra-red, visible, and ultra-violet lights were an increase in the H_2O and mineral salt content of the blood and also, temporarily, of the skin. There was also, in general, an increased elimination of total N and of purines. NUTR. ABS.

Enzymes : a discovery and its consequences. E. F. ARMSTRONG (Nature, 1933, **131**, 535—537). L. S. T.

Adsorption of enzymes. A. J. J. VAN DE VELDE (Bull. Acad. roy. Belg., 1932, [v], **18**, 1095—1115).—The adsorbing powers of various earths for some proteolytic and amylolytic enzymes were determined. A. J. M.

Enzymes of "kabitofu," a Chinese food. R. H. BUN (J. Agric. Chem. Soc. Japan, 1932, **8**, 273—279).—The aq. extract of "kabitofu" (prepared from soya-bean curd with *Aspergillus* sp., *Penicillium* sp., and *Rhizopus reflexus*) contained diastase, invertase, emulsin, oxidase, catalase, and trypsin- and erepsin-like enzymes. The actions of lipase and deamidase were weak; the presence of maltase, rennin, a pepsin-like protease, and peroxidase could not be proved. CH. ABS.

Catalase. V. Catalase activity of hæmin complexes. K. G. STERN (Z. physiol. Chem., 1933, **215**, 35—46; cf. this vol., 92).—The coupling of hæmin with N bases increases its catalase activity. The hæmochromogens (with hæmin-Fe^{II}) are inferior to the parahæmatins (with hæmin-Fe^{III}). In no case is the activity of the same order as that of catalase. The hæmin–globin complexes possess a certain activity, weakest in the case of hæmoglobin. The activity may be due to the presence of free hæmatin. Certain parahæmatins (deutero-, meso-, hæmato-, pyrro-, and phyllo-hæmin) were almost inactive with the exception of hæmatomethæmoglobin, the activity of which is due to hæmatohæmin. A stroma-protein–protohæmin complex was only slightly active, helicorubin almost inactive except in presence of C_5H_5N, by which the active hæmochromogen is liberated. J. H. B.

Yellow oxidation enzyme. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1933, **258**, 496—498).—The free pigment of the enzyme (cf. this vol., 313) sublimes unchanged in a vac.: formula $(C_{13}H_{13}N_4O_2)_2$ or $(C_{12}H_{12}N_4O_2)_n$. Its absorption curve is given; baryta hydrolysis yields a colourless solution containing urea. P. W. C.

Peroxidase. W. GRIMMER and M. TEITELBAUM (Milch. Forsch., 1933, **14**, 473—475).—A solution of peroxidase was prepared from the Pb acetate serum (I) of skimmed milk. The albumin was pptd. with saturated $(NH_4)_2SO_4$, washed free from sugar, and redissolved. The albumin was digested with 1% pancreatin and the peroxidase repptd. with $(NH_4)_2SO_4$, redissolved by dilution with the min. of H_2O, and dialysed until free from NH_3. The solution, containing only 0·4% of solids, was 15 times as strong in peroxidase as the original (I); the Fe content was very small. E. B. H.

Specificity of intracellular dehydrogenases. IV. Effect of hydrogen-ion concentration. V. Toxicity of arsenic, selenium, and tellurium compounds in frog and fish muscle. M. E. COLLETT, M. RHEINBERGER, and E. G. LITTLE (J. Biol. Chem., 1933, **100**, 267—269, 271—275).—IV. There is a sp. optimum p_H for the dehydrogenases of succinic (I), citric (II), lactic (III), glycerophosphoric (IV), and *l*-malic (V) acids in frog muscle but not in that of goldfish.

V. The frog-muscle dehydrogenases of (I), (II), (III), (IV), (V), and $AcCO_2H$ are differentiated by the different toxic actions of AsO_4''', AsO_3''', SeO_4'' SeO_3'', and TeO_3''. The seasonal variations of frog muscle activity are different for the different reactions. Gold-fish muscle does not show the same specificity. H. D.

Isolation of xanthine-oxidase from milk. J. TOYAMA (J. Biochem. Japan, 1933, **17**, 131—133).—The separated cream from milk, on extraction with Et_2O and drying the residue in a vac., yields a white powder (0·15% of the milk), rich in xanthine-oxidase. The prep. is stable in the absence of O_2, is practically free from protein, and contains 0·00335% Fe, 0·653% P, and 5·1% N. F. O. H.

Biological oxidations. II. Oxidation of lactic acid by α-hydroxyoxidase and its mechanism. E S. G. BARRON and A. B. HASTINGS (J. Biol. Chem., 1933, **100**, 155—182).—Suspensions of gonococci in 0·9% aq. NaCl kept at 3° lose their ability to oxidise glucose and $AcCO_2H$, retaining their power to oxidise α-OH-acids. The velocity of oxidation of lactic acid by α-hydroxyoxidase so obtained, as determined by O_2 consumption and $AcCO_2H$ determination, shows the reaction to be unimol. Q_{10}, the temp. coeff. between 25° and 35°, is 2·23, and the crit. energy increment is 14,900 g.-cal. per mol. Whilst exposure of the enzyme prep. to 52° for 2 hr. inhibits completely the oxidation with O_2, the ability of the enzyme to oxidise lactic acid in the presence of a reversible oxidation–reduction dye such as cresyl-blue is not destroyed. This is believed to indicate that two components, an activating co-enzyme and an oxidising enzyme, are concerned. The inhibiting effects of 0·01*M*-KCN, 0·002*M*-H_2S, 0·1*M*-valeronitrile, 0·01*M*-iodoacetic acid, 0·224*M*-urethane, saturated aq. phenylcarbamide, and 0·224*M*-valeramide on the activating co-enzyme are nil, nil, 7%, nil, 26%, 42%, 29%, respectively, and on the oxidising enzyme 100%, 100%, 100%, 62%, 28%, 52%, 71%, respectively. The catalytic effect of hæmin on the oxidation by the activating co-enzyme is small, that of nicotine–hæmin much greater, this being in accordance with previous work on reduction potentials by Barron and Hoffman (A., 1930, 639). The mechanism of the oxidation by α-hydroxyoxidase is explained in terms of electronic transfers. A. L.

Enzymic action of glycerol extracts of the livers of various animals in the liver- and muscle-

glycogen of the rabbit, liver-glycogen of *Bufo vulgaris*, and glycogen of oysters. Y. HAYASHI (Japan. J. Gastroenterol., 1932, 4, 209—214).—The rates of hydrolysis were measured by digestion with taka-diastase and pancreatin; oyster glycogen was least readily hydrolysed. Glycerol extracts of livers also caused hydrolysis; the liver extract is usually most active with glycogen from the same species. CH. ABS.

Enzyme action. V. Ageing of amylases in aqueous solution. K. V. GIRI and V. SUBRAHMANYAN. **VI. Heat-inactivation of pancreatic amylase.** K. V. GIRI (J. Indian Inst. Sci., 1932, **15, A**, 107—116, 117—121).—V. Dialysed and undialysed amylase preps. from malted barley and malted cumbu (*Pennisetum typhoideum*) lose their activity on keeping, the loss of liquefying being > that of saccharifying activity. Dialysed malt-amylase in buffered solutions is most stable at the optimum p_H (4·6). Undialysed taka-diastase is most stable at p_H 6·2, which is somewhat above the optimum for activity (p_H 5·0). The rate of inactivation of the undialysed is > that of the dialysed preps.

VI. The amylase activity of solutions of pancreatin, determined by the amount of sugar produced from starch, under standard conditions, decreases on keeping at 40°, the curve first following a unimol. course. The deviation from the strict unimol. law suggests the existence of > one enzyme. The rate of inactivation is min. at p_H 6·5—7·0. The energy of activation, calc. from observations at 30 and 40°, is 39,100 g.-cal. for p_H 6·5 and 41,000 g.-cal. for p_H 7·0. W. O. K.

Complement of amylases. X. Activation of pancreatic amylase by glutathione. H. BORCHARDT and H. PRINGSHEIM (Biochem. Z., 1933, **259**, 134—137; cf. A., 1932, 1063).—Dil. KCN activates pancreatic amylase (I) to the same extent as does glutathione (II). Oxidised (II) counteracts the toxic effect of Cu on (I). Pyrophosphate and probably also the complex produced by the interaction of Cu and the SH groups do not activate (I). The activation of (I) by hæmin (Cosack, A., 1931, 1190) is not confirmed. W. McC.

Similarity of the kinetics of invertase action *in vivo* and *in vitro*. III. J. M. NELSON and B. G. WILKES (J. Gen. Physiol., 1933, **16**, 571—577).—The hydrolytic activity of living cells of *Saccharomyces cerevisiæ* on sucrose at various concns. is identical with that of an invertase prep. from the same yeast. This confirms the view that yeast-invertase exerts its activity in a region close to the cell surface (this vol., 93). F. O. H.

Specific action of lipase. III. Liver-lipase of various animals. J. C. KERNOT and H. W. HILLS (Z. physiol. Chem., 1933, **215**, 8—9; cf. A., 1932, 776).—Of the *Cyprinoidea* examined, only the herbivorous species carp and roach show a preferential hydrolysis of the *l*-ester of Et *dl*-mandelate. The liver-lipase of the emu has a similar action in contradistinction to that of many animal species. J. H. B.

Asymmetric ester hydrolysis by enzymes. VII. Configuration specificity of (human) liver-esterase according to kinetic treatment of the various processes. G. M. SCHWAB, E. BAMANN, and P. LAEVERENZ. **VIII. Comparison of the optical selection of liver-esterase in various stages of development of the organ.** E. BAMANN, S. MAHDIHASSAN, and P. LAEVERENZ (Z. physiol. Chem., 1933, **215**, 121—141, 142—146; cf. A., 1931, 874).—VII. The rate of hydrolysis of Et *d*-, *l*-, and *dl*-mandelate by human liver-esterase was studied. The marked deviation from the mass-action law in the hydrolysis of the racemate is due to the *d*-ester inhibition of the *l*-ester fission. The ratio of the reaction vals. of *l*- and *d*-ester fission is 130 : 5·5. In the case of the *l*-ester there are two hydrolysable compounds formed, $ES\_$ and $E(S\_)_2$, the fission of both of which is inhibited by *d*-ester. EtOH inhibits the breakdown by forming a compound $ES\_$–EtOH, hydrolysed with difficulty. The high affinity, 130, with which the *l*-ester forms the hydrolysable $ES\_$ compound differs widely from the val. 1·59 with which it eliminates the *d*-ester from the hydrolysable ES_+.

VIII. The esterase derived from human liver of various ages shows little variation, although that obtained from the newly-born infant is slightly more active than that of the embryo. J. H. B.

Configuration specificity of ester-synthesising enzymes. P. ROna and E. CHAIN (Biochem. Z., 1933, **258**, 480—495).—Bu α-chloropropionate, α- and β-hydroxybutyrate, phenylchloroacetate, β-phenyl-α-hydroxypropionate, and styrylglycollate, and the butyrates of CHMePr·OH, CHEtPr·OH, methyl-, ethyl-, propyl-, and ethylene-amylcarbinols are prepared enzymically, using the esterase of pig's pancreas. Ester synthesis always proceeded asymmetrically except for the esters of mandelic and phenylchloroacetic acids. P. W. C.

Reduction of urobilin to urobilinogen in the body, with special reference to the kidneys. M. OSHIMA (Japan. J. Gastroenterol., 1932, **4**, 102—107).—Reduction by organ pulp (kidney>liver) is max. in 3 hr. at p_H 7·5—7·8. CH. ABS.

Hydrolysis of hexose diphosphoric ester by bone-phosphatase. A new fructose monophosphate. M. MACLEOD and R. ROBISON (Biochem. J., 1933, **27**, 286—297).—Hydrolysis of hexose diphosphate (1 : 6-diphosphofructofuranose) by bone-phosphatase gives a mixture of aldoses and ketoses, whilst partial hydrolysis gives aldose and fructose monophosphates. The chief aldose ester is probably glucose 6-phosphate. Besides fructose 6-phosphate, a new *l*-rotatory fructose ester, probably fructose 1-phosphate, has been obtained. H. G. R.

Glucosulphatase. III. T. SODA and C. HATTORI (Bull. Chem. Soc. Japan, 1933, **8**, 65—69).—The presence of glucosulphatase (I) (A., 1931, 1331; 1932, 92) in 20 molluscs (various classes) is reported. With few exceptions, the activity of (I) from *Gastropoda* is >(I) from *Pelecypoda*. H. B.

Influence of bile acids on autolysis of genital glands. K. TANAKA (J. Biochem. Japan, 1933, **17**, 111—116).—The liberation of guanine, adenine hypoxanthine, xanthine, and arginine during the

autolysis of bull's testes is increased by addition of cholic acid. F. O. H.

Crystalline pepsin. V. Isolation from bovine gastric juice. J. H. NORTHROP (J. Gen. Physiol., 1933, **16**, 615—623).—Pepsin (I) was obtained from the juice by saturating with $(NH_4)_2SO_4$, dissolving the ppt. in 60% $COMe_2$, pptg. with 75% $COMe_2$, repeatedly pptg. with half-saturated $MgSO_4$, and finally crystallising from warm H_2O. In cryst. form and in optical and proteolytic activity, (I) is identical with the prep. (II) from pig's gastric mucosa (A., 1930, 1317; 1931, 1090; 1932, 1166). The solubility of (I) and (II) in acetate buffer half-saturated with $MgSO_4$ at 26° is, however, additive and hence (I) and (II) are different but closely related. F. O. H.

Adsorption of enzymes on protein. I. Pepsin adsorption. H. DYCKERHOFF and G. TEWES (Z. physiol. Chem., 1933, **215**, 93—120).—All proteins examined can adsorb pepsin and rennin under favourable conditions. The cryst. plant globulins retain their structure. The p_H optimum for caseinogen hydrolysis is 2—3·5 for small amounts of pepsin acting for a short time, but 4 for higher concns. and longer time. Probably the hydrolysis at p_H 2 is due to an enzyme different from that active at p_H 4. Enzyme adsorption by protein is favoured by high enzyme concn. The amorphous and the cryst. globulin-pepsins obtained by mixing solutions of the components show activities equal to that of Northrop's crystals. The cryst. form retains its activity on recrystallisation. Pepsin solution shaken with solid cryst. protein gives crystals less active than Northrop crystals, but reaching their activity on recrystallisation. If opportunity is afforded for autodigestion, an amorphous ppt. is obtained with spherical structure, resembling synthetic polypeptides. This form is more active than the cryst. preps., but shows a similar constancy of enzyme content on repptn. J. H. B.

Histochemistry of enzymes. K. LINDERSTRØM-LANG and H. HOLTER. **IV. Peptidase content of some marine invertebrates.** K. LINDERSTRØM-LANG (Z. physiol. Chem., 1933, **215**, 167—178; cf. this vol., 426).—The peptidase activity of the unincubated eggs of *Urechis caupo* (I) and *Dendraster excentricus* (II) corresponds with the hydrolysis of $0{\cdot}6\times10^{-3}$ to $1{\cdot}3\times10^{-3}$ mg. of alanylglycine per hr. at p_H 7·7 and 40°. The eggs of (II) are about twice as active as those of (I), and when halved, the total activity is equal to the sum of the parts, the half containing the nucleus being the more active. During the incubation of the eggs of (I) the activity first falls, rises after 3—6 hr., and again falls after 20—30 hr. J. H. B.

Influence of various organic compounds on urease. T. TAKEUCHI (J. Biochem. Japan, 1933, **17**, 47—59).—The action of urease in PO_4''' buffer at p_H 6·8 is accelerated by glycine and alanine, retarded by arginine, histidine, methyl-, acetyl-, chloro-, and glycyl-carbamide, succinic monoureide, ureidoglutaric acid, glycyl-glycine and -aspartic acid (I); aspartic and glutamic acids, asparagine, hydantoic acid, glycyl-asparagine, and ureidosuccinic acid are without action. The presence of (I) shifts the p_H optimum of the enzyme from 6·9 to 7·1. Hydroxycarbamide has an inhibitory action which, as with NH_2OH and p-$C_6H_4(OH)_2$, is related to its reducing power. The relation between the structure of the above compounds and their interference with urease action is discussed. F. O. H.

Action of metals on enzymes. M. JACOBY (Biochem. Z., 1933, **259**, 211—222).—Reproducible quant. results are obtained in the determination of the min. amount (I) of a metal required to inactivate urease completely and of the min. amount (II) required to produce just noticeable toxic effects. All these can be reversed by cysteine, thioglycollic acid, and pyrophosphate as well as by KCN (all of which act by removing the metal from the enzyme) and (I) can be quantitatively defined by the amount of KCN required fully to restore the activity. As measured by (II) the order of toxicity is Hg>Cu>Ni>Ag>Fe; as measured by (I) Ag and Hg are equally toxic, and Cu, although more toxic than these, cannot poison > 95% of the enzyme. Pb and Zn have very slight toxic effects. The metals cannot be separated from the enzyme by dialysis. W. McC.

Nucleic acid in *Saké* pressed cake and brewer's yeast. M. KIMURA (J. Soc. Chem. Ind. Japan, 1933, **36**, 85B—86B). P. G. M.

Putrefaction products of beer yeast. I. K. YOSHIMURA and K. NISHIDA (J. Agric. Chem. Soc. Japan, 1932, **8**, 309—312).—The filtrate from the putrefaction of dried yeast (8 kg.) in H_2O (40 litres) at 29·1° for 13 days afforded: NH_4OH 252·90 g., leucine 518·0 g., and (as hydrochlorides) hypoxanthine 11·80, putrescine 12·60, tyramine 4·74, histamine 2·64, and cadaverine 4·80 g. CH. ABS.

Comparison of different criteria of death in yeast. O. RAHN and M. N. BARNES (J. Gen. Physiol., 1933, **16**, 579—592).—The harmful effects of heat (I), aq. $HgCl_2$ (II), ultra-violet light (III), and X-rays (IV) on yeast cultures were determined by loss of power of reproduction (V), loss of fermentation (VI), change in staining reaction to methylene-blue (VII), loss of membrane permeability (VIII), and coagulation of the protoplasm (IX), the order (V)—(IX) being one of decreasing rapidity of occurrence. Thus with (I) or (II), the ratio of the intervals before the appearance of (V) : (VI) : (VIII) : (IX)=1 : 2 : 3 : 40, whilst with (III) or (IV) quite different ratios are obtained. Death, as indicated by any of the above criteria, is not followed by recovery at a later stage. F. O. H.

Effect of agar-agar on the growth of *Aspergillus niger*. A. I. VIRTANEN and L. PULKKI (Suomen Kem., 1933, **6**, B, 58).—Addition of approx. 0·1% of agar to nutrient media increases the dry matter production of *A. niger* cultures by 130%. A. G. P.

Acid and alcohol production by *Aspergillus*. VIII. Species of *Aspergillus* and the production of acids. K. SAKAGUCHI (J. Agric. Chem. Soc. Japan, 1932, **8**, 433—444).—The quantity and kind of acid are species-sp. CH. ABS.

Absorption of nickel by *Aspergillus niger* grown on Raulin's medium containing nickel sulphate.

M. MOKRAGNATZ (Bull. Soc. Chim. Yougoslav., 1932, **3**, 221—225).—The Ni content of the mycelium increases with that of the medium. In no case is Ni completely removed from solution by the mould. R. T.

Aspergillin, the pigment of the spores of *Aspergillus niger*. I. A. QUILICO and A. DI CAPUA (Atti R. Accad. Lincei, 1933, [vi], **17**, 93—98).—The yield of aspergillin (I) varies widely with the strain used and with the medium on which it is grown. High yields are given by the Pollacci strain and by one isolated from a cheese, when grown on molasses–agar. The method of separating (I) is described. T. H. P.

Biochemical transformation of sugar by the action of moulds. Transformation of fumaric acid, accumulation of formic acid, and chemistry of oxalic acid production. T. CHRZASZCZ and M. ZAKOMORNY (Biochem. Z., 1933, **259**, 156—167; cf. A., 1931, 394).—Fumaric acid (Ca salt) is a satisfactory source of C for the growth of various species of *Penicillium* and *Aspergillus*, which convert it chiefly into HCO_2H (I) and CO_2, small amounts of oxalic (II), glyoxylic (III), and occasionally citric and malic acids also being produced, according to the species of mould used. The acids are produced in the order (III), (I), (II), (II) being then converted into CO_2, but only (I) accumulates in large amounts when conditions remain favourable for the growth of the moulds. When these are unfavourable or when the normal order of the processes is altered, (II) accumulates. (II) resists direct oxidation, but readily serves as a medium for the growth of the moulds. W. McC.

Specificity of the intracellular globulin of *Fusarium lini*. C. I. NELSON (J. Agric. Res., 1933, **46**, 183—187).—The "sap" is expressed from the mycelial mass after pre-treatment with Et_2O and electrodialysed. The resulting liquid is centrifuged. The extracted globulin possesses high antigenic specificity. A. G. P.

Carbon nutrition of *Polytoma uvella*. A. LWOFF (Compt. rend. Soc. Biol., 1931, **107**, 1070—1072; Chem. Zentr., 1932, ii, 3569).—AcOH and $PrCO_2H$ are the only sources of C. A. A. E.

Physiology of *Cladosporium*. F. P. DEMMLER (Phytopath. Z., 1932, **5**, 275—313).—Under normal metabolic conditions the organism differs from many others in producing no acid of appreciable dissociation. Inorg. neutral salts in concns. 0·05—0·16*M* have little effect on growth. In very acid media sol. starch is produced. The organism behaves as a facultative anaerobe (submersed) if glycerol is supplied as a source of C, and in nutrients of high salt concn. *Cladosporium* utilises $NH_4^{\cdot}$ readily, NO_3' very slowly, and glycine under certain conditions. The utilisation of N materials is largely controlled by the C source supplied. A. G. P.

Organic nutrition of *Ankistrodesmus falcatus* (Corda), Ralfs. B. ALEEF (Zentr. Bakt. Par., 1933, II, **87**, 340—348).—Best growth occurred with glucose, sucrose, or peptone as a source of C. As a N source glycine and peptone, but not asparagine or urea, were utilised. NH_4 salts of org. acids were more readily assimilated than those of mineral acids. Nitrates of Ca, K, and Na favoured growth, but $NaNO_2$ was inhibitory. A. G. P.

Biological oxidation of carbohydrate solutions. II. Oxidation of sucrose in the presence of different inorganic nitrogen compounds. III. Nitrogen, phosphorus, and potassium balances in percolating filters. S. H. JENKINS (Biochem. J., 1933, **27**, 245—257, 258—273).—Using NH_4Cl, $NaNO_2$, and $NaNO_3$ there is no significant difference in the degree of biological oxidation of sucrose. A considerable loss of N was observed, particularly where carbohydrate oxidation was most active.

III. Recovery of P and K was not quant., possibly owing to inadequate methods of analysis. Liberation of N from NH_3 and org. compounds of N may be carried out entirely within the cell of an organism. The loss of N does not arise from formation of NH_3, NO_2', or NO_3' and subsequent denitrification. H. G. R.

Acetic acid bacteria in Formosa. I. S. TANAKA (J. Agric. Chem. Soc. Japan, 1932, **8**, 962—990).—*B. ascendens*, Henneberg, *B. acetosum*, Henneberg, *B. aceti*, Hansen, and *B. xylinum*, Brown, were isolated from saké wort and vinegar. 4·2—7·0% of acid is produced; the optimum p_H is 4—6. CH. ABS.

Mechanism of oxidation processes. XXXIII. Dehydrogenation reactions with butyric acid bacteria. H. WIELAND and M. G. SEVAG (Annalen, 1933, **501**, 151—162).—The O_2 consumption of a mixture of glucose (or EtOH) and *B. acidi butyrici* (I) at 34·5° is optimal at 8 (phosphate buffer). The ratio CO_2 evolved : O_2 consumed for glucose is 0·8—0·84 after 315—375 min., indicating that oxidation of intermediate products occurs; the corresponding ratio for glycerol is about 0·6. Lactic acid is oxidised at about the same rate as glucose, but the ratio $CO_2 : O_2$ is < the calc. val., indicating that the change $OH{\cdot}CHMe{\cdot}CO_2H + O \longrightarrow AcCO_2H$ occurs at a faster rate than $AcCO_2H \longrightarrow CO_2 + MeCHO$. Succinic, citric, and β-hydroxybutyric acids and AcOH are not oxidised by (I). A larger O_2 consumption is found for EtOH+(I) than for the other alcohols examined; PrOH and $Pr^{\beta}OH$ react similarly, as do $Bu^{\alpha}OH$ and $Bu^{\beta}OH$. Reaction with MeCHO, EtCHO, PrCHO (a large amount of CO_2 is produced in this case, probably by β-oxidation), and $Pr^{\beta}CHO$ is slower than with the corresponding alcohols. The catalase activity of (I) is diminished by KCN (*N*/200—*N*/800). Oxidation of glucose and EtOH is similarly retarded, but not to the same extent as in the case of acetic acid bacteria (A., 1929, 219). The rate of decolorisation of methylene-blue by (I)+glucose and the above alcohols does not parallel the corresponding O_2 consumptions. PrOH, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, and $Bu^{\beta}OH$ are dehydrogenated by benzoquinone+(I) at p_H 6·8. H. B.

Lactic fermentation. G. P. LE GALLIC (Compt. rend. Soc. Biol., 1931, **107**, 146—148; Chem. Zentr., 1932, ii, 3569).—The quantity of lactic acid formed in lactose–caseinogen–peptone bouillon by *Streptococcus acidi lactici* increases with the addition of K_2CO_3; p_H—log[lactate']=const. (about 2·9). A. A. E.

New sporing lactic acid bacterium (*Lactobacillus sporogenes*, nov. sp.). L. M. HOROVITZ-

VLASSOVA and N. V. NOVOTELNOV (Zentr. Bakt. Par., 1933, II, **87**, 331—333).—The organism produces lactic acid from glucose, sucrose, lactose, mannitol, arabinose, starch, and dextrin. A. G. P.

Gluconic acid fermentation. V. *B. hoshigaki* var. *rosea mobilis saccharosum*. T. TAKAHASHI and T. ASAI (J. Agric. Chem. Soc. Japan, 1932, **8**, 1180—1190).—The bacteria were grown in 100 c.c. of yeast extract with glucose (10 g.) at 26—28° for 18 days; the yield of gluconic acid (I) was 94·5% of the total sugar. Sucrose is inverted and (I) produced from sucrose, maltose, dextrin, raffinose, and sorbitol. The max. yield of (I) (14·3%) was obtained with 20% glucose solution. Growth and acid production are, respectively, optimal at 28—30° and 26—28°. AcOH is not oxidised or decomposed. The bacterium did not grow or produce acid in 7% EtOH, 2·5% AcOH, or 2·0—2·5% NaCl solution. CH. ABS.

Factors involved in the biological production of acetone and butyl alcohol. L. WEINSTEIN and L. F. RETTGER (J. Bact., 1933, **25**, 201—238).—A prolamine (I) or allied substance is necessary for the production from carbohydrates of $COMe_2$ and BuOH by *Clostridium acetobutylicum* (II). In the absence of (I), the fermentation of glucose, xylose, and arabinose yields normal amounts of $COMe_2$, but little or no BuOH (normal ratio 1 : 2). Fermentation of acid hydrolysates of sawdust etc. yields $COMe_2$ only, but the addition of zein increases the production of both $COMe_2$ and BuOH. The latter is not derived from (I), which appears necessary for the proper metabolism of (II) and may also have a physical effect on the substrate. A. G. P.

Butyl alcohol–acetone fermentation. I, II. M. TSUCHIYA (J. Agric. Chem. Soc. Japan, 1932, **8**, 1209—1221, 1267—1280).—I. Maize was fermented by *B. granulobacter pectinovorum*. Dil. wort gave the higher yield of $COMe_2$. Addition of soya-bean cake, rice bran, oryzanin, phytin, or various proteins did not increase the yield. Maize yielded more $COMe_2$ than kao-liang.

II. Tapioca and sweet potato were used as source of carbohydrate; molasses does not ferment. The yield of $COMe_2$ was best when soya bean (or cake) was used as source of protein. For tapioca addition of kao-liang gave good results. CH. ABS.

Acetylmethylcarbinol fermentation. L. M. HOROVITZ-VLASSOVA and E. A. RODIONOVA (Zentr. Bakt. Par., 1933, II, **87**, 333—339).—$CHAcMe{\cdot}OH$ is produced by a no. of organisms, especially those of the *subtilis* group, which can utilise for this purpose sugars, polysaccharides, and glycerol. Smaller proportions of $\beta\gamma$-butylene glycol and sometimes Ac_2 are formed simultaneously. The former may be converted by the organism into $CHAcMe{\cdot}OH$ or with free access to O_2 may be oxidised to Ac_2. A. G. P.

Microbiology of the soil. VII. Nitrifying organisms. S. VINOGRADSKY (Ann. Inst. Pasteur, 1933, **50**, 350—432).—The activity of nitrifying organisms is inhibited by certain org. nutrient-containing materials, and nitrification does not occur until the microbial mineralisation of these is practically complete. NH_3, even in small concns., retards the development of *Nitrobacter*, which does not become active until NH_3 is almost entirely converted into NO_2'. The isolation of a no. of species of nitrifying organisms on SiO_2 gel media is described. The general p_H range of activity is 6·0—9·2. Certain species of *Nitrosomonas* tolerate $p_H < 6{\cdot}0$. The distribution and activity of certain species in soils of different types are recorded. A. G. P.

Silica bacteria. A. BRUSSOFF (Arch. Mikrobiol., 1933, **4**, 1—22).—The isolation of *B. siliceus* (nov. sp.) from soil is described. SiO_2 is accumulated by this organism and subsequently eliminated as minute granules. A. G. P.

Detoxification with special reference to sodium ricinoleate. I. T. H. RIDER (J. Lab. Clin. Med., 1932, **18**, 15—23).—Na ricinoleate (I) prepared from crude castor oil soap usually contains Na oleate (II), stearate (III), linoleate (IV), and dihydroxystearate (V). (III) and (V) do not appear to detoxify tetanus toxin; (II) and (IV) are much less effective than (I). The prep. of pure (I) is described. CH. ABS.

Lipin content of various types of tubercle bacillus. E. REMY (Biochem. Z., 1933, **259**, 238—239; cf. this vol., 190).—Polemical. W. McC.

Shaffer–Hartmann and Hagedorn–Jensen methods in determining polysaccharide in tuberculin. B. MUNDAY and F. B. SEIBERT (J. Biol. Chem., 1933, **100**, 277—285).—The Hagedorn–Jensen method (I) is more suitable for polysaccharide (II) determination than the Shaffer–Hartmann owing to its greater sensitivity to the pentoses. Free NH_2-acids must be removed before the determination; the Folin–Wu reagent (III) does not remove tryptophan (IV) and is therefore unsatisfactory in mixtures containing free NH_2-acids. The Somogyi $ZnSO_4$ reagent is less satisfactory, whilst the $HgSO_4$ and $Hg(NO_3)_2$ pptns. remove (II) besides (IV). Hence pptn. of N-containing material before hydrolysis with (III) or after hydrolysis with the Hg reagent and determination of the reducing substances by (I) give equally good results. H. D.

Growth factors of lower organisms. G. L. PESKETT (Biol. Rev., 1933, **8**, 1—45).—A review. NUTR. ABS.

Culture media containing carbamides. V. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1933, **15**, 55—61).—$CS(NH_2)_2$ at concns. below 1·25% has but little influence on the activity of *B. lactis acidi* and *B. ureæ*, or on *Saccharomyces*; *B. fluorescens liquifaciens*, however, is more sensitive. H. F. G.

Microbicidal action of organic acids and their copper salts. A. JANKE and F. BERAN (Arch. Mikrobiol., 1933, **5**, 54—71).—The growth-inhibiting (antiseptic) action and lethal effects of a no. of Cu, Bi, and Cd salts of org. acids on various bacteria and fungi are recorded. Buffering (to p_H 5·0) with NaOH appreciably reduced the toxicity of the acids. Introduction of additional CO_2H groups into fatty acid mols. or of their Cu salts reduced their inhibitory action. The introduction of a CO_2H group in the *o*-position to a phenolic OH or of OH in the *o*-position to the CO_2H group in an aromatic acid increased the

activity of the respective compounds. The activity of free acids was in general > that of the Cu salts, among which the salicylate and glycollate showed especially high toxicity. $CuCl_2$ was more toxic than $CuSO_4$. The growth-inhibiting action of Cu salts was smallest at the optimum growth p_H of the various organisms. *B. subtilis* was more sensitive to the inhibitory action of Cu salts and relatively less sensitive to lethal doses than were non-sporing organisms. Cd and Bi acetates and salicylates were less active than the corresponding Cu salts. A. G. P.

Irradiation of bacteriological media by ultra-violet rays. J. PROKS (Lait, 1933, **13**, 331—337).—Media of peptonised gelatin or gelose, in whey, were irradiated and subsequently inoculated with cultures of *St. lactis* or *cremoris*. Comparison with controls showed that the rate of development of micro-organisms was retarded considerably in the irradiated media, the effect increasing with time of irradiation. The count was higher in media irradiated before than after inoculation. Similar results were obtained with *B. coli*, *Sarcina lutea*, and *Torula lactis*. In pasteurised milk irradiated and subsequently inoculated with *St. lactis* the development of acidity was slightly slower than with that of the sample of milk inoculated but not irradiated. E. B. H.

Certain properties of toxicity curves. G. F. GAUSE (Protoplasma, 1933, **17**, 548—553).—The mechanism of the killing action of toxic substances on various organisms is of a composite character, each individual process predominating over a definite range of concn. of the poison. Toxicity curves therefore show more or less abrupt changes of direction. The Ostwald equation relating concn. and toxicity is applicable to each branch of the curve. Similar curves represent the action of mixed poisons, *e.g.*, $HgCl_2$+quinine on *Paramecium caudatum*.
A. G. P.

Influence of nutrition on adrenaline action. K. YOSHIO (J. Biochem. Japan, 1933, **17**, 11—27).—The hyperglycæmia (I) due to injection of adrenaline is greater and of longer duration with dogs on a carbohydrate-free diet (II) than with dogs on a carbohydrate-rich diet (III). With (II) the extent of (I) is also influenced by the relative amounts of fat and protein in the diet. In each case the lower is the content of glycogen in the muscle and liver the greater is the extent of (I). Hence the character of (I) due to adrenaline is not directly related to the condition of the glycogen depots of the body.
F. O. H.

Effect of insulin, adrenaline, and phloridzin on blood-phosphate and -lactic acid in rabbits. S. YAMADA (J. Biochem. Japan, 1933, **17**, 61—89).—Following the administration of normal doses of insulin (I), both the inorg. PO_4 (II) and lactic acid (III) decrease, whilst with convulsive doses there are slight increases, that in (III) being due not to direct glucose oxidation, but to a deficiency in the supply of O_2 to the tissues. Adrenaline (IV) produces a rise in (III), but (II) is unchanged. Phloridzin produces a slight fall in (III), whilst there is a slight increase followed by a slow and steady decrease in (II). The changes in hexose mono- and pyro-phosphate (V) during these reactions indicate that (I) promotes the conversion of (III) by way of hexose phosphate into glycogen, whilst (IV) promotes the opposite reaction. During hyperglycæmia (V) appears to promote the degradation of glucose into (III), a reaction not influenced by (I). F. O. H.

Action of insulin and adrenaline on the excretion of sulphur and nitrogen. B. M. JAKOBSON and H. REINWEIN (Arch. exp. Path. Pharm., 1933, **170**, 84—93).—Administration of insulin (I) to dogs produces an increased excretion of N which is not due to increased protein catabolism, since the urinary S remains const. and since the effect does not occur after diuresis induced by H_2O. Adrenaline (II) also produces an increased excretion of N in moderately starved dogs, whilst in severely starved dogs there is a decrease. Unlike (I), (II) causes an increased excretion of S, especially in dogs to which glucose has been orally administered until glycosuria results. That the increased excretion of S is not dependent on a hyperglycæmia follows from the increase due to injection of (II) into dogs previously rendered hypoglycæmic by injection of (I). F. O. H.

Purity of insulin preparations. N. A. NIELSEN (Skand. Arch. Physiol., 1933, **65**, 305—310).—The blood-sugar-raising component of impure insulin is more readily detected by the discharge of glycogen in the perfused liver than by the production of a preliminary hyperglycæmia when injected into the whole animal. NUTR. ABS.

Effect of thyreoglobulin on the secretion of insulin and adrenaline. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1932, **110**, 1001—1003; Chem. Zentr., 1932, ii, 3732).—Thyreoglobulin increases the secretion of insulin (I) and adrenaline (II), as does thyroxine (III), but less uniformly. In the organism (III) or a similar compound is liberated from thyreoglobulin. The increase in secretion of (I) is due to the increased production of (II). A. A. E.

Effect of thyroxine on glycogen content of cartilage. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1933, **86**, 383—386).—The glycogen of the liver, heart, and skeletal muscle of rabbits was greatly reduced after the animals had received thyroxine intravenously; the greater the no. of injections and amount injected the more marked was the diminution. The glycogen content of cartilage (ear and tracheal) was unaffected. NUTR. ABS.

Relations between the effects on animal growth of thymocrescin and thyroxine. W. W. NOWINSKI (Biochem. Z., 1933, **259**, 182—190; cf. A., 1932, 970).—As regards their growth-promoting effects on young rats and their effects on the sex organs thyroxine and thymocrescin act antagonistically.
W. McC.

Distribution of iodine in central nervous system after administration of thyroid products. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1933, **86**, 275—289).—In healthy rabbits the I content of the mid brain (I) and thereafter of the medulla was > that of other parts of the central nervous system (II). Administration of thyroxine caused a rise in the I content of (II), and especially

of (I). Oral administration of dried thyroid produced similar results noticeable only in (I). KI and di-iodotyrosine had no apparent effect. NUTR. ABS.

Changes in chemistry and secretion of bile under influence of thyroxine. S. LEITES and R. ISABOLINSKAJA (Klin. Woch., 1933, **12**, 149—150).—Injection or ingestion of thyroxine in dogs with permanent bile fistulæ greatly decreased the quantity of bile, and the bile salts, Ca and K, decreased in proportion, their % remaining unchanged. The cholesterol in the fistula fluid did not decrease and its concn. therefore greatly increased. NUTR. ABS.

Detoxication of thyroid hormone. I. E. HESSE, K. R. JACOBI, and G. BREGULLA [with H. DICKMANN and R. NAGEL] (Arch. exp. Path. Pharm., 1933, **170**, 13—25).—The toxicity of thyroid gland preps. (I) in mice is decreased by the feeding of egg-white, a prep. from rye germ, and myrcene. With dogs, 3·0 g. per kg. per day of (I) (D.A.B. VI) causes death in 15—41 days, whereas such a dose is harmless when 0·4 mg. per kg. body-wt. of Cu is added to the diet. Egg-white, $Fe^{\cdot\cdot}$, and $Fe^{\cdot\cdot\cdot}$ are also effective. The deprivation of fat from the liver and adipose tissue due to (I) is inhibited by Cu, which, however, is without action on the N and carbohydrate metabolism. The above action of Cu is due not to deposition of Cu in the liver or heart, but probably to the formation of non-toxic Cu derivatives of thyroxine. F. O. H.

Substances with thyroid-like action from artificially iodinated protein. I. ABELIN (Naturwiss., 1933, **21**, 223).—Substances not yet identified which possess both the morphogenetic and metabolic effects of thyroid gland have been obtained by decomp. of iodinated protein. Formation of products of this nature outside the thyroid is possible. R. K. C.

Maternal and fœtal distribution of parathyroid and thyroid hormones. S. UJIIE (Tohoku J. Exp. Med., 1932, **20**, 34—64).—The placenta is permeable to the hormones of the fœtus. CH. ABS.

Influence of parathyroid hormone on blood-calcium. G. MOSCHINSKI (Arch. exp. Path. Pharm., 1933, **170**, 1—7).—Following subcutaneous injection of parathyroid extract (I) into rabbits, the blood-Ca level (II) immediately rises, attains a max. after 15—20 min., then falls, and rises to a second max. val. 3 hr. after injection, after which the level falls to normal vals. The amount of (I) injected has no influence on the times of occurrence of the max. and min. vals. Injection of $CaCl_2$ (III) or Ca gluconate (IV) produces a max. val. of (II) in 30 min., the max. with (IV) being > with (III); no second max. occur. Injection of both (I) and (III) or (IV) produces an approx. summation of the two effects; the max. val. of (II) is high and the hypercalcæmia is prolonged. F. O. H.

Thyreotropic hormone of the anterior pituitary lobe. K. JUNKMANN and W. SCHOELLER (Klin. Woch., 1932, **11**, 1176—1177; Chem. Zentr., 1932, ii, 2480).—The effects on the rabbit's thyroid of injection of an aq. extract of the anterior pituitary lobe are described, and a unit is specified. By purification a powder of which 1 mg. represents 80—120 units was obtained. The hormone (I), which is insol. in org. liquids, rapidly loses its activity in aq. solution, is thermolabile, and is readily adsorbed by colloids. It is not dialysable through collodion or parchment; it appears to be related to the albumoses and peptones, and it resembles the gonadotropic anterior pituitary hormone, the posterior pituitary substances, and insulin. 1 kg. of dry, fat-free ox anterior pituitary lobe affords 0·25—0·5 million units. It was not found in normal human urine. Purified (I) had no gonadotropic properties, and prolan has no thyreotropic properties. (I) is not identical with Paal's hormothyrin, and does not affect the blood-$COMe_2$ of the rat. A. A. E.

Diabetic effect of anterior pituitary extracts in the dog. B. A. HOUSSAY, A. BIASOTTI, E. DI BENEDETTO, and C. T. RIETTI (Compt. rend. Soc. Biol., 1933, **112**, 494—496).—Normal, hypophysectomised, and thyroidectomised dogs, injected intraperitoneally with alkaline anterior pituitary extracts, developed hyperglycæmia, glycosuria, acetonuria, increased resistance to insulin, prolonged blood-sugar curves, hyperlipæmia, hypercholesterolæmia, and increased plasma-protein. Such actions are apparently sp., since control injections of other tissue extracts were without effect. NUTR. ABS.

Action of proteolytic enzymes on the oxytocic principle of the pituitary gland. J. M. GULLAND and T. F. MACRAE (Nature, 1933, **131**, 470; cf. A., 1932, 655).—The activity of the oxytocic hormone is destroyed slowly by aminopolypeptidase and rapidly by dipeptidase and proteinase from brewer's yeast. The inactivation is due apparently to an enzyme in these preps. having a p_H optimum at 7·4. Papain preps. also destroy the hormone rapidly. L. S. T.

Inhibition of œstrus by extracts of the anterior lobe of the pituitary body. M. C. D'AMOUR and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1933, **47**, 269—280).—From ox anterior pituitary lobes (I) and from whole sheep pituitaries (II), extracts have been prepared, best by extracting at an alkaline p_H, which inhibit œstrus in the adult female white rat and stimulate œstrus in the immature rat. The extracts made from (II) are more active in respect of both functions than those prepared from (I). Gland desiccated by $COMe_2$ may be satisfactorily used as the source of the extract. Extracts made from control tissues have no œstrus-inhibiting power. W. O. K.

Prolan and tumour growth. Inhibiting effect of prolan on implanted carcinoma in the white mouse. H. ZONDEK, B. ZONDEK, and W. HARTOCH (Klin. Woch., 1932, **11**, 1785—1786; Chem. Zentr., 1932, ii, 3433—3434).—The growth was largely inhibited by prolan but not by Ca or K salts, glucose, thyroxine, adrenaline, insulin, pituitrin, or folliculin. Prolan-*A* behaves similarly. A. A. E.

Excretion of the sexual hormones by the salivary glands. M. TRANCU-RAINER (Compt. rend. Soc. Biol., 1931, **106**, 1001—1002; Chem. Zentr., 1932, ii, 3731).—In pregnancy the saliva always contains the follicular-ripening and luteinising hormone. Tests for œstrin in the 2nd, 3rd, and 7th month were positive (*e.g.*, 500 mouse units per litre). A. A. E.

Colour reactions of the follicular hormones. E. SCHWENK and F. HILDEBRANDT (Biochem. Z., 1933, **259**, 240—242).—The β (I) and δ (II) forms and the dihydro-derivative (III) of (II) of the follicular hormone give the reaction of Montignie (A., 1932, 868), but pregnandiol and crude testicular hormones do not. (I) and (II) and also the hydrate (IV) of the hormone give the reaction of Gerngross and Voss, but (II) and Gerard's equilin (A., 1932, 433) do not. (I) and (IV) differ from (II) with regard to the colours which they develop on coupling with diazo-compounds, the results in this case being similar to those produced by *ar*-tetrahydronaphthols. Formulæ for (I) and (II) based on deductions from these reactions and in harmony with recent views are suggested. W. McC.

Reduction of the follicular hormone. E. SCHWENK and F. HILDEBRANDT (Naturwiss., 1933, **21**, 177).—Reduction converts the CO into a CH·OH group, affording the *dihydro-hormone*, $C_{18}H_{24}O_2$, m.p. 168—170° (*benzoate*, $C_{25}H_{28}O_3$, m.p. 187·5—190°), which gives a green H_2SO_4 solution with a blue fluorescence, and has an activity of 30×10^6 mouse units per g. in the Allen–Doisy test. The mother-liquor yields a *substance*, $C_{18}H_{24}O_2$, m.p. 198—204°, with an activity of 20×10^6 mouse units per g. A. C.

Constitution of the follicular hormone. A. BUTENANDT, H. A. WEIDLICH, and H. THOMPSON (Ber., 1933, **66**, [*B*], 601—604).—The hormone hydrate (I) is transformed by molten KOH into a phenoldicarboxylic acid (II), $C_{18}H_{22}O_5$, probably containing the CO_2H groups in the 1 : 5 position and formed by fission of a five-member ring between two *sec.*-OH groups. The hormone is not an intermediate, since it yields different products. (II) is smoothly dehydrogenated by Se to CO_2 and *hydroxy*-1 : 2-*dimethylphenanthrene* (III), m.p. 190—191° (*Bz* derivative, m.p. 210°; *Me ether*, m.p. 153°), which could not be oxidised to an *o*-quinone. (III) is converted by distillation with Zn dust into 1 : 2-*dimethylphenanthrene* (IV), m.p. 140° (*picrate*, m.p. 148°), also obtained synthetically. The production of (IV) from ætiobilianic acid (V) establishes the close relationship of (V) and (I). H. W.

Effect of liver extracts on blood-sugar. H. KAHLER and R. RIEDEL (Klin. Woch., 1933, **12**, 151—152).—The extracts had no significant effects on blood-sugar of rabbits (intravenously) or man (intramuscularly). NUTR. ABS.

Reactivation of the blood-forming action of liver by constituents of gastric mucosa. F. INUKAI and W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1933, **20**, 178—188).—When liver is fed to rabbits, the red blood-cell count and the Sahli hæmoglobin index increase, but liver digested with commercial pepsin (I) does not exert a similar action. Liver digested with fresh pig gastric mucosa (II) gives a positive result, whilst liver inactivated by digestion with (I) is reactivated by the addition of dried (II). (II) is itself without erythropoietic activity. Reactivation was not obtained with dried small intestine, œsophagus, or spleen. The active principle in (II) is thermolabile, extractable by H_2O or EtOH, but not by Et_2O. Its relationship to the substance curative in pernicious anæmia is obscure. W. O. K.

Review of vitamins and avitaminoses. W. WEISE (Arch. Schiffs- Trop.-Hyg., 1933, **37**, 44—53, 103—112, 152—160). NUTR. ABS.

A provitamin-*A*. A. WINTERSTEIN (Z. physiol. Chem., 1933, **215**, 51—58).—The fruit rind of *Gonocaryum pyriforme* contains lycopene, α- and β-carotene, and a cryst. *provitamin*-A, m.p. 160—165°, absorption bands 529·5, 492, 458, and 429 mμ in CS_2. The new product restored growth in *A*-deficient rats. J. H. B.

Determination of vitamin-*A* in oils. A. CHEVALLIER and P. CHABRE (Compt. rend. Soc. Biol., 1933, **112**, 375—376).—By biological tests the ratio of the vitamin-*A* potencies of three fish oils was found to be the same as the ratio of their absorptions at 328 mμ. The results by the two methods agreed within 13% and were in the range of error of the biological test. NUTR. ABS.

Value of determinations of vitamin-*A* by the reaction of Carr and Price. W. A. G. VAN EVERDINGEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1339—1347).—Measurements were made with a vac. thermo-element and with a photo-electric cell of the changes with time in absorption at 460, 610, and 615—650 mμ of mixtures of cod-liver oil and $SbCl_3$ in $CHCl_3$. Reproducible results could not be obtained, and it is concluded that the band at 608—630 mμ is the resultant of several reactions, and it remains to be proved that the vitamin-*A*–$SbCl_3$ reaction is one of these. R. K. C.

Reaction of Carr and Price as a test for vitamin-*A*. M. VAN EEKELEN, A. EMMERIE, H. W. JULIUS, and L. K. WOLFF (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 1347—1359).—Determinations of blue vals. of vitamin-*A* concentrates with a tintometer, a stuphometer, by photometry of the absorption spectrum, and by measurement of the absorption of monochromatic light of λ 620 mμ, gave concordant results. By treatment of concentrates with fuller's earth the 580 mμ chromogen is selectively absorbed, and may be eluted with 96% EtOH. In an experiment with rats, only the fraction containing the 620 mμ chromogen was active, contrary to Heilbron. The inhibition of the 620 mμ band in unsaponified cod-liver oils is due to the presence of an unsaturated acid not identical with linoleic or oleic acid. In presence of large amounts of carotenoids the $SbCl_3$ reaction is used for determination of vitamin-*A* after extraction of xanthophyll and allowance for the carotene present. R. K. C.

Determination of vitamin-*A* in oils by a spectrophotometric method. A. CHEVALLIER and P. CHABRE (Biochem. J., 1933, **27**, 298—302).—Measurement of the intensity of absorption at 3280 Å., taking into account pigment and free acidity of the oil, agrees fairly well with the biological test. H. G. R.

Relative velocities of the photochemical reactions of carotene and vitamin-*A* with radiation of wave-length 2650 Å. W. J. DANN (Biochem. J., 1933, **27**, 274—278).—Contrary to the observation

of Bowden and Snow (A., 1932, 656) vitamin-*A* is not formed from carotene by irradiation, the former being rapidly destroyed. H. G. R.

Effect of heat on the vitamin-*A* content of milk. M. LUNDBORG (Biochem. Z., 1933, **259**, 27—29).—The vitamin-*A* content of fresh whole milk is reduced by > 50% on heating (with vigorous stirring) at 63° for 30 min. and by 10% on boiling for 2 min. W. McC.

Effects of vitamins-*A* and -*D* on antibody production and resistance to infection. M. R. GREENE (Amer. J. Hyg., 1933, **17**, 59—101).

Vitamin-*A* in six varieties of frozen cherries. M. T. POTTER and M. A. DICKSON (J. Home Econ., 1933, **25**, 47—52).—The amount of frozen cherries containing 1 unit of vitamin-*A* was approx. 0·250 g. of the sour variety, 0·375 g. of the hybrid, and between 0·375 g. and 0·500 g. of the sweet variety. NUTR. ABS.

Extraction of the antineuritic (B_1) vitamin from dried brewers' yeast. A. SEIDELL (J. Biol. Chem., 1933, **100**, 195—203).—Samples of dried brewer's yeast vary greatly in their vitamin-B_1 content. The extraction of this factor by aq. MeOH, EtOH, and $COMe_2$ depends mainly on the concn. of the H_2O, and the addition of HCl increases the extraction of both vitamin and yeast solids. The best solvent is 70% aq. MeOH or EtOH or $COMe_2$ with 1% HCl, this giving 80% of vitamin and 10% of yeast solids in the extract. A. L.

Differential extraction from dried brewers' yeast of the antineuritic (B_1) and the growth-promoting (B_2) vitamins and their biological standardisation. Relation of hæmin to vitamin-B_2. M. I. SMITH (J. Biol. Chem., 1933, **100**, 225—235).—The differential extraction of vitamins-B_1 and -B_2 by percolation of dried brewers' yeast separately with MeOH, EtOH, and $COMe_2$ containing varying amounts of H_2O and HCl is studied. MeOH with 5% HCl removes both factors equally, and 76% aq. EtOH or 70% aq. $COMe_2$ both containing 1% HCl removes 80% of B_1 and no B_2, further additions of HCl or H_2O increasing the solubility of both factors. Hæmin of hæmatin administered to rats fed on a *B*-free diet supplemented with B_1 does not promote growth or prevent dermatitis. There is therefore no relationship between B_2 and hæmin or hæmatin. A. L.

Crystalline preparations of vitamin-B_1. H. W. KINNERSLEY, J. R. O'BRIEN, and R. A. PETERS (Biochem. J., 1933, **27**, 232—239).—Separation by Na phosphotungstate, $AuCl_3$, and crystallisation from EtOH yields a cryst. prep. of higher vitamin-B_1 activity than previously described. H. G. R.

Large-scale preparation of vitamin-B_1 and -B_4 concentrates. H. W. KINNERSLEY, J. R. O'BRIEN, R. A. PETERS, and V. READER (Biochem. J., 1933, **27**, 225—231).—Using the C adsorption method with baker's yeast, details are given for obtaining vitamin-B_1 and -B_4 concentrates. H. G. R.

Vitamin-B_4. R. TSCHESCHE (Ber., 1933, **66**, [*B*], 581—582).—The alleged vitamin-B_4 of Barnes *et al.* (this vol., 325) is identified as adenine. H. W.

Vitamin-*B* and the assimilation of sugar by the pigeon. Comparative action of fructose, glucose, galactose, and various disaccharides in a lipin-rich diet. R. LECOQ (Compt. rend., 1933, **196**, 807—809).—The carbohydrate component in the proposed diet for the study of avitaminosis-*B* in the pigeon (A., 1931, 530) was successively fructose (I), glucose (II), galactose (III), sucrose (IV), maltose (V), and lactose (VI). With (I), (II), and (III) the amounts of dried yeast necessary for maintenance of life forms the series (III)>(II)>(I), in agreement with that of the rates of absorption from the alimentary tract (A., 1926, 429), whilst the disaccharides form the series (VI)>(IV)>(V). Birds fed with (VI) or (III) and a large amount of vitamin-*B* survive only for a short period. F. O. H.

Effect of the composition of the nutrient medium on the production of vitamin-*B* by bacteria. M. SCHIEBLICH (Biochem. Z., 1933, **259**, 19—26; cf. A., 1931, 881).—Bacteria [*B. mycoides* (I) and *B. prodigiosum* (II)] which produced only small or moderate amounts of vitamin-*B* (III) when grown on the medium (IV) previously used produce considerably greater amounts in a medium (V) containing peptone and glucose to which citric acid and $NaNH_4$ phosphate are added. The ratio between the amounts produced by (I) and (II) remains the same as when (IV) is used. On (V) *B. lactis aerogenes* produces as much (III) as does (II), but if the glucose is replaced by starch, this bacterium produces less (III). *Vibrio alcaligenes* (Petruschky) produces as much (III) in (V) as does (I). W. McC.

Chemical nature of vitamin-*C*. J. L. SVIRBELY and A. SZENT-GYÖRGYI (Biochem. J., 1933, **27**, 279—285).—Prep. of ascorbic acid (I) from Hungarian paprika, where it occurs in relatively large quantities, is described. The *iso*propylidene derivative is a moderate antiscorbutic and the recovered acid fully active. (I) readily disappears from the adrenal gland of animals on a vitamin-*C*-free diet. H. G. R.

Chemical nature of vitamin-*C* or the *C*-vitamins. L. RANDOIN and R. NETTER (Bull. Soc. Chim. biol., 1933, **15**, 275—304).—A review.

Determination and distribution of ascorbic acid (vitamin-*C*) and glutathione in animal tissues. T. W. BIRCH and W. J. DANN (Nature, 1933, **131**, 469—470).—Ascorbic acid (I) occurs in various organs in amounts comparable with glutathione (II), and except in the suprarenal cortex up to 40% of the glutathione I titre may be accounted for by this acid. (I) and (II) may be two linked factors in one system of oxidation in the animal cell. L. S. T.

Vitamin-*C* and the suprarenal cortex. II. Loss of potency of guinea-pig suprarenals in scurvy. Determination of antiscorbutic activity (hexuronic acid) by chemical means. L. J. HARRIS and S. N. RAY (Biochem. J., 1933, **27**, 303—310).—Guinea-pig suprarenal loses its antiscorbutic activity, together with hexuronic acid (I), on a vitamin-*C*-free diet, unlike some other species (dog and rat) which can synthesise vitamin-*C*. A method of determining (I), using 2 : 6-dichlorophenol-indo-

phenol, has been evolved and a correlation established between (I) and vitamin-*C* in many sources, supporting the theory of their identity. H. G. R.

Alleged antiscorbutic activity of a mixture of methylnornarcotine and glycuronic acid. W. J. Dann (Biochem. J., 1933, **27**, 220—224).—Contrary to the observation of Rygh and Rygh (A., 1932, 1294), the mixture is devoid of activity. H. G. R.

Methylnornarcotine and vitamin-*C*. J. Reschke (Z. physiol. Chem., 1933, **215**, 164—166).—Methylnornarcotine prepared according to the method of Rygh and Rygh (A., 1932, 1294) failed to protect guinea-pigs against scurvy. J. H. B.

Antiscorbutic vitamin and glycuronic acid. E. M. P. Widmark and G. Glimstedt (Z. physiol. Chem., 1933, **215**, 147—150).—Contrary to the statement of Rygh and Rygh (A., 1932, 1294), the urine of guinea-pigs on a scorbutic diet gives a positive naphthoresorcinol reaction for glycuronic acid. J. H. B.

Vitamin-*C* in Japanese green tea. M. Miura and M. Tsujimura (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1933, **20**, 129—144).—Fresh Japanese green tea contains considerable quantities of vitamin-*C* (I), but stored samples tend to contain less, especially when stored for several years. Black tea fresh or stored contains practically no (I), whilst Bancha (coarse tea) contains at most only small quantities. W. O. K.

Vitamin-*C* in commercially sterilised milk and Japanese green tea. M. Miura and N. Okabe (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1933, **20**, 145—161).—A monkey, rendered scorbutic by a vitamin-*C*-free diet, improved, but did not completely recover when given 150 c.c. of commercially sterilised milk per day. An infusion of fresh Japanese green tea (about 0·5 g. per day) effected complete recovery. W. O. K.

Winesap apple as source of vitamin-*C*. M. T. Potter (J. Home Econ., 1933, **25**, 52—56).—The protective dose of the apples for guinea-pigs is approx. 10 g. Nutr. Abs.

Effect of *C*-avitaminosis on the lipase and catalase content of the animal body. P. Suomalainen (Biochem. Z., 1933, **259**, 200—202).—In guinea-pigs *C*-avitaminosis is not accompanied by appreciable changes in the lipase contents of the liver and pancreas or in the catalase content of the liver and blood. W. McC.

Properties of ergosterol and calciferol. A. L. Bacharach, E. L. Smith, and S. G. Stevenson (Analyst, 1933, **58**, 128—135).—The properties of ergosterol and calciferol are described. Consts. suggested are: ergosterol, m.p. 162—164°, $-157°$, $[\alpha]_D^{20} > -123\ 5°$ (both in $CHCl_3$ solution), and ultra-violet absorption 281 mμ $\lessdot 320$; calciferol, m.p. 115—117°, $[\alpha]_{546\cdot1}^{20} > +122°$, $[\alpha]_D^{20} > +103°$ (in EtOH solution), ultra-violet absorption $E_{1\ cm}^{1\%}$ 281 mμ $\lessdot 470$, and antirachitic activity $\lessdot 40 \times 10^6$ international units per g. T. McL.

Effect of irradiated ergosterol after removal of parathyroid glands from rats. D. W. Asher and J. H. Jones (J. Biol. Chem., 1933, **100**, 333—431).—The blood-Ca, bone-ash, lipins, H_2O, and org. matter of 50- and 75-days-old parathyroidectomised rats, fed on a Steenbock basal diet minus the milk ration, were compared with those to which 2000 units of irradiated ergosterol were fed daily. The serum-Ca of the untreated rats was at tetanic level, whilst that of the treated rats was higher but below normal. Bone analyses showed little difference between the two groups. H. D.

Parathyroid glands and toxicity of irradiated ergosterol. J. H. Jones (J. Biol. Chem., 1933, **100**, 343—348).—Rats in which parathyroid tetany had been induced were treated with irradiated ergosterol (I) and the min. lethal dose was found to be between 10,000 and 13,000 units per day per 100 g. body-wt., which was not appreciably < the normal control. The degree of hypercalcæmia produced by doses of 9750—19,500 units of (I) is not affected by parathyroidectomy; hence the toxicity of (I) is not due to stimulation of parathyroid tissue to greater activity. H. D.

Vitamin-*D* and the conservation of calcium in the adult. II. Vitamin-*D* and calcium conservation in adult rats fed on low calcium diets. III. Vitamin-*D* and the teeth of rats. V. M. Templin and H. Steenbock (J. Biol. Chem., 1933, **100**, 209—216, 217—224).—II. Adult rats fed for 8 months on a low-Ca diet (0·058%) and no vitamin-*D* (I) developed a prematurely senile condition with considerable loss in wt. Blood-Ca was reduced, but although the muscles became hypertonic, no tetany was observed. The femur-ash (II) was reduced in wt. by 10%. Introduction of moderate amounts of (I) into the diet of a parallel series of rats caused only 6·5% loss in wt. of (II), wt. losses in the animals were reduced, serum-Ca was increased, and the parathyroids had almost normal size as compared with control animals.

III. The incisor teeth of lactating female rats fed on a standard ration which did not maintain normal ash content of the bones showed normal Ca content, liberal addition of (I) having no effect. Administration of a diet low in Ca failed, however, to maintain the normal mineral composition of the teeth and bones even in non-lactating animals. Additions of (I) to this last diet caused almost normal mineralisation of the teeth. A. L.

Influence of fat-soluble vitamin on the amount of cholesterol in the blood in rabbits. S. Kusaka (Japan. J. Gastroenterol., 1932, **4**, 304—311).—Cod-liver oil and biosterol reduce the total cholesterol in the blood of rabbits by about 20%; hypercholesterolæmia follows. Ch. Abs.

Enriching yeast with vitamin-*D* by irradiation with ultra-violet rays. V. Vadimov, A. Voznaya, and V. Semashko (Elektr. Selsk. Choz., 1932, **2**, No. 8, 20—38).—Yeast and direct ultra-violet irradiation were more beneficial to chicks than cod-liver oil. Ch. Abs.

Antirachitic value of sardine oil for growing chicks. F. E. Mussehl and C. W. Ackerson (Poultry Sci., 1933, **12**, 31—33).—0·5% of sardine oil in the diet provided adequate protection against rickets. Nutr. Abs.

Influence of vitamin-*D* on hatchability and egg production. H. D. BRANION and J. B. SMITH (Poultry Sci., 1932, **11**, 261—265).—Irradiated ergosterol is not as efficient as cod-liver oil. CH. ABS.

Bone-ash method of determining effectiveness of vitamin-*D* supplements. J. L. ST. JOHN, C. KEMPF, and L. BOND (Poultry Sci., 1933, **12**, 34—36).—Ash determinations on different portions of the tibia from 8-week-old chicks, receiving a basal diet, with various increasing supplements of vitamin-*D*, showed that the vals. were very different for anatomically different parts of the same bone. NUTR. ABS.

Absorption spectrum of the vitamin-*E* fraction of wheat-germ oil. P. BOWDEN and T. MOORE (Nature, 1933, **131**, 512).—At liquid air temp. the broad diffuse bands become sharper and show detailed structure. Well-defined bands occur with max. at 4850, 4520, 4260, and 2550 Å. Exposure to air or O_2 at room temp. has no effect: H_2O_2 slightly increases absorption at 2400 Å., whilst O_3 destroys all bands except 2550 Å. and finally produces continuous absorption in the ultra-violet. L. S. T.

Determination of atmospheric carbon dioxide necessary for assimilation [by plants]. H. BRIESE (Landw. Versuchs-Stat., 1933, **115**, 75—129).—In a comparison of various methods that of Lundegardh proved most satisfactory. A modification of the apparatus is described by means of which the time of operation is reduced. A. G. P.

Seasonal fluctuations of chlorophyll assimilation by Algerian plants. C. KILLIAN (Compt. rend., 1933, **196**, 804—807).—The CO_2 assimilation and the humidity, light-strength, and temp. under which the determinations were performed are discussed in relation to the ecological characteristics of the plants. F. O. H.

Photoactivity of chlorophyll. A. H. ROFFO (Strahlenther., 1932, **45**, 115—124).—The photoactivity of chlorophyll persists for $>$ 1 month after its extraction from the plant and is of higher intensity if the extraction is carried out in the cold. As with cholesterol, the photoactivity is attributed to some form of mol. oxidation. NUTR. ABS.

Catalase activity and respiration in the leaves of growing barley. M. N. POPE (J. Agric. Res., 1933, **46**, 35—40).—Respiration rates were high in young leaves and decreased towards maturity. Catalase activity was low in early growth, rising to a max. at maturity and subsequently declining. A negative correlation between respiration rates and catalase activity in young leaves is recorded. With advancing maturity the relationship became irregular. A. G. P.

Respiration and ion intake [by plants]. H. LUNDEGARDH and H. BURSTROM (Planta [Z. wiss. Biol.], 1933, **18**, 683—699).—From solutions of nitrates (except NH_4NO_3) the intake of anions is more rapid than that of cations, especially in the case of Mg. From solutions of chlorides the cations were the more rapidly taken up, although considerable cation exchange occurs. Respiratory CO_2 serves partly to neutralise the excess of cation and partly to maintain a slightly acid reaction (p_H 5·8—6·2) in the nutrient solution. With a heavy excess of cations, CO_2 elimination is insufficient for this purpose and the p_H of the solution rises. Where cation intake predominates and the p_H of the solution falls, CO_2 elimination from the roots reaches a min. The presence of colloidal SiO_2 in the medium does not disturb the regulation of the reaction of the solution by CO_2. Interrelationships between respiratory activity and the p_H of the medium do not involve variations in the permeability of the root cells, but are explicable as an equilibrium between the diffusion pressure of CO_2 and the p.d. between the solution and the protoplasm of the cells. A. G. P.

Co-enzymes and banana respiration. J. M. NELSON and C. HEMPERLY (J. Amer. Chem. Soc., 1933, **55**, 1102—1106).—Aq. extracts of (and the expressed juice from) banana pulp contain material which activates yeast *apo*zymase but to a smaller extent than yeast cozymase. The activity is not lost by short boiling, but is lost when a solution (p_H 6·4) is evaporated; the activator is largely destroyed by alkali (p_H 9·4), is fairly resistant to acid (p_H 1), and diffuses through a collodion membrane. The action of the activator is increased by a little $MgCl_2$; MeCHO has practically no effect. Banana pulp also contains phosphatase and carboxylase. H. B.

Nitrogen fixation by alders (*Alnus*). A. I. VIRTANEN and S. SAASTAMOINEN (Suomen Kem., 1933, **6**, B, 57—58).—In sand cultures *Alnus* grown in N-free nutrients and inoculated with nodule organisms produced better growth than those uninoculated but supplied with NH_4NO_3. A. G. P.

Carbohydrates and carbohydrate metabolism of foliage. II. Inversion of sucrose in leaves after treatment with ether. H. SCHROEDER and F. HERRMANN (Biochem. Z., 1933, **259**, 231—237; cf. A., 1931, 1197).—The use of Et_2O (Chibnall, A., 1923, i, 635) is unsatisfactory when investigating carbohydrate metabolism in foliage, since the invertase is not destroyed, and hence hydrolysis of sucrose is not stopped. Steam or boiling EtOH may be used. Since Et_2O does not destroy enzymes it may be employed when they are to be detected or determined indirectly. Post-mortal alterations due to enzymes may also occur in expressed juices. W. McC.

Processes of fat formation in plants. S. IVANOV and P. KLOKOV (Allgem. Oel- u. Fett-Ztg., 1933, **30**, 149—152).—The linolenic acid content of linseed (in Moscow) increases during ripening, whilst the oleic acid, and particularly the linoleic acid, content decreases. Formation of fat in the plant is considered to proceed according to the scheme: (*a*) glucose→glycerol, (*b*) glucose→saturated→unsaturated fatty acids, (*c*) fatty acid plus glycerol→fat. MeCHO, $EtCO_2H$, hexoic, octoic, and decoic acids were identified in unripe sunflower-, mustard-, and flax-seed; it is suggested that the lower acids are first formed in all seeds, but that, in northerly climates, they are transformed into higher fatty acids as ripening proceeds. E. L.

Phosphatides of plant cells. V. GRAFE (Protoplasma, 1933, **17**, 602—609).—The role of phos-

phatides in the physiological process of plant cells is reviewed and discussed. A. G. P.

Decoic acid from the seed fat of the California bay tree. C. R. NOLLER, I. J. MILLNER, and J. J. GORDON (J. Amer. Chem. Soc., 1933, **55**, 1227—1228).—The Me esters of the fatty acids (prepared by alcoholysis of the fat) are separable into Me decoate (28%) and laurate (54%). The free fatty acids consist of octoic (1%), decoic (37%), and lauric (62%). H. B.

Pyrethrum flowers. V. Presence of pyrethrolon and methylpyrethrolon in the flowers. C. B. GNADINGER and C. S. CORL (J. Amer. Chem. Soc., 1933, **55**, 1218—1223; cf. Ripert, B., 1931, 1154).—Pyrethrins I and II are freed from pyrethrolon (I) and its Me ether (II) by treatment of a solution in light petroleum with aq. $KMnO_4$; (I) and (II) are destroyed, whilst the former are only oxidised slightly. (I) and (II) are not present in the light petroleum extracts of freshly harvested flowers from three sources. Aged (10 months) flowers contain autoxidised pyrethrins which are more readily oxidised by aq. $KMnO_4$ in Et_2O than pyrethrins I and II. H. B.

Presence of anthocyanins or oxyflavones in aleurone grains of *Gramineæ*. J. CHAZE (Compt. rend., 1933, **196**, 952—955).—The aleurone cells of red maize seeds (*Zea*) contain oxyflavone compounds (I) and adsorbed anthocyanins (II). In other varieties of yellow or white maize (I) may be converted into (II) during germination. A. C.

Anthocyanins. III. Distribution of leucoanthocyanins. G. M. ROBINSON and R. ROBINSON (Biochem. J., 1933, **27**, 206—212).—Leuco-anthocyanins (I) are extracted with boiling 1% HCl together with anthocyanins (II) and anthocyanidins (III). (II) can then be hydrolysed before (I) is attacked. (III) is removed by $C_5H_{11}\cdot OH$ and, after further concn., (II) is obtained from the decomp. of (I). H. G. R.

Pigment of "Kuro-mame." C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1933, **9**, 17—18).—Cyanin was isolated from the H_2O-sol. pigment. A. A. L.

Glucosides of *Philyrea latifolia*, L. A. KRAMER (Compt. rend., 1933, **196**, 814—816).—Philyrin (A., 1886, 1040), m.p. 162° (block), $[\alpha]_D$ +46·71°, is hydrolysed by H_2SO_4, emulsin, or powdered *Aspergillus niger*, yielding glucose (33·92%) and philygenol (I), $C_{21}H_{24}O_6$, m.p. 134·5° (block), $[\alpha]_D$ +121·70°. (I), which has a phenolic and three OMe groups, yields protocatechuic acid on fusion with alkalis. *P. latifolia* yields a second glucoside, syringin (A., 1889, 159), which also occurs in *P. decora*. F. O. H.

Biochemistry of *Salix*. V. *iso*Salipurposide. C. CHARAUX and J. RABATE (Compt. rend., 1933, **196**, 816—818).—The yellow part of the cambium of *S. purpurea*, L., yields iso*salipurposide* (I), m.p. 175°, $[\alpha]_D$ −19·01° (hydrated), −20·4° (anhyd.). Hydrolysis by H_2SO_4 or emulsin gives glucose and salipurpol, indicating isomerism with salipurposide (A., 1931, 1100). A structure of the flavone type for (I) is advanced. F. O. H.

Presence of mannitol in the genus *Delphinium*. R. JARETZKY and C. SCHAUB (Arch. Pharm., 1933, **271**, 171—174).—All of 25 species examined contained mannitol. R. S. C.

Reducing sugar of the flower of *Matricaria chamomilla*, L. C. BÉGUIN (J. Pharm. Chim., 1933, [viii], **17**, 241—248).—Little, if any, glucose is present, but considerable quantities of fructose have been obtained. β-Methylglucoside is absent, as indicated by attempted hydrolysis with emulsin. The Jerusalem artichoke is the only other plant known to contain fructose without glucose. A part of the reducing power of camomile extracts is due to non-carbohydrate substances. P. G. M.

Preparation of *l*-galactose from linseed mucilage. E. ANDERSON (J. Biol. Chem., 1933, **100**, 249—253).—A method is described for the prep. of *l*-galactose from linseed and from linseed mucilage (I) giving yields of 0·4 and 12%, respectively, for the crude product. (I) contains 11% of galactose as determined by hydrolysis and conversion into mucic acid after removal of galacturonic acid by $BaCO_3$. A. L.

X-Ray investigation of Konnjaku-mannan. I. SAKURADA and K. HUTINO (J. Soc. Chem. Ind. Japan, 1933, **36**, 90—92B).—Not only do the spectra of the α- and β-modifications differ, but the former gradually dissolves in H_2O at room temp., whilst the latter is insol. at 100°. The product obtained by pptn. of a 1% solution with 20 vols. of 95% EtOH shows the α-spectrum. By evaporation of a 1% solution at 40—100° or by treatment with excess of hot aq. $Ca(OH)_2$ the β-modification is obtained. P. G. M.

Amount and distribution of oxalic and malic acids in the coffee plant. E. HERNDLHOFER (Biochem. Z., 1932, **259**, 168—174).—The fruit of the plant has low contents of oxalate (I) and malate (II) as compared with other parts, and these contents remain unchanged during development and ripening, and also, after harvesting, during the drying. During germination, large amounts of both acids are produced in the seeds, which, at other times, are almost free from them, although the shells of the fruit contain them. The max. content of the acids is attained in the stems and roots of the young plants after 6 months, but subsequently it decreases. The leaves attain their max. content of the acids somewhat later. In the mature plants (I) accumulates in the bark and older parts, but (II) falls to a min. in all parts. Succinic, citric, and tartaric acids are not found in the coffee plant. W. McC.

Differences in the amino-acid content of the chief protein (glycinin) from seeds of several varieties of soya bean. F. A. CSONKA and D. B. JONES (J. Agric. Res., 1933, **46**, 51—55).—In the varieties examined, the tryptophan content of the glycinin was 1·89—2·84% and cystine vals. were 0·74—1·46%. Variations are ascribed to differences in the relative proportions in which the globulins comprising the glycinin fractions occur in different varieties. Nutritional aspects of these variations are discussed. A. G. P.

Proteins of Indian foodstuffs. IV. Fenugreek (*Trigonella fœnum graecum*). Y. V. S. RAU and M. SREENIVASAYA (J. Indian Inst. Sci., 1932, **15A**, 122—124).—Flour prepared from the seeds of fenugreek contained ash 3·55%, Et_2O extractives 8·10%, crude protein 29·90%, starch 2·11%, cellulose 21·00%, lignin 2·23%, other carbohydrates 33·02%. Two protein fractions isolated by extraction with 6% NaCl solution have been analysed. One has the properties of a globulin, contains S but no P, and has a very high content of histidine (11·6%), whilst the other, probably an albumin, contains both P and S. W. O. K.

Vegetable proteins. I. Preparation of purified edestin. G. FLORENCE, J. ENSELME, and M. POZZI (Bull. Soc. Chim. biol., 1933, **15**, 135—146).—Edestin was prepared from hemp-seed (I) by various methods and the composition and the ultra-violet absorption of 0·01*N*-HCl solutions of the products were determined. A product with the highest content of N (18·7%) and with the lowest content of cyclic NH_2-acids and absorptive power was considered the most pure. For its prep. defatted (I) was extracted at 60° with 5% NaCl, the extract allowed to cool slowly, and the ppt. recrystallised from 5% NaCl in the same way. F. O. H.

Cystine and sulphur content of bushes and grasses in a Karroid area (Fauresmith). M. HENRICI (18th Rep. Dir. Vet. Serv., Union S. Afr., 1932, 579—595).—No relationship between protein, S, and cystine could be established. The cystine content was usually about 0·02% on the dry matter, the highest vals. being found in plants at the time of vigorous growth. The total S content and cystine contents of the bushes were > those of the grasses. NUTR. ABS.

Arginine content of chlorophyll-defective leaves. H. VON EULER and D. BURSTRÖM (Z. physiol. Chem., 1933, **215**, 47—50).—Although the arginine (I) content of barley seedlings is a function of time of germination, no difference was observed between chlorophyll-normal and -defective mutants of the same age. Variegated pelargonium contains 50—100 times as much (I) in the white leaf-edges as is present in the green inner portions of leaf. J. H. B.

Ratio of chlorophyll-*a* to chlorophyll-*b* in mutants defective in the pigment. H. HELLSTRÖM and D. BURSTRÖM (Biochem. Z., 1933, **258**, 221—227).—In some barley mutants defective in chlorophyll the ratio of chlorophyll-*a* to -*b* (I) is the same as in normal barley and in other plants, but certain defective mutants contain practically no (I). W. McC.

Permeability in *Chara ceratophylla*. I. Normal composition of cell sap. R. COLLANDER. **II. Permeability to non-electrolytes.** R. COLLANDER and H. BÄRLUND (Acta Bot. Fennica, 1930, No. 6, 1—20; No. 11, 1—114). I. The total salt concn. of the sap is about 1·5%, protein < 0·1%, and other org. compounds ≯ 0·3%. These vals. lie between those of *Valonia macrophysa* and *Nitella clavata*, but are > the salt concn. of the nutrient solutions. The mechanism of salt transport is discussed.

II. The permeability of the cells to a large no. of non-electrolytes was determined. Urea will not penetrate the membrane at p_H 4·8, but it will do so at p_H 7·0; it is considerably more toxic than NH_2·CO·NHMe (I). An increase in the concn. of the outer solution has no effect on the distribution ratio. As compared with living cells, the dead cells show a much increased permeability to all non-electrolytes; the effect is particularly marked in the case of sucrose, glycerol, and urea, less so with substances of the type of MeOH and (I). Lipin-sol. substances, such as Me_3 citrate, diffuse into the cell relatively rapidly. The presence of more than one non-electrolyte has no effect on the permeability to a solution of a single substance. In general, alcoholic OH groups reduce and esterification increases penetrating power, whilst, in a homologous series, the latter varies directly with the length of the C chain. The mechanism of the permeability of the cell membrane is discussed. P. G. M.

Protein metabolism of potash-deficient plants. K. SCHMALFUSS (Phytopath. Z., 1932, 5, 207—249).—A deficiency of K in the nutrient of higher plants is associated with a smaller total dry-matter production, but a higher % of dry matter and of N in the tissues. The latter results from an increased proportion of sol. N rather than protein-N. The distribution of the N fractions depends on environmental conditions and on whether it is supplied as $NH_4^{\cdot}$ or NO_3'. The abnormalities resulting from K deficiency are more marked when Ca than when Na is substituted for K in the nutrient. Relationships between the K supply, the activity of the plant colloids, and the carbohydrate metabolism are also discussed. A. G. P.

Chemical transformations of phosphorus in the growing maize plant with results on two first-generation crosses. E. E. DE TURK, J. R. HOLBERT, and B. W. HOWK (J. Agric. Res., 1933, **46**, 121—141).—Phytin is absent from all organs of the yellow dent maize plant prior to pollination and appears in the developing seeds (but not in other organs) about 14 days after pollination. At this period the P gradient in the plant rises steadily in the order root, stalk, shank, ears. During germination phytin disappears fairly rapidly from the seed. During the growth of the plants the % of phospholipin and of acid-insol. (0·2% HCl) org. P (I) in the dry matter varied but little. There was a general tendency for the (I) and the inorg. P (II) to decrease as growth advanced. Translocation of P within the plant occurs only with (I) and (II). A. G. P.

Application of the biometric method to the investigation of the role of mineral matter in the life of plants. N. T. DELEANU (Bul. Tutunului, 1932, **21**, 215—241).—Comparison of analytical data of plant tissues expressed as % of fresh or dry wt. of material may yield misleading results. The vals. in abs. wt. of constituent as % of the max. content which is attained at the flowering period have been calc. Three stages of growth are differentiated: (*a*) "development period" with an increasing intake of nutrients, (*b*) the true assimilation period ("period of protoplasmic constancy") in which the N and P contents of the tissue remain unchanged,

and (*c*) the negative translocation period during which a proportion of the nutrient returns to the soil. Leaves take up only sufficient nutrients to maintain the chemical processes in the cells and do not accumulate a reserve. Stage (*c*) represents the rejection of minerals now surplus to requirement. Simultaneously surplus protein is broken down and is translocated as NH_2-acids or NH_4 salts. Surplus Ca is not returned to the soil, but is pptd. as oxalate. The elimination of free H_2O during flowering frequently precedes that of surplus minerals and is an independent process. Cell membranes vary in permeability during the three growth stages. In tobacco the second flowering period is accompanied by a similar series of movements of mineral matter. A. G. P.

Iodine content of food in coastal mid-China. W. H. ADOLPH and P. C. WHANG (Chinese J. Physiol., 1932, **6**, 345—352).—I is found in vegetable and marine foods in the Soochow–Shanghai area to a considerable extent, the largest amounts occurring in cabbage and *Laminaria*, which have 0·8 and 240 pts. per 10^6 of dry wt., respectively. The average daily intake per person in this area, which is non-goitrous, is $32—66 \times 10^{-6}$ g. per day. A. L.

Injurious effects of manganese and iron deficiencies on the growth of citrus. A. R. C. HAAS (Hilgardia, 1932, **7**, No. 4, 181—204).—A deficiency of Mn produces in citrus leaves chlorosis, but no mottling. Gum spots appear on both sides of the leaves, which in acute stages absciss prematurely. Shoots die back and exude gum. Roots are not affected. Chlorosis may also result from excessive concns. of Mn in the nutrient, even in the presence of much Fe. Subnormal amounts of Fe accumulate in Mn-deficient leaves. Leaf mottling, as well as chlorosis, takes place in Fe-deficient leaves. A. G. P.

Bromine in plant pathology. F. MERKENSCHLAGER (Pharm. Ztg., 1933, **78**, 162).—A summary of the knowledge of the action of Br compounds, particularly eosin, on germination and growth of seeds. E. H. S.

Substance causing withering in plants. M. LUDTKE and H. ACHMED (Biochem. Z., 1933, **257**, 256—266).—The growth in artificial media of *Fusarium vasinfectum*, Atk., and *F. lycopersici*, Sacc., on their respective plant hosts is studied. Parasitic withering is due to an amine produced during growth of the culture. P. W. C.

Effect of dyes on plant pathogenic micro-organisms. H. H. THORNBERRY (Trans. Illinois State Acad. Sci., 1931, **23**, 200—203).—Me-violet (1 in 50,000) inhibits bacterial spot of peach (*B. pruni*); malachite-green is more toxic than Me-violet. Me-violet, gentian-violet, and malachite-green (1 in 100,000) cause disjunction of apple cells, apparently owing to stimulation of enzymic activity. CH. ABS.

Virus diseases and intracellular inclusions in plants. F. M. L. SHEFFIELD (Nature, 1933, **131**, 325—326). L. S. T.

Virus diseases of the potato: comparison of the carbohydrate metabolism of normal with that of leaf-roll potatoes. E. BARTON-WRIGHT and A. MCBAIN (Trans. Roy. Soc. Edin., 1932, **57**, 309—349).—Numerous analyses of various parts of potato plants in respect of reducing sugars, sucrose (I), and starch (II) indicate that in healthy plants (I) is the sugar of translocation, whilst in those affected with leaf-roll the transport of (I) is prevented in consequence of the damaged condition of the phloem through which it usually passes. The stoppage of (I) translocation accounts for the accumulation of (II) in the leaf laminæ and the reduction in the no. of tubers. A certain amount of carbohydrate translocation occurs in leaf-roll plants through the ground parenchyma in the form of hexose. In normal plants the first carbohydrate product of photosynthesis is hexose, which then condenses to (I) and (II). W. O. K.

Eliminating the use of calcium carbonate in preparing plant tissue for analysis. F. E. DENNY (Contr. Boyce Thompson Inst., 1933, **5**, 103—114).—The practice of adding $CaCO_3$ to prevent hydrolysis of sugars by org. acids in plant material prepared for analysis is unnecessary and in material treated with boiling EtOH does not fulfil its intended purpose. The action of org. acids on inulin is similar to that on sugars and the risk of hydrolysis is no greater. A. G. P.

Applications of the H_2SO_4–HNO_3–$HClO_4$ method of destroying organic matter. R. FABRE and E. KAHANE (Ann. Chim. Analyt., 1933, [ii], **15**, 49—56).—The method described (this vol., 308) is applicable to the determination of As, Hg, Cu, Mn, and Cr. R. S. C.

Semi-micro-method for determination of carbon in biological fluids. H. R. KANITZ (Biochem. Z., 1933, **257**, 361—362).—Certain details of Osuka's method are more clearly defined and an example of its use is given (cf. A., 1932, 550). P. W. C.

Colorimetric determination of glutathione. R. FLEMING (Compt. rend. Soc. Biol., 1931, **106**, 259—260; Chem. Zentr., 1932, ii, 3445).—The colour developed by thiol compounds (comparison substances thiolactic acid and cysteine hydrochloride) and Na nitroprusside is comparable with that of a dil. acid solution of neutral-red. The comparison must be made at const. temp. (22°). Determination thus of the glutathione in fresh brewer's yeast gives higher vals. than those afforded by iodometric titration. A. A. E.

Principles of ultrafiltration as applied in biological studies. W. J. ELFORD (Proc. Roy. Soc., 1933, **B**, **112**, 384—406).—The factors influencing ultrafiltration with graded collodion membranes have been investigated using dyes, metal sols, proteins, and bacterial and virus suspensions as disperse systems. The particle sizes of suspensions, determined by filtration, agree with vals. otherwise obtained. Theoretical considerations are presented which account for the fact that the pore size of a limiting membrane is $>$ the size of retained particles in colloidal disperse systems. A. C.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1933.

General, Physical, and Inorganic Chemistry.

Glow discharge in highly dried molecular gases. A. GUNTHER-SCHULZE and F. KELLER (Z. Physik, 1933, **81**, 528—538).—When dried with P_2O_5, H_2 gave a new highly coloured discharge; N_2 and O_2 became chemically very active, attacking even Pt. A. B. D. C.

Spectrum of H_2. Bands ending on $2p^3\Pi$ levels. II. O. W. RICHARDSON and P. M. DAVIDSON (Proc. Roy. Soc., 1933, **A**, **140**, 25—58).—The band systems coming from $3d^3\Sigma$, $3d^3\Pi_{ab}$, and $3d^3\Delta_{ab}$ and ending on $2p^3\Pi_{ab}$ levels, which have been previously described (A., 1931, 887), are reconstructed and extended. The properties of the levels are discussed, and some of the principal consts. determined. L. L. B.

Theory of uncoupling and formulæ for the Stark effect in hydrogen. J. K. L. MACDONALD (Proc. Roy. Soc., 1932, **A**, **138**, 183—204).—Mathematical. L. L. B.

Anode glow discharge. A. GUNTHER-SCHULZE and F. KELLER (Z. Physik, 1933, **81**, 799—815).—Measurements of the anode fall in potential show that the fast electrons from the cathode move much farther from the cathode than has hitherto been assumed. The unperturbed anode fall is 20·5 volts in H_2, 30 volts in N_2, and 14 volts in O_2. Presence of dark spaces and velocity distributions of electrons in the anode column are discussed. A. B. D. C.

Continuous electron affinity spectrum of hydrogen. C. K. JEN (Physical Rev., 1933, [ii], **43**, 540—547).—Mathematical. The intensity distribution in the continuous emission spectrum due to the capture of electrons by normal H atoms and the absorption coeff. in the corresponding absorption spectrum due to the neutralisation of negative H ions are calc. by wave mechanics. N. M. B.

Absolute probability of excitation of helium 2^1P at zero angle. J. E. TAYLOR and R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1933, **2**, 383—385).—The impact of 40—400-volt electrons with He atoms has been investigated, the inelastically scattered electrons at zero angle being observed. The probability of 2^1P excitation is approx. a linear function of the energy of the incident electrons. The excitation probability is lower than that predicted by recent theories. J. W. S.

Structure of the emission line 6708 of lithium. L. ALLEGRETTI (Atti R. Accad. Lincei, 1932, [vi], **16**, 33—35).—In the arc spectrum of Li the above line consists of two principal components with a separation of 0·155 Å., and a third less intense line separated by 0·149 Å. from the component of greater wave-length. O. J. W.

Stark effect. E. U. CONDON (Physical Rev., 1933, [ii], **43**, 648—654).—Discussions on the Stark effect in at. spectra are illustrated by data on Ni, Li, C, and A. N. M. B.

Fine structure of the metastable $^2D_{5/2,3/2}$ terms of nitrogen. V. TSCHULANOVSKY (Z. Physik 1933, **82**, 134—136). A. B. D. C.

Optical properties of the alkali metals. R. W. WOOD (Nature, 1933, **131**, 582).—New observations with thin films are described. L. S. T.

Anode spot in a neon tube. T. TAKAMINE, T. SUGA, and A. YANAGIHARA (Nature, 1933, **131**, 584).—The anode spot in a discharge tube filled with Ne is intermittent in its emission. L. S. T.

Band and line fluorescence in sodium vapour excited by absorption. A. JABŁONSKI, P. PRINGSHEIM, and R. ROMPE (Z. Physik, 1932, **77**, 26—34).—Fluorescence was excited in Na vapour at 300—400° by the continuous spectrum in the blue-green and red; a study of the relative intensities of the bands and lines on addition of He, A, and N_2 revealed that the excited Na_2 mol. is dissociated by collision. A. B. D. C.

Perturbed series of the spectrum of ionised aluminium. L. PINCHERLE (Atti R. Accad. Lincei, 1932, [vi], **16**, 35—40).—Mathematical. The calc. divergence of certain series in the spectrum of Al II from the Ritz form agrees with the theory of Shenstone and Russell (A., 1932, 439). O. J. W.

Arc spectra of chromium, manganese, cobalt, and nickel in the red and near infra-red. H. SLEVOGT (Z. Physik, 1933, **82**, 92—118).—The region studied was 6000—9000 Å. A. B. D. C.

Isotope displacement and nuclear moment of zinc. H. SCHÜLER and H. WESTMEYER (Z. Physik, 1933, **81**, 565—570).—Hyperfine structures of some Zn II lines give isotopes 64, 66, 67, and 68, and the nuclear moment of 67 as 3/2. A. B. D. C.

Nuclear moment of arsenic. M. F. CRAWFORD and A. M. CROOKER (Nature, 1933, **131**, 655—656).—The nuclear moment of As is $1\frac{1}{2} \times h/2\pi$. Details of the hyperfine structure of the spectrum of As IV are recorded. L. S. T.

Intensity relations in the cadmium spectrum. J. L. VERHAEGHE (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 71—73).—The intensity relations of certain Cd lines, exhibited by alloys of Ag and Cd containing 4% and 1% Cd, are discussed. W. R. A.

Paschen–Back effect of hyperfine structure and polarisation of resonance radiation. Cadmium (6^1P_1—5^1S_0). N. P. HEYDENBURG (Physical Rev., 1933, [ii], **43**, 640—647).—Experimental data for the polarisation of Cd λ 2288 Å. resonance radiation, changing from 76·7% in zero field to 100% in a strong field ‖ electric vector of the exciting light, are in good agreement with results calc. on the Goudsmit–Darwin theory of the Paschen–Back effect, and give $12{\cdot}6\times10^{-3}$ cm.$^{-1}$ for the separation of the two levels into which the 6^1P_1 level of Cd (odd isotopes) is split. N. M. B.

Significance of Hg A bands at 2365 and 2285 A. and of the Hg_2 band at 1690 Å. W. FINKELNBURG (Z. Physik, 1933, **81**, 781—784). A. B. D. C.

High-frequency discharge in gases. T. V. IONESOU and (MME.) I. MIHUL (Compt. rend., 1933, **196**, 1292—1294; cf. A., 1932, 554; this vol., 9).—On applying a magnetic field parallel to the axis of a tube containing gas at 0·001—0·1 mm. Hg and perpendicular to the field produced by a Mesny oscillator, if the latter be moderately heated but little light is emitted and that mainly at the electrode. This disappears at the strength of field for which the free electrons are in resonance with the external electric field. A stronger magnetic field greatly increases the light, indicating that such a field reduces the potential required to maintain the discharge, but it again diminishes on further increase of the field. C. A. S.

Fine structure of the arc lines of lead and tin. S. B. L. MATHUR (Phil. Mag., 1932, [vii], **14**, 270—275). N. M. B.

Uniform positive column. F. L. JONES (Phil. Mag., 1933, [vii], **15**, 958—968).—Theoretical. H. J. E.

Evidence for a spinning photon. I. Intensity relations in the Raman spectrum of hydrogen. S. BHAGAVANTAM (Indian J. Physics, 1932, **7**, 107—138).—The intensity and polarisation of the lines in the Raman spectrum of H_2 are compared with the vals. calc. from wave mechanics (cf. Manneback, A., 1931, 21). J. W. S.

Verification of Compton's arc theory by measurement of the arc gas temperature at different pressures. L. S. ORNSTEIN, H. BRINKMAN, and A. BEUNES (Z. Physik, 1932, **77**, 72—81). A. B. D. C.

Discharge delay in homogeneous electric fields and in air at atmospheric pressure. R. STRIGEL (Wiss. Veroff. Siemens-Konz., 1932, **11**, No. 2, 52—74). A. J. M.

Visible part of the Northern Light spectrum. L. VEGARD (Z. Physik, 1933, **81**, 556—559).—Correction of wave-lengths already given (A., 1932, 1187). A. B. D. C.

Determination of Lande's g-factor by means of the Einstein–de Haas effect with pyrrhotine. F. COETERIER (Naturwiss., 1933, **21**, 251—252).—Pyrrhotine, a compound of Fe and S, is easily magnetised in one plane, but at right angles to this is almost non-magnetic. The magnetism depends partly on orbital moment, and not alone on spin moment (cf. ferromagnetism). The relative presence of orbital and spin moments can be determined by finding the Lande g-factor, which is 0·6, indicating both orbital and spin moments in the magnetism, the two being in opposite directions. A. J. M.

True and apparent intensity distribution in spectral lines. II. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, 1933, **81**, 428—434).—The integral equation of I (this vol., 201) is applied to particular cases. A. B. D. C.

Possible variation in energy of atomic processes occurring in a small interval of time. W. KUHN and H. MARTIN (Z. Physik, 1933, **81**, 482—490).—Association of spectral line width with life period leads to contradictions in the energy range of a predissociated mol.; thermodynamics requires that this range be defined by the width of the illuminating line when this line is narrower than the spectral line of the mol., but introduction of an intermediate level requires the range to be measured by the life period in the intermediate level. The contradiction is not restricted to predissociation, but arises from the wave and corpuscular descriptions of nature being complementary. A. B. D. C.

Correspondence theory of line width. H. CASIMIR (Z. Physik, 1933, **81**, 496—506).—The relation of radiation damping to line width is treated by Heisenberg's method, and is applied to Raman lines. A. B. D. C.

Structure of some ultra-soft X-ray lines. J. A. PRINS (Z. Physik, 1933, **81**, 507—515).—The structure of Ag M and W N lines are given, and C K lines are dependent on experimental conditions. A. B. D. C.

Scattering of hard X-rays by solids. S. CHYLINSKI (Physical Rev., 1932, [ii], **42**, 153—166). N. M. B.

Weak lines in K spectra of rhodium and molybdenum. H. HULUBEI and (MLLE.) Y. CAUCHOIS (Compt. rend., 1933, **196**, 1294—1297).—Re-examined with the author's spectrograph (cf. A., 1932, 902) the K spectra of Rh and Mo are slightly corrected and extended; β_0 at 548·23 X for Rh and 635·65 for Mo are new (cf. Ross, Physical Rev., 1932, ii, **39**, 536, 748). C. A. S.

L absorption discontinuities of gold. F. M. UBER and C. G. PATTEN (Physical Rev., 1932, [ii], **42**, 229—232).—The vals. obtained agree with those obtained for Hg (cf. A., 1931, 1105). N. M. B.

Fluorescence yield from the L_{III} level of uranium. R. J. STEPHENSON (Physical Rev., 1933, [ii], **43**, 527—533).—The fluorescence yield for the L_{III} level, or the ratio, no. of fluorescence quanta emitted/no. of incident quanta absorbed, gave the val. 0·67. The relative intensities of the α to the β lines

in the K fluorescence spectra of Mo agree with the val. from the characteristic spectrum; similar agreement is shown for the α and β lines in the fluorescence spectrum from the L_{III} level of U. The ratio of the at. absorption coeffs. on the short and long wave-length side of the L_{III} discontinuity is 2·27. N. M. B.

Effect of chemical combination on the X-ray emission spectrum of sulphur. J. VALASEK (Physical Rev., 1933, [ii], **43**, 612—614).—With an improved method eliminating effects of chemical reaction with the target, the wave-lengths of S $K\alpha$ and β lines were measured for S, FeS, CoS, NiS, Cu_2S, and ZnS. The $K\beta$ line in ZnS is a triplet. The $K\beta$ lines of CoS and NiS are reported. N. M. B.

Absorption coefficients for X-rays in the neighbourhood of the L edges for the elements gold, platinum, and silver. M. WOLF (Ann. Physik, 1933, [v], **16**, 973—984; cf. this vol., 3).—From the absorption coeffs. determined, the no. of dispersion electrons in the three L levels of Au, Pt, and Ag were obtained. A. J. M.

Diffuse scattering of X-rays from sylvine. II. G. G. HARVEY (Physical Rev., 1933, [ii], **43**, 591—595; cf. A., 1931, 1205).—The average at. structure factors of the $K^{\cdot}$ and Cl' ions were calc., taking account of the incoherence of part of the scattering, from abs. intensity measurements, of the diffuse scattering of X-rays of wave-length 0·71 Å. for the angle range 5—110°. Results are in good agreement with vals. for A, and with theoretical vals. N. M. B.

Absolute X-ray reflectivities of single crystals of calcite, rock-salt, Rochelle salt, and barite. P. KIRKPATRICK and P. A. ROSS (Physical Rev., 1933, [ii], **43**, 596—600).—Using Ag $K\alpha$ radiation, the integrated reflexion, % reflexion, and rocking-curve width were derived for each crystal and wave-length. Scattering factors to show the variation with wave-length in the neighbourhood of the Ba K limit were found for barite. N. M. B.

Influence of oxygen and sulphur on the photo-electric effect of alkalis (K and Na). P. V. TIMOFEEV and V. V. NALIMOV (Z. Physik, 1933, **81**, 687—696).—The max sensitivity, I/I_0, for photo-cells illuminated with the full spectrum from a filament lamp at 2700° abs. was obtained with 40×10^{-5} g. per sq. cm. of adsorbed O_2 for K, and with 60×10^{-8} for Na. The effect of adsorbed S and the structure of the sensitive surface are discussed. A. B. D. C.

Positive electrons. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1933, **196**, 1105—1107).—That positive electrons, and not negative ones brought to a focus by the chamber, are emitted when Pb is subjected to the neutrons and γ-rays produced by Po+Be is rendered almost certain by placing the source behind a Pb plate closing an orifice in a cylindrical chamber and subjecting the emitted electrons to a magnetic field. With a field of 1100 gauss and considering only electrons of energy $>10^6$ ev. there were for 10 negative electrons from the Pb 2·83 positive from the Pb and 1·76 positive or negative distributed on the walls of the chamber; with 640 gauss corresponding figures for electrons of energy $>0{\cdot}5\times10^6$ ev. are 4·5 and 3·6; the positive electrons have a smaller energy than the negative. With an Al plate the vals. are 0·53 and 1·3. Interposition of 2 cm. of Pb between source and chamber reduces the no. of positive electrons issuing from the Pb by 50%, implying that the emission of positive electrons is probably due to the γ-rays (cf. this vol., 441). C. A. S.

Reflexion of electrons from standing light waves. P. L. KAPITZA (Proc. Camb. Phil. Soc., 1933, **29**, 297—300).—Theoretical.

Variation with angle of emission of the radiation from metals bombarded with slow electrons. C. BOECKNER (Bur. Stand. J. Res., 1932, **9**, 583—591).—Pt, W, and Ag cylinders were bombarded with electrons of energy 7 volts and the intensity of light emitted at different angles was compared. The results indicate that the radiation is emitted uniformly in all directions from a layer beneath the surface of the metal. D. R. D.

Variation of secondary emission with heat treatment. P. L. COPELAND (J. Franklin Inst., 1933, **215**, 435—443).—Targets contaminated with grease give high secondary emission on electron bombardment. When heated they recover to a val. characteristic of the metal. H. J. E.

Diffraction of very rapid electrons. M. KOSMAN and A. ALICHANIAN (Naturwiss., 1933, **21**, 250).—Apparatus for producing very rapid electrons up to 520 kv., and for studying their diffraction at Ag foil, is described. A. J. M.

Diffraction of low-speed electrons by a tungsten single crystal. W. T. SPROULL (Physical Rev., 1933, [ii], **43**, 516—526).—Using a new magnetic deflexion method, the intensity of the secondary beams was measured when the (1—1—2) and (1—0—0) planes of a W crystal were bombarded normally by primary electrons. Strong beams in the AA' azimuth of the (1—1—2) plane were governed in every case by the vol. equation and not, as theoretically required, by the surface equation. Vals. obtained are W_a 5·52, and W_i 1 volt. N. M. B.

Electron affinity spectrum. O. OLDENBERG (Physical Rev., 1933, [ii], **43**, 534—539).—Attempts to observe an electron affinity spectrum of at. I, emitted by the combination of neutral electronegative atoms and electrons, using three methods: hollow cathode, positive column with a rare gas added, and glowing filament, were unsuccessful. The failure is probably due to the capture of electrons by halogen atoms being unlikely as compared with the combination of positive ions and electrons. N. M. B.

Photo-electric investigation of the influence of matter on slow electrons. G. LANG (Ann. Physik, 1933, [v], **16**, 781—792).—Using monochromatic light of 2540 Å. and a photo-electric cell, which incorporated a thin layer of Pt sputtered on a quartz plate as cathode, the emission of slow electrons was investigated under various conditions of pressure and cathode thickness. W. R. A.

Scattering of electrons in thin films. G. O. LANGSTROTH (Proc. Roy. Soc., 1933, A, **140**, 159—

178).—Measurements have been made of the angle distribution of electrons scattered between 65° and 160° by celluloid and Al films of varying thickness, and of the total no. of electrons scattered back from various thicknesses of Al film with >186 volts energy, for primary voltages of 8—24 kv. L. L. B.

Elastic and inelastic scattering with angle in helium. T. EMMERSON and R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1933, **2**, 386).—Preliminary results are reported from experiments on the electron scattering by He at low pressure. At zero scattering angle and low electron speed the inelastic scattering is very small, but rises to a max. at an angle $<10°$, in disagreement with theory. J. W. S.

Energy of the beams in electron diffraction. F. C. POULTNEY and R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1933, **2**, 387—390).—Investigation of the velocities of electrons diffracted by passage through a thin film has been repeated, greater resolution being obtained by deviating the rays through 90° in the field. The velocities are the same to $\pm 0{\cdot}3\%$ and no trace of electrons the energy of which is < that of the main beam by the amount lost in X-ray excitation is found. J. W. S.

Quantum theory of inelastic electron collisions. L. GOLDSTEIN (Ann. Physique, 1933, [x], **19**, 305—420).—Mathematical. Following a general survey, calculations made for various series of levels are applied to ionisation stages, and compared with experimental results. N. M. B.

Scattering of electrons by ions and the mobility of electrons in a cæsium discharge. C. BOECKNER and F. L. MOHLER (Bur. Stand. J. Res., 1933, **10**, 357—363).—From measurements of the electrical gradient and the electron temp. and concn. the mobilities of electrons in the positive column of a Cs discharge are calc. The cross-section of the Cs atom deduced from the mobilities at low electronic concn. is $3{\cdot}3\times10^{-11}$ sq. cm. for electron energies of about 0·33 volt, and appears to increase linearly with ionic concn. in the discharge, the variation being due to scattering of electrons by ions. This variation gives a val. 75×10^{-14} sq. cm. for the ionic cross-section of 0·33-volt electrons, a magnitude explicable by electrostatic interaction between ions and electrons. J. W. S.

Diffusion of electrons by atoms. J. WINTER (Compt. rend., 1933, **196**, 1299—1301).—Mathematical. The effect of a sphere of spherically symmetrical potential on a de Broglie wave is considered. C. A. S.

Width of the discharge in the electron counter. E. GREINER (Z. Physik, 1933, **81**, 543—555).—In the Geiger–Müller counter the discharge spreads through the whole tube by means of ultra-violet radiation. A. B. D. C.

Cathodic disintegration of platinum by mercury ions. J. E. HENDERSON and (MISS) E. GIDEON (Physical Rev., 1933, [ii], **43**, 601—604).—Disintegration per positive ion increased linearly with the energy of the ion up to 2000 volts. Approx. two atoms of Pt are ejected per incident ion of 1000 volts energy. N. M. B.

Polarisabilities of ions from spectra. J. E. MAYER and (MISS) M. G. MAYER (Physical Rev., 1933, [ii], **43**, 605—611).—Data corrected for penetration effect and for higher order distortion of the ion are calc. for Li, Be^{++}, B^{+++}, C^{++++}, Na^{+}, Mg^{++}, Al^{+++}, K^{+}, Ca^{++}, Rb^{+}, Sr^{++}, and Cs^{+} from the corresponding spectra. N. M. B.

At. wt. of iodine. GUICHARD (Compt. rend., 1933, **196**, 1024—1025).—Baxter and Butler's doubts as to the purity of I_2O_5 and its suitability for at. wt. determinations are criticised, and 126·91 is recommended as the at. wt. of I (cf. A., 1914, ii, 723; 1931, 543; this vol., 203). C. A. S.

At. wt. of lead from Bedford cyrtolite. G. P. BAXTER and C. M. ALTER (J. Amer. Chem. Soc., 1933, **55**, 1445—1448).—The at. wt. is $205{\cdot}92\pm0{\cdot}02$ from determinations of the ratio $PbCl_2:2Ag$. The result is discussed. J. G. A. G.

Attempt to separate isotopes by reversible fractional distillation. H. J. HENRIQUES and R. E. CORNISH (J. Physical Chem., 1933, **37**, 397—399).—Fractional distillation of CH_2Cl_2 in a column 6·09 m. long gave no separation of Cl^{35} and Cl^{37}. H. J. E.

Photochemical separation of isotopes. W. KUHN and H. MARTIN (Z. physikal. Chem., 1933, **B**, **21**, 93—137).—A more detailed account of the partial separation of the isotopes of Cl previously reported (A., 1932, 1186) is given. The fact that separation has been achieved indicates that the probability of decomp. of excited mols. which absorb strictly discontinuously in the region of sharp absorption bands may be finite. It is estimated that of mols. which have passed to the quantum state p'—4, q'—1 by absorption of the line 2816·179 Å. about one fifth decompose and the remainder return to the normal state. Since the photochemical method employed is purely chemical, the isotopes of an element cannot be identical in chemical properties. It seems possible that there may be cases where, using such a method, practically complete separation can be achieved by a single irradiation. R. C.

Origin of the various kinds of lead. O. HAHN and L. MEITNER (Naturwiss., 1933, **21**, 237—238).—Pb^{207} has the same origin as Pb^{206} and Pb^{208}. The various forms arose at different periods of the cosmic era. It is doubtful whether the larger part of ordinary Pb arose from U isotopes or from Th. A. J. M.

Wave mechanical model of the neutron. S. FLÜGGE (Z. Physik, 1933, **81**, 491—495).—Theoretical. A. B. D. C.

Orbits of electrons released by neutron excitation. L. MEITNER and K. PHILIPP (Naturwiss., 1933, **21**, 286—287).—The no. and energy of electrons from a Po+Be source are much > those from a Po source alone. In a magnetic field, the majority of these electrons were deflected in a direction opposite to that expected of negatively-charged particles. They may be " positive " electrons (cf. this vol., 549). A. J. M.

Neutrons in the nucleus. I, II. A. LANDÉ (Physical Rev., 1933, [ii], **43**, 620—623, 624—626).—I. Mass defects show that the isotopes of an element

differ only by the no. of neutrons incorporated by them.

II. The no. of neutrons in the nuclei is illustrated by a model showing the building up of successive shells of neutrons. N. M. B.

Condensation chamber photographs of atomic disintegration by rapid protons. F. KIRCHNER (Naturwiss., 1933, **21**, 250—251).—The at. disintegration of B by rapid protons gives rise to a considerable no. of nuclear particles of range both $>$ and $<$ (1·5—6 cm.) that noted by Cockcroft and Walton (3 cm.) (cf. this vol., 111). A. J. M.

Atomic disintegration by ultra-radiation. W. MESSERSCHMIDT (Naturwiss., 1933, **21**, 285—286).—The at. nucleus of a substance absorbing ultra-radiation can be completely disintegrated by it. A bundle of very rapid corpuscular rays, having a range of 20 cm. in Pb, is then released. A. J. M.

Range of particles from atomic disintegration at low voltages. R. DOPEL (Z. Physik, 1933, **81**, 821—823).—Li and B disintegrated with 40-kv. canal rays gave particles of range in agreement with those observed on disintegration with several hundred kv. A. B. D. C.

Collisions between neutrons and protons. P. AUGER and G. MONOD-HERZEN (Compt. rend., 1933, **196**, 1102—1104; cf. this vol., 205).—The distribution of the rapid and slow protons ejected from H by neutrons produced by Po+Be as regards direction, and for the slow protons also length of path, determined by means of a Wilson expansion chamber, confirm the distinction between them. The probability of emission between θ and $\theta+d\theta$ (θ being measured from the direction of incident neutron, assumed to be direct from the source) is, for the swift protons, $a_1 \sin\theta\cos\theta\, d\theta$, and for the slow ones approx. $a_2 \sin\theta\, d\theta$ (a_1, a_2 being consts.); the length of path of the latter is 1—14 mm., with a max. for about 5 mm. These results indicate as regards the swift protons elastic frictionless collisions between the neutrons and protons, as regards the slow ones the existence of slow neutrons diffused by the material of the expansion chamber. C. A. S.

Diffusion of recoil atoms in air. (MLLE.) C. CHAMIE (Compt. rend., 1933, **196**, 1107—1109).—A collecting plate was placed at varying distances, $x > 0{\cdot}13$ mm., from active deposit of Th (path in air at 760 mm. and 15°, 0·13 mm.), and the intensity of ionisation measured. The intensity decreases exponentially, $I=I_0e^{-kx}$ for $x > 0{\cdot}13 < 0{\cdot}5$ mm., and linearly for $x > 0{\cdot}5$ mm., indicating diffusion of the recoil atoms in air. C. A. S.

Entry of the disintegrating α-particle into the nitrogen nucleus and a general relation between heights of nuclear barriers and atomic number. E. C. POLLARD (Proc. Leeds Phil. Soc., 1933, **2**, 357—358).—Previous results (cf. A., 1932, 894) are amplified. The height of the barrier is, except for the lightest elements, approx. proportional to the at. no. N. M. B.

Atomic radiations of short range from heavy elements. H. PETTERSSON and J. J. SCHINTLMEISTER (Naturwiss., 1933, **21**, 222—223).—Substances in thin layers in the gaseous state were bombarded with a beam of α-rays from Po. With a special apparatus the presence of short-range radiations from Xe mixed with He was shown, the proportion of new particles to total no. scattered being 0·66. The particles must be either scattered α-particles with greatly reduced range due to inelastic collisions, or else products of the disintegration of the Xe nucleus. A mixture of 40% Kr and 60% He yielded a similar group of particles with even smaller range. A. J. M.

Fundamental state of nuclear α-particles. G. GAMOW (Nature, 1933, **131**, 618—619). L. S. T.

Theoretical decay curves for various ratios of radium-*B* to radium-*C*, and of thorium-*B* to thorium-*C*. J. A. CRANSTON and C. BENSON (J. Roy. Tech. Coll., 1933, **3**, 47—51). A. R. P.

Radioactivity of samarium and the formation of hibernium haloes. J. H. J. POOLE (Nature, 1933, **131**, 654).—A discussion (cf. this vol., 442). L. S. T.

Chemical detection of artificial transmutation of elements. F. A. PANETH and P. L. GÜNTHER (Nature, 1933, **131**, 652—653).—In the bombardment of O_2 by α-rays such Ne as may be formed falls below the ratio 1 atom Ne to 10^5 α-particles, the present limit of detection of Ne in He. Bombardment of NaF and KF also gave indefinite results. No formation of He has been observed after the bombardment of substances by β-rays or by neutrons. When H_2O, C, K, Sn, or Hg is bombarded by the unfiltered rays of Th-*B* and -*C*, the He formed, within a 10% limit of error, corresponds with the no. of α-particles shot into the substance; with compounds such as paraffin, palmitic acid, and Ph_2, surpluses of up to 100% have been obtained. L. S. T.

Early history of the determination of atomic charge. ANON. (Nature, 1933, **131**, 569—570). L. S. T.

Evaporation phenomena with mercury droplets and their influence on the measurement of the elementary quantum of electricity. R. NESTLE, K. SCHÄFER, and E. REGENER (Z. Physik, 1933, **81**, 700—702).—Polemical against Lustig and Reiss (this vol., 111). A. B. D. C.

Transport phenomena in Einstein–Bose and Fermi–Dirac gases. I. E. A. UEHLING and G. E. UHLENBECK (Physical Rev., 1933, [ii], **43**, 552—561).—Mathematical. N. M. B.

Significance of experimental determinations of the mean specific ionisation by cosmic rays from comparison measurements with an ionisation chamber and counter. W. KOLHÖRSTER and L. TUWIM (Z. Physik, 1933, **81**, 435—439).—Recent applications of quantum mechanics explain the high sp. ionisation (135 ions per cm.) previously observed (*ibid.*, 1931, **73**, 130); the criticism of Locher (this vol., 556) is discounted. A. B. D. C.

Origin of cosmic radiation. H. ALFVÉN (Nature, 1933, **131**, 619—620).—The origin of cosmic rays can be explained without new hypotheses by applying the kinetic theory of gases to the conditions of space. L. S. T.

Absorption curves of ultra-radiation and their explanation. E. REGENER (Physikal. Z., 1933, **34**, 306—323).—Results of determinations of the intensity of ultra-radiation in the sea and in the stratosphere are given, and the absorption curves are analysed. The nature of ultra-radiation is discussed. A. J. M.

Dependence of ionisation by cosmic radiation on pressure. B. GROSZ (Z. Physik, 1932, **78**, 271—278).—An equation is given. A. B. D. C.

The neutron, atom building, and a nuclear exclusion principle. W. D. HARKINS (Proc. Nat. Acad. Sci., 1933, **19**, 307—318).—The neutron is held to constitute a new element of zero at. no. The emission of γ-rays by nuclei excited by neutrons is discussed. The no. of neutrons (neutronic no.) is even for almost every known at. nucleus. A nuclear exclusion principle and pairing of neutrons are deduced. N. M. B.

Law of force between neutron and proton. E. C. POLLARD (Proc. Leeds Phil. Soc., 1933, **2**, 397—400).—The relation between height of the nuclear barrier and the nuclear charge is used to determine vals. for the polarisability of a neutron. J. W. S.

Tetrahedral field of action of atoms. III. Probable cause. R. REINICKE (Ann. Guebhard-Severine, 1932, **8**, 217—244; cf. A., 1932, 563, 901).—The author's theory is discussed from the viewpoint of electronic configurations. J. W. S.

Three-dimensional periodic orbits in the field of a non-neutral atom. M. A. EL-SHERBINI (Phil. Mag., 1932, [vii], **14**, 304—310).—Mathematical. N. M. B.

Vector model and the Pauli principle. M. H. JOHNSON, jun. (Physical Rev., 1933, [ii], **43**, 627—631; cf. A., 1932, 315).—Mathematical. N. M. B.

Almost closed shells. M. H. JOHNSON, jun. (Physical Rev., 1933, [ii], **43**, 632—635).—Mathematical. Shortley's results (cf. A., 1932, 668) are extended, by a development of Heisenberg's treatment, to several almost closed shells with other electrons not in the shells. N. M. B.

Nuclear magnetic moments. S. GOUDSMIT (Physical Rev., 1933, [ii], **43**, 636—639).—Mathematical. Formulæ for the calculation of nuclear magnetic moments from observed hyperfine structure separations are deduced. N. M. B.

Theory of metals. R. PEIERLS (Z. Physik, 1933, **81**, 697—699).—A theory different from that of Wilson (this vol., 116) is preferred. A. B. D. C.

Quantum mechanics of diatomic systems. M. BORN and S. FLÜGGE (Ann. Physik, 1933, [v], **16**, 768—780).—Mathematical. W. R. A.

Evaporation of incandescent wires in a vacuum. III. L. PRÁSNIK (Z. Physik, 1932, **77**, 127—132; cf. A., 1932, 565).—Theoretical. The effect of heat conductivity is taken into account. A. B. D. C.

Optics in the service of chemistry. B. K. SINGH (J. Indian Chem. Soc., 1933, **10**, 7—26).—A lecture.

Optical properties of photographic layers. E. LAU and J. JOHANNESSON (Z. Physik, 1933, **82**, 37—47).—A study of the scattering of light by photographic plates revealed that for low intensity scattering by the gelatin predominates, Ag particle-scattering reaching a max. at 50% image intensity. Microphotometer records are best obtained with diffuse light with dense images, and contrast can be increased by rubbing magnesia on the film surface of the plate and examining with light incident on the glass surface. A. B. D. C.

Light filter for the middle ultra-violet. H. J. BACKSTRÖM (Naturwiss., 1933, **21**, 251).—3 cm. thickness of a solution containing 1·75*M*-(pure)$NiSO_4$ and 0·5*M*-$CoSO_4$ is recommended for transmission of light of wave-lengths in the neighbourhood of 300 mμ. Other filters are described. A. J. M.

Investigations in the Schumann region. H. HESE, A. ROSE, and R. GRÄFIN ZU DOHNA. **I. Schumann spectrograph for precision measurements.** H. HESE. **II. Simple fluorite spectrograph and its application to absorption photographs.** A. ROSE (Z. Physik, 1933, **81**, 745—751, 751—763).—I. The spectrograph is designed for absorption spectra of org. compounds.

II. The ultra-violet transmission of B_2O_3, and absorption of O_2, CH_4, C_2H_2, and C_6H_6 were investigated between 2050 and 1250 Å. A. B. D. C.

New band in the water vapour discharge. W. H. RODEBUSH and M. H. WAHL (J. Amer. Chem. Soc., 1933, **55**, 1742).—The spectrum of the electrodeless discharge in H_2O vapour contains a band, with the head at λ 3564 Å., which is attributed to the presence of OH^+. J. G. A. G.

Band system of SrO in the near infra-red. K. MAHLA (Z. Physik, 1933, **81**, 625—646).—Rotational and band analyses of bands near 8000 Å. are recorded. A. B. D. C.

Band spectra of the monoxides ScO, YO, and LaO. G. PICCARDI (Gazzetta, 1933, **63**, 127—138; cf. A., 1932, 1074).—Analysis of the oscillation bands in the emission spectra of the vapour of the oxides shows that the bands are due in each case to the diat. neutral mol. The fine structure of the bands could not be investigated. O. J. W.

Rotation-vibration spectrum of water vapour. II. W. BAUMANN and R. MECKE. **III.** K. FREUDENBERG and R. MECKE (Z. Physik, 1933, **81**, 445—464, 465—481).—II. Rotation lines in bands at 9420, 9060, 8227, and 7227 Å. are interpreted according to Mecke's scheme (this vol., 445).

III. Rotation lines in bands at 6994, 6524, 5952, 5924, and 5722 Å. are interpreted according to Mecke's scheme, and formulæ are given expressing the moments of inertia in terms of the vibrational quantum nos. A. B. D. C.

Optical investigation of perylene and its derivatives. IV. Ultra-violet absorption spectrum of 1 : 12-derivatives and isomerides. C. HUA-CHIH and H. CONRAD-BILLROTH (Z. physikal. Chem., 1933, **B**, **20**, 333—339; cf. A., 1932, 107).—1 : 12-Perylene peroxide has an absorption curve quite different from that of 1 : 12-perylenequinone, and

seems to have a cyclic peroxide structure. The curves of 3 : 10-dihydroxyperylene and -perylenequinone are similar, whilst the curve of 1 : 12-dihydroxyperylene is unlike that of 1 : 12-perylenequinone. The absorption of hexahydroperylene supports Zinke and Schniderschitsch's structure (A., 1929, 803), not Zinke and Benndorf's (A., 1932, 507). R. C.

Absorption of halogen derivatives of methane in near ultra-violet, and their dissociation energies. T. IREDALE (Z. physikal. Chem., 1933, B, **20**, 340—344).—A discussion of the absorption spectra of CH_3I, CH_2I_2, and CHI_3 and the methods of determining the energy of the halogen–C linking shows that the spectroscopic vals. of this energy are as yet uncertain. R. C.

Absorption spectra [of the Na salt of tetraiodophenolphthalein and phenoltetraiodophthalein]. E. H. HARVEY (Amer. J. Pharm., 1933, **105**, 199—200).—Curves are given for solutions in EtOH. The latter salt is more sensitive to p_H changes. R. S. C.

Infra-red absorption spectra of halogen derivatives of methane. J. LECOMTE (Compt. rend., 1933, **196**, 1011—1013).—Using a special spectrograph with rotating prisms of NaCl or KCl the absorption spectra of the liquid halogen, X, derivatives of CH_4 have been determined for λ 6·9—20 μ. In most cases there are two max., in good agreement with the Raman lines. λ of both max. increases as X changes in the order Cl, Br, I; increase in the no. of X atoms causes the λ of the max. of greater λ to increase, that of the max. of smaller λ to decrease. Secondary zones of absorption are explicable by combination frequencies in the cases of CX_4 and CHX_3. C. A. S.

Rotation–vibration spectrum of ethylene in the near infra-red. W. SCHEIB and P. LUEG (Z. Physik, 1933, **81**, 764—775).—The band at 8715 Å. was investigated, and gives the intermediate moment of inertia as $28{\cdot}85\times10^{-40}$ g.-cm.^{2} Taking the C–H distance as 1·08 Å., the C–C distance is 1·34 Å. C–C separations are 1·54, 1·34, and 1·19 A. for single, double, and triple linkings, respectively. A. B. D. C.

Interpretation of polyatomic spectra. L. TISZA (Z. Physik, 1933, **82**, 48—72).—Selection rules for Raman and infra-red spectra are deduced by the group theory for harmonic and combination tones, and for rotational structure. A. B. D. C.

Raman effect in *X*-ray region. II. W. KAST and F. WÜRSTLIN (Z. Physik, 1933, **81**, 581—583).—Two examples of a supposed Raman effect are due to known *X*-ray spectral lines. A. B. D. C.

Raman effect of glycerol. R. BÄR (Z. Physik, 1933, **81**, 785—789).—15 lines were obtained in the Raman spectrum, but the continuous spectrum can be due only to fluorescence (cf. Carrelli and Went, this vol., 337). A. B. D. C.

Raman spectrum of silicon trichlorobromide. M. DE HEMPTINNE, J. WOUTERS, and (MLLE.) M. FAYT (Bull. Acad. roy. Belg., 1933, [v], **19**, 318—324).—On excitation with the Hg 4358·34 Å. line $SiBrCl_3$ shows Raman frequencies of 410, 362, 325, 201, 183, and 123 cm.$^{-1}$, the 362 cm.$^{-1}$ frequency being very strong. The fundamental frequencies for this mol. are calc. and compared with the data for $SiHCl_3$. J. W. S.

[Raman effect and] ethylenic linking : hexenes. (MLLE.) H. VAN RISSEGHEM, (MLLE.) B. GREDY, and L. PIAUX (Compt. rend., 1933, **196**, 938—940; cf. A., 1932, 897).—The Raman spectra between 1250 and 1700 cm.$^{-1}$ (omitting the band near 1450) of Δ^{α}- and Δ^{β}-(*cis* and *trans*)hexene, δ-(*cis* and *trans*)- and γ-methyl-Δ^{β}- and δ-methyl-Δ^{γ}-pentene, and $\beta\gamma$-dimethyl-Δ^{β}-butene include lines at 1252—1262, 1296—1306, 1350—1416, and 1642—1676. Methods of prep., b.p., and some f.p. and *d* are given. C. A. S.

[Raman effect and] acetylenic linking : disubstituted acetylenes. (MLLE.) B. GREDY (Compt. rend., 1933, **196**, 1119—1122; cf. A., 1931, 284).—The Raman spectra of 11 hydrocarbons RC:CR′, where R is Ph, C_5H_{11}, or C_6H_{13}, and R′ Me, Et, Pr, Bu, or C_4H_3, are tabulated. All show two unequal lines between 2200 and 2300 cm.$^{-1}$; Ph lowers the frequency. In its absence the strongest line is at 2234; if R′ is Me there are strong lines at 378 and 1380. All have a doublet at 1300—1330. There is some ground for supposing the presence of two characteristic lines to indicate a new form of isomerism. C. A. S.

Depolarisation of light by liquids holding crystalline particles in suspension in relation to the birefringence of these particles. S. PROCOPIU (Ann. Sci. Univ. Jassy, 1933, **17**, 111—117).—The depolarisation is due to the magnetic birefringence of the particles. A proportionality relation between the depolarisation and the no. of particles and their birefringence has been developed theoretically and confirmed by experiment. This method may be used for the determination of the magnetic birefringence of colloid particles. J. W. S.

Depolarisation of light diffused by a uniaxial crystal with optic axis parallel to diffused light. J. CABANNES (Compt. rend., 1933, **196**, 977—979).—If a uniaxial crystal be examined with its axis in the direction of the diffused ray all the Raman lines are completely depolarised. This is inconsistent with the Langevin mol. model and the ellipsoid of refractivity. An explanation is based on the Kramers–Heisenberg theory (cf. A., 1932, 212; this vol., 113, 208). C. A. S.

Diffusion of light in highly turbid media. V. A. FABRIKANT, V. L. GINSBURG, and V. L. PULVER (Z. Physik, 1933, **81**, 795—798).—Theoretical.

Theory of fluctuations and critical opalescence. Y. ROCARD (J. Phys. Radium, 1933, [vii], **4**, 165—185).—Mathematical (cf. this vol., 113).

Mechanism of photochemical dissociation. L. GOLDSTEIN (J. Phys. Radium, 1933, [vii], **4**, 123—131).—Mathematical. The nature of the intensity of continuous absorption bands for a mol. having an electric moment in its fundamental electronic state, and the bands accompanying dissociation processes are calc. N. M. B.

Total reflexion of *X*-rays at liquids. H. STEPS (Ann. Physik, 1933, [v], **16**, 949—972).—The reflexion of *X*-rays at free liquid surfaces has been investigated. The properties of surfaces as regards

image formation were compared. Those of glycerol and H_2O were specially good. A. J. M.

Physical proof of Gurwitsch radiation. B. RAJEWSKY (Naturwiss., 1933, **21**, 299).—Notes on the work of Siebert and Seffert (cf. this vol., 335). A. J. M.

Intensity of fluorescence of sodium salicylate. P. DUBOULOZ (Compt. rend., 1933, **196**, 1221—1222; cf. A., 1932, 319).—Using the method previously described, save that dextrin was absent, curves relating intensity of fluorescence to wave-length of incident light have been obtained with a C arc and a W-filament lamp, confirming previous results (cf. A., 1927, 497). C. A. S.

Inhibitive action of organic substances on fluorescence of uranine. J. BOUCHARD (Compt. rend., 1933, **196**, 1317—1318; cf. this vol., 337).—For a given concn., s, of 14 org. substances (chiefly amines or phenols) the fluorescent power of uranine in 0·1*N*-NaOH decreases exponentially with its concn.; and similarly for a fixed concn. of uranine and variable concn. of org. substance. For 18 others (chiefly sugars, amines, or amides) the result is independent of s. C. A. S.

Emission of phosphors. III. Behaviour of samarium in the oxides of group II. R. TOMASCHEK and O. DEUTSCHBEIN (Ann. Physik, 1933, [v], **16**, 930—948; cf. A., 1932, 1076).—The emission spectra of Sm phosphors with CaO, SrO, BaO, MgO, and BeO were obtained. The structures of these spectra depend on the previous history of the prep. and on the cryst. structure. A. J. M.

Spatial structure of phosphorescent mixtures. A. SCHLOEMER (J. pr. Chem., 1933, [ii], **137**, 40—46).—The middle point of a phosphorescent centre is occupied by an active ion or an electrically differentiated group of atoms. It is surrounded by mols. or groups thereof, the arrangement of which is either that of a crystal lattice in which the orientation is disturbed by the active middle point, or that which maintains within a solvate. The active ion plays the part of the dissolved substance and the fundamental mass that of the solvent. H. W.

Constitution of phosphorescence centres in fluorite. S. IIMORI (Sci. Pap. Inst. Phys. Chem. Res., Tokyo, 1933, **20**, 189—200; cf. A., 1931, 1111).—The nature of the primary matter, previously denoted P_1, in the lumino-transformation of fluorite is further discussed. J. W. S.

Luminescence of alkaline-earth tungstates containing lead. F. E. SWINDELLS (J. Opt. Soc. Amer., 1933, **23**, 129—132).—Pb is an activator for the phosphorescence of Ca and Sr tungstates, the optimum concn. being about 0·01 g.-mol. $PbWO_4$ per g.-mol. of alkaline-earth tungstate. Higher concns. of Pb produce a very great increase in fluorescent and phosphorescent power of $SrWO_4$, optimum Pb concn. being 0·2 and 0·4 g.-mol. for the respective effects, whereas high Pb concn. in $CaWO_4$ decreases the luminescent power. N. M. B.

Transformation of translational into vibrational energy in molecular collision processes. J. FRANCK and A. EUCKEN (Z. physikal. Chem., 1933, **B**, **20**, 460—466).—In determining the frequency of this transformation the mutual perturbation of the potential curves of the colliding individuals plays an important part; it is probably this effect, rather than the purely mechanical transfer of energy, which is the decisive factor. This affords a qual. explanation of the differences in yield. R. C.

Investigation of transformation of translational into vibrational energy on collision of various molecules by means of sound dispersion measurements. A. EUCKEN and R. BECKER (Z. physikal. Chem., 1933, **B**, **20**, 467—474).—Measurements of the velocity of sound of frequency 3×10^5 hertz have shown that He, H_2, HCl, and CH_4 promote the transformation of translational into intramol. vibrational energy of Cl_2 and CO_2; A has no effect. These observations support the theory previously advocated (cf. preceding abstract). R. C.

Inner photo-electric effect in cuprous oxide. D. NASLEDOV and L. NEMENOV (Z. Physik, 1933, **81**, 584—604).—Conductivity measurements were made for Cu_2O in the dark and when illuminated at room and at liquid air temp.; the inner photo-electric effect is very small, being inappreciable for layers of resistance 10^4 ohms per cm., but giving a 600-fold increase in conductivity of layers of 10^7 ohms per cm. at liquid air temp. A. B. D. C.

Photo-electric effect in single crystals of cuprite. R. DEAGLIO (Compt. rend., 1933, **196**, 1303—1305).—(*a*) When light falls perpendicularly on one gilt surface of a parallelepiped cut from a single crystal of cuprite two opposite surfaces of which are covered with a film of Au, a current passes externally from the illuminated to the dark surface—about 10^{-7} amp. for light of 25 candles. (*b*) If the light fall on two opposite ungilt surfaces a current still passes, the direction of which changes when the light falls close to the gilt surface which, except when it falls there, is the negative pole. If a current is passed through the cuprite arranged as (*a*), the photo-electric effect gradually disappears through deposition of Cu below the Au cutting off the light. These facts point to the cuprite becoming electrolytically conducting when exposed to light, and give a more satisfactory explanation of Dember's effect (cf. A., 1931, 999; Physikal. Z., 1932, **33**, 207). C. A. S.

Non-additive effect of radiations of different wave-lengths on cuprous oxide photo-cells. C. LAPICQUE (Compt. rend., 1933, **196**, 1301—1303; cf. A., 1931, 1112). C. A. S.

Photo-effects in semi-conductors. B. LANGE (Trans. Electrochem. Soc., 1933, **63**, 69—81).—Current theories are critically reviewed and a new theory is advanced. The close parallelism between the spectral sensitivity of the photo-electric response of a Cu_2O cell of the "front wall" type and that of the photo-electric change in its resistance indicates the identity of the electrons of the "barrier" film photo-effect and those of the internal photo-effect. H. J. T. E.

Proof of a limiting layer in the cuprous oxide barrier layer cell. F. ROTHER and H. BOMKE (Z. Physik, 1933, **81**, 771—775).—Diffusion occurs

in the thermal formation of Cu_2O from Cu giving a reaction in the solid state. Several zones of different conductivity were observed, and it is suggested that the hypothetical barrier layer consists of a non-conducting layer of the purest oxide. A. B. D. C.

Relation of characteristic vibrations and the external photo-electric effect. III. Coal-tar dyes in the ultra-violet. F. Hlučka (Z. Physik, 1933, **81**, 521—527).—Measurements in the ultra-violet confirm relations already given (this vol., 447). A. B. D. C.

New detector. J. Cayrel (Compt. rend., 1933, **196**, 1216—1218).—If aq. H_2S is electrolysed with a crystal of galena as anode the crystal becomes covered with a brown powder consisting of finely-divided S in a more or less colloidal condition. Galena so treated gives with Cu greatly improved *B* rectification, due to formation of CuS at the point of contact (cf. A., 1920, ii, 526). C. A. S.

Cæsium–oxygen–silver photo-electric cell. C. H. Prescott, jun., and M. J. Kelly (Trans. Electrochem. Soc., 1932, **62**, 207—232).—The cell consists of a Ni wire anode and an oxidised Ag foil cathode on which Cs is deposited by heating a mixture of Cs_2CrO_4, Cr_2O_3, and Al. The active cathode surface appears to be a film of free Cs of at. dimensions adsorbed on a matrix of Cs_2O and Ag containing free Cs and small amounts of Ag_2O. The characteristics of the cell are described.

New photo-electric phenomenon. A. Etzrodt (Physikal. Z., 1933, **24**, 338—340).—The effect noted by Majorana (A., 1932, 898, 1189) is not primarily photo-electric, but is due to the effect of heat rays on the resistance of the conducting metal. A. J. M.

New photo-electric phenomenon. Q. Majorana (Physikal. Z., 1933, **34**, 340).—A reply to Etzrodt (preceding abstract). It is maintained that the effect is photo-electric. A. J. M.

Photo-electric conductivity and absorption of Lenard phosphors in the red and infra-red spectral region. L. Weber (Ann. Physik, 1933, [v], **16**, 821—843).—Photo-electric conductivity of a phosphor was produced by means of the superposition of a photo-electric effect on the centre (especially for short waves) and on the main constituent, *e.g.*, CaS, for long waves. Two experimental methods indicate that absorption of the phosphor in the red and infra-red consists of a superposition of absorption bands from the fundamental constituent and the selective absorption bands of the phosphorescence centres. W. R. A.

Dependence of breakdown strength on thickness for very thin layers of Ta_2O_5. G. Just (Z. Physik, 1933, **82**, 119—133).—The breakdown potential is proportional to layer thickness for layers between 15 and 250 mμ, the factor of proportionality being $2{\cdot}0\times10^6$ volts per cm. A. B. D. C.

Calculation of electric moments. G. Allard (Compt. rend., 1933, **196**, 1095—1097; cf. A., 1931, 894).—The correctness of the method of calculating the electric moment of a mol. by vectorial addition of the partial moment of each of the linkings in the mol., considered as directed along that linking, is demonstrated by wave mechanics. C. A. S.

Dielectric constant and conductivity of ionised gases. T. V. Ionescu and C. Mihul (Ann. Sci. Univ. Jassy, 1933, **17**, 78—110).—The dielectric const. and conductivity of ionised air have been measured by a resonance method at wave-lengths of 200—2090 cm. at different accelerating potentials. The changes with wave-length exceed those anticipated theoretically, and lead to the conclusion that ionised air possesses a characteristic frequency $3{\cdot}16\times10^7$ independent of the electronic density. It is suggested that some of the electrons are attached to mols. of gas, whilst the others are free, and that these two categories exert different influences on the variation of dielectric const. and conductivity with frequency. The large proportion of ionised gas in the higher strata of the atm. may account for the great penetrating power of short electric waves. J. W. S.

Dielectric polarisation. VI, VII. E. C. E. Hunter and J. R. Partington (J.C.S., 1933, 309—313).—VI. The dipole moments ($\times10^{18}$) of $Et_2N_2O_2$, $Bz_2N_2O_2$, and *s*-Me_2SO_3 in C_6H_6 are 1·5, 0·4, and 2·9, respectively, and that of NH_2NO_2 in dioxan is 3·75. The parachors obtained for Et, Pr, and *n*-Bu hyponitrites agree with the formula HO·N:N·OH for the acid. The constitutions of NH_2NO_2 and N_2O are discussed.

VII. The dipole moments ($\times10^{18}$) of $MeNO_2$, $EtNO_2$, and $BuNO_2$ in C_6H_6 solution are 3·02, 3·19, and 3·29, respectively. Induction apparently occurs in the hydrocarbon chain, the effect of the NO_2 group extending at least as far as the third C atom. Since the val. for $PhNO_2$ is 3·9, the moment of NO_2 is smaller in the aliphatic than in the aromatic series. M. S. B.

Dipole moments of some benzene derivatives. H. Poltz (Z. physikal. Chem., 1933, **B**, **20**, 351—356).—The measured dipole moments of the nitro- and iodo-toluenes agree with the vals. calc. from group moments by vectorial addition. With *m*-$C_6H_4I{\cdot}NO_2$ the agreement is also good, but with the *o*- and *p*-compounds there are divergences, which largely disappear when Smallwood and Herzfeld's method of calculation (A., 1930, 841) is used. R. C.

Dielectric constant of liquids. IX. Aqueous solutions of carbamide. G. Devoto (Gazzetta, 1933, **63**, 119—121; cf. A., 1932, 794).—Vals. of ε are given for solutions of carbamide at 15°. O. J. W.

Dipole moments and structures of the organic azides and aliphatic diazo-compounds. N. V. Sidgwick, L. E. Sutton, and W. Thomas (J.C.S., 1933, 406—412).—The electrical dipole moments of the following compounds have been determined at 25°: PhN_3 1·55, *p*-$C_6H_4Me{\cdot}N_3$ 1·96, *p*-$C_6H_4Cl{\cdot}N_3$ 0·33, Ph_2CN_2 1·42, $(p\text{-}C_6H_4Me)_2CN_2$ 1·94, $(p\text{-}C_6H_4Cl)_2CN_2$ 0·62, Ph·NCO 2·23, and *p*-$C_6H_4Cl{\cdot}NCO$ 0·82. The negative end of the dipole is directed away from the C_6H_6 ring. The data for the azides and diazo-compounds are in favour of the ring structure (I) $R{-}N\!<\!\overset{|}{\underset{|}{N}}\!\!>$ rather than either of the open-chain

structures (II) R—N=N—N or (III) R—N←N=N, but the possibility of a state of continuous and rapid oscillation between the forms (II) and (III) is not ruled out. The latter view also receives some support from the val. of the heat of formation of the azides. M. S. B.

Nature of electrical conductivity of α-silver sulphide. C. WAGNER (Z. physikal. Chem., 1933, **B**, **21**, 42—47).—Transport, conductivity, and diffusion data are mutually reconcilable if conduction is preponderatingly electronic and the share of Ag ions in it is comparatively small. The proportion of electrolytic conduction has been approx. determined by e.m.f. measurements with the cell Pt(S)|Ag_2S|Ag. R. C.

Conductivity of α-silver sulphide. II. W. JOST and H. RÜTER (Z. physikal. Chem., 1933, **B**, **21**, 48—52; cf. A., 1932, 446).—Transport experiments with Ag_2S–Cu_2S mixed crystals reveal certain anomalies, and Faraday's law is not valid for conduction in Ag_2S at 220° at high c.d. These observations are explained by Wagner's theory of the formation of Ag_2S films on Ag (this vol., 564) and of conduction in α-Ag_2S (cf. preceding abstract). R. C.

Drude's theory of optical activity. W. KUHN (Z. physikal. Chem., 1933, **B**, **20**, 325—332).—The mol. model on which Drude based his theory is incapable of optical activity. He incorrectly calculated the interaction with the incident light. R. C.

Refractive index of a liquid. S. C. GLADDEN (Rev. Sci. Instr., 1933, [ii], **4**, 231—232).—A simple watch-glass method was used; results are given for H_2O, PhMe, C_6H_6, and CCl_4. N. M. B.

Spectrochemistry of pyridone and pyridine derivatives. K. VON AUWERS (Z. physikal. Chem., 1933, **164**, 33—43).—The sp. depression of C_5H_5N is reduced by halogens, I having the most marked effect. By formation of active conjugations the groups –CO_2R, –CO·R, and –CHO cause exaltation, the effect increasing in this order. The sp. exaltation of a C_5H·N derivative with an active conjugation is reduced by entrance of Cl into the nucleus. Et_2 chelidamate has m.p. 125°. R. C.

Magnetic birefringence of liquid oxygen. P. LAINÉ (Compt. rend., 1933, **196**, 1218—1220, 1594).—The magnetic birefringence of O_2 at 90·6° abs. for λ 5460 is −1·96 (that of $PhNO_2$ at 17° being 1), giving C_m = $-5{\cdot}33\times10^{-12}$. This is incompatible with the mol. O_2 possessing symmetry of revolution around an axis uniting the centres of the constituent atoms unless this axis be a direction of low and not of high refractivity. C. A. S.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. V. *n*-Propyl propionate, *iso*butyl acetate, ethyl acetoacetate, and ethyl oxalate. A. DE M. BEANLAND and E. J. EVANS (Phil. Mag., 1933, [vii], **15**, 905—929; cf. A., 1932, 323).—The magneto-optical and ordinary dispersion of each liquid, measured in the visible and ultra-violet spectrum, are represented by formulæ. The wave-lengths of the absorption bands of the four liquids are 0·1088, 0·1080, 0·1089, and 0·1105 μ, and the calc. vals. $\times 10^{-7}$ of e/m are 0·99, $1{\cdot}01_5$, $0{\cdot}87_3$, and 0·91 e.m.u., respectively. H. J. E.

Magnetic susceptibilities of hydrochloric acid and lithium chloride solutions. A. F. SCOTT and C. M. BLAIR, jun. (J. Physical Chem., 1933, **37**, 475—482).—Data for aq. HCl agree with those of Hocart (A., 1929, 628), but not with those of Farquharson (A., 1931, 1118). The χ–concn. curve is linear when $c < 19\%$, after which χ decreases suddenly, the data above 22% LiCl falling on a different straight line (cf. A., 1929, 247; 1932, 678). D. R. D.

Magnetic susceptibility of complex compounds. II. L. CAMBI and L. SZEGÖ (Ber., 1933, **66**, [*B*], 656—661; cf. A., 1932, 10).—The magnetic susceptibility of dithio-compounds $Fe(CS_2{\cdot}NHR)_3$ [R=Me or Et] is that typical of Fe^{III} salts and follows the Weiss–Curie law. Compounds $Fe(CS_2{\cdot}OR)_3$ [R=Et] and $Fe(CS_2R)_3$ [R=Ph or *p*-C_6H_4Br] behave analogously to $K_3Fe(CN)_6$, whereas those of the type $Fe(CS_2{\cdot}NR'R'')_3$ [R′=R″=Me, Et, Pr, Bu, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, $C_{12}H_{25}$, or $C_{16}H_{33}$] exhibit a susceptibility varying according to the temp. between the limits calc. for Fe^{III}. The simultaneous existence of magnetic-isomeric forms is thus recognised, the equilibrium of which depends on the temp. and the more or less polar nature of the acid radical. H. W.

Paramagnetic saturation of potassium chrome alum. C. J. GORTER, W. J. DE HAAS, and J. VAN DEN HANDEL (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 158—167).—Measurements have been made with a new apparatus down to 1·34° abs. and a field strength of 21 œrsteds. The results agree with the Bose–Stoner theory (A., 1927, 805; 1929, 1371). No influence of orbital magnetism could be detected. M. S. B.

Magnetic behaviour of some chromium compounds at low temperatures. C. J. GORTER, W. J. DE HAAS, and J. VAN DEN HANDEL (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 168—173).—The magnetic susceptibilities of samples of basic $Cr_2(SO_4)_3$, Cr_2O_3, and $[CrCl_2(H_2O)_4]Cl,2H_2O$ (I) have been determined between 14° and 290° abs. The val. for (I) alone follows approx. the theoretical law for Cr compounds. The reasons for the deviations are discussed. M. S. B.

Paramagnetic properties of crystals of the rare earths. II. H. A. KRAMERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 17—26; cf. this vol., 340).—The paramagnetism of a cryst. powder, particularly that of CeF_3, and the paramagnetic rotation in the crystals, particularly in tysonite, are deduced mathematically. W. R. A.

Law of discontinuous distribution of ferromagnetic Curie points. I. Influence of distance between magnetic atoms. R. FORRER (J. Phys. Radium, 1933, [vii], **4**, 109—117; cf. A., 1932, 452).—A necessary condition for ferromagnetism is that the distance between magnetic atoms should lie between definite limits, the "effective distance." The limits for Fe and Mn are 2·7—3, and for Co and Ni 2·4—2·5 Å., the former applying also to Fe–Mn combinations. Distances greater and less than the effective

distance lead to variable paramagnetism and const. paramagnetism, respectively. N. M. B.

Magnetisation of ferromagnetic crystals. F. BITTER (Physical Rev., 1933, [ii], **43**, 655—660; cf. this vol., 212).—Photographs are given of models representing a function for the energy of a crystal as a function of the direction of magnetisation in the case of undistorted crystals of Ni and Fe, and Fe distorted by compression and extension. For the last-named, magnetisation curves are calc. and illustrated. N. M. B.

Ferromagnetism of ferric oxide. H. SACHSE (Naturwiss., 1933, **21**, 299).—The conclusion of Danilow *et al.* (cf. this vol., 340) that trigonal Fe_2O_3 can exist in para- and ferro-magnetic forms according to heat treatment is contrary to the fact that ferromagnetic Fe_2O_3 is cubic and that when heated it affords the trigonal paramagnetic form. It is usual to ascribe the ferromagnetism of trigonal Fe_2O_3 to the presence of small quantities of Fe_3O_4. A. J. M.

Interatomic distances and ferromagnetism. E. C. STONER (Proc. Leeds Phil. Soc., 1933, **2**, 391—396).—The relative interaction energy J_0 associated with ferromagnetism of electron pairs in neighbouring atoms in Fe, Co, and Ni is calc. For Fe $\partial J_0/\partial V$ is positive and for Ni negative, indicating that interaction is a max. for R vals. between those of Co and Ni. R vals. (ratio of interat. distance to sum of effective radii) are calc. for a no. of unlike at. pairs with incomplete d shells and the results are discussed. J. W. S.

Atomic moments in ferromagnetic metals and alloys with non-ferromagnetic elements. E. C. STONER (Phil. Mag., 1933, [vii], **15**, 1018—1034).—Theoretical. From Sadron's results for alloys (A., 1932, 112, 679) the decrease in magnetic moment of Ni (in Bohr units) per atom of alloyed Cu, Zn, Al, or Sn is shown to equal the valency of the substituted atom. H. J. E.

Photo-stationary states of some geometrically isomeric acids. A. R. OLSON and F. L. HUDSON (J. Amer. Chem. Soc., 1933, **55**, 1410—1424).—Photo-stationary concns. of maleic and fumaric, citraconic and mesaconic, and *cis*- and *trans*-cinnamic acids have been determined conductometrically in aq. solution at 0—90° in monochromatic light of wave-lengths 2536 and 3130 Å. Photo-decomp. was negligible. Previous consideration of potential energy curves for photo-stationary states (A., 1931, 578) is extended to these cases in which the isomerides have different absorption coeffs. The importance of using monochromatic light is emphasised. J. G. A. G.

Regularities among hydrides. A. KREBS (Z. Physik, 1933, **81**, 776—780).—Nuclear separation plotted against at. no. gives two smooth curves for hydrides between Li and F. A. B. D. C.

Three-electron linking in chlorine dioxide. L. O. BROCKWAY (Proc. Nat. Acad. Sci., 1933, **19**, 303—307).—Energies of possible electronic structures are discussed. Electron diffraction photographs of the gas lead to the val. $1{\cdot}58 \pm 0{\cdot}03$ Å. for the Cl—O distance, in close agreement with the theoretical val. 1·57 Å., and giving definite evidence for the three-electron linking. N. M. B.

Form and vibrational frequencies of the NO_2 molecule. L. HARRIS, W. S. BENEDICT, and G. W. KING (Nature, 1933, **131**, 621).—Critical (cf. this vol., 336). Evidence is advanced for the view that the atoms in the NO_2 mol. form an obtuse-angled triangle. L. S. T.

Pseudo-atoms. A. ERLENMEYER and M. LEO (Helv. Chim. Acta, 1932, **15**, 1171—1186).—Measurement of the mol. extinction coeff. of azo-dyes made by coupling β-naphthol with diazotised *p*-amino-diphenyl ether, -diphenylmethane, and -benzophenone, respectively, reveals a close resemblance between the first two, which is not shared by the third. This supports the conception of ·CH_2· as pseudo-oxygen. Solubilities of the sulphate, chloride, bromide, and iodide of HgMe decrease in the order named; the halides are sol. in aq. NH_3, KCN, or $Na_2S_2O_3$, and the sulphate forms no double salt with Al sulphate. The radical is therefore regarded as pseudo-silver and not, as formerly held, as a pseudo-alkali metal. The subject is discussed theoretically. F. L. U.

Volumes of alkyl groups and their orienting powers. R. J. W. LE FÈVRE (Nature, 1933, **131**, 655).—Reasons for expecting an orientation contrary to electronic theories for certain types of compound are given and are supported by the nitration and halogenation of cymene. Me appears to possess a greater *o*-directive influence than Pr^{β}. L. S. T.

Orientations of molecules in the *p*-benzoquinone crystal. K. S. KRISHNAN and S. BANERJEE (Nature, 1933, **131**, 653—654; cf. this vol., 682).—Magnetic susceptibility measurements show that the mol. planes in the *p*-benzoquinone crystal are almost coincident with the (201) plane. Optical properties support this view. L. S. T.

Mosaic structure of crystals. F. BLANK (Physikal. Z., 1933, **34**, 353—368).—A summary.

Specially suitable standard substance for the accurate determinations of lattice constants by the Debye-Scherrer method. K. MOELLER (Naturwiss., 1933, **21**, 223).—TlCl is recommended. A. J. M.

Movement of liquid drops on growing crystals. L. KOWARSKI (Compt. rend., 1933, **196**, 1091—1093; cf. A., 1932, 796).—When *p*-toluidine is slowly sublimed and deposited on a razor edge, superfused droplets appear under certain temp. conditions on the crystals although the temp. is below the m.p., indicating indirect contact between crystal and liquid. The appearances are figured. C. A. S.

Effect of etching on the relative intensities of the components of double Laue spots obtained from a quartz crystal. M. Y. COLBY and S. HARRIS (Physical Rev., 1933, [ii], **43**, 562—563).—The investigations of Cork (cf. this vol., 213) are extended. N. M. B.

Interatomic electrons in crystal lattices. R. FORRER (Compt. rend., 1933, **196**, 1097—1099; cf. A., 1932, 449, 452).—The author's theory of effective contacts and interat. electronic orbits applies satis-

factorily to the Curie points of Fe_2O_3, Fe_3O_4 and δ-Fe, and to the m.p. of Bi and Sb, indicating the presence of such electrons in a crystal lattice. C. A. S.

Influence of the initial grain size on the final grain size of crystals during recrystallisation. R. ALEXANDRU (Bull. Sci. Polytech. Timisoara, 1933, **4**, 122—129).—Samples of electrolytic Fe with grain sizes between 200 and 24 grains per sq. mm. were deformed by rolling, and allowed to recrystallise at 650—750°. An initial grain size of approx. 157 grains per sq. mm. gave a max. grain size in the product. H. J. E.

Scattering of *X*-rays from powdered crystals. G. E. M. JAUNCEY and F. PENNELL (Physical Rev., 1933, [ii], **43**, 505—515; cf. this vol., 115).—The "average scattering" from powdered crystals of KCl, CaS, NaF, and MgO was determined for a wide band of *X*-rays entering a wide window of an ionisation chamber (cf. Coven, A., 1932, 1072); the spectral distribution of the intensity was obtained by reflexion from rock-salt, and the scattered intensities were compared with those from paraffin. Data are in good agreement with vals. calc. from the theory of diffuse scattering. N. M. B.

Dependence of crystallisation velocity on molecular structure. M. E. KRAHL (J. Amer. Chem. Soc., 1933, **55**, 1425—1429; cf. A., 1932, 450).—The linear velocity of crystallisation increases to a const. max. val. with increased supercooling. Data for 32 substitution derivatives of C_6H_6, CH_4, C_2H_6, C_2H_4, and $C_{10}H_8$ support the hypothesis that, of a series of isomerides, the most symmetrical compound crystallises fastest. The velocity is independent of temp. and time of melting, the no. of remeltings, and the time of ageing of the melt. J. G. A. G.

Nickel carbide and its relation to other carbides of elements from scandium to nickel. B. JACOBSON and A. WESTGREN (Z. physikal. Chem., 1933, **B**, **20**, 361—367).—In Ni_3C, prepared by heating Ni at 270—300° in CO, the Ni atoms have hexagonal closest spherical packing, and the unit cell has *a* 2·646 and *c* 4·329 Å. The C atoms occupy the largest interstices in the Ni lattice, and seem to form a definite array. Ni_3C is probably so unstable that it falls outside the scope of Hagg's rule (A., 1931, 414), to which it would otherwise be an exception. R. C.

Metals and alloys. XII. Nature and structure of lattices of binary magnesium compounds. E. ZINTL and E. HUSEMANN (Z. physikal. Chem., 1933, **B**, **21**, 138—155).—The following lattice consts. have been obtained: Mg_3P_2, *a* 12·03; Mg_3As_2, *a* 12·33; Mg_3Sb_2, *a* 4·573, *c* 7·229; Mg_3Bi_2, *a* 4·671 *c* 7·403 Å. The lattices are co-ordinated and anti-isomorphous with those of oxides M_2O_3. R. C.

Crystal structure of the compound $LaAl_4$. A. ROSSI (Atti R. Accad. Lincei, 1933, [vi], **17**, 182—185; cf. A., 1932, 575).—Cleavage takes place along the (001) pinacoid faces, and the lattice distance between cleavage planes is 5·1 Å. or an integral multiple thereof. The unit cell has *a* 13·2 Å., *c*/*a* 0·77; $d_{calc.}$ 3·69, $d_{obs.}$ 3·86. O. J. W.

Crystal structure of yttrium vanadate. E. BROCH (Z. physikal. Chem., 1933, **B**, **20**, 345—350).—*Yt vanadate*, prepared by heating Yt earths with NH_4VO_3, has the space-group The unit cell has *a* 7·126 and *c* 6·179 Å., and contains 4 $YtVO_4$ mols. R. C.

Possible form of Si_3O_8 groups in silicates. T. ITO (Proc. Imp. Acad. Tokyo, 1933, **9**, 53—55).—A chain arrangement of the Si and O in Si_3O_8 groups is suggested, and used to account for the cleavage properties of certain silicates with Si : O = 3 : 8. H. J. E.

Crystal structure of cancrinite from Dodo, Korea. I. S. KÔZU and K. TAKANE (Proc. Imp. Acad. Tokyo, 1933, **9**, 56—59; cf. this vol., 252).—The mineral crystal belongs to the hexagonal pyramidal hemihedral hemimorphic class [*a* 12·72, *c* 5·18 Å.; 1 mol. of $3(Na_2AlO_4{\cdot}Si_2O_4),2CaCO_3$ in unit cell; space-group C_6^6]. H. J. E.

Crystal structure of cancrinite from Dodo, Korea. II. S. KÔZU and K. TAKANE (Proc. Imp. Acad. Tokyo, 1933, **9**, 105—108).—A model of the arrangement of atoms in the unit cell of the crystal is suggested. H. J. E.

Crystal structure of diaspore. K. TAKANE (Proc. Imp. Acad. Tokyo, 1933, **9**, 113—116).—The unit cell has *a* 4·43, *b* 9·36, *c* 2·80 Å., and contains 2 mols. of $H_2Al_2O_4$; space-group H. J. E.

Diaspore from Shokozan. B. YOSHIKI (Proc. Imp. Acad. Tokyo, 1933, **9**, 109—112).—The mineral forms prismatic crystals, of the approx. formula $Al_2O_3{\cdot}H_2O$. Facial angles and optical properties are recorded. H. J. E.

Crystal structure of tenorite (cupric oxide). G. TUNELL, E. POSNJAK, and C. J. KSANDA (J. Washington Acad. Sci., 1933, **23**, 195—198).—The unit monoclinic cell has a_0 4·66, b_0 3·40, c_0 5·09 A., all ±0·02 Å.; β 99° 30′±30′. C. W. G.

Crystal structure of *o*-iodobenzoic acid. H. P. KLUG (J. Amer. Chem. Soc., 1933, **55**, 1430—1436).—The monoclinic crystals have 4 mols. in the unit cell, with $a:b:c = 0{\cdot}745:1:0{\cdot}2863$, β = 90° 43′ 47″, and a_0 11·30, b_0 15·17, c_0 4·336 Å.; space-group C_{2h}^5. The closest distances of approach between I atoms of adjacent mols. are 3·99 and 4·34 Å. J. G. A. G.

Crystal structure of anthracene. Quantitative *X*-ray investigation. J. M. ROBERTSON (Proc. Roy. Soc., 1933, **A**, **140**, 79—98).—A detailed account of work already noted (this vol., 216). L. L. B.

Ill-defined fibre-diagrams of cellulose derivatives. C. TROGUS and K. HESS (Z. physikal. Chem., 1933, **B**, **21**, 7—17).—The lack of sharpness in such diagrams is entirely a consequence of the conditions of separation of the cellulose derivative, and has no relation to the structure of the cellulose mol. Cellulose nitrate separates from solution in an org. solvent as a cryst. solvate, from which the normal ester lattice is formed by topochemical decomp. R. C.

***X*-Ray fibre-diagram of glucomannan.** I. SAKURADA and K. HUTINO (Z. physikal. Chem., 1933, **B**, **21**, 18—24).—Konnjakumannan (A., 1928, 873) exists in an amorphous form, sol. in H_2O, and a cryst. insol. form. When the gel is stretched, the micelles orient themselves in the direction of stretching; orientation

has also been observed in dried films and frozen discs of the gel. On swelling in H_2O the lattice of the cryst. form is distended, the effect being most marked across the fibre-axis. The unit cell contains three hexose residues. R. C.

Alternations in the properties of *N*-monoalkylmalonic acids. Malkin's views concerning the alternation phenomena. P. E. Verkade and J. Coops (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 76—87).—A crit. examination of *X*-ray work on alternation phenomena in crystals. W. R. A.

Structure of cyanuric triazide $(C_3N_3)(N_3)_3$. T. C. Sutton (Phil. Mag., 1933, [vii], **15**, 1001—1018).—$(C_3N_3)(N_3)_3$ forms holohedral hexagonal prisms, terminated by a single hexagonal pyramid (axial ratio 0·684; *d* 1·71; $a=b=c=8{\cdot}66$ Å., d 5·94 Å.; 2 mols. in unit cell). A model of the unit cell has been constructed, which represents the observed properties of the crystal. The azide group is a short chain of 3 N atoms, linked to the (C_3N_3) group by the middle N. C_3N_3 forms a hexagonal ring resembling C_6H_6. H. J. E.

Effect of tension on the electrical resistance of single antimony crystals. (Miss) M. Allen (Physical Rev., 1933, [ii], **43**, 569—576; cf. this vol., 217).—The adiabatic tension coeff. of resistance was determined for various orientations. The coeff.–orientation curves resemble those of Bi. The six coeffs. defining the resistance behaviour under deforming forces are found with and without strain corrections. N. M. B.

Change in magnetic induction under constant field strength during cold working and the recovery on heating. G. Tammann and H. J. Rocha (Ann. Physik, 1933, [v], **16**, 861—864).—Curves showing the recovery of magnetic induction of Fe, Ni, and mixed crystals of Fe and Ni are given. W. R. A.

Change of resistance of a semi-conductor in a magnetic field. J. W. Harding (Proc. Roy. Soc., 1933, **A**, **140**, 205—222).—Mathematical. Wilson's theory of semi-conductors (*ibid.*, 1931, **A**, **134**, 277) gives the correct form of the curve required to explain the experimental results both for low and high fields, and the correct order of magnitude for the resistance change. L. L. B.

Effect of water on the plasticity of rock-salt. A. Smekal (Naturwiss., 1933, **21**, 268).—The view is expressed that recent work on the taking up of H_2O by rock-salt does not necessarily establish a direct causal connexion between the entrance of H_2O and plasticity of the crystal. A. J. M.

Strength and elastic limit of thin rods of rock-salt, single crystals of zinc, and glasses. E. Jenckel (Z. Elektrochem., 1932, **38**, 569—578).

Mechanism of plastic deformation. A. V. Stepanov (Z. Physik, 1933, **81**, 560—564).—During plastic deformation the deformation energy is transformed into heat in the small zones bordering slip, and this localisation of heat causes a temporary dissociation of the lattice around the zones. A. B. D. C.

Polymorphic transformations of iron at the A3 and A4 points. A. V. Svetchnikov (Rev. Met., 1932, **29**, 583—587).—Calculations based on lattice measurements show that the sp. vol. of Fe is decreased by 3·4% at the A3 transformation and increased by 0·9% at the A4 point. On plotting the sp. vol. of α-, γ-, and δ-Fe against the temp. the vals. for α- and δ-Fe lie almost on a straight line and those for γ-Fe on a smooth curve concave to the vol. axis and meeting the α–δ line at the m.p. of Fe. It is concluded therefore that α- and δ-Fe are the same phase. A. R. P.

Superconductivity. L. Brillouin (Compt. rend., 1933, **196**, 1088—1090).—Theoretical. Superconductivity can occur if a certain relation (illustrated by curves) holds between the energy and momentum of the electron in a crystal lattice. This is very improbable except in a face-centred cubic lattice in which the electrons are almost bound, as is the case in superconductors. The explanation is consistent with the effect of a magnetic field on superconductivity, and its appearance at a definite temp. (cf. A., 1930, 1082). C. A. S.

Thermo-electric powers of nickel and nickel–chromium alloys near the Curie point. A. W. Foster (Proc. Leeds Phil. Soc., 1933, **2**, 401—405).—The thermo-electric powers of Ni (99·5%) and Ni–Cr alloys (Ni 98·5, Cr 1%, and Ni, 97·5, Cr 2%) have been measured against Cu. The change in the sp. heat of electrons at the Curie point is lowered very rapidly by the addition of Cr. J. W. S.

Theory of heat conduction at low temperatures. W. Kroll (Z. Physik, 1933, **81**, 425—427).

Effect of magnetic field on the heat conductivity of gases. I. H. Senftleben and J. Pietzner (Ann. Physik, 1933, [v], **16**, 907—929).—The conductivity of paramagnetic gases is decreased by the application of a magnetic field. The effect is independent of field strength (H) for the higher vals. of H, and alteration of temp. has no influence beyond a certain limit. The effect is independent of pressure for low pressures. A. J. M.

Jump in the expansion coefficient of liquid helium in passing the λ-point. W. H. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 147—152).—Theoretical. A relation is deduced between the inclination of the λ-curve in the p–T diagram of He, the jump in sp. heat, and the jump in the expansion coeff. at 2·19° abs. $\Delta a=-0{\cdot}0648$. This val. is in harmony with the results of Onnes and Boks for the density of liquid He between 1·8° and 2·5° abs. M. S. B.

Specific heats of tungsten, molybdenum, and copper. H. L. Bronson, H. M. Chisholm, and S. M. Dockerty (Canad. J. Res., 1933, **8**, 282—303).—The vals. of C_p at 0—500° for Cu, Mo, and W are determined by the method of mixture, and for Cu by electrical heating also. They are given by: Cu, $C_p=0{\cdot}09292+0{\cdot}0000136T-452/T^2$; Mo, $C_p=0{\cdot}06069+0{\cdot}000012T-361/T^2$; W, $C_p=0{\cdot}03199+0{\cdot}00000328T-129/T^2$. H. A. P.

Active oxides. LXIII. Specific heats of crystalline zinc hydroxide and the calculation of the affinity between zinc oxide and water. G. F. HÜTTIG and H. MÖLDNER (Z. anorg. Chem., 1933, **211**, 368—378; cf., A., 1932, 1211).—The mean sp. heat of cryst. $Zn(OH)_2$ at −185° to 10·6°, −79° to 17·5°, and 16·9—49·8° was measured. The total heat (U) and the affinity (A) for the formation of stable cryst. $Zn(OH)_2$ from ZnO and H_2O were calc. for different vals. of T. The equilibrium diagram of the system ZnO–H_2O was plotted, and the effect of activation of ZnO on the equilibrium discussed. H. J. E.

Heat of vaporisation of hydrogen fluoride. J. H. SIMONS and J. W. BOUKNIGHT (J. Amer. Chem. Soc., 1933, **55**, 1458—1460).—The heat of vaporisation at 748 mm. is 97·5 g.-cal. per g. The agreement with the val. calc. from v.-d. and v.-p. data shows that the heat of vaporisation does not involve the heat of dissociation of H_6F_6. J. G. A. G.

Calculation of specific heats of solids. K. HONNEFELDER (Z. physikal. Chem., 1933, **B**, **21**, 53—64).—The sp. heats at not too low temp. of Cu, Cd, Zn, W, Sn, Zn blende, fluorspar, quartz, rock-salt, and sylvine calc. from the Debye–Born–von Karman theory agree more or less satisfactorily with the observed vals. Below about 15—25° abs., however, for W, Zn, and Cd the calc. vals. are 70% below the observed vals. R. C.

Isomorphism and alternation in the m.p. of the normal alcohols, acetates, bromides, acids, and ethyl esters from C_{10} to C_{18}. J. D. MEYER and E. E. REID (J. Amer. Chem. Soc., 1933, **55**, 1574—1584).—The m.p. of n-decyl to n-octadecyl alcohol do not show detectable alternation, whilst those of the corresponding bromides do so. The m.p. of the acetates and the isomeric Et acylates both show alternation. Decided arrests are found in the curves of the alcohols from C_{12} to C_{18}. Cetyl and octadecyl acetates exhibit two f.p. (α- and β-forms), but heptadecyl acetate shows only one; below cetyl, the acetates of the odd alcohols exhibit two f.p., whilst those of the even alcohols show one. Many of the acetates and Et acylates exhibit dimorphism. H. B.

Thermal properties of halides. V. Influence of constitution on m.p., b.p., heats of vaporisation, and volumes of halides. VI. Vapour pressures and vapour densities of beryllium and zirconium halides. O. RAHLFS and W. FISCHER (Z. anorg. Chem., 1933, **211**, 321—348, 349—367; cf. A., 1932, 1195).—V. The b.p. and m.p. of the halides in the main groups of the periodic table are plotted as functions of valency, and their b.p. as functions of the cation radius. Vals. for λ/T_B and σ/T_S are tabulated (λ=heat of vaporisation at abs. b.p., T_B; σ—heat of sublimation at the abs. sublimation temp., T_S). The ratio of the mol. vol. at m.p. and b.p. to the mol. vol. of cryst. state at 0° abs. for the halides is plotted against T_F/T_B (T_F=abs. m.p.).

VI. The v.p., v.d., and m.p. of $BeCl_2$, $BeBr_2$, BeI_2, $ZrCl_4$, $ZrBr_4$, and ZrI_4 were measured. $BeCl_2$ and $BeBr_2$ at their b.p. are approx. 50% associated to Be_2Cl_4 and Be_2Br_4. The Zr compounds are unimol. ZrI_4 dissociates at 1000° into ZrI_2 and I_2. Be halides and $ZrCl_4$ attack SiO_2, forming $SiCl_4$. No oxychloride of Si is formed from SiO_2 and SiCl. at 630°. H. J. E.

Ebulliometric and tonometric researches on chemically pure liquids. I. A. ZMACZYNSKI (Rocz. Chem., 1933, **13**, 181—192).—The vals. of A, B, and C in the equation $t=A+Bt_{H_2O}+Ct^2_{H_2O}$ (t is the b.p. of the liquid, and t_{H_2O} that of H_2O) have been determined at 330—2000 mm. pressure, for EtBr, CS_2, $COMe_2$, $CHCl_3$, C_6H_6, PhMe, PhCl, and PhBr, using a differential ebullioscope fitted with a rectifying column. R. T.

Revision of isotherm measurements of Kohnstamm and Walstra. A. MICHELS and A. J. J. GERVER (Ann. Physik, 1933, [v], **16**, 745—750; cf. Kohnstamm and Walstra, A., 1914, ii, 800).—A table of pv vals. for H_2 is given. W. R. A.

Vapour pressure of liquid and solid carbon dioxides. C. H. MEYERS and M. S. VAN DUSEN (Bur. Stand. J. Res., 1933, **10**, 381—412).—The v.p. of CO_2 has been redetermined over the temp. range −56·60° to 31·0°. Empirical equations which represent the v.p. for the liquid and solid states, respectively, have been developed. The results accord with those of other investigators. J. W. S.

Physical properties of divinyl ether. F. T. MILES and A. W. C. MENZIES (J. Physical Chem., 1933, **37**, 425—430).—Over the range −30° to +60°, the v.p. of $(CH_2{:}CH)_2O$ is given by $\log p_{mm.}=21{\cdot}73592-2085{\cdot}11/T-4{\cdot}81530 \log T$. Between 0° and 25°, $d=0{\cdot}79601-1{\cdot}14582t\times10^{-3}-2{\cdot}5706t^2\times10^{-6}\pm2\times10^{-4}$. The orthobaric v.d. is 0 002994 at the b.p., 28·35°± 0·04. The latent heat of vaporisation at the b.p. is 89·4 g.-cal. per g. Trouton's const. is 20·8 and Hildebrand's is 14·2 at −21°. D. R. D.

Vapour pressure of *trans*-di-iodoethylene. L. F. BROADWAY and R. G. J. FRASER (J.C.S., 1933, 429—430).—The v.p. has been determined between −8° and 20° by the mol. effusion method and may be expressed by the equation $\log p_{mm}=-2130/T+5{\cdot}86$. The calc. latent heat of sublimation is 9720 g.-cal. per mol. M. S. B.

Equation of state of real fluid. S. C. BRADFORD (Engineering, 1933, **135**, 439).—Work previously reported (cf. A., 1930, 1119) leads to a new definition of temp.: the mean kinetic energy of a particle of a perfect gas, or the temp. of a thermometer filled with a perfect gas in equilibrium with the substance under observation. From this definition, with the help of λ, the ratio of the most probable particle speed in the liquid to that in a perfect gas, and A an association factor, the kinetic relations and an equation of state for a real fluid, in agreement with experimental data, are deduced. N. M. B.

Values of b and $\sqrt{a}$ for the alkali metals, halogens, and molten alkali halides. Determination of the critical temperature and pressure from various independent data. J. J. VAN LAAR (Chem. Weekblad, 1933, **30**, 294—304).—The calculations (from published data) are given in detail. H. F. G.

Viscosity, thermal conductivity, and diffusion in gaseous mixtures. XXII. Temperature coefficient of molecular diameter and its relation to Maxwell diameter, lattice size, and nuclear separation. M. TRAUTZ (Ann. Physik, 1933, [v], **16**, 751—767).—Vals. of mol. diameters deduced from physical data are compared and the temp. coeff. is derived for a large no. of gases and vapours. W. R. A.

Demonstration apparatus for liquefaction of helium. F. SIMON and J. E. AHLBERG (Z. Physik, 1933, **81**, 816—820). A. B. D. C.

Possibility of attaining any low temperature. F. SIMON (Z. Physik, 1933, **81**, 824—831, 838—839). A. B. D. C.

Attainment of lowest temperature by compression of liquid helium. W. MEISSNER (Z. Physik, 1933, **81**, 832—837).—Compression cools liquid He; the possibility of attaining lower temp. is indicated. A. B. D. C.

Thermodynamic functions of hydrocarbon gases from spectroscopic data. L. S. KASSEL (J. Amer. Chem. Soc., 1933, **55**, 1351—1362).—Approx. methods of evaluating the free energies and entropies of polyat. mols. are applied to CH_4, C_2H_4, and C_2H_2 between 250° and 5000° abs. J. G. A. G.

Determination of the constant σ of the Stefan–Boltzmann radiation law. C. MÜLLER (Z. Physik, 1933, **82**, 1—36).—An accurate determination of σ gave the val. $5{\cdot}774(\pm 0{\cdot}02)\times 10^{-12}$ watt × cm.$^{-2}$ × degree^{-4}. A. B. D. C.

Viscosity, heat conductivity, and diffusion of gaseous mixtures. XXIII. Absolute Enskog–Chapman diameter of gas molecules and their temperature coefficients. M. TRAUTZ (Ann. Physik, 1933, [v], **16**, 865—886; cf. A., 1932, 14).—The calculation of mol. diameters from viscosity is discussed, with special reference to the various types of mol. models. The temp. coeffs. of the diameters are calc., and the physical interpretation of these numbers is discussed. A. J. M.

Determination of composition of certain azeotropic mixtures, using a universal fractional distillation apparatus. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1933, **13**, 193—200).—A fractionating apparatus adapted for use at increased or reduced pressures is described. The composition of the azeotropes of EtOH and C_6H_6 varies with the pressure: b.p. 0°, 4·5%; b.p. 35·5°, 12%; b.p. 76·5°, 21%; b.p. 160°, 45% EtOH. A mixture of EtOH and C_6H_6 can hence be separated by successive distillation at high and low pressures. The H_2O content of the azeotrope of Et_2O and H_2O of b.p. 34·15° is 1·3%, and of b.p. 114° 4·5%; by distillation at 114° (11 atm.) H_2O is distilled off in the azeotropes, leaving anhyd. Et_2O. The composition of EtOH–H_2O azeotropes does not vary with pressure; for this reason Lewis' method for the prep. of anhyd. EtOH by fractionation under pressure is not possible. R. T.

Azeotropic hydrobromic acid solutions at pressures of 100—1200 mm. W. D. BONNER, L. G. BONNER, and F. J. GURNEY (J. Amer. Chem. Soc., 1933, **55**, 1406—1409).—The composition, *d*, v.p., and b.p. of "const.-boiling" solutions are recorded. J. G. A. G.

Heat of mixing of normal liquids. V. KIREJEV (Z. anorg. Chem., 1933, **211**, 423—426).—An expression for the heat of mixing, developed from that of van Laar and Lorenz (A., 1925, ii, 870), agrees with experimental vals. for CS_2–C_6H_6 and CS_2–Me_2O mixtures. H. J. E.

System water–phenol. III. Electrical conductivities. O. R. HOWELL and C. HANDFORD (Trans. Faraday Soc., 1933, **29**, 640—653).—Electrical conductivities of mixtures of PhOH and H_2O have been determined at 20—70°. The form of the conductivity (κ)–concn. curves, which show a max. is attributed to the formation of the compound, $(PhOH_2^{\cdot})(OH')$ and its subsequent dissociation. The acidity of dil. aq. PhOH affords evidence for the alternative dissociation: $PhOH+H_2O \rightleftharpoons PhO'+OH_3^{\cdot}$. The κ–temp. curve for each concn. is smooth and is represented by the equation $\kappa_t-\kappa_{20°}+\alpha(t-20°)+\beta(t-20°)^2$. The curves obtained by plotting α and β against the concn. exhibit an inflexion for the equimolar mixture. M. S. B.

Rate of diffusion of metals in gold and silver. W. JOST (Z. physikal. Chem., 1933, **B**, **21**, 158—160).—The rates of diffusion of Pd, Pt, and Cu in Au and of Pd in Ag have been determined over a wide temp. range by an *X*-ray method. R. C.

Diffusion of mercury on rolled tin foils. F. W. SPIERS (Phil. Mag., 1933, [vii], **15**, 1048—1061; cf. A., 1932, 906).—From *X*-ray analysis, the amalgam has a hexagonal structure (*a* 3·23, *c* 3·00 Å.; 1 atom in unit cell). It is shown by resistance measurements to be a secondary solid solution. H. J. E.

Are liquid sodium amalgams colloidal? H. E. BENT (J. Physical Chem., 1933, **37**, 431—436).—Polemical against Paranjpe and Joshi (this vol., 118) Liquid Na amalgams are true solutions with properties independent of the mode of prep. D. R. D.

Elastic properties of single crystals of silver–gold alloys. H. RÖHL (Ann. Physik, 1933, [v], **16**, 887—906).—The Young's and torsion moduli of single crystals of the mixed crystal system Ag–Au have been determined. The elastic properties of the system are quite as anisotropic as those of the pure components. The system does not obey the mixture rule for any given direction. The velocity of sound, and its dependence on direction, have been calc. for Au and Ag. A. J. M.

Relation between mean atomic volume and composition in copper–zinc alloys. E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1933, **A**, **140**, 179—191).—In the Cu–Zn series the mean at. vol. of both phases present in a mixed region remains const., but the const. at. vol. of one phase depends on the second phase. The increase in at. vol. when a Cu atom is replaced by a Zn atom is attributed to the fact that the Zn atom is not "spherical" and packs differently in the various phases. A detailed analysis is made of the ε- and η-phases. For pure Zn $a=2{\cdot}659$ Å., $c=1{\cdot}856$ at room temp. L. L. B.

Variation of mean atomic volume with temperature in copper–zinc alloys, with observations on the β-transformation. E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1933, **A**, **140**, 191—204).—The changes in mean at. vol. with temp. (350—800°), for the α-, β-, and γ-phases of Cu–Zn alloys, have been studied by *X*-ray precision analysis. The mean at. vol. of both the constituents in a mixed region shows a change (probably owing to a change in solid solubility), whereas the mean at. vol. in the pure phases remains const. Both the β- and γ-phases in the β+γ region show a min. mean at. vol. at about 500°, whilst the α-phase in the α+β region shows a max. val. at the same temp. The β-transformation which occurs at about 470° is discussed in the light of the experimental data. L. L. B.

***X*-Ray analysis of iron–tin alloys.** W. F. EHRET and A. F. WESTGREN (J. Amer. Chem. Soc., 1933, **55**, 1339—1351).—The solubility of Sn in α-Fe increases from 9·8% at 680° to 18·8% at 900°, and the edge of the body-centred α-Fe lattice increases linearly with concn. of Sn from 2·896 to 2·925 Å. The cell consts. of the hexagonal β-phase are a_1 5·292, a_2 4·440, and the unit cell contains three FeSn mols. The β′-phase is present in alloys containing 27—59% Sn annealed at 680°, whilst the β″-phase in alloys containing 27—48% Sn and annealed at 860° is hexagonal and contains two Fe_2Sn per unit cell for which a_1=5·449 Å., a_2 =4·353 Å. A γ-phase is present in certain alloys quenched from 750—900°. The unit cell of the $FeSn_2$ phase contains 12 atoms, and is hexagonal, with a_1 5·317, a_3 9·236. The results are discussed in relation to previous work (B., 1931, 1053). J. G. A. G.

Metals and alloys. X. Valency electron rule and atomic radii of base metals in alloys. E. ZINTL and G. BRAUER. **XI. Lattice structure of NaIn and deformation of atoms in alloys.** E. ZINTL and S. NEUMAYR (Z. physikal. Chem., 1933, **B**, **20**, 245—271, 272—275).—X. *X*-Ray examination of binary alloys of alkali and alkaline-earth metals with other metals in equi-at. proportions has shown the existence of numerous phases with the structure of β-brass and NaTl. The no. of valency electrons per atom varies, however, from 1 to 2½, so that the rule that in body-centred alloy phases there are always three valency electrons for each two atoms is not valid for alloys of very electronegative metals. In such alloys the interat. distance is < corresponds with additivity, an effect which is ascribed to diminution in the at. radius of the base component. It is inferred that the concn. of valency electrons does not determine the structure if the components of an alloy differ greatly in polarisability. The miscibility of conc. Li alloys has been investigated.

XI. The alloy NaIn has the NaTl structure with a 7·297 Å. In this the radii of Na and Tl are both 1·58 Å. The at. radii deduced from NaTl structures show that the contraction of base metals in alloys is the greater the larger are their atoms and the smaller the atoms of the more electropositive component. R. C.

Non-substituted mixed crystals of iron. E. SCHEIL (Z. anorg. Chem., 1933, **211**, 249—256).—Crystals of α- or γ-iron in which atoms such as C or N can be inserted in virtue of their small at. radius are chemically reactive at a temp. 200—300° lower than are those in which Fe atoms are substituted. Spacial considerations lead to the conclusion, supported by observation, that γ-iron will accommodate a larger proportion of C or N than will α-iron, but that the foreign atoms will become mobile at a lower temp. in the latter. F. L. U.

Formation of layers in the systems alkali hydroxide–water–ammonia. E. WEITZ and U. HEUBAUM (Ber., 1933, **66**, [*B*], 790—792).—The behaviour of aq. NaOH or KOH towards NH_3 under high pressure shows that the solubility of each substance in H_2O is depressed by the presence of the other. H. W.

Physical properties of heterogeneous ternary mixtures. P. M. MONVAL (J. Chim. phys., 1933, **30**, 195—197; cf. A., 1928, 1084).—A reply to Brun (A., 1932, 1091). F. L. U.

Solubility of silver in mercury. II. R. E. DERIGHT (J. Physical Chem., 1933, **37**, 405—416).—Between 20° and 80°, the solubility of Ag in Hg is given by $\log N = -1105{\cdot}8/T + 0{\cdot}5894$. D. R. D.

Transformations of salts of tervalent metals in solution. V. Solubility of chromic sulphate and of potassium and sodium chrome alums. C. MONTEMARTINI and E. VERNAZZA (L'Ind. Chimica, 1933, **8**, 445—446; cf. A., 1932, 708, 827, 912, 996).—Saturated aq. solutions at 18° contain $K_2SO_4,Cr_2(SO_4)_3,24H_2O$ 28·2, $Cr_2(SO_4)_3,17H_2O$ 84·8, and $Na_2SO_4,Cr_2(SO_4)_3,24H_2O$ 94·8%. The % of violet fraction is 51·75, 51·68, and 51·70, respectively. Thus the equilibrium violet—green form of $Cr_2(SO_4)_3$ is not affected by alkali sulphate, and is almost independent of the concn. T. H. P.

Distribution of radium in fractional precipitation of radiferous barium chloride. (MME.) B. E. MARQUES (Compt. rend., 1933, **196**, 1309—1311).—Steadily increasing proportions of the Ba and Ra contained in equal amounts of a $BaCl_2$+$RaCl_2$ solution were pptd. by aq. HCl. The proportion of Ra which is pptd. decreases steadily as the total amount of the ppt. increases. C. A. S.

Influence of temperature and pressure on adsorption of hydrogen by nickel. II. J. SMITTENBERG (Rec. trav. chim., 1933, **52**, 339—351; cf. this vol., 346).—Two further preps. of Ni have been used in the determination of adsorption isotherms at 18°, 122°, 208°, and 300°, and of isobars at 760 mm. The adsorption capacity of Ni is diminished not only by rise in the temp. of reduction, but also by calcination of the oxide prior to reduction. Adsorption of H_2 by Ni is a complex process consisting of at least two superposed phenomena which, for the isotherm at 300°, can be satisfactorily expressed by a combination of two formulæ. F. L. U.

Energy exchange at platinum–hydrogen interface. H. H. ROWLEY and K. F. BONHOEFFER (Z. physikal. Chem., 1933, **B**, **21**, 84—92).—The coeff. of accommodation, α, of H_2 on bright Pt is 0·22 at room temp. and increases as the temp. falls, reaching at 110° abs. the val. 0·37; the coeff. is independent of

the pressure between 0·03 and 0·3 mm. This high val. of α is ascribed to reflexion occurring on an adsorbed film of H, and the negative temp. coeff. is possibly due to α for rotational energy having a large negative temp. coeff. For an approx. 50% mixture of ortho- and para-H_2 α at 140° abs. is about 10% < and at 180° about 15% < for ordinary H_2, which shows that α is smaller for rotational than for translational energy. α is considerably increased by the presence of adsorbed O on the Pt. R. C.

Adsorption of sulphur dioxide and carbon dioxide at small equilibrium pressures. A. MAGNUS and H. GIEBENHAIN (Z. physikal. Chem., 1933, **164**, 209—222).—Various forms of wood charcoal have been used as adsorbents and measurements made with SO_2 at 0—300° and CO_2 at 0° and pressures of about 0·001—5 mm. None of the isotherms for SO_2 has the double point of inflexion reported by Polanyi and Welke (A., 1928, 580) for Aussig C, and the differential heat of adsorption calc. from the isotherms diminishes continuously with the amount adsorbed, without passing through a min. at low pressures. For CO_2 many of the isotherms are markedly concave to the pressure axis at low pressures, but become linear at higher pressures, which is taken to mean that the active centres of highest adsorption potential are first occupied, after which only physical adsorption occurs, corresponding with the linear part of the isotherms. By treatment of the C with small amounts of O_2 at 380—700° part of the active centres could be burned away. For a given form of C the isotherm for CO_2 at 0° is very similar to that for SO_2 at 100°. R. C.

Gas adsorption on electrically conducting films during their condensation from molecular rays. M. C. JOHNSON and T. V. STARKEY (Proc. Roy. Soc., 1933, **A**, **140**, 126—140).—A const. stream of Hg vapour, with or without the addition of H_2, O_2, A, CO_2, or various ionised gases, is condensed into an electrically conducting film on a target cooled with liquid air. The curves obtained are in accord with microscopical observations relating to the growth of loosely-aggregated structures from Hg vapour in presence of a gas. L. L. B.

Influence of combined oxygen on the adsorption of vapours by porous solids. I. L. J. BURRAGE (J. Physical Chem., 1933, **37**, 505—510).—Charcoal which had been heated in vac. at 800° for 80 hr. still contained traces of CO and CO_2. A method for removing these by flushing with CCl_4 is described. With this O-free C, reversible isothermals, consisting of a series of rectangular steps, were obtained for CCl_4 by the static method, equilibrium being instantaneous. D. R. D.

Desorption of *n*-butylamine from charcoal. H. J. PHELPS and R. B. VALLENDER (Biochem. J., 1933, **27**, 435—441).—Desorption (I) of NH_2Bu^a from charcoal in H_2O or an equi-vol. mixture of H_2O and EtOH occurs as a two-stage process. In the primary rapid stage up to 50% (I) occurs within 10 min. The second stage is slow and is inhibited at 0°. H. D.

Mode of retention of sulphur by carbon. J. P. WIBAUT (Z. anorg. Chem., 1933, **211**, 398—400: cf. this vol., 221).—Part of the S adsorbed by C can be removed (as CS_2) only by heating to 1000°. A chemisorption, resembling that of O_2 by C, is suggested. H. J. E.

Adsorption of Congo-red by animal charcoal. G. ROSSI and A. MARESCOTTI (Annali Chim. Appl., 1933, **23**, 62—66).—The degree of dispersion of Congo-red solutions varies appreciably with the dilution. The fact that the adsorption by animal charcoal in solutions of different concn. does not follow Boedecker's law is probably due to this change in the degree of dispersion. T. H. P.

Adsorption of electrolytes from neutral solutions by calcium carbonate. J. JEBAVY (Z. Zuckerind. Czechoslov., 1933, **57**, 264—268, 269—272).—The adsorption of $CaSO_4$, Ca citrate, and Ca aspartate from neutral solution by twelve different varieties of calcite and of aragonite has been determined; the concns. of the solutions used correspond with the concns. of the salts in diffusion juice. The adsorption falls in the order: citrate, sulphate, aspartate, and for all forms of calcite is > for aragonite; it varies with the temp. and method of prep. of the adsorbent. The presence of free CaO increases the adsorption. H. F. G.

Inner adsorption in crystalline salts. VI. D. BALAREV (Kolloid-Beih., 1933, **37**, 324—341; cf. this vol., 122).—The theory of the mosaic structure of crystals and the consequent inner adsorption at the surface of the elementary crystal blocks has been applied to the formation of solid solutions. The elementary blocks of colloidal dimensions are considered to be slightly disoriented with respect to one another, so that the unoriented ions or atoms constitute variable linkings between the individual blocks. The following main types are distinguished: (*a*) typical mixed crystals (*e.g.*, KCl–KBr), (*b*) typical solid solutions (*e.g.*, C_6H_6 and I), (*c*) typical inner adsorption (*e.g.*, K_2SO_4 and H_2O), but it is emphasised that progression from one type to another is continuous. E. S. H.

Influence of foreign substances on the adsorption of liquid by non-swelling powders. H. FREUNDLICH, O. ENSLIN, and G. LINDAU (Kolloid-Beih., 1933, **37**, 242—280).—The max. amount of H_2O, w_∞, taken up by homodisperse powders of different chemical nature (SiO_2, Al_2O_3, Fe_2O_3, MgO, TiO_2, As_2S_3, PbS, ZnS, FeS_2, and Cu_2S,Fe_2S_3) is almost const., although differences appear when the powder is heterodisperse or when the particles are very small or rough. With homodisperse SiO_2, increases rapidly as the particle size is increased from 8 to 45 μ, but varies little further up to 150 μ. A marked increase of w_∞ is observed in Al_2O_3 particles between 7 and 32 μ. Similar results are obtained when the hydrophilic SiO_2 particles are made hydrophobic by adsorption of dyes and when the hydrophobic As_2S_3 particles are made hydrophilic by adsorption of gelatin or casein. Addition of 0·1*M*-$BaCl_2$ does not change w_∞ unless the particle size is > 30 μ, when w_∞ is increased and a looser packing is observed. The rate of imbibition of H_2O by SiO_2 is high, but is decreased greatly by adding small amounts of a basic, strongly adsorbable dye (crystal-violet); the acid dye Me-

orange has no effect. The velocity of imbibition of H_2O by hydrophobic As_2S_3 is correspondingly increased by adsorption of gelatin, casein, etc.; ovalbumin has little effect. E. S. H.

Adsorption of radon by silica gel. R. Livingston and L. H. Reyerson (J. Physical Chem., 1933, **37**, 534—535).—The distribution coeff. for Rn between SiO_2 gel containing 5% H_2O and free space (Rn per g. of gel/Rn per c.c. of space) is 144 (cf. A., 1932, 803). The adsorptive capacity of Pyrex glass is much < that of SiO_2 gel. D. R. D.

Adsorption by colloidal clay. E. Ungerer (Z. Pflanz. Düng., 1933, **29**, **A**, 38—50).—Adsorption of basic dyes by clay colloids (< 0·2 μ) conforms to the general adsorption isotherm. The adsorption of methylene-blue (and of cinchonine) is related to the adsorption capacity determined by the $BaCl_2$ method. Sparingly sol. compounds (*e.g.* $BaSO_4$, $CaCO_3$; Li, Ba, Ca, and Mg phosphates) are decomposed by the clay in aq. suspension, liberating free anions. The bearing of this on the mobility of anions in soil and on the formation of alkali soils is discussed. A. G. P.

Hygroscopic moisture of cellulose. XI. Mechanism of adsorption of water vapour by cellulose. S. Oguri (J. Soc. Chem. Ind., Japan, 1933, **36**, 67B).—The absorption of H_2O by cotton cellulose is not an effect of simple dissolution and chemical reaction. From the thermal viewpoint there is scarcely any difference between absorption and condensation of H_2O vapour in the case of standard cotton cellulose. Theories of the mechanism of H_2O absorption are discussed. It is probable that this is due to the attraction of OH groups in the mol. Almost half the OH groups in the cellulose mol. are unsuitably oriented to attract H_2O. V. E. Y.

Adsorption of various ammonium compounds in soils. K. Nehring and A. Keller (Kolloid-Beih., 1933, **37**, 293—323).—The adsorption of $NH_4^{\cdot}$ by soils is in accordance with the Freundlich isotherm, and the amount adsorbed is influenced by the lyotropic character of the anion present. The adsorbent power of acid soils is increased when the $H^{\cdot}$ is replaced by $Ca^{\cdot\cdot}$, and particularly by $Na^{\cdot}$. Adsorption of $NH_4^{\cdot}$ by acid soils is very marked in $(NH_4)_2HPO_4$ and $(NH_4)_2C_2O_4$, but is reduced considerably when $CaCO_3$ is added to the soil. In acid soils the effects of concn. and nature of the anion are more marked than in neutral soils. E. S. H.

Mechanism of precipitation processes. XII. Processes in which cadmium salts participate. Z. Karaoglanov and B. Sagortschiev (Z. anorg. Chem., 1933, **211**, 227—232; cf. A., 1932, 584).—CdS pptd. from $CdBr_2$ by Na_2S contains a proportion of $CdBr_2$ which increases with time, and depends on the concn. of $CdBr_2$, but not on the presence of acids. With K_2CO_3, a much smaller proportion of precipitant is retained. $CdCl_2$ behaves similarly. When $CdSO_4$ is used, this is also contained in the ppt. with Na_2S or K_2CO_3, but the amount does not change with time. $Na_2C_2O_4$ in all cases gives a ppt. free from secondary products. The results are referred to the fact that CdS is the least and CdC_2O_4 the most sol. of the ppts. examined. F. L. U.

Co-precipitation. IV. Co-precipitation of alkali ions with calcium oxalate. Adsorbent properties of the latter. V. Co-precipitation of anions with calcium oxalate. I. M. Kolthoff and E. B. Sandell (J. Physical Chem., 1933, **37**, 443—458, 459—473).—The order of adsorption of alkali metal ions by CaC_2O_4,H_2O (I) is the same as that for co-pptn., viz., $Na>K>NH_4$. These effects are diminished by an excess of $Ca^{\cdot\cdot}$ in the solution and increased by excess of C_2O_4'', except in very conc. solutions, where irregularities are observed. Under the conditions used in the analytical pptn. of (I), contamination is slight. The purest (I) is obtained by pptn. at room temp. from fairly conc. solutions at 4—6, the mixture being then heated for 24 hr. on the steam-bath. Co-pptn. decreases with rising temp. The amount of alkali metal co-pptd. is an exponential function of its concn.

V. The order of co-pptn. of anions with (I) is: $IO_3'>CrO_4''=SO_4''>BrO_3'>Cl'=Br'=I'$. OH' is also strongly adsorbed by, and co-pptd. with, (I), recrystallisation failing to remove it unless acid is present. The amount of IO_3', CrO_4'', SO_4'', and OH' pptd. may be sufficient to affect analytical work, whereas only traces of Cl', Br', or I' are pptd. under the conditions most favourable to co-pptn. Co-pptn. is favoured by high temp. and excess of $Ca^{\cdot\cdot}$, and suppressed by excess of C_2O_4''. In the case of IO_3', which has been investigated in most detail, the amount co-pptd. is an exponential function of $[IO_3']$. D. R. D.

Interrelation of electrokinetic behaviour and cation exchange of iron phosphate. J. B. Hester (J. Amer. Chem. Soc., 1933, **55**, 1442—1445).—The cation exchange capacity of Fe phosphate pptd. at p_H 3—9 is a min. for p_H 4·4. Thus high base exchange accompanies high electrokinetic potential of the colloid. J. G. A. G.

Theory of formation of surface films on metals. C. Wagner (Z. physikal. Chem., 1933, **B**, **21**, 25—41).—The rate of formation of surface films on metals by reaction with O_2, S, or halogens is in many instances determined by the rate of diffusion in the film. Assuming that diffusion occurs almost exclusively by migration of ions and electrons, the rate of formation of the film may be calc. from affinity, conductivity, and transport nos. of ions and electrons. The results for the systems Ag–S and Cu–O agree with experiment. In the system Ag–halogen the mechanism is possibly similar. R. C.

Structure of unimolecular films. I. Surface potentials of films of long-chain compounds. R. J. Fosbinder and A. E. Lessig (J. Franklin Inst., 1933, **215**, 425—433).—The method of Schulman and Rideal (A., 1931, 299) was modified, and their results with myristic and palmitic acids were confirmed. A liquid condensed film of stearolactone has a limiting mol. area of 31 sq. Å., agreeing with the val. calc. for the lactone ring. H. J. E.

Structure of surface films. XVII. γ-Hydroxystearic acid and its lactone. N. K. Adam (Proc. Roy. Soc., 1933, **A**, **140**, 223—226).—γ-Hydroxystearolactone forms a condensed film of area about 29 sq. Å. at zero compression on H_2O, dil. acid,

and dil. alkali. On *N*-NaOH the lactone films undergo rapid expansion, due to hydrolysis to the acid. The acid forms a liquid expanded film at and above room temp. on slightly acid solutions, and a condensed film near 0°. The OH group has a tendency to approach the CO_2H group and the underlying H_2O. L. L. B.

Behaviour of surface films of unsaturated compounds. A. H. HUGHES (J.C.S., 1933, 338—344).—Unimol. films of long-chain aliphatic compounds on aq. solutions have been examined by surface pressure and surface potential methods. In the series oleic, petroselic, and Δ^a-*iso*oleic acids, the dipole system of the double linking has a marked adhesion for the H_2O surface as compared with a saturated hydrocarbon chain. Proximity to a CO_2H group greatly increases the dipole moment of a double linking. A double linking in a five-membered ring, as in chaulmoogric acid, also has a dipole moment > that of a double linking in a straight chain. A triple linking has a dipole moment > that of a double linking, thus causing greater adhesion to the H_2O surface. The behaviour of a conjugated double-linking system has been studied in α- and β-elæostearic acid and their additive compounds with maleic anhydride. Both acids undergo autoxidation in the unimol. film, but this is completely inhibited by the presence of 0·12% of quinol in the underlying solution. M. S. B.

Molecular phenomena at an oil–water surface: application to testing [lubricating oils]. J. J. TRILLAT and L. LEPRINCE-RINGUET (Compt. rend., 1933, **196**, 1214—1216).—The change of the interfacial tension produced by the addition of a foreign substance depends on the electric moment of the latter. In the case of a paraffin–H_2O surface *cyclo*hexanol produces a marked decrease in interfacial tension, whereas *cyclo*hexane has no effect; this is due to orientation of the mols. of the former. Measurements of interfacial tension indicate changes in lubricating oils due to heat, ultra-violet light, use, etc.; a decrease implies acid formation. C. A. S.

Interfacial phenomena in the formation of crystals with continuous or discontinuous distribution of microscopic components. L. IMRE (Z. Elektrochem., 1932, **38**, 535—543).—The analogy between crystal growth and adsorption of ions on heteropolar crystal surfaces is discussed at length. The relative ease of adsorption of two kinds of ion is not const. over the whole cryst. surface; a const. difference of adsorption potential occurs only when the ions are similar, and in these cases the difference is independent of temp. H. F. G.

Wetting velocity and flotation. H. FREUNDLICH, O. ENSLIN, and G. LINDAU (Kolloid-Beih., 1933, **37**, 281—286).—PbS and FeS_2 are wetted very rapidly and ZnS and Cu_2S,Fe_2S_3 slowly by H_2O. After treatment with oleic acid all are wetted slowly, whilst SiO_2 is wetted rapidly. Rapid wetting by aq. NaOH or KCN occurs at a definite concn., which varies with the particular sulphide, thus offering a means of separation. E. S. H.

Diffusion of monatomic gases through fused silica. T. ALTY (Phil. Mag., 1933, [vii], **15**, 1035—1048).—The assumption that atoms of inert gases diffuse along narrow cracks of mol. dimensions in the SiO_2 agrees with experimental data. Atoms enter the cracks directly from the gas phase, and not from an adsorbed surface layer. H. J. E.

Copper membrane gas-molecule sieve. Callendar's theory of osmosis. D. L. WARRICK and E. MACK, jun. (J. Amer. Chem. Soc., 1933, **55**, 1324—1332).—The porosity of a Cu membrane made by vac. distillation of the Zn from thin sheet brass at 400—900° increases with rise of temp. and duration of heating. Membranes prepared at low temp. have about 10^{12} pores (diam. 6—20 Å.) per sq. cm., and the transpiration of gases through the membrane is a mol. process rather than one of viscous flow. The separation of C_6H_6 or Et_2O from gases of smaller mol. diam. is only partly possible owing to clogging of the pores. Callendar's theory of osmosis is supported by approx. agreement between calc. and observed rates of osmotic flow through a Cu membrane separating H_2O and aq. sugar solutions. J. G. A. G.

Absorption and osmosis. I. F. A. H. SCHREINEMAKERS and C. L. DE VRIES (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 180—189).—A membrane absorbs substances to which it is permeable and changes its character in the process. These changes have been studied for pig's bladder in aq. Na_2CO_3, aq. $(CH_2{\cdot}CO_2H)_2$, and aq. tartaric acid (I), and for cellophane in aq. (I). M. S. B.

Permeability of protein–cellulose membranes. G. FLORENCE and J. LOISELEUR (Bull. Soc. Chim. biol., 1933, **15**, 395—401).—Clear membranes can be obtained only when the protein–cellulose solutions are allowed to dry completely at room temp., and these become permeable only on imbibition of solutions such as dil. aq. HCO_2H or EtOH. The permeability increases with the % protein, and is greatest for casein (cf. A., 1931, 167). H. D.

Cryoscopic effects in mixtures of solvents and their relation to solubility of solute. O. ANDERS (Z. physikal. Chem., 1933, **164**, 145—175).—The solubilities of I, S, and Na_2CrO_4 in C_6H_6, AcOH, and mixtures of these at 0°, 20°, and 30° and of $AgClO_4$ in AcOH and C_6H_6 at 20° have been measured. The f.-p. depression of the eutectic and other mixtures of C_6H_6 and AcOH by the above solutes and by CrO_3 and the composition of all the phases in equilibrium at the f.p. of these solutions have been determined. Addition of a small amount of a solute to the C_6H_6–AcOH mixture having the eutectic composition causes enrichment of the solid phase separating on freezing in the component in which the solute has the smaller solubility. The f.-p. depression data exhibit abnormalities which are due partly to salting-out effects and partly to polymerisation. Na_2CrO_4 is largely dissociated, whilst $AgClO_4$ is associated and somewhat miscible with C_6H_6 in the solid state. R. C.

Solvent action. VI. Optical rotatory powers of β-octanol, *d*-amyl alcohol, and their derivatives. H. G. RULE, (MISS) E. B. SMITH, and J. HARROWER (J.C.S., 1933, 376—387).—The rotatory powers in solution of the 15 *sec.*-β-octyl and *d*-amyl

compounds examined are closely related to the dipole moment of the solvent, provided that mono-substituted derivatives of the same hydrocarbon are employed for comparison. For 11 compounds the rotatory powers tend to vary inversely as the polarity of the solvent, but for the more highly polar substances the reverse relation tends to hold. The explanation is discussed in terms of the theory of dipoles. The graph for the rotatory power of β-octanol on progressive dilution with C_6H_{14} is irregular, probably owing to variations in the degree and mode of association of the alcohol mols. in solution. Other alcohols display similar changes in polarisation. Other octyl derivatives, however, yield smooth curves without max. and min., which behaviour is also normal. M. S. B.

Solubilities, conductivities, and b.-p. elevations of solutions of organic and inorganic compounds in liquid hydrogen fluoride. K. FREDENHAGEN [with G. CADENBACH and W. KLATT] (Z. physikal. Chem., 1933, **164**, 176—200).—In its ability to dissolve org. and inorg. compounds and form highly conducting solutions, HF surpasses all other solvents, even H_2O. HF and H_2O are as solvents almost entirely dissimilar, in spite of the small difference in their dielectric consts. HCl, HBr, and HI are not measurably sol. in HF and do not affect its conductivity. The only anion which can exist in HF solution is F′, and the ion pptn. reactions which occur in aq. solution are not observed. Whilst fluorides ionise in the same way as in H_2O, other electrolytes ionise according to such schemes as $AcOH+HF=AcOH,H^{\cdot}+F'$, and $KNO_3+2HF=K^{\cdot}+HNO_3,H^{\cdot}+2F'$, as is shown by b.-p. elevation and conductivity data. HF dissolves numerous neutral org. compounds, including carbohydrates, ethers, and ketones, yielding solutions often with conductivities > those of the most highly conducting aq. solutions. Here the ions are formed by dissociation of solvates, *e.g.*, $MeOH+HF=MeOH,H^{\cdot}+F'$. It is suggested that in a solution in a binary solvent an atom or group of a solute can form an ion only if its affinities for the cationic and anionic constituents of the solvent are unequal. R. C.

Determination of molecular b.-p. elevations in hydrogen fluoride. K. FREDENHAGEN and G. CADENBACH (Z. physikal. Chem., 1933, **164**, 201—208).—The mol. b.-p. elevation is 1·90°. R. C.

Diffusion of electrolytes. B. W. CLACK (Phil. Mag., 1933, [vii], **15**, 1061—1062; cf. Davies, this vol., 347).—A correction. H. J. E.

Cryoscopic determination of hydration of ions of potassium chloride. G. BOURION and E. ROUYER (Compt. rend., 1933, **196**, 1111—1113; cf. this vol., 460).—On the assumption previously made, the hydration for *M*-KCl is represented by $KCl,8{\cdot}62H_2O$, and for 0·5*M*-KCl by $KCl.10{\cdot}2H_2O$ (cf. A., 1908, ii, 1009; 1928, 954). C. A. S.

Lowering of eutectic points: a ternary eutectic. H. MULLER (Compt. rend., 1933, **196**, 1109—1111; cf. A., 1932, 913).—The mol. lowering for the eutectic (100 H_2O, 10·3 KNO_3, 4·7 K_2SO_4; −3·02°) is 16·5. C. A. S.

Partial molal volumes of cobalt sulphate and of cadmium iodide [at 25°]. R. C. CANTELO and H. E. PHIFER (J. Amer. Chem. Soc., 1933, **55**, 1333—1338).—The data refer to 0·005—2·29*M* aq. solutions. For $CoSO_4$, $V=14{\cdot}06c^{\frac{1}{2}}-3{\cdot}514$, for KCl, $V=3{\cdot}652c^{\frac{1}{2}}+26{\cdot}23$, and for CdI_2, $V=67{\cdot}16$, where V is the partial molal vol. and c is mol. concn. The results are discussed in relation to the theory of complete ionisation. J. G. A. G.

Colorimetry of titanium. III. H. GINSBERG (Z. anorg. Chem., 1933, **211**, 401—411; cf. this vol., 43).—Coloured solutions obtained by adding H_2O_2 to Ti solutions containing H_3PO_4, H_2SO_4, $KHSO_4$, and $Al_2(SO_4)_3$ obey the Lambert–Beer law at concns. 4—0·2 mg. of Ti per 100 c.c. The determination of Ti with the abs. colorimeter (A., 1932, 1225) is described. H. J. E.

Alkali tartrates and chromium. J. P. MATHIEU (Compt. rend., 1933, **196**, 1222—1224; cf. this vol., 26).—Measurements of optical activity, α, circular dichroism, δ, and absorption for solutions containing varying proportions of Cr^{III}, NaOH, and Na tartrate indicate the existence, besides the chromitartrate, of one or more intermediate compounds, and also of a compound, for which α is negative for blue, and positive for red light, and for which δ is positive. C. A. S.

Birefringence of cerium salts in aqueous and non-aqueous solution. C. HAENNY (Compt. rend., 1933, **196**, 1297—1298; cf. A., 1932, 677, 909).—Magnetic birefringence–concn. curves of aq. solutions of $Ce(NO_3)_3$, $Ce_2(SO_4)_3$, and $CeCl_3$ are convex to the axis of concn. The birefringence of the nitrate is much the strongest; it is diminished by excess HNO_3, and the magnitude of this effect increases more rapidly than the HNO_3 concn. EtOH solutions of $Ce(NO_3)_3$ and $CeCl_3$ are also strongly birefringent; Ce^{IV} salts are only slightly so. These facts indicate a connexion between birefringence and magnetic moment. C. A. S.

Subsidence of starch milk. SPROCKHOFF and HONSCH (Z. Spiritusind., 1933, **56**, 59).—Potato starch suspensions of *d* 1·07—1·15 were allowed to subside in a vertical glass tube 1 m. long and of 45 mm. bore; deposition was regarded as complete as soon as the upper surface of the deposit offered a firm resistance to a glass rod with flattened end. For suspensions of equal concn. the time required for deposition is proportional to the height of the liquid, and for a given height the time required is proportional to the original concn. In practice moderately tall vats and low concn. are recommended as most favourable to the separation of fibrous matters from the starch. J. H. L.

Application of Wiener's general mixture formula to colloid-disperse systems. H. FREUNDLICH and F. ROGOWSKI (Kolloid-Beih., 1933, **37**, 215—222).—The variation of n with concn. in sols of Al_2O_3, SiO_2, TiO_2, ThO_2, mercurisulphosalicylic acid, gelatin, ovalbumin, and cellulose acetate and nitrate is not consistent with Wiener's theory. E. S. H.

Influence of saline impurities on osmotic pressure of colloidal solutions. A. BOUTARIC (J. Chim. phys., 1933, **30**, 181—185).—Expressions

for the osmotic pressure of a colloidal electrolyte against its ultra-filtrate are derived for cases where the non-diffusible ion is n-valent, and where the salt impurity is uni-uni- and uni-bi-valent. F. L. U.

Dependence of the ultra-filtrate from a sol of "ferric hydroxide" on rate of ultra-filtration; Donnan equilibrium and p_H of sols. J. W. McBain and W. L. McClatchie (J. Amer. Chem. Soc., 1933, **55**, 1315—1323; cf. A., 1932, 994).—The concn. of the filtrate from fairly conc., well-dialysed $Fe(OH)_3$ sol decreases many-fold with increasing rate of ultra-filtration through cellophane membranes at pressures between 1 and 100 atm. That the p_H of a rapidly obtained ultra-filtrate is < that of a sol of a positive colloid (with very slow ultra-filtration, the p_H is much greater) supports the view that in the slow process the ultra-filtrate approaches the Donnan membrane distribution due to the presence of charged colloids, whereas in the rapid process the regions immediately surrounding the particles are sampled. The importance of these results in relation to previous work is emphasised. J. G. A. G.

Reversal of lyotropic series in flocculation experiments. A. Voet and F. Balkema (Rec. trav. chim., 1933, **52**, 371—377).—The coagulating power of univalent anions for Au sols which have had their charge reversed by $Al^{\cdots}$ or $Th^{\cdots\cdot}$ is in the order $CNS' > I' > NO_3' > ClO_3' > Br' > Cl'$, showing an inversion of the usual order. Peculiarities in the coagulation of hydrated and non-hydrated sols are explained by the reduction of the dielectric const. of H_2O by accumulation of ions in the double layer. F. L. U.

Coagulation of colloidal sulphur solutions by gelatin. G. Rossi and G. Scandellari (Annali Chim. Appl., 1933, **23**, 67—71).—Coagulation of highly-dialysed colloidal sulphur solutions by gelatin yields large flocks, which are formed only within very narrow limits of gelatin concn. and redissolve with excess. The coagulation thus differs essentially from that caused by KCl. T. H. P.

Depolarisation of light on passing through colloidal solutions. V. Petrescu (Ann. Sci. Univ. Jassy, 1933, **17**, 15—69).—Of 14 colloids examined none shows any light depolarisation in the sol state, either fresh or after ageing. The corresponding gels, however, exhibit the property to a degree which depends on the age of the sols from which they are formed. For suspensions of V_2O_5 and $CaCO_3$ the angle of depolarisation varies as the square of the radius of the particles. A modified form of Pokrovski's formula agrees well with experiment. J. W. S.

Stability of lithium urate sols. S. Prakash (J. Indian Chem. Soc., 1933, **10**, 35—39).—The ageing of sols has been followed by measurement of electrical conductivity. The sol is hydrophobic and gels formed from it have little stability. A. S. C. L.

Influence of non-electrolytes on the coagulation of $Ce(OH)_4$ sol dialysed to different extent. M. Prasad and M. V. Nabar (J. Indian Chem. Soc., 1933, **10**, 53—56).—Alcohols sensitise the sol to coagulation, their efficiency increasing with chain-length. Sugars protect, sucrose being more efficient than glucose. These effects become more marked when the stabilising ions are removed. A. S. C. L.

Double layer of silver iodide sol. E. K. W. Verwey (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 225—233).—The adsorption of $AgNO_3$ and KI by undialysed AgI sols has been determined potentiometrically and colorimetrically. The ageing of dialysed and undialysed sols has been studied quantitatively by changes in adsorptive power. It may take place rapidly without increase in size of particles or slowly with increase. Adsorption of the peptising ion appears to take place at edges or irregularities on the surface of the submicroscopic crystals. These active points decrease in no. as the crystals gradually assume a more regular and perfect form. M. S. B.

Variation of the electrical charge of colloidal particles. V. Effect of the manner of preparation of As_2S_3 sol on cataphoresis in presence of electrolytes. J. Mukherjee, S. Roychoudhury, and S. G. Rajkumar (J. Indian Chem. Soc., 1933, **10**, 27—32).—The influence of various electrolytes on cataphoretic velocity has been studied; the mechanism of their action is discussed. A. S. C. L.

Electrokinetic phenomena. XI. Action of univalent electrolytes on electric mobility of proteins. H. A. Abramson (J. Gen. Physiol., 1933, **16**, 593—603).—The velocities (I) of natural and heat-denatured ovalbumin and of gelatin in various concns. of acetate buffer were determined. The decrease in (I) due to increased concn. suggests a simple relation between (I) and the effective reciprocal thickness of the electric double layer. Such a relation may be derived theoretically from the assumption that the electric charge of proteins is primarily determined by the $[H^+]$ of the medium (cf. A., 1932, 695). F. O. H.

Colloid chemical studies on rosin sizing. I, II. K. Kanamaru and T. Tsuchida (J. Soc. Chem. Ind. Japan, 1933, **36**, 102—110B).—The influence of KCl, NaCl, $MgCl_2$, K_2SO_4, HCl, H_2SO_4, NaOH, $AlCl_3$, $Al_2(SO_4)_3$, and $Th(NO_3)_4$ on the ζ potential and turbidity of sols of abietic acid and its Na salt is in accordance with the valency rule. $AlCl_3$ and $Th(NO_3)_4$ cause a reversal in the sign of charge of the particles, and a sharp min. is observed in the turbidity–concn. curve where the ζ potential–concn. curve intercepts the concn. axis. Changes in the concn. of electrolyte affect the potential and the turbidity in the same manner. $Al_2(SO_4)_3$ does not reverse the sign of charge. E. S. H.

Influence of lyotropic substances on the mutarotation and gelatinisation of gelatin–water mixtures. II. Substances with two hydrophilic groups. J. R. Katz and J. F. Wienhoven (Rec. trav. chim., 1933, **52**, 385—388; cf. this vol., 226).—Comparison of substances containing two hydrophilic groups with those containing only one shows parallelism between the influence on surface tension and that on the mutarotation and gelatinisation of 3% gelatin. Substances with several SO_3H groups, and o-$C_6H_4(OH)\cdot CO_2H$ form an exception to this rule. F. L. U.

Transformations of gelatin. I. Scattering of light. II. Ultra-filtration. J. DUCLAUX and F. HIRATA (J. Chim. phys., 1933, **30**, 213—231).—Scattering of light by gelatin sols and gels has been measured at concns. 0—2·1%, temp. 5—40°, and p_H 3·5—9. Gelatin exists in two forms, one of which (<2%) scatters white light strongly with max. at p_H 5, whilst the other scatters blue light feebly, the scattering increasing continuously with the p_H. Gelatinisation does not involve an increase in the vol. of the particles, but is due to formation of a network. The fraction of gelatin which can pass an ultra-filter increases continuously with rise in temp. between 0° and 70°. F. L. U.

Influence of small quantities of electrolytes on the course of gelatinisation of potato starch by heat. E. WIEGEL (Z. Spiritusind., 1933, **56**, 62—63).—The changes in viscosity of 1% suspensions of air-dried potato starch in H_2O or electrolyte solutions, in the course of heating from 20° to 95° and maintaining at 95° for several hr., were measured by Wo. Ostwald's method ("Kleine Praktikum der Kolloidchem.," 7th Ed., 1930, 41) and are represented by graphs. In most cases a pronounced max. was obtained ½—1 hr. after 95° had been attained. The max. val. is greatly influenced by the rate of heating to 95°. For a standard rate of heating the max. val. is lowered considerably by small quantities of electrolytes. J. H. L.

Rhythmic precipitates. II. Influence of light and ageing. T. ISEMURA (Bull. Chem. Soc. Japan, 1933, **8**, 108—112).—The rhythmic bands formed by the action of $AgNO_3$ solution on a gelatin jelly containing $K_2Cr_2O_7$ do not become irregular when the system is exposed to light, even direct sunlight, but they become closer and their number increases. Previous reports to the contrary are ascribed to irregular irradiation. Ultra-violet radiation retards band formation and causes the bands to become finer and closer together; this effect does not occur with $CuCrO_4$ bands in SiO_2 gel. The Ag_2CrO_4 bands produced in an aged gelatin gel and in a gel of the same age, but warmed and allowed to re-set before the $AgNO_3$ is added, are identical; the influence of ageing is thus related to a reaction between the $K_2Cr_2O_7$ and the gelatin and not to the gel structure. The effect of ageing is less pronounced with $CuCrO_4$ bands in SiO_2 gel. H. F. G.

Distribution of cations and anions in swelling gelatin. W. VON MORACZEWSKI (Biochem. Z., 1933, **259**, 387—397).—In Ca salt solutions at p_H below the isoelectric point the gelatin is richer in anions (Cl', I', CNS') and poorer in cations than the outer fluid; at p_H above the isoelectric point the gelatin is richer in cations but has the same anion content as the outer fluid. For K and NH_4 salts the results are much less definite. P. W. C.

Swelling of gels in presence of denaturing agents. N. JERMOLENKO and A. LOBANOVITSCH (Biochem. Z., 1933, **259**, 374—380).—Denaturing substances (CH_2O, PhOH, EtOH, MeOH) decrease the swelling. The effects of these substances and those of hydrating substances (KCNS, KI, carbamide) in mixtures are additive. The characteristic p_H–swelling curve is still given in presence of denaturing substances. The latter retard the liquefaction of gelatin by certain salts (KCNS, KI) at room temp. P. W. C.

Denaturation of proteins. X. Acid and alkali titration curves of crystalline ovalbumin. XI. Effect of denaturation on capillary activity of solutions of certain proteins. W. J. LOUGHLIN (Biochem. J., 1933, **27**, 99—105, 106—111).—X. Titration curves for undenatured cryst. ovalbumin (I) with the glass electrode (A., 1930, 1151) agree with those given by the H_2 (A., 1932, 996) or quinhydrone electrodes (A., 1932, 181). The curves for (I) are identical with those for the denatured protein for p_H 2·5—6; the agreement on the alkaline side is not so satisfactory (cf. A., 1930, 628; 1931, 316). The method of coagulating the protein may influence the titration on the alkaline side.

XI. The dynamic surface tension (s) of solutions of natural and of denatured but unflocculated (I) and oxyhæmoglobin (II) has been determined. With natural (I), s has a min. val. at the isoelectric point (cf. A., 1928, 121). Both natural proteins lower the s of H_2O, but the p_H–s curves for (II) are more regular than those for (I). In both cases denaturation lowers s to an extent which depends on p_H. The increased capillary activity on denaturation is due to the increased size of the micelles. F. O. H.

Effect of ultrasonic waves on gels, especially thixotropic jellies. H. FREUNDLICH, F. ROGOWSKI, and K. SÖLLNER (Kolloid-Beih., 1933, **37**, 223—241).—Apparatus for producing intense ultrasonic waves is described. The waves have the effect of liquefying those gels that can be liquefied normally by shaking, but no permanent change is brought about, as the subsequent solidification time is not altered. Liquefaction occurs first at the air boundary. Non-thixotropic gels do not exhibit the phenomenon. The swelling and peptisation of caoutchouc in various org. media and of gelatin in H_2O are accelerated by ultrasonic waves, apparently by reason of local heating at the gel–liquid boundary. SiO_2 gels do not liquefy under the influence of ultrasonic waves, but lose their elasticity and become slightly turbid after long exposure; the original elasticity is regained on keeping the gel. E. S. H.

Study of syneresis. G. ROSSI and A. MARESCOTTI (Gazzetta, 1933, **63**, 121—127).—The concn. of salt in the liquid obtained by the syneresis of agar-agar dissolved in aq. gelatin solutions containing Na and K halides is in general > (but for some KI solutions <) the concn. in the original gelatin solution. This sp. influence of the salt ions on syneresis is probably of importance in certain biological processes. O. J. W.

Complex coacervation. XVII. Specific effects in the mixed coacervation type 4—1 of gum-arabic sol. H. G. B. DE JONG, J. H. VAN DER HORST, and A. LAFLEUR (Biochem. Z., 1933, **260**, 161—169).—The auto-complex coacervation of gum-arabic sol has been examined in respect to (*a*) the effects of cations and anions of neutral salts of the types 2—1 and 1—1, and (*b*) the effects of various alcohols as desolvation agents. H. W. D.

Complex coacervation. XV. Coacervation and precipitation of types 4 and 4—1 by sodium arabate sol. H. G. B. DE JONG and K. C. WINKLER. **XVI. Mechanism of the union of oppositely-charged ions.** H. G. B. DE JONG (Biochem. Z., 1933, **259**, 436—441, 442—452).—XV. Previous experiments (A., 1931, 908; 1932, 693) with gum-arabic sol are repeated using Na arabate sol, with similar results, quant. differences being chiefly due to the substitution of $Ca^{\cdot\cdot}$ by $Na^{\cdot}$.

XVI. Further experiments with Na nucleate sol are discussed in relation to the attachment of oppositely-charged ions at the inner surface of the double layer. P. W. C.

Change of state of viscous systems. VII. Extension of theory to solid substances. H. UMSTATTER (Kolloid-Beih., 1933, **37**, 287—292; cf. *ibid.*, 1932, **34**, 1).—Theoretical. E. S. H.

Chemical equilibrium in vapour of a mixture of hydrocarbons. H. A. WILSON (Proc. Roy. Soc., 1933, **A, 140**, 1—8).—The author's theory (A., 1927, 1139; B., 1929, 503) is applied to mixtures containing naphthenes and *cyclo*paraffins as well as paraffins and unsaturated hydrocarbons. With liquid and vapour both present, the naphthene fraction increases with rise of temp., but falls with the pressure; when vapour only is present, it falls with the temp. but rises with the pressure. The variation of the C_6H_6 fraction with temp. and pressure is also considered. L. L. B.

Role of the solvent in electrolytic dissociation. A. R. MARTIN (Nature, 1933, **131**, 584—585).—A criticism (cf. this vol., 354). L. S. T.

Equilibrium law of electrolytes. K. JABŁCZYNSKI and J. WOJCIECHOWSKA (Rocz. Chem., 1933, **13**, 167—175).—The expression $n^{4/3}/n_0=K$ (where n_0 is the concn. of undissociated salt, and n that of one of its ions) is verified cryoscopically for various concns. of H, Li, Na, K, NH_4, and Ag nitrate, H, Na, NH_4, and K perchlorate, $KBrO_3$, $NaBrO_3$, KIO_3, and HIO_3. A const. val. is obtained for K on the assumption that certain ions are hydrated ($H^{\cdot}$ 9, $Li^{\cdot}$ 11, $Na^{\cdot}$ 3, $K^{\cdot}$, $NH_4^{\cdot}$, $Ag^{\cdot}$, NO_3', BrO_3', and IO_3' 0, and ClO_4' 4 mols. H_2O), and that Na, K, NH_4, and Ag nitrates are associated. Since $LiNO_3$ and HNO_3 do not exhibit association, the same must apply to NO_3' ions, whence it follows that complexes of the type $[M(NO_3)_2]'$ must be formed. The vals. of K for acids diminish in the order $HI>HBr>HCl>HNO_3>HClO_4>HIO_3$, and a similar series is obtained for K salts of certain of these acids. R. T.

Dissociation constants of acids. G. N. BURKHARDT (Chem. and Ind., 1933, 330).—A reply to Wynne-Jones (cf. this vol., 464). E. S. H.

Ionisation of sulphuric acid. H. M. DAWSON (Proc. Leeds Phil. Soc., 1933, **2**, 359—364).—The hydrolysis of EtOAc in solutions of H_2SO_4 is due to the joint catalytic effects of the $H^{\cdot}$ and HSO_4' ions. Since the first-stage ionisation is practically complete, it is possible to derive the $[H^{\cdot}]$ for dil. solutions of H_2SO_4 from the measured reaction velocities and the catalytic coeffs. for the two reactive ions. The second-stage ionisation const. $K_2=0{\cdot}010$; this val. affords a satisfactory account of the reaction velocity data for a wide range of H_2SO_4 solutions. N. M. B.

Extent of dissociation of zinc sulphate. I. A. COWPERTHWAITE (Trans. Faraday Soc., 1933, **29**, 593—596).—The conclusion reached from e.m.f. data (A., 1932, 126), that $ZnSO_4$ is completely ionised up to $0{\cdot}01M$, is supported by the Debye–Hückel theory as extended by La Mer and his colleagues. M. S. B.

One-third basic aluminium acetate solution. I. C. ROHMANN (Arch. Pharm., 1933, **271**, 219—247).—The degree of hydrolysis of Al diacetate (I) increases from 14·4 for $1{\cdot}15N$ to 32% for $0{\cdot}060N$ solution. The p_H is only slightly affected by the temp. of prep. or by dilution. The solution is shown by electrometric titrations to have excellent buffer capacity with max. at p_H 3·6, 4·7, and 10·5. Conductivity measurements indicate that (I) behaves as a salt of a univalent cation and univalent anion. F.-p. measurements support the view that (I) is associated in solution. The sediment formed during various methods of prep. always gives the same X-ray diagram and appears to consist of (I) with a slight excess of OAc. R. S. C.

Phase changes in the ordinary and extended sense classified according to the corresponding singularities of the thermodynamic potential. P. EHRENFEST (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 153—157).—Discontinuities in curves of both first and second order, due to phase change, are discussed. M. S. B.

Alkaline-earth hydrides. P. REMY-GENNETÉ (Ann. Chim., 1933, [x], **19**, 263—352).—A crit. review of data relating to the dissociation of CaH_2 and experimental details of results previously published (Bull. Soc. chim., 1929, [iv], **45**, 699; Compt. rend., 1929, **189**, 579). The chief difficulty in the determination of the dissociation pressure of CaH_2 is the volatility of Ca. This has been overcome by enclosing the heated CaH_2 in an Fe tube with a thin wall which, when hot, is permeable to H_2, but not to Ca vapour. The H_2 pressure has thus been determined for the temp. range 815—965°. The results are satisfactorily represented by the equation $\log p=0{\cdot}0091799T-8{\cdot}503$. There is no indication of the existence of a subhydride CaH. These results are in good agreement with those of Hurd and Walker (A., 1931, 800). The heat of formation calc. from Nernst's theorem is approx. 41,000 g.-cal. M. S. B.

Transition points of salt hydrates in various non-aqueous solvents. W. W. LUCASSE and H. J. ABRAHAMS (J. Physical Chem., 1933, **37**, 511—519).—The method previously described (A., 1926, 799) has been extended by using different solvents (MeOH, EtOH, $Pr^{\alpha}OH$, *iso*-$C_5H_{11}{\cdot}OH$, C_5H_5N, $COMe_2$, and glycol). The transition temp. is in general independent of the solvent and identical with that obtained by other methods. Mean vals. are: $LiNO_3,3H_2O \longrightarrow 2LiNO_3,H_2O$, 29·5°; $CaCl_2,6H_2O \longrightarrow \beta$-$CaCl_2,4H_2O$, 28·7°; $CdBr_2,4H_2O \longrightarrow CdBr_2,H_2O$, 35·5°; $Zn(NO_3)_2,6H_2O \longrightarrow Zn(NO_3)_2,3H_2O$, 35·3°; $ZnBr_2,2H_2O \longrightarrow ZnBr_2$, 35·3°; $CoCl_2,6H_2O \longrightarrow CoCl_2,H_2O$ (?), 31·3° in C_5H_5N or MeOH and 29·7° in glycol. D. R. D.

Change in the transformation temperature of copper sulphate at 56° with the solvent medium. H. J. Abrahams and W. W. Lucasse (J. Physical Chem., 1933, **37**, 521—524).—The transition point of $CuSO_4$ at about 56° (probably α-$CuSO_4,5H_2O \longrightarrow \beta$-$CuSO_4,5H_2O$) has been determined by the authors' method (cf. preceding abstract), using glycerol–EtOH mixtures as solvent. The transition temp. falls from 53·1° with 10% glycerol to 49·6° with 80%. D. R. D.

Chemical systems of Lenard phosphors. I. R. Schenck and H. Pardun. **II.** R. Schenck (Z. anorg. Chem., 1933, **211**, 209—221, 303—320).—I. The systems MS–Bi_2S_3 (M=Ca, Sr, Ba) have been studied with reference to the chemical changes occurring during absorption and emission of light by phosphors. From the determination of equilibria in the reaction $Bi_2S_3+3H_2 \rightleftharpoons 2Bi+3H_2S$ at 507° in presence of varying amounts of MS it appears that BaS and SrS, but not CaS, combine with Bi_2S_3 thus: $S''+Bi_2S_3 \longrightarrow (Bi_2S_4)''$. Heats of formation of the thiobismuthites from the respective sulphides are calc. by two independent methods, that of $CaBi_2S_4$ being assumed = 0.

II. The phosphor system is regarded as analogous to a storage battery, electrons being transferred from cation to anion during absorption of light energy, which is emitted during the reverse change. This view receives support in the agreement of the differences between the heats of formation of Ca, Sr, and Ba thiobismuthites with those between the energies of electron transference in the corresponding phosphors calc. from the wave-length of their α-emission bands. The reaction which gives rise to the bands is therefore $M^{\cdot}+(Bi_2S_4)' \longrightarrow M^{\cdot\cdot}+(Bi_2S_4)''$. F. L. U.

Phloridzin crystals. P. Gaubert (Compt. rend., 1933, **196**, 554—556).—Addition of a dye (0·1—0·5%) to hydrated phloridzin, $C_{21}H_{24}O_{20},2H_2O$, leads to the formation of larger crystals, probably rhombic. The hydrated crystals, *d* 1·431, heated in vaseline at about 105° give off H_2O and without melting pass into the anhyd. substance, *d* 1·452, m.p. about 150°. The behaviour on heating the crystals in air is described in detail (cf. A., 1932, 101). C. A. S.

Foreign matter in solid solution and stability of crystals. P. Gaubert (Compt. rend., 1933, **196**, 942—944; cf. this vol., 451, and preceding abstract).—The influence of the presence of $\gtrsim 1\%$ of various dyes on the dehydration, cleavage, and refractivity of crystals of hydrated phloridzin is described. It is suggested that the presence of minute quantities of foreign substances may explain the varying behaviour of many minerals, *e.g.*, laumontite, of different origins. C. A. S.

System $(NH_4)_2SO_4$–H_2SO_4–H_2O. P. Locuty and P. Laffitte (Compt. rend., 1933, **196**, 1311—1314; cf. A., 1921, ii, 45).—The system has been examined at 30°, 50°, and 70°; the resultant curves are similar and indicate the compounds $(NH_4)_2SO_4,H_2SO_4$, $3(NH_4)_2SO_4,H_2SO_4$, and $4(NH_4)_2SO_4,H_2SO_4$. C. A. S.

System $HgBr_2$–KBr–EtOH. (Mlle.) M. Pernot (Compt. rend., 1933, **196**, 1314—1316; cf. A., 1931, 695).—With pure EtOH, $HgBr_2$,KBr,EtOH is formed as colourless crystals, in which EtOH is rapidly replaced by H_2O on exposure to the atm. With 95 vol.-% EtOH the crystals are $HgBr_2$,KBr,H_2O. C. A. S.

Ternary system palmitic, margaric, and stearic acids. R. L. Shriner, J. M. Fulton, and D. Burks, jun. (J. Amer. Chem. Soc., 1933, **55**, 1494—1499).—F.p. for the ternary system of palmitic, m.p. 62·2—62·4°, margaric, m.p. 59·9—60°, and stearic, m.p. 69·6—69·8°, acids are recorded. H. B.

Reciprocal system in absence of the solvent. A. P. Palkin (Acta Univ. Asiæ Mediæ, Chem., 1930, **6**, No. 4, 1—40).—I. $AgCl+KBr \rightleftharpoons AgBr+KCl$. The reaction $\longleftarrow$ shows a small heat effect, 0·3 kg.-cal., but the equilibrium tends to the AgBr side owing to the slight solubility or slight dissociation of the salt. The eutectoid line is characteristic. Its projection on a vertical plane is convex with a max. near AgBr. The binary systems AgBr–AgCl and KBr–KCl form an unbroken series of solid solutions, whilst AgBr–KBr and AgCl–KCl each have a eutectic.

II. $AgBr+KI \rightleftharpoons AgI+KBr$. The system is similar to the previous one. The reaction $\longrightarrow$ is accompanied by a positive heat effect of 8·8 kg.-cal. In the binary system AgI–KI an unstable *compound*, KI,4AgI, decomp. 267°, is formed. Both systems represent a link between the purely reciprocal and the irreversible types. M. S. B.

Gaseous thermal diffusion—the principal cause of discrepancies among equilibrium measurements on the systems Fe_3O_4–H_2–Fe–H_2O, Fe_3O_4–H_2–FeO–H_2O, and FeO–H_2–Fe–H_2O. P. H. Emmett and J. F. Shultz (J. Amer. Chem. Soc., 1933, **55**, 1376—1389; cf. A., 1932, 1090).—By means of a static method incorporating special precautions the following equilibrium ratios, P_{H_2O}/P_{H_2}, have been found: 0·334, 0·419, 0·501, 0·603, and 0·678 at 600°, 700°, 800°, 900°, and 1000° for the Fe–FeO system, 0·107, 0·214, and 0·283 at 400°, 500°, and 550° for the Fe–Fe_3O_4 system, and 2·35, 1·16, and 0·461 at 800°, 700°, and 600° for the FeO–Fe_3O_4 system. Thermal diffusion accounts for previous static vals. being as much as 40% too high (cf. A., 1931, 41), and the degree of thermal separation in H_2O–H_2 mixtures at 400—500° in a tube with a temp. gradient has been determined. It is calc. that thermal diffusion may lead to errors $\gtrsim 8\%$ in the CO_2/CO ratio for the system Fe–CO_2–FeO–CO. J. G. A. G.

Equilibrium in the system SnO_2–H_2–Sn–H_2O. Indirect calculation of the values of the water-gas equilibrium constants. P. H. Emmett and J. F. Shultz (J. Amer. Chem. Soc., 1933, **55**, 1390—1395).—By means of the technique previously described (preceding abstract), the statically determined equilibrium ratio, P_{H_2O}/P_{H_2}, for the reaction $0{\cdot}5SnO_2+H_2 \rightleftharpoons 0{\cdot}5Sn+H_2O$ is 1·66, 2·22, 2·84, and 3·53, at 650°, 700°, 750°, and 800°, respectively. That previous results (cf. A., 1928, 594) are about 25% too high is attributed to thermal diffusion. The new vals. combined with data for the Sn–C–O system give consts. for the water-gas equilibrium in accord with direct determinations. J. G. A. G.

Field of saturation of potassium and sodium chlorides in quinary sea-salt systems. II. D. LANGAUER (Rocz. Chem., 1933, **13**, 201—212).—The solubility of KCl and NaCl in solutions of a const. concn. of $MgCl_2$ and a variable concn. of $MgSO_4$, and *vice versa*, has been determined at 83°, 90°, and 100°. R. T.

Value of the determination of free energy change for organic compounds. D. B. KEYES (Science, 1933, **77**, 202—204). L. S. T.

Heat of formation of silicon tetrafluoride, carbon tetrafluoride, and silicon carbide. H. VON WARTENBERG and R. SCHÜTTE (Z. anorg. Chem., 1933, **211**, 222—226).—The vals. obtained in kg.-cal. are: $Si(cryst.)+2F_2=SiF_4+360\pm3$; $C(graphite)+2F_2=CF_4+162\pm2$; and (by fluorination of SiC) $Si(cryst.)+C(graphite)=SiC+31\pm6$. F. L. U.

Moving boundary method for the determination of transport numbers. G. S. HARTLEY and J. L. MOILLIET (Proc. Roy. Soc., 1933, **A**, **140**, 141—158).—Theoretical. The fundamental relations between the transport no., mobility, and equiv. conductivity of a radical are worked out, and the equations for the displacement of concns. in conducting solutions are derived. If there is a moving boundary between two electrolyte solutions with a common ion, and if the leading non-common ion is faster than the following non-common ion, the two solutions become separated up to a limit determined by diffusion, the leading ion remains at const. concn., and the following (or indicator) solution automatically attains a const. concn. Experimental work on both rising and falling boundaries is discussed. The independence of the boundary velocity of the initial concn. of the indicator solution is limited by the effects of temp. and concn. correction. L. L. B.

Change of transport numbers in a membrane due to the concentration of electrolyte, and a theory of transport number in the pores of a membrane. S. ÔKA (J. Soc. Chem. Ind. Japan, 1933, 36, 93—98B).—Experiments with hardened filter paper, two kinds of collodion, collodion impregnated with hæmoglobin, parchment paper, cellophane, and parchment paper dyed with Congo-red show that the transport nos. depend on the concn. of the solution and that the relative effects of the membranes are small at high concn. and become more marked at lower concns. In explanation it is suggested that the capillary pores of a membrane contain (*a*) the membrane ion, (*b*) the ions in the outer double layer, (*c*) free anions, (*d*) free cations. E. S. H.

Ludwig–Soret effect and ionic mobilities in cuprous bromide–silver bromide mixed crystals. H. REINHOLD and R. SCHULZ (Z. physikal. Chem., 1933, **164**, 241—276).—The equilibrium diagram for the system CuBr–AgBr has been determined. The Ludwig–Soret effect changes in sign on passing through a concn. of 50 mol.-% and also on passing through 200°. Transport nos. have been measured at 170—290° with mixed crystals containing 30—90 mol.-% AgBr; their temp. coeffs. change in sign in the same temp. and concn. region as the Ludwig–Soret effect. In the region of stability of the high-temp. form of AgBr the sp. conductivity of mixed crystals containing 65, 80, and 90 mol.-% AgBr may be represented by $\kappa=\kappa_1+\kappa_2=A_1e^{-E_1/RT}+A_2e^{-E_2/RT}$, the consts. of which can be evaluated from transport data. $(E_1—E_2)$ has the same val. as the difference of the heats of transport. A relation between the Ludwig–Soret effect and relative ionic mobilities in mixed crystals, deduced from Wagner's theory (Ann. Physik, 1929, [v], **3**, 629), agrees with the above results. Diffusion coeffs. have been measured in mixed crystals containing 50, 65, and 80 mol.-% AgBr, and the results in conjunction with Einstein's equation give vals. for the ionic conductivities of the same order as the observed vals. R. C.

Electrical conductivities of solutions of water in sulphur dioxide. M. DE K. THOMPSON and F. C. JELEN (Trans. Electrochem. Soc., 1933, **63**, 91—105).—The sp. conductance of anhyd. SO_2, measured by a d.c. method immediately after distillation into a Pyrex cell with smooth Pt electrodes, decreases notably with successive distillations, but becomes nearly const. after 5—10 distillations. The vals. increase on keeping for periods up to ½ hr., and Ohm's law is not obeyed, the apparent sp. conductance decreasing with increase of applied voltage between 44 and 990 volts per cm. The lowest immediate val. obtained at −20° to 0° was approx. 10^{-9} mho per cm. Cooling from 20° to −60° causes a marked increase in conductivity. The sp. conductance of SO_2 containing up to 0·004% of H_2O does not differ appreciably from that of anhyd. SO_2 measured under the same conditions, but with higher concns. of H_2O the sp. conductance increases rapidly, reaching $0·77\times10^{-6}$ at 0·1% H_2O and $3·4\times10^{-6}$ at 1% H_2O at 0°, the latter concn. being near the saturation val. The temp. coeff. of conductivity changes sign between 0·064 and 0·15% H_2O. Sp. conductances $>10^{-6}$ mho per cm. were measured by the a.c. method. H. J. T. E.

Conductivity of Grignard reagents in ether solutions. W. V. EVANS and F. H. LEE (J. Amer. Chem. Soc., 1933, **55**, 1474—1477).—The order of conductivity at −10° to 20° is: MgEtBr (max.), $MgBu^nBr$, $CH_2Ph{\cdot}MgBr$, MgPhBr, $MgBr_2$ (min.); all have negative temp. coeffs. Except with 2*M*-MgPhBr, fall in temp. causes increase in the conductivity. The mol. conductivity of MgEtBr decreases with dilution. H. B.

Interpretation of electrolytic part of conduction in amalgams and other alloys. II. C. WAGNER (Z. physikal. Chem., 1933, **164**, 231—233; cf. A., 1932, 230).—Comments on Schwarz' paper (cf. following abstract). An approx. expression for transport no. in a solid alloy is deduced. R. C.

Theory of electrolysis phenomena in metallic solutions. K. SCHWARZ (Z. physikal. Chem., 1933, **164**, 223—230).—Skaupy's theory (A., 1907, ii, 327) that in a molten metallic solution the force opposing the action of the applied field on the ions is the friction of the electrons on the ions is irreconcilable with experimental data, but the assumption that the migration of the ions is determined only by the resultant of the electrostatic force and electrohydrostatic buoyancy leads to a relation between

transport no., density of charge, ρ, and mobility which agrees with available data, and indicates that that component of the solution having the greater ρ will migrate to the cathode. Hg is apparently completely dissociated into electrons and $Hg^{\cdot}$ or $Hg_2^{\cdot\cdot}$. R. C.

Standard battery. R. B. Elliott and G. A. Hulett (J. Physical Chem., 1933, 37, 489—493).—Details are given for the construction and maintenance of a Weston cell battery. On closing the circuit, the e.m.f. falls about 0·200 mv. during the first 30 sec. and then remains const. at 1017·489±0·003 mv., independent of temp. D. R. D.

Haber's glass cell. J. Zirkler (Z. Physik, 1932, 77, 126; cf. A., 1931, 914).—The e.m.f. of a cell symmetrical with respect to a glass membrane is probably a piezo-electric effect due to strains in the glass. This cell may be adapted to measure e.m.f. without diffusion, and thus verifies Nernst's views on the association of strong electrolytes. A. B. D. C.

Use of the tungsten–nickel electrode system in neutralisations. N. H. Furman and G. W. Low, jun. (J. Amer. Chem. Soc., 1933, 55, 1310—1315).—The W–Hg_2Cl_2 and the Ni–Hg_2Cl_2 electrodes are most sensitive in the p_H regions in which phenolphthalein and Me-orange, respectively, change colour. The W–Ni system is satisfactory in the titration of a weak or a strong base with a strong acid. J. G. A. G.

Mechanism of hydrogen–oxygen electrode. K. Bennewitz and W. Neumann (Z. physikal. Chem., 1933, 164, 277—294).—The potential, ε, of a Pt electrode in contact with a mixture of H_2 and O_2 has been measured. A platinised electrode reacts so rapidly compared with the rate of diffusion that if H_2 is in excess above the stoicheiometric ratio it behaves as a H_2 electrode, whilst if the O_2 is in excess it acts as an O_2 electrode, although in the latter case the reversible potential is not reached, which may be accounted for by the oxide theory (A., 1932, 24). With a bright Pt electrode the relation between ε and the composition of the gas mixture is most satisfactorily accounted for on the lines of Erdey-Gruz and Volmer's theory (A., 1930, 1376). R. C.

Oxidation-reduction potential of the system thioglycollic acid–dithioglycollic acid. E. Larsson (Svensk Kem. Tidskr., 1933, 45, 65—72).—This system gives reproducible potentials with a Pt electrode in a N_2 atm., and these are unaffected by traces of O_2. The presence of 10^{-6} equiv. Fe per litre causes non-reproducible potentials, and renders the system sensitive to O_2. R. P. B.

Determination of the isoelectric point [of aqueous lead monoxide]. L. V. Andrews and D. J. Brown (J. Physical Chem., 1933, 37, 417—424).—The e.m.f. of cells of the type Hg, HgO, aq. KOH|H_2O, PbO, HgO, Hg indicates that the activity of OH′ in saturated aq. PbO is $1·84\times10^{-4}$ for red PbO and $2·82\times10^{-4}$ for $3PbO,H_2O$. Hence K for the dissociation $PbO,xH_2O \rightleftharpoons PbOH^{\cdot}+OH'$ is $2·7\times10^{-4}$. The isoelectric point, given by the concn. of KOH at which $E=0$ for the cell Hg, HgO, aq. KOH|aq. KOH, PbO, HgO, Hg, is $5·6\times10^{-3}$. The basic character of HgO is too weak to affect the results. D. R. D.

Electrochemical phenomena in the catalytic decomposition of hydrogen peroxide by platinum. R. Wolff (Compt. rend., 1933, 196, 1113—1116).—The p.d. at a Pt electrode in M-H_2O_2 is a linear function of the p_H of the solution over the range p_H 1·25—11·3. The potential is supposed to be connected with the catalytic decomp. of the H_2O_2. C. A. S.

Analysis of chemical reactions. G. Grigercsik (Ann. Sci. Univ. Jassy, 1933, 17, 195—198).—Mathematical. J. W. S.

Optimum temperatures in exothermic gaseous reactions. (Mlle.) A. E. Korvezee and F. E. C. Scheffer (Rec. trav. chim., 1933, 52, 321—326).—Theoretical. Expressions giving the temp. at which the max. quantity of the product of a reversible gaseous reaction is formed are derived, having regard to the rate of flow of the gas through a heated tube. The two cases $A \rightleftharpoons B$ and $2A \rightleftharpoons B+C$ are considered. F. L. U.

Photographic analysis of explosion flames. W. A. Bone (Proc. Roy. Inst., 1933, 27, 698—730).—A lecture.

Minimal critical pressure of explosions. K. S. G. Doss (J. Indian Chem. Soc., 1933, 10, 57—59).—Theoretical and polemical against Semenov (A., 1928, 847). A. S. C. L.

Hydrogen–oxygen reaction. Adsorption of hydrogen on Pyrex and quartz. A. T. Williamson (J. Amer. Chem. Soc., 1933, 55, 1437—1441).—The rate of adsorption of H_2 at 760 mm. on SiO_2 and Pyrex in the range 400—542° has been determined. True adsorption equilibrium vals. have been obtained for Pyrex only after prolonged contact. Alyea's theory of the upper explosion limit of the H_2–O_2 reaction is inconsistent with the results (cf. A., 1931, 688). J. G. A. G.

Mechanism of the upper limit of inflammation of electrolytic gas mixtures. N. Semenov, A. Nalbandjan, and Dubowizky (Trans. Faraday Soc., 1933, 29, 606—611).—Experiments on the inflammation of electrolytic gas in presence of at. H show that the upper limit of inflammation still exists, contrary to the observation of Haber and Oppenheimer (A., 1932, 576). The presence of at. H enlarges the region of inflammation, but does not alter its form. The extinction curve has also a similar form. The inflammation limits depend in some way on the no. of initial centres, and the chain theory of inflammation must be restricted, *i.e.*, the interaction of chains must be included in the theory. At. O has a much stronger action than at. H, and extremely small concns. lower the inflammation temp. 80—100°. This supports Semenov's theory of the mechanism of chain development in the inflammation region (A., 1930, 299). M. S. B.

Effect of nitrogen in combustion processes. H. H. Gray (Chem. and Ind., 1933, 351—352).—The work of Bone and his co-workers is discussed. The inactivity of N_2 is questioned, and it is suggested

that the retardation by N_2 of combustion in gaseous mixtures, particularly those containing CO, is due to a reaction between C and N_2. H. F. G.

Reaction regions. XXIV. Explosion regions of gas mixtures in which an oxygen compound is used in place of oxygen. Nitrous oxide as oxygen provider. III. Explosion regions CH_4–N_2O–A and CH_4–(N_2+0·5O_2)–A. W. P. JORISSEN and A. A. VAN DER DUSSEN (Rec. trav. chim., 1933, **52**, 327—332; cf. A., 1930, 708).—The lower and upper explosion limits in the mixture CH_4+N_2O are respectively 2·2 and 36·6% CH_4, whilst the corresponding vals. for CH_4+(N_2+0·5O_2) mixtures are 4·3 and 22·9. The quenching action of A does not differ greatly in the two cases. F. L. U.

Reaction between sodium vapour and cyanogen halides. J. CURRY and M. PÓLANYI (Z. physikal. Chem., 1933, **B**, **20**, 276—282).—In the homogeneous reactions with CNCl and CNBr at 300—400° the ratio of NaCN : NaX (X=Cl or Br) formed in the primary reaction varies from about 1 : 50 to 1 : 150, falling as the temp. rises. It is concluded that two primary reactions occur simultaneously: Na+CNX ⟶ NaX+CN, Na+CNX ⟶ NaCN+X. R. C.

Oxidation of ammonium sulphite and preparation of ammonium sulphate from gaseous sulphur dioxide, ammonia, and water vapour. S. I. VOLFKOVITSCH and D. L. ZIRLIN (Z. anorg. Chem., 1933, **211**, 257—271).—The rate of oxidation of aq. $(NH_4)_2SO_3$ by air increases with rise of temp. Owing to simultaneous decomp., the optimum temp. is 70°. Cu and MnO_2 have a weak catalytic influence. The best results were obtained with a large surface of SiO_2 gel. Oxidation of solid $(NH_4)_2SO_3$ was very incomplete under all conditions. The product obtained by electrostatic pptn. from a mixture of SO_2, NH_3, H_2O vapour, and air at 18° contained ⩾ 9·2% of $(NH_4)_2SO_4$. F. L. U.

Organic thermochemical measurements. Velocities and heats of saponification of amides. III. General results and their interpretation. E. CALVET (J. Chim. phys., 1933, **30**, 198—212).—The results of the work previously described (A., 1932, 344; this vol., 353) are summarised and discussed. F. L. U.

Kinetics of reactions of iodine with ferrous salts. II. Discussion of results. A. BERTHOUD and S. V. ALLMEN (J. Chim. phys., 1933, **30**, 186—194; cf. this vol., 469).—When KF is used to suppress the reverse change, the velocity of the reaction between I and $FeSO_4$ in aq. solution at first decreases to a min. with increasing [I′], then increases to a max., and finally attains a limiting val. The velocity increases with [Fe″] and ∝ [I] except in the region between the min. and max. It ∝ 1/[H·]. The effect of other ions has also been studied. The thermal coeff. is about 3 at 20—30°. F. L. U.

Energy of activation. V. K. LAMER (J. Amer. Chem. Soc., 1933, **55**, 1739—1741; cf. A., 1931, 1132).—The energy of activation, E, of the reaction between $CH_2Br·CO_2Na$ and $Na_2S_2O_3$ decreases, whilst that of the reaction between Na β-bromopropionate and $Na_2S_2O_3$ increases, with rise of temp. T, and added salts have marked effects on E. The dependence of the relation between E and T on the heat capacity, free energy, and entropy of activation is considered. J. G. A. G.

Kinetics of the addition of iodine to β-phenylpropiolic acid. E. A. MOELWYN-HUGHES and A. R. LEGARD (J.C.S., 1933, 424—429).—The addition of I to CPh:C·CO_2H in aq. solution is bimol. In moderate concns., reaction is between the anions CPh:C·CO_2′ and I_3′. Comparison with the velocity coeff. calc. from the collision theory indicates that only ternary collisions involving H_2O mols. are effective. Below 2·5×10 k rises rapidly, due to preponderance of addition of HIO to CPh:C·CO_2′, proceeding at 100 times the velocity calc. from the collision theory. J. S. A.

Effect of the solvent on reaction velocity. III. Interaction of persulphate and iodide ions. F. G. SOPER and E. WILLIAMS (Proc. Roy. Soc., 1933, **A**, **140**, 59—70).—The equation $k=P\times Ze^{-E/RT}$ is proposed for reaction velocity in solution. P is a probability factor varying with temp. and connected with the polar nature of reagents and products. $Ze^{-E/RT}$ is the collision frequency of mols. having the necessary activation energy. Alternative ideas for the physical nature of P are proposed: (*a*) the solvent exerts its effect on the breakdown of the intermediate crit. complex, causing a resolution into those substances, resultants, or reactants for which it has a greater affinity; and (*b*) the solvent exerts its effect in aiding or hindering the articulation of the reactant mols. to form the crit. complex. In both cases the effect of polar, as compared with non-polar, solvents will be to favour the formation of polar mols., and thus to accelerate or retard the reaction velocity, according as the resultants or the reactants are the more polar. A study of the kinetics of the oxidation of iodide by S_2O_8″ ions over the range of ionic strength from μ=0·001 to 0·025 and where the product ions are of dissimilar charge favours alternative (*a*), but this explanation may be obscured by disturbances due to the high charge of the crit. complex. L. L. B.

Verification of a mechanism involving a reactive intermediate compound. Rate of oxidation of oxalate by hypobromous acid. B. MAKOWER and H. A. LIEBHAFSKY (Trans. Faraday Soc., 1933, **29**, 597—606).—The rate of the reaction $HOBr+HC_2O_4' \longrightarrow H_2O+2CO_2+Br'$, measured in the absence of Br_2, is virtually independent of Br′ over the concn. range 10^{-9} to $10^{-6}M$. The val. of k_1 ($2·7\times10^3$ at 0°) is in close agreement with that deduced by Griffith and others (A., 1932, 344) and is thus direct evidence for the theory that halogens in H_2O solution are oxidising agents only through the intermediary of the hypohalous acids or their ions. Agreement is also obtained for the measured and calc. vals. of the activation energy of the reaction, 15,700 g.-cal. In alkaline solution there is an increase in rate which is independent of H· and is accounted for by a second rate-determining step: $OBr'+HC_2O_4' \xrightarrow{k_2} HCO_3'+CO_2+Br'$. Assuming 10^{-9} as the dissociation const. of HOBr at 0°, $k_2=3\times10^5$. The val. of k_1 is not affected by diffused daylight. M. S. B.

Thermal reactions of phosphorous acid with bromine and chlorine. R. O. GRIFFITH and A. MCKEOWN (Trans. Faraday Soc., 1933, **29**, 611—618).—The reaction between H_3PO_3 and X_2 in presence of HX and the corresponding neutral salt, where X is Cl or Br, is bimol., but is retarded by $H^{\cdot}$ or X'. The data are interpreted in terms of two simultaneous processes of the type $X_2+H_2PO_3'+H_2O \longrightarrow H_3PO_4'+2HX$ and $X_2+HPO_3''+H_2O \longrightarrow HPO_4''+2HX$. M. S. B.

Mechanism of simple substitution processes and Walden inversion. I. E. BERGMANN, M. PÓLÁNYI, and A. SZABO (Z. physikal. Chem., 1933, **B**, **20**, 161—174).—The rates of reaction of NaI with *d*-CHIMePr and with *d*-CHIMeBu in $COMe_2$ solution at 30°, leading to racemisation (cf. this vol., 31), have been measured. The reactions of I′ with the corresponding chlorides (A., 1925, i, 494) and with the bromides are apparently of this same type. CHClPhMe dissolved in SO_2 gradually racemises owing to the configurative lability of the positive carbonium ion formed by ionisation. R. C.

Theory of explosive reactions. H. MURAOUR (Chim. et Ind., 1933, **29**, 507—514).—The vals. of A and B in the Arrhenius formula $K=Be^{-A/RT}$ recently calc. by Roginski (A., 1932, 1003) for numerous explosives are criticised on the ground that the formula is applicable only when rise in temp. produces an increase in the reaction velocity without modifying the nature of the reaction. In numerous cases considerable changes in the nature and amount of the reaction products occur with rise in temp., and in some cases products formed at low temp. act as catalysts in the further decomp. of the substance. According to the manner in which the necessary energy is supplied to the explosive, decomp. may take place in one or other of the following ways: thermal decomp. below the explosion temp., decomp. by inflammation which may or may not be followed by detonation according to the rate of decomp., and true detonation. The mechanism of these processes is explained theoretically. Bombardment of NI_3 with electrons, ultra-violet rays, X-rays, or the α-rays from polonium fails to produce detonation. A. R. P.

Reaction between a gas and a solid. Absorption of carbon dioxide by calcium oxide and by calcium hydroxide. H. W. B. RYAN (Fac. Sci. [London], Spec. Bull., No. 2, 15 pp.).—The rate of absorption of dry CO_2 by dry CaO is very small, and a surface film of $CaCO_3$ causes almost complete cessation of the reaction; in presence of H_2O vapour, however, the $CaCO_3$ crust falls away from the surface. The curve showing the increase with time of the wt. of $Ca(OH)_2$ placed in a dry CO_2 atm. passes through a max., and subsequently becomes parallel to the time axis; its form agrees closely with a theoretical equation, of general applicability, based on the rate of absorption of the CO_2 and the rate of evaporation of the liberated H_2O. An equation is derived also for the absorption of moist CO_2 by moist $Ca(OH)_2$. H. F. G.

" Transition points " of bismuth and copper. J. A. HEDVALL, R. HEDIN, and E. ANDERSSON (Z. anorg. Chem., 1933, **212**, 84—90).—The rates of attack of Bi by 1·84*N*-HNO_3 or 0·13*N*-I in aq. KI and of Cu by 1·84*N*-HNO_3 showed discontinuities at approx. 75° and 70°, respectively, these being the transition temp. of Bi and Cu observed dilatometrically by Cohen (cf. A., 1914, ii, 206; 1915, ii, 471). H. J. E.

Laws of combustion of (*a*) colloidal [explosive] powders, (*b*) nitrocellulose colloidal powders. H. MURAOUR and G. AUNIS.—See B., 1933, 365.

Corrosion of metals. P. F. THOMPSON.—See B., 1933, 392.

Thermal decomposition of crystals of barium azide. F. E. HARVEY (Trans. Faraday Soc., 1933, **29**, 653—658).—In the thermal decomp. of single crystals of dehydrated BaN_6 for the temp. range 100—130°, an induction period is observed similar to that in the case of Hg fulminate (this vol., 470). The reaction accelerates at a rate which increases as the tenth power of the time and the acceleration obeys the law, $\log(dp/dt-dp_0/dt)=k_1t+\text{const.}$, previously found to hold for fulminate and Pb styphnate. Towards the end the reaction is unimol. A black cryst. residue is left. During decomp. nuclei of Ba are produced. M. S. B.

Reactions in the solid state. J. A. HEDVALL (Svensk Kem. Tidskr., 1933, **45**, 80—106).—Reactions between solids are greatly influenced by cryst. form, particle size, and thermal history. The presence of liquid or gas is in most cases a secondary effect, reaction taking place by the motion of atoms or ions in the solid lattice. Melting does not always increase the reaction velocity. The loosening of the lattice by thermal vibration may be greatly affected by the presence of other solids even in very small amounts. Abnormal activity is often shown at the transition temp. between two cryst. forms. Experiments on the effect of ultra-violet and X-rays on three reactions gave negative results. R. P. B.

Homogeneous catalysis of the para-ortho-hydrogen transformation by paramagnetic substances. L. FARKAS and H. SACHSSE (Sitz. Preuss. Akad. Wiss. Phys.-Math. Klasse, 1933, **6**, 14 pp.).—In the gaseous phase the transformation is a first-order reaction in presence of O_2, NO, or NO_2. The collision efficiency is approx. equal ($1:10^{12}$) in each case, is independent of temp., and is the same when O_2 is used in aq. solution. The gaseous catalyst undergoes no chemical change. The paramagnetic ions $Cu^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, and $Mn^{\cdot\cdot}$ (as sulphates in 0·5*M* aq. solution) aid the transformation, the velocity increasing in the order of ions given. For a const. amount of a given salt the velocity of the transformation increases with dilution. E. S. H.

Intensification by alkali carbonate or hydrogen carbonate of catalytic oxidation by traces of mineral substances. G. CARPENTIER (Union pharm., 1932, **72**, 65—67; Chem. Zentr., 1932, ii, 3761).—St. Nectaise H_2O (6 g. HCO_3' per litre; traces of Cu, Co, Mn, and Fe) gives reactions with Meyer's, Escaïch's, and the benzidine reagents. The reactions are not given by H_2O from which insol. carbonates, co-pptg. the active metals, have separated. A. A. E.

Complex formation and catalysis. I. Increase of the rate of reduction of molybdic acid by complex formation. P. KRUMHOLZ (Z. anorg. Chem., 1933, **212**, 97—108; cf. this vol., 580).—The rate of reduction of MoO_3 to Mo^V compounds by NaI+0·05—0·2*N*-HCl is accelerated by addition of H_3PO_4, H_4SiO_4, or H_4GeO_4, due to formation of the complexes $H_3PO_4,12MoO_3$, $H_4SiO_4,12MoO_3$, and $H_4GeO_4,12MoO_3$. Addition of H_2SO_4 to MoO_3 reduces the catalytic activity of H_3PO_4, the H_2SO_4 itself forming complexes. The catalytic action of the above complexes is discussed in relation to their stability. H. J. E.

Effect of various compounds on the stability of hydriodic acid. W. J. HUSA and L. MAGID (J. Amer. Pharm. Assoc., 1933, **22**, 279—289).—The accelerating effect of 0·5*N* solutions of iodides on the rate of decomp. of 0·1*N*-HI decreases in the following order: Fe^{II}, Mn, Sr, Na, K, Li, Mg, Ca, NH_4. Ba and Hg iodides have strong retarding effects and Zn and Cd iodides slight effect. With const. p_H increase in iodide concn. increases the rate of decomp. of HI, and with const. iodide concn. increase of p_H increases the rate. HCl has a greater effect than H_2SO_4. $Ni^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, and $Co^{\cdot\cdot}$ have sp. catalytic effects in increasing the rate of decomp. $NiCl_2$, $FeCl_2$, and $CoSO_4$ markedly accelerate, $Al_2(SO_4)_3$ and $CdCl_2$ markedly retard, and $MnSO_4$, $MgCl_2$, $SrCl_2$, $BaCl_2$, $ZnCl_2$, $CaCl_2$, and KCl slightly retard decomp. NH_4Cl, LiCl, and NaCl have no effect. E. H. S.

Peroxidative and catalytic action of ferrous salts. II. S. GOLDSCHMIDT and S. PAUNCZ (Annalen, 1933, **502**, 1—19; cf. A., 1928, 251).—Comparison of the absorption curves of mixtures of $FeSO_4$, $OH{\cdot}CH_2{\cdot}CO_2H$ (I), and $OH{\cdot}CH_2{\cdot}CO_2Na$ with those of $FeSO_4+H_2SO_4$ indicates that complex $Fe^{\cdot\cdot}$ salts of (I) are not produced in any appreciable quantity. Max. oxidation of EtOH (to MeCHO and AcOH) with H_2O_2 in presence of $FeCl_2$ or $FeSO_4$ and mineral acid occurs independently of the anion of the $Fe^{\cdot\cdot}$ salt at p_H about 0·7; the no. of equivs. of H_2O_2 activated by 1 equiv. of $Fe^{\cdot\cdot}$ is affected by the anion. No consumption of H_2O_2 occurs with $K_4Fe(CN)_6$ or Na pentacyanoaquoferroate [which, contrary to Kuhn (A., 1926, 1215), possesses catalytic activity]. When EtOH is added to a mixture of H_2O_2 and $FeCl_2$, a renewed consumption of H_2O_2 occurs and the EtOH is oxidised, thus showing that all the $Fe^{\cdot\cdot}$ is not oxidised to $Fe^{\cdot\cdot\cdot}$ by the H_2O_2. Catalytic decomp. of H_2O_2 by $Fe^{\cdot\cdot}$ salts proceeds in two stages (first rapid; second slowly), is influenced by the anion (max. with Cl'), and decreases with rise in $[H^{\cdot}]$ (independently of the anion). Catalytic decomp. with $FeCl_2$ and HCl can occur more readily in presence of EtOH than in its absence. Both types of reaction are considered to be chain reactions. H. B.

Primary salt effects in reactions in which the substrate is neutral. N. N. T. SAMARAS (J. Physical Chem., 1933, **37**, 437—441).—Theoretical. D. R. D.

Catalysts for production of hydrogen by means of the water-gas reaction. IX. Reduction of ferric oxide catalyst during catalysis. X. Activity of triferric tetroxide catalyst. R. YOSHIMURA.—See B., 1933, 426.

Are traces of water really necessary for the occurrence of many reactions? M. BODENSTEIN (Z. physikal. Chem., 1933, **B**, **20**, 451—459).—The inhibition of reactions necessitating the penetration of solid surfaces by intensive drying may be due to blocking of the interfaces by films of resultants, the mols. of which would diffuse away in adsorbed H_2O films and form discrete crystals. Those gas reactions which are inhibited are chain reactions or are delimited by chain reactions under the experimental conditions. The drying either introduces impurities which terminate the chains or prevents chains starting. R. C.

Catalytic oxidation of carbon monoxide. (MME.) L. S. MATHIEU-LEVY (Compt. rend., 1933, **196**, 1319—1321; cf. A., 1927, 407; 1931, 904).—The catalytic activity of Mn dioxide (measured by the rise of temp. caused by the oxidation of CO) immediately after stoving is $<$ that of a sample which has adsorbed Fe, and this is $<$ one that has adsorbed Mn^{II}, but as regards resistance to ageing the order is reversed, and the effect of adsorption of Cu is opposite to that of Fe or Mn^{II}. Activity is increased by prolonged stoving, which effects dehydration and increases the O content, *e.g.*, from $MnO_{1·65}$ to $MnO_{1·79}$, whilst an oxide which had adsorbed Cu was reduced from $MnO_{1·91}$ before to $MnO_{1·79}$ after catalysis. C. A. S.

Ability of metal oxides to decompose nitrous oxide, and their position in periodic system. G. M. SCHWAB, R. STAEGER, and H. H. VON BAUMBACH (Z. physikal. Chem., 1933, **B**, **21**, 65—83).—The catalysed decomp. of N_2O on various oxides has been investigated. For the oxides of metals of a given group of the periodic system the apparent heat of activation, q, increases with decrease in the at. no. of the metal. On oxides of the principal sub-groups of the second and third groups the reaction is of the first order, whereas on ZnO, CdO, and CuO it is retarded by O_2, and on In_2O_3 by N_2O. For SrO q is not affected by partial poisoning with air, which shows that the active centres are all alike. For a given catalyst q does not vary materially with the method of prep., showing the active centres to have approx. the same energy content irrespective of their mode of formation. R. C.

Adsorption of nitrogen by iron synthetic ammonia catalysts. P. H. EMMETT and S. BRUNAUER (J. Amer. Chem. Soc., 1933, **55**, 1738—1739).—The ratio of the initial rates of adsorption of N_2 at 400° by Fe alone, Fe promoted with Al_2O_3, and Fe promoted with Al_2O_3 and K_2O is approx. equal to the ratio of the rates of NH_3 synthesis performed immediately after the adsorption. The rates of N_2 adsorption are consistent with this process being the first step in NH_3 synthesis. The energy of activation of desorption of N_2 from the surface of Fe catalysts is 49,000—57,000 g.-cal. (cf. A., 1931, 1247). J. G. A. G.

Decomposition of nitrous oxide on glowing platinum and platinum–iridium. J. LUKE and R. FRICKE (Z. physikal. Chem., 1933, **B**, **20**, 357—

360).—Schwab and Eberle's observations on the decomp. on glowing Pt (this vol., 33) have been confirmed. On a Pt–Ir wire the reactions follows Hinshelwood's equation (A., 1925, ii, 310) and the activity of the wire gradually decreases during use. If the wire is rubbed continually during the reaction, the velocity increases again, presumably owing to the formation of new active centres, but when rubbing ceases it falls abruptly. R. C.

Rare earths. XXXVIII. Electrolytic preparation of rare-earth amalgams. II. Decomposition of lanthanum amalgam to obtain the metal. R. E. Meints, B. S. Hopkins, and L. F. Audrieth (Z. anorg. Chem., 1933, **211**, 237—240; cf. A., 1931, 805).—La amalgam can be prepared by electrolysing a 20% solution of $LaCl_3,H_2O$ in EtOH. The pure metal is obtained by heating the amalgam contained in a crucible made of rare-earth oxides in a vac. furnace, finally at 1000°. Ce and Nd are obtained similarly. F. L. U.

New form of electrolytically deposited chromium. B. Rassow and L. Wolf.—See B., 1933, 352.

Plating of metallic surfaces with aluminium in an aluminium chloride–sodium chloride melt. V. A. Plotnikov and N. N. Graziansky.—See B., 1933, 352.

Preparation of macroscopic thallium crystals by electrolysis. A. Sprantsman (Acta Comm. Univ. Tartuensis, 1933, **A**, **24**, 3—5).—The crystals were prepared by electrolysing aq. Tl_2SO_4, using a Pt anode and a Cu cathode covered by a film of paraffin. The form of the crystals depends on the concn. and temp. of the solution, and on the product of the free acid and applied p.d., but is independent of c.d. between 0·01 and 0·10 amp. per sq. dm. E. S. H.

Theory of addition agent action [in electrodeposition of metals]. R. Taft.—See B., 1933, 431.

Cyanide-free bath for deposition of copper on steel. C. G. Fink and C. Y. Wong.—See B., 1933, 431.

Free cyanide in copper electroplating. L. C. Pan.—See B., 1933, 432.

Theory of corrosion. I. Relation between passivity and corrodibility of metals. W. J. Muller (Korrosion u. Metallschutz, 1932, **8**, 253—260; Chem. Zentr., 1932, ii, 3782).—If a metal, having a natural coating, when immersed in an electrolyte, becomes more noble, the phenomenon is termed self-passivation; it is related to increase in the size of the pores of the layer. If the coating is affected by dissolution or colloidal swelling or solvation, the phenomenon is not observed, and the coating is not protective. A. A. E.

Formation of silane in hydrogen discharge. E. Hiedemann (Z. physikal. Chem., 1933, **164**, 20—32).—In the electric discharge in H_2 in quartz vessels there is much less fatigue of the pressure decrease than in glass vessels (cf. A., 1931, 440). There is no fatigue in the amount of condensable gas ultimately formed, which supports the view that the fatigue in glass is due to Na remaining adsorbed on the wall. In presence of condensed Hg, HgH, but practically no silane, is formed. A review of the literature shows that all attempts to demonstrate the existence of neutral unexcited H_3 have failed, and that no conclusive evidence of the existence of neutral highly excited H_3 has been obtained. R. C.

Heterogeneous reactions in the silent electrical discharge. II—IV. S. Miyamoto (J. Sci. Hiroshima Univ., 1932, **A**, **3**, 79—97, 99—115, 117—136; cf. this vol., 33).—Further observations on the reaction of H_2 with 60 solid inorg. substances are recorded. F. L. U.

Graphitic oxidation at low pressure by electric discharge or by Röntgen irradiation. V. Sihvonen (Suomen Kem., 1933, **6**, 59—60B).—The reactions and equilibria which occur when electric discharges of various intensities are passed between Pt and graphite electrodes in either CO_2+CO or in O_2 are summarised with special reference to graphitic oxidation. J. W. B.

[Decomposition of methane by condensed sparks.] P. Montagne (Bull. Soc. d'Encour., 1933, **132**, 183—186; cf. A., 1928, 589).—A max. of 75% of the CH_4 may be transformed into C_2H_2 and H_2 by a condensed spark at 1—11 mm. pressure, the C_2H_2 decomposing on further sparking into C and H_2. The amount of C_2H_2 increases with the capacity at const. pressure, and is almost independent of the pressure at const. capacity. Small amounts of C_3H_4, C_2H_6, and C_3H_8 are formed. The amount of CH_4 decomposed in a d.c. discharge is much smaller. H. J. E.

Photosynthesis of hydrogen chloride. I. New experimental method; inhibiting effect of hydrogen chloride. II. "Oxygen-free" mixtures. M. Ritchie and R. G. W. Norrish (Proc. Roy. Soc., 1933, **A**, **140**, 99—112, 112—125).—I. A method for the measurement of rates of reaction and quantum efficiencies in the formation of HCl involves the determination of light absorption by the Cl_2 in the reaction mixtures. HCl exerts a marked inhibiting effect in H_2–Cl_2 mixtures containing O_2.

II. The quantum efficiency of the photochemical reaction between H_2 and Cl_2 can be represented over a wide range by the expression $\gamma=(2{\cdot}8\times10^3[H_2][Cl_2])/([Cl_2]+1{\cdot}7[HCl])(I_{abs.})^{0{\cdot}4}$. A max. quantum yield of $1{\cdot}2\times10^5$ is obtained. The velocity of HCl formation is proportional to a power of the intensity of the absorbed light approaching 0·5 (actually 0·6). Reaction chains are terminated mainly by self-neutralisation. The at. mechanism for such O_2-free mixtures involves Nernst chains, of which the at. reactions compare closely with those of the corresponding H_2–Br reaction. L. L. B.

Photochemical reaction of hydrogen and chlorine. A. J. Allmand (Nature, 1933, **131**, 656).—A reply to criticism (this vol., 132). L. S. T.

Behaviour of dry chlorine–hydrogen mixture in light. F. Bernreuther and M. Bodenstein (Sitz. Preuss. Akad. Wiss. Phys.-Math. Klasse, 1933, **6**, 25 pp.).—Experiments on the union of highly-purified and intensively-dried Cl_2 and H_2 under the influence of visible and ultra-violet light show that

the presence of H_2O vapour is not necessary. The contrary results of previous investigators are attributed to the presence of impurities. E. S. H.

Photochemical kinetics of reaction between chlorine, hydrogen, and oxygen. M. Bodenstein and P. W. Schenk (Z. physikal. Chem., 1933, **B**, **20**, 420—450).—The formation of HCl and H_2O from streaming mixtures of H_2 and Cl_2 with a considerable amount of O_2 can be represented by the scheme (1) $Cl_2+h\nu=2Cl$, (2) $Cl+H_2=HCl+H$, (3) $H+Cl_2=HCl+Cl$, (4) $H+O_2+M=HO_2+M$, (5) $Cl+O_2+M=ClO_2+M$, with slight modifications. The yield of H_2O depends on the ratio $[H_2]:[Cl_2]:[HCl]$, which indicates that (4) is followed by reactions of HO_2 with H_2, Cl_2, and HCl. Acceptable schemes for these reactions have been worked out. Reaction (3) has a heat of activation 1900 g.-cal., the collision efficiency is 1/21, and there is also a steric factor, < 1. Reaction (4) occurs after every triple collision in which the steric conditions are favourable. Since the velocity coeff. of $H+HCl=H_2+Cl$ is only 10^{-3} to 10^{-4} times that of reaction (3), the formation of HCl cannot be hindered by HCl at room temp. The formation of HCl can be represented by Thon's equation (A., 1927, 323) modified to take into account the Cl atoms formed in reaction (1). The results are compatible with the mechanism $H+O_2+H_2=H_2O+OH$, $2OH+M=H_2O_2+M$ for the formation of H_2O_2 sensitised by Hg, but not with the chain mechanism $H+O_2+H_2=H_2O_2+H$. R. C.

Photochemical decomposition of chlorine monoxide between 2350 and 2750 Å., and interpretation of its absorption spectrum in this region. H. J. Schumacher and R. V. Townend (Z. physikal. Chem., 1933, **B**, **20**, 375—384).—The quantum yield at 20° is 4·5, indicating that the primary process after light absorption is dissociation into 2Cl and O. The Cl atoms then react with the Cl_2O as previously described (A., 1932, 237). Neither O atoms nor O_3 react with Cl_2O. R. C.

Solarisation. VI. Solarisation by physical development. H. Arens (Z. wiss. Phot., 1933, **31**, 317—323).—Solarisation occurs with secondary physical development only and always when it is produced with primary physical development. Emulsions showing solarisation with chemical development show less and may show no solarisation with physical development. Br′, if added at peptisation, reduces the production of solarisation. This effect is removed by washing, and is not restored by further addition of Br′. Increased temp. of peptisation increases solarisation, and inhibits the protective action of Br′. J. L.

Present position of the problem of fine grain [in photography]. K. Fischer (Z. wiss. Phot., 1933, **31**, 297—316).—A review. The methods considered for the production of fine grain together with high sensitivity are: (1) composition and prep. of the emulsion, (2) efficiency of the plate, (3) hypersensitisation, (4) special developers; bleaching and redeveloping or sulphiding, (5) optical diffusion of the image on enlargement. J. L.

Colour centres of the latent image in the electric field. O. Stasiw (Nachr. Ges. Wiss. Gottingen, 1932, 261—267; Chem. Zentr., 1932, ii, 3674).

Additive coloration of alkali halide crystals. E. Mollwo (Nachr. Ges. Wiss. Gottingen, 1932, 254—260; Chem. Zentr., 1932, ii, 3673—3674).

Effect of solvent on reaction velocity. IV. Rate and critical increments of some chlorination reactions. R. E. Roberts and F. A. Soper (Proc. Roy. Soc., 1933, **A**, **140**, 71—78).—Velocity coeffs. and crit. increments of the chlorination of certain phenolic ethers and anilides have been determined in a series of solvents, and in some cases zero crit. increments were observed. As in reactions where the polar nature of reactants and resultants are markedly different, *e.g.*, the formation of quaternary NH_4 salts, the calc. reaction rates are anomalous. L. L. B.

Photochemical reaction of monoalkylmalonic acids. D. Coster and A. van der Ziel (Z. physikal. Chem., 1933, **B**, **20**, 385—397).—On irradiation of *n*-monoalkylmalonic acids with sunlight, the light of a Hg arc, or *X*-rays, there are formed new substances of unknown character, which are not fatty acids. They have 2 mols. between the surfaces of identity. R. C.

Photosynthesis in tropical sunlight. VI. Presence of formaldehyde in rain-water. N. R. Dhar and A. Ram (J. Physical Chem., 1933, **37**, 525—531).—Freshly collected rain-water contains up to 1 mg. of CH_2O per litre, the largest quantity being obtained when the shower has been preceded by bright sunlight. Probably the CH_2O is formed in the upper atm. by the reaction $CO_2+H_2O=CH_2O+O_2$ under the action of ultra-violet light. D. R. D.

Photo-reduction of carbonic acid by chlorophyll. R. Willstatter (Naturwiss., 1933, **21**, 252—253).—This takes place only in presence of small quantities of O_2. The H atoms of the chlorophyll react singly, and not in pairs, an application of Haber's principle. It is supposed that a monodehydrochlorophyll is first formed: chlorophyll $+O_2=O_2H$+monodehydrochlorophyll. By wandering of a H atom to the $Mg–H_2CO_3$ complex, the dehydrocompound is produced. In the later stages, the light reaction, dehydrochlorophyll$+H_2O=OH$+monodehydrochlorophyll, —— dehydrochlorophyll+H (going to the $Mg–H_2CO_3$ complex), takes place. After the giving up of 4 H atoms, the dehydro- and monohydrocompounds regenerate chlorophyll in the light: monodehydrochlorophyll $+H_2O-OH+$chlorophyll. The radicals O_2H and OH may again furnish monodehydrochlorophyll or give H_2O, O_2, and H_2O_2. A. J. M.

Reaction mechanism of photosynthesis. K. Shibata and E. Yakushiji (Naturwiss., 1933, **21**, 267—268).—The chlorophyll–H_2CO_3 complex can add 4 H_2O by co-ordination at the Mg. The light energy absorbed by the coloured mol. activates the H_2O to give H and OH, four quanta being used. The H_2CO_3 acts as acceptor to the four active H atoms thus obtained, and becomes reduced to CH_2O and H_2O; $H_2CO_3+4(H\ldots OH)=2H_2O+CH_2O+4OH$. The four OH radicals remaining combine forming

H_2O_2, which is then decomposed by leaf catalase into O_2 and H_2O. This reaction mechanism explains the taking up of four quanta, as shown experimentally by Warburg. The Blackman reaction, dependent on temp., is the catalytic decomp. of the H_2O_2. The O_2 given off in photosynthesis is derived entirely from H_2O. The action of leaf catalase can be shown by investigating the action of a sp. catalase poison, *e.g.*, NH_2OH, which soon stops the evolution of O_2. A. J. M.

Decomposition of ozone by α-particles and by thermal means. B. LEWIS (J. Physical Chem., 1933, **37**, 533—534).—The rate of decomp. of O_3 by α-particles from Rn at room temp. follows the equation $-d[O_3]/dt=dp/dt-K[O_3]^{1\cdot5}$, where K is independent of p and $[O_2]$. The no. of mols. decomposed per ion pair $\propto [O_3]^{2\cdot3}$. The rate of thermal decomp. of O_3 at 85° follows an equation of the same type, but K varies with p and initial concn. of O_2. D. R. D.

Destruction of highly polymerised molecules by ultrasonic waves. A. SZALAY (Z. physikal. Chem., 1933, **164**, 234—240).—The mols. of starch, gum arabic, and gelatin are disintegrated by the action on the solution of a frequency of 722,000 hertz. Sucrose, paraformaldehyde, and hexamethylenetetramine are slightly decomposed. R. C.

Isolation of halogen compounds of the rare gases. A. VON ANTROPOFF, H. FRAUENHOF, and K. H. KRUGER (Naturwiss., 1933, **21**, 315; cf. A., 1932, 1007).—The red compound previously isolated, and stated to be Kr chloride, has now been shown to be a compound of NO and HCl. This does not, however, explain the decrease in pressure observed and does not prove that Kr chloride does not exist. A. J. M.

"Variegated" hydrogen. A. GUNTHER-SCHULZE and F. KELLER (Naturwiss., 1933, **21**, 235—236).—If a heavy discharge is passed through H_2 which has been intensively dried with P_2O_5, a new modification is produced which gives an extraordinarily colourful glow discharge. It is proposed to call the new form "variegated" ("Bunter") H_2. A. J. M.

Parahydrogen. E. JOSEPHY (Angew. Chem., 1933, **46**, 256—258).—A review.

Reactions of atomic hydrogen with alkyl halides. H. M. CHADWELL and T. TITANI (J. Amer. Chem. Soc., 1933, **55**, 1363—1376).—Under the conditions employed, the reactivity of at. H with Me halides increases from zero for MeF to 100% decomp. for MeI, thus indicating that the heat of activation decreases rapidly in the series MeF to MeI. The products are CH_4, C_2H_6, and a trace of C_2H_4, the proportions of which do not vary greatly with relative [H]. EtCl and EtBr yield the same products containing higher $[C_2H_6]$. In general, the % decomp. decreases with decreasing at. H : alkyl halide ratio. Decomp. of the chlorides affords HCl, whilst that of the bromides and iodides yields the H halide and free halogen, the proportion of which decreases with increase of [H]. The primary reaction for the Me halides is $MeX+H \longrightarrow Me+HX$, and the subsequent steps are discussed. J. G. A. G

Sodium nitrosyl. E. ZINTL and A. HARDER (Ber., 1933, **66**, [*B*], 760—761).—The action of NO on Na in liquid NH_3 at −50° gives *Na nitrosyl* (I), $(NaNO)_n$, which is not identical with Na hyponitrite. (I) and H_2O yield N_2O, NaOH, Na hyponitrite, and NO_2'. A reducing action of (I) towards Fehling's solution, HgO, or Ag_2O–NH_3 could not be certainly established. (I) does not react with NH_4Cl in liquid NH_3 or yield a hydroxamic acid with PhCHO. N_2O is vigorously evolved by the action of HCl–anhyd. Et_2O. H. W.

Influence of substituents in the bases and the anions on the co-ordination index of a metal. I. N. COSTACHESCU and A. ABLOV. **II.** A. ABLOV (Ann. Sci. Univ. Jassy, 1933, **17**, 149—172, 173—187).—I. The ammines derived from $Cu(OAc)_2$ (I) or halogen-substituted (I) and 6-methylquinoline, β-naphthoquinoline, 2-methylquinoline, quinoline, and C_5H_5N are described.

II. The ammines derived from $(CH_2Ph\cdot CO_2)_2Cu$, (I), Cu amygdalate, benzilate, glycollate, phenoxyacetate, cupriglycollate, cupribenzilate, and cupriamygdate and NH_3, C_5H_5N, β-picoline, and $(CH_2\cdot NH_2)_2$ are described. The compositions of these compounds are compared and discussed with reference to the influence of substituent groups. J. W. S.

Silver ferrites. VIII. Orthoferric hydroxide with a side-chain. A. KRAUSE and I. GARBACZÓWNA (Z. anorg. Chem., 1933, **211**, 296—302; cf. this vol., 474).—Oxidation of aq. $FeSO_4$ with dil. H_2O_2 gives a red orthohydroxide sol which is quickly converted into a yellow ppt. consisting of its sulphate. The latter, when treated with aq. NH_3, yields a brick-red orthohydroxide having a T-shaped mol. with 8 atoms of Fe. The "ageing" of this substance in presence of alkali has been followed by the Ag ferrite method. The end-product is goethite. F. L. U.

Complexes of silver and zinc with nitrogen bases. A. TAMISIER (Bull. Soc. chim., 1933, [iv], **53**, 157—166).—The composition and stability of the compounds have been determined by the solubility method and, for Zn complexes, by the partition method also. The Ag ammines contain 2 mols. of base to 1 atom of Ag and, in agreement with earlier measurements, the primary saturated aliphatic amines give Ag compounds of practically the same stability, with the exception of NH_2Me, which gives an ammine of lower stability. The stability is also diminished by the presence of a double linking, an alcoholic group, or nuclear N as in C_5H_5N. Zn gives several complexes with NH_3 or mixtures of the complexes containing 2 and 4 mols. of NH_3 per atom of Zn, respectively. From determinations of the stability of NH_2Me and NH_2Pr complexes this appears to decrease with increasing length of chain. More than one ammine is present in these cases also. M. S. B.

Existence of the element 87. P. REMY-GENNETÉ (Bull. Soc. chim., 1933, [iv], **53**, 140—144).—A review of the evidence for the existence of eka-cæsium (I) and a criticism of Allison's magneto-optical method of analysis (A., 1930, 1541). From the universal association of Li and the heavy alkali metals in mineral waters and minerals, and also the asso-

ciation of alkali metals and He in certain minerals rich in He, but lacking in U and Th, Lepape concluded that the He of the ancient lagoon deposits is due to the disintegration of (I) which has practically disappeared from the earth's surface. M. S. B.

Colorations in glasses and various compounds due to alkali metal vapour. J. Hoffmann (Z. anorg. Chem., 1933, **211**, 272—276).—The origin of the colours produced by Na vapour at 500—700° in various glasses, quartz, Na_2SO_4, $Na_4P_2O_7$, and Na borates is discussed. F. L. U.

Properties and constitution of tricalcium phosphate. A. Sanfourche (Compt. rend., 1933, **196**, 935—936).—$Ca_3(PO_4)_2,H_2O$ loses no H_2O below 180° and then only 33%, at 475° 75%, and at 900° 95%, complete dehydration requiring a bright red heat. It is also more acid (p_H 6·8) than $CaHPO_4$ (p_H 7·5) (cf. A., 1932, 696). These facts are explicable if the H_2O is "H_2O of constitution," the substance being an acid salt of "hydroxyphosphoric acid" $H_6P_2O_9$, the "neutral salt" of which is $4CaO,P_2O_5$ (cf. *ibid.*, 1204). This acid thus forms the link between H_3PO_4 and $P(OH)_5$ (cf. A., 1904, i, 807). C. A. S.

Preparation of phosphorescent zinc sulphide. R. Coustal (Compt. rend., 1933, **196**, 1306—1307; cf. A., 1930, 576).—By fusing ZnS under 160 kg. of N_2 the optimum concn. of Cu for phosphorescence is shown to be 10^{-5} when prepared at 2000°; with no Cu the product is probably slightly phosphorescent. C. A. S.

Spontaneous oxidation of zinc and the nature of "pyrophoric" zinc. W. S. Sebborn (Trans. Faraday Soc., 1933, **29**, 659—663).—When finely-divided Zn (either ordinary commercial Zn dust or Zn sponge prepared electrolytically) is moistened with 10% NaOH or KOH in presence of air or O_2, but not of an inert gas, and the excess H_2O is removed by filter paper, a reaction occurs after a few min. Heat is evolved and oxidation to ZnO takes place with incandescence. The presence of NaOH or KOH is essential, probably in order to remove the protective surface of ZnO. With Cd the reaction is much less vigorous. M. S. B.

Ammines of double chlorides. L. T. Caton (Ann. Sci. Univ. Jassy, 1933, **17**, 199—204).—The *compounds* $[CdCl_6](SrAm_2)(CdAm_2),3H_2O$ (where Am $=NH_2Ph$ or C_5H_5N) are formed by the addition of powdered $SrCl_2,2CdCl_2,7H_2O$ to a solution of the amine in equal vol. of anhyd. EtOH, with subsequent agitation and addition of excess of light petroleum (b.p. 55—75°). J. W. S.

Mercurous oxide. R. Fricke and P. Ackermann (Z. anorg. Chem., 1933, **211**, 233—236).—The *X*-ray diagram of "Hg_2O" prepared by different methods shows only interferences characteristic of HgO, with some diffuse blackening due to Hg. No satisfactory evidence of the existence of Hg_2O has yet been produced. F. L. U.

Oxides and hydrated oxides of aluminium. J. D. Edwards and M. Tosterud (J. Physical Chem., 1933, **37**, 483—488).—The different forms of Al_2O_3 and its hydrates are described. It is shown by chemical, *X*-ray, and thermal analysis that there is a second form of Al_2O_3,H_2O, distinct from diaspore (cf. this vol., 214). D. R. D.

Alkali aluminium silicates. VII. Behaviour of mineral zeolites towards liquid ammonia. E. Gruner (Z. anorg. Chem., 1933, **211**, 385—397; cf. A., 1932, 482).—The dehydration of zeolites and their base-exchange products by the Biltz NH_3 extraction method (A., 1928, 852, 854) resembles that of permutites. Part of the H_2O in Ca zeolites is present as $[Ca(H_2O)_2]^{\cdot\cdot}$ (removable by NH_3), and part as H_2SiO_3 or H_4SiO_4 (partly removable by NH_3). H_2O in the anion is not extracted by NH_3. Alkali zeolites yield no H_2O on treatment with NH_3. Formulæ are suggested for desmin, alkali desmins, chabasite, alkali chabasites, heulandite, and alkali heulandites. H. J. E.

Halides of the rare earths. VII. Halides of thulium and lutecium. G. Jantsch, N. Skalla, and H. Grubitsch (Z. anorg. Chem., 1933, **212**, 65—83; cf. A., 1932, 1194).—Anhyd. $TuCl_3$, m.p. 821±3°, and $LuCl_3$, m.p. 892±2°, were prepared by heating the hydrated chlorides in HCl at 350°. TuI_3, m.p. 1015±10°, and LuI_3, m.p. 1045±10°, were prepared by heating the chlorides in HI at 600°. The thermal decomp. of these compounds was studied. Partial reduction to Tu or Lu occurred on heating the halides in H_2 at 700—900°. H. J. E.

Germanium. XIII. Calcium germanide and unsaturated germanium hydride. P. Royen and R. Schwarz (Z. anorg. Chem., 1933, **211**, 412—422; cf. this vol., 79).—The *compound* CaGe was prepared from Ge and Ca or CaH_2 at 950°. Acid hydrolysis of CaGe yielded the *compound* GeH_2, an amorphous yellow non-volatile solid, sol. in conc. NaOH to form H_2, GeH_4, and Na_2GeO_2. GeH_2 reacts explosively with O_2, forming Ge and H_2O. H. J. E.

Preparation of germanous iodide and action of silver nitrate on halogen derivatives of methane. A. Tchakirian (Compt. rend., 1933, **196**, 1026—1028).—Although $GeHCl_3$ boils at 75°, in presence of H_2O nothing distils over below 102°, the solution, *d* 1·6, finally containing 0·5 g. $GeCl_2$ and 0·3 g. HCl per c.c. Acid solutions of KI and $GeCl_2$ give GeI_2; MeI added to aq. (but not dry) $GeCl_2$ slowly forms GeI_2, as also does CH_2I_2, but to a smaller extent. CHI_3 (in $CHCl_3$ solution) and PhI have no action. On mixing EtOH solutions of $AgNO_3$ and $CH_{4-n}X_n$ no action occurs with X=Cl, n=2, 3, or 4; X=Br, n=2 or 3. In all cases when n=1 AgX is pptd., the order of rapidity being I>Br>Cl, as also when n=2 and X=I. These results point to the following formulæ: $[C^{+IV}X_4]^0$, $[C^{+II}X_3]^-H^+$, $[C^0X_2H_2]^0$, $[C^{-II}H_3]^+X^-$, and $[C^{-IV}H_4]^0$ (cf. A., 1931, 322; 1932, 830). C. A. S.

Thermal decomposition of ammonium [dihydrogen] phosphate. (Mme.) Réchid (Compt. rend., 1933, **196**, 1163—1165; cf. this vol., 475).—$(NH_4)H_2PO_4$ was heated for varying periods at a series of temp., 218—800°; the product in each case was dissolved in H_2O at 0°, and excess EtOH added, when an oil, which frequently crystallised, is pptd.; it is neither ortho- nor pyro-phosphate. These facts

and conductometric determinations compared with those for the Na salt show that first passes partly into a dimetaphosphate, thence into a hexametaphosphate at 218°, and thereafter perhaps into a tetrametaphosphate; but at the same time NH_3 is steadily lost, more and more free metaphosphoric acid in the insol. form being formed, and this alone remaining after 5 min. at 800°. This explains the supposed formation of an insol. NH_4 metaphosphate (cf. A., 1900, 651). C. A. S.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XVII. Vanadic acids, polyvanadates, and vanadium salts as examples of the formation and decomposition of multimolecular inorganic compounds in solution. G. JANDER and K. F. JAHR (Z. anorg. Chem., 1933, **212**, 1—20; cf. this vol., 475).—From measurements of ionic diffusion coeffs., alkali vanadate solutions are shown to contain successively mono-, di-, tetra-, and penta-vanadate ions, with increasing p_H. Each type of ion is stable over a definite p_H range. Pentavanadic acid corresponds with the hexavanadic acid previously reported (Dullberg, A., 1903, ii, 733). Tetravanadic acid is transformed into pentavanadic acid through the intermediate octavanadic acid. H. J. E.

Complex acids. IX. Tantalic acid. Reactions of alkali niobate and tantalate solutions with organic acids. H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1933, 419—424; cf. A., 1932, 999).—Conductometric and potentiometric titration of K tantalate solutions affords no evidence of the existence of definite K tantalates. Comparison of the p_H data with those found for Nb_2O_5 provides an explanation of the CO_2 separation of Weiss and Landecker.

HCO_2H, $CH_2Cl{\cdot}CO_2H$, AcOH, and $CH_2Ph{\cdot}CO_2H$ caused immediate pptn. of Ta_2O_5; Nb_2O_5 was pptd. only by excess AcOH and $CH_2Ph{\cdot}CO_2H$. $H_2C_2O_4$ and hydroxy-acids caused no pptn. of either Nb_2O_5 or Ta_2O_5, although lactic, tartaric, and malic acids form no definite complexes. Relatively large amounts of $H_2C_2O_4$ are needed to dissolve Ta_2O_5. J. S. A.

Constitution of nitrosylsulphuric acid, and the reactions in the lead chamber. L. CAMBI (Atti R. Accad. Lincei, 1933, [vi], **17**, 204—206).—The formation of additive compounds by NO, and its autoxidation and reduction, are discussed in relation to the reactions in the Pb chamber, and, in particular, to the formation of H_2SO_5N. H. F. G.

Complex metallic salts of sulphamide: an optically active inorganic salt. F. G. MANN (J.C.S., 1933, 412—419; cf. A., 1932, 1101).—$SO_2(NH_2)_2$ is of the class of chelate co-ordinating groups unable fully to saturate 6-co-ordination metals. This is not due to combination of 2 mols. only in the *trans*-position, since $Na[(H_2O)_2Rh(N_2H_2SO_2)_2]$, having been resolved into optical isomerides having $[M]_{5780}$ +31° and −34°, has the *cis* structure. The *compounds* $X[(H_2O)_2Rh(N_2H_2SO_2)_2]$ (where X=H, NH_4, *d*-α-phenylethylamine, and *d*-nor-ψ-ephedrine), the stable *dihydrate* $Na_3RhCl_6,2H_2O$, and the *compounds* $X[(NH_3)(OH)Pt(N_2H_2SO_2)_2]$, where X=Na, K, H, were prepared. J. S. A.

"Blue acid." E. BERL, K. WINNACKER, and H. H. SAENGER (Z. anorg. Chem., 1933, **211**, 379—384; cf. A., 1932, 1219).—A reply to criticism by Manchot (this vol., 240). The compound H_2SO_4,NO is formed from 100% H_2SO_4 and NO under pressure. N_2O_3 and SO_2 are not necessary. They are formed in a side reaction. H. J. E.

Colorimetric studies on heteropolymolybdates. P. KRUMHOLZ (Z. anorg. Chem., 1933, **212**, 91—96).—Extinction coeff. measurements on the yellow solutions obtained on adding successive amounts of H_3PO_4, Na_2SiO_4, or Na_2GeO_4 to molybdic acid at const. temp. show maxima, attributed to the complexes $H_3PO_4,12MoO_3$, $H_4SiO_4,12MoO_3$, and $H_4GeO_4,12MoO_3$ in solution. Excess of H_3PO_4 converts $H_3PO_4,12MoO_3$ into colourless $H_3PO_4,9MoO_3$. The Si and Ge compounds are more stable, and form no corresponding products with excess of H_4SiO_4 or H_4GeO_4. H. J. E.

Preparation of telluric acid. L. I. GILBERTSON (J. Amer. Chem. Soc., 1933, **55**, 1460—1461).—Te or TeO_2 is refluxed with a 2 : 1 (vol.) mixture of 30% H_2O_2 and conc. H_2SO_4. J. G. A. G.

Influence of substitution on co-ordination number. R. RASCANU (Ann. Sci. Univ. Jassy, 1933, **17**, 70—77).—$UO^{\cdot\cdot}$ compounds form ammines with NHPhAc containing 3 mols. of the latter and various nos. of mols. of H_2O. With NPhMeAc, however, the ammines contain only 2 mols. of the amine, and attempts to former higher ammines or hydrated ammines have proved unsuccessful. The prep. and properties of the *compounds* $UO_2Ex_2(NO_3)_2$, $UO_2Ex_2Cl_2$, and $UO_2Ex_2Br_2$ (Ex=NPhMeAc) are described. J. W. S.

Fluorides of bivalent metals. II. Behaviour of metal fluorides towards ammonium, potassium, and sodium fluorides. A. KURTENACKER, W. FINGER, and F. HEY (Z. anorg. Chem., 1933, **211**, 281—295; cf. this vol., 476).—Solubility measurements at 20° and 50° in the systems MF_2–$M'F$–H_2O (M=Ni, Co, Zn, Cd, Cu; M'=NH_4, K, Na) are given in tables and triangular diagrams. With NH_4F double salts $MF_2,2NH_4F,2H_2O$ are formed in every case. Mixed crystals are not formed. With KF the solid phase consists of an extensive range of mixed crystals the constitution of which is doubtful. The same is true of NaF. F. L. U.

Preparation and properties of atomic chlorine. G. M. SCHWAB and H. FRIESS (Naturwiss., 1933, **21**, 222).—At. Cl was prepared by passing a discharge through purified Cl_2 in a Wood's tube of quartz. To distinguish between at. and mol. Cl use was made of the effect on a thermocouple of the heat of recombination. The recombination follows a first-order equation, and takes place on the walls. The life period of the atoms was 6×10^{-3} sec. S and red P react with Cl slowly, Cu and Cr_2O_3 more quickly. Sn destroys the activity of the gas completely at first, then melts, and volatilises, after which the activity of the gas returns. The % concn. of Cl remains approx. const. between pressures of 0·03 and 0·1 mm. A. J. M.

Tervalent rhenium and univalent ruthenium. W. MANCHOT and J. DUSING (Z. anorg. Chem., 1933, **212**, 21—31; cf. A., 1932, 133).—In the autoxidation by O_2 at 20° of the green solution containing Re^{III}, obtained by electrolytic reduction of K_2ReCl_6, 1 equiv. of O_2 is absorbed rapidly, the solution becoming brown. Three additional equivs. of O_2 are absorbed more slowly, the solution becoming deep red, violet, and then almost colourless. The violet colour is attributed to Re^{VI}. Oxidation by $KMnO_4$ gives the same colour changes. In aq. HCl Re^{III} absorbs only 1 equiv. of O_2, K_2ReCl_6 crystallising out. Re^{III} is reduced by NaH_2PO_2, probably to Re^{II}, H_2 being evolved. Aq. NaH_2PO_2 and salts of Re^{III} or Ti^{III} reduce salts of Ru^{III} or Ru^{II} to Ru^{I}, H_2 being evolved. H. J. E.

Crystalline systems of microcrystalline ferric oxides. A. GIRARD and G. CHAUDRON (Compt. rend., 1933, **196**, 925—927; cf. this vol., 351).—Magnetisation–temp. curves indicate that the apparently colloidal ppt. obtained by rapid oxidation at room temp. of $Fe(OH)_2$ in excess of O_2 in a basic medium consists of very fine particles of cubic Fe_2O_3; the similar ppt. obtained in an acid medium is not ferromagnetic and gives a hazy rhombohedral *X*-ray diagram. Rapid dehydration of lepidocrocite results in a mixture of cubic and rhombohedral Fe_2O_3; hydrolysis of $LiFeO_2$ or $KFeO_2$ at room temp., as also oxidation at 100° of pptd. hydrated Fe_3O_4, give the cubic variety. C. A. S.

Active iron. O. BAUDISCH (Science, 1933, **77**, 317—319).—A discussion of Fe oxides. L. S. T.

Ferrous hydroxide, and a ferromagnetic ferric hydroxide. G. SCHIKORR (Z. anorg. Chem., 1933, **212**, 33—39).—Aq. $FeSO_4$ and aq. NaOH evolve H_2 on mixing only when excess of $FeSO_4$ is present. The prep. of greyish-white $Fe(OH)_2$ under these conditions is described. On oxidising this $Fe(OH)_2$ with air or H_2O_2 the dried product has the formula $FeO{\cdot}OH$, and is ferromagnetic. Oxidation of aq. $FeSO_4$ in presence of $(NH_4)_2SO_4$ and aq. NH_3 yielded a green hydroxide containing < 2 atoms of Fe^{II} per atom of Fe^{III}. H. J. E.

Analogy between iron and ruthenium: sodium rutheninitropentacyanide. W. MANCHOT and J. DUSING (Z. anorg. Chem., 1933, **212**, 109—112; cf. A., 1930, 899).—The *compounds* $Na_4Ru(CN)_6$ and $Na_4Ru(CN)_6,3H_2O$ were prepared by acting on aq. $RuCl_3$ with excess of NaCN. The *compound* $Na_2Ru(NO)(CN)_5$, prepared by warming $Na_4Ru(CN)_6$ with aq. HNO_3 on a H_2O-bath, resembles the K salt, already described. Characteristic reactions are given with alkali sulphides and salts of Ag, Cu, Ni, and Co. It resembles $K_2Fe(NO)(CN)_5$. H. J. E.

Optical activity. III. *d*- and *l*-Cobaltioxalates. C. H. JOHNSON and A. MEAD (Trans. Faraday Soc., 1933, **29**, 626—640).—$[Co(C_2O_4)_3]'''$ has been resolved into its optical isomerides through the difference in solubility of the strychnine salts, and *strychnine l-cobaltioxalate* has been isolated. The analyses, absorption coeffs., and variation of rotatory power with wave-length have been determined for strychnine and K *d*- and *l*-cobaltioxalates. The mol. rotatory power of K *d*-cobaltioxalato is probably the highest recorded for a pure substance. The curves of rotatory dispersion are not symmetrical with respect to the active absorption band, the position of zero rotation (6280 Å.) being displaced about 250 Å. towards the long wave-length from the max. absorption at 6020 Å. The results are discussed in relation to Kuhn's work (A., 1930, 980; 1932, 111). Strychnine salts of *d*- and *l*-cobaltioxalates crystallise with 14 and 10 H_2O, respectively. The solid *l*-salt racemises completely when kept for a few weeks, but the *d*-salt quickly loses about 25% of its activity and then remains practically unchanged. M. S. B.

Preparation of normal nickel carbonate by Senarmont's method and the formation of solid solutions of nickel chloride in nickel carbonate. J. KRUSTINSONS (Z. anorg. Chem., 1933, **212**, 45—48).—$NiCO_3$ made by heating $CaCO_3$ with aq. $NiCl_2$ in a sealed tube at 180° (Senarmont, Ann. chim. phys., 1850, [iii], **30**, 138) always contains $NiCl_2$, which is shown by *X*-ray analysis to be in solid solution in $NiCO_3$. Pure $CoCO_3$ may be made by Senarmont's method. H. J. E.

Complex compounds of ethylenic substances with platinum salts. P. PFEIFFER and H. HOYER (Z. anorg. Chem., 1933, **211**, 241—248).—Ethylenic substances react with K_2PtCl_4 to give yellow complex compounds which are often too sol. to be crystallised alone, in which case they may be purified with the help of other complex salts. The following *compounds* or cryst. derivatives are described:

$[Cl_3Pt(Z)][Co\ en_2Cl_2]$, where $Z=CH_2{:}CH{\cdot}CH_2{\cdot}OH$, $CH{\cdot}CH{\cdot}CH_2{\cdot}OAc$, $CHMe{:}CH{\cdot}CH_2{\cdot}OH$, $CHMe{:}CH{\cdot}CH_2{\cdot}OAc$, or $CHMe{:}CH{\cdot}CHO$;

$[Cl_3Pt(CHMe{:}CH{\cdot}CH_2{\cdot}OH)]_2[Pt(NH_3)_4]$;

$[Cl_3Pt(CHMe{:}CH{\cdot}CH_2{\cdot}OH)][Co\ en_2(C_2O_4)]$;

$[Cl_3Pt(CHMe{:}CH{\cdot}CH_2{\cdot}OH)]K$. No reaction occurred in the absence of an ethylenic linking. F. L. U.

Mathematical formula for chemical analysis in a two-phase system. J. F. MCCLENDON (Science, 1933, **77**, 189—190).—A formula for calculating the total "unknown" from two extractions (CCl_4 from aq. solution) is given. L. S. T.

Quantitative analysis in small and ultra-small amounts of liquid by means of potentiometric titration. I. Titrations in macro-drops. K. SCHWARZ (Mikrochem., 1933, **13**, 6—17).—The drop to be titrated is suspended in a wire ring which forms one electrode. For acidimetric and oxidation titrations a Pt ring is used, for $AgNO_3$ titrations a Ag ring. The p.d. between this and a comparison electrode (Ag in 0·001*N*-$AgNO_3$) is measured by a Lindemann electrometer. Quantities of the order 10^{-6} g. may be determined within 1%. J. S. A.

Differing spectrographic sensitiveness of an element when isolated and when mixed with other elements. V. GAZZI (Annali Chim. Appl., 1933, **23**, 71—75).—The amount of an element revealed by the spark spectrum, using C electrodes, is greatly diminished when other elements are present. The observations are especially disturbed when a trace of an element, such as Fe, occurring in the electrodes is sought. T. H. P.

Indirect volumetric determinations. V. C. BORDEIANU (Arch. Pharm., 1933, **271**, 209—215).—Titrations involving back-titration are theoretically more accurate if only a slight excess of reagent is used. This is verified for five simple determinations. An apparatus for the prep. and storage of carbonate-free NaOH solution is described. R. S. C.

Simple quinhydrone electrode. K. ŠANDERA (Chem.-Ztg., 1933, **57**, 303).—A soil extract or other solution is placed in a small crystallisation dish, and in this is stood a porcelain or glass crucible having a porous bottom and containing a solution of standard p_H. Pt electrodes dip in the inner and outer vessels. A. G.

Recombination of hydrogen atoms. I. I. AMDUR [with A. L. ROBINSON] (J. Amer. Chem. Soc., 1933, **55**, 1395—1406).—Objections to the calorimetric determination of at. H in mixtures with H_2 are immaterial under certain conditions. The contribution of wall reaction to the total rate of combination of at. H is small, but H_2 mols. are approx. four times as efficient as H atoms in causing recombination at ternary collisions. J. G. A. G.

Potentiometric determination of very small amounts of chloride. K. SCHWARZ and C. SCHLOSSER (Mikrochem., 1933, **13**, 18—30).—On account of the solubility of AgCl, titration of Cl′ is not possible in aq. solutions more dil. than $0{\cdot}001N$. In 80% EtOH potentiometric titration is possible down to $[Cl']=2\times10^{-5}N$ and in 98% $COMe_2$ down to $[Cl']=2\times10^{-6}N$. J. S. A.

Volumetric determination of chlorine ions in presence of sodium fluosilicate. S. K. CHIRKOV (J. Appl. Chem., Russia, 1932, **5**, 1103—1106).—The solution is made just alkaline with NaOH (phenolphthalein) and titrated with $AgNO_3$ (K_2CrO_4). CH. ABS.

Detection and determination of free chlorine in chlorinated drinking water. L. W. WINKLER.—See B., 1933, 414.

Colorimetric determination of iodine by means of chloroform. K. L. MALJAROV and V. B. MATSKIEVITSCH (Mikrochem., 1933, **13**, 85—90).—The presence of Na_2SO_4, $MgSO_4$, or $CaSO_4$ in concns. up to 200 g. per litre does not interfere, but in presence of $>$ 15 g. NaCl, 12·5 g. $CaCl_2$, or 10 g. $MgCl_2$ per litre, low results are obtained. Empirical formulæ are given for correction of results in presence of the above salts. J. S. A.

Determination and occurrence of iodine in phosphate rock. W. L. HILL and K. D. JACOB.—See B., 1933, 346.

Modification of the Willard–Winter method for fluorine determination. W. D. ARMSTRONG (J. Amer. Chem. Soc., 1933, **55**, 1741—1742; cf. this vol., 242).—A sharper end-point is obtained with 3 drops of 0·05% aq. Na alizarinsulphonate in 40 c.c. of F′ solution. J. G. A. G.

Determination of hydrogen fluoride in air. Y. D. GOLDENBERG (J. Appl. Chem., Russia, 1932, **5**, 1088—1096).—Absorption in $Ti(SO_4)_2$–H_2SO_4 is satisfactory. Air is washed with H_2O, PO_4''' is separated with $AgNO_3$; the max. flow of air is 120 litres per hr. CH. ABS.

Analysis of liquid sulphur dioxide. F. A. EUSTIS.—See B., 1933, 384.

Determination of sulphurous acid and alkali sulphites by potassium permanganate. E. CARRIÈRE and R. LIAUTÉ (Compt. rend., 1933, **196**, 933—934; cf. A., 1909, ii, 264).—H_2SO_3 is accurately determined if its solution is poured into a known amount of acid aq. $KMnO_4$, $0{\cdot}02N$ in $KMnO_4$ and $<5{\cdot}5N$ in H_2SO_4, and the excess $KMnO_4$ is titrated: $5H_2SO_3+2HMnO_4=3H_2SO_4+2MnSO_4+3H_2O$. Na_2SO_3 can be determined by means of neutral or alkaline aq. $KMnO_4$: $3Na_2SO_3+2KMnO_4+H_2O=3Na_2SO_4+2KOH+2MnO_2$. C. A. S.

Oil-field water analysis. I. Determination of sulphate by benzidine. II. Volumetric determination of calcium in presence of magnesium. D. G. JONES and C. E. WOOD.—See B., 1933, 366.

Nephelometric determination of sulphate in drinking water. H. MOHLER.—See B., 1933, 366.

Determination of nitrogen by Kjeldahl's method. A. FRIEDRICH (Mikrochem., 1933, **13**, 91—115).—A summary of literature.

Presumed and actual errors in macro- and micro-Kjeldahl distillation. E. SCHULEK and G. VASTAGH (Z. anal. Chem., 1933, **92**, 352—356).—The chief errors arise from use of rubber stoppers and connexions, and from mechanical spraying of alkali, which may be eliminated by regulating the excess of alkali used. Dissolution of alkali from glass condensers is negligible. J. S. A.

Conductometric titration of ammonium salts, zinc salts, and cyanates by the visual method. O. PFUNDT (Angew. Chem., 1933, **46**, 218—219).—The method gives accurate results in the titration of NH_4Cl, $(NH_4)_2SO_4$, and NH_4NO_3, either alone or mixed with alkali salts, using $0{\cdot}5N$-NaOH, but phosphates interfere. $ZnCl_2$, but not $ZnSO_4$, may be similarly titrated with NaOH, inflexions in the curve being obtained when all the free acid is neutralised and when all the Zn is converted into $Zn(OH)_2$. Visual conductometric titration of aq. NaCNO or KCNO with N-$AgNO_3$ gives accurate results when the concn. is 150 mg. in 50—60 c.c. A. R. P.

Volumetric determination of nitrates with ferrous sulphate as reducing agent. I. M. KOLTHOFF, E. B. SANDELL, and B. MOSKOVITZ (J. Amer. Chem. Soc., 1933, **55**, 1454—1457).—20 mg. of KNO_3 are rapidly determined to within 0·5% and 2 mg. of NO_3' to 3% by reduction at 100° in an atm. of CO_2 with excess of $FeSO_4$ in conc. HCl and $(NH_4)_6Mo_7O_{24}$ as catalyst. ClO_3', BrO_3', and IO_3' interfere, but Mn'' and PO_4''' have no effect. J. G. A. G.

Diphenylaminesulphonic acid as a reagent for the colorimetric determination of nitrates. I. M. KOLTHOFF and G. E. NOPONEN (J. Amer. Chem. Soc., 1933, **55**, 1448—1453; cf. A., 1931, 1141).—Optimum conditions have been found, and determinations, accurate to within 5%, are made when

the colour produced by adding 0·1 c.c. of 0·006*M*-Na diphenylaminesulphonate to a cooled mixture of 10 c.c. each of conc. H_2SO_4 and a solution containing 0·001—0·05 mg. of NO_3' and 8—12 g. of KCl per litre is compared with standards prepared at the same time. NO_2' interferes and is removed by boiling with NH_4Cl. J. G. A. G.

Chromometric method of determination of NO_3'. J. Wierciński (Przemysł Chem., 1933, **17**, 57—59).—The $NaNO_3$ content of commercial $NaNO_2$ is determined by adding the solution dropwise to boiling acidified aq. carbamide in an atm. of CO_2, thus eliminating NO_2', and reducing residual NO_3' to NH_2OH by addition of $CrCl_2$, excess of which is determined by titration with standard $Fe_2(SO_4)_3$ in presence of KCNS as indicator. This method gives more accurate results than does direct titration with $KMnO_4$. R. T.

Determination of phosphorous, hypophosphorous, phosphoric, and hypophosphoric acids. W. Jung (Diss., Berlin, 1930; Bied. Zentr., 1932, **3**, A, 153).—Phosphites are oxidised by I in $NaHCO_3$ solution, and hypophosphites in acid solution. Hypophosphates are oxidised by $K_2Cr_2O_7$.

Colorimetric determination of phosphoric acid in argillaceous products. P. Urech.—See B., 1933, 345.

Colorimetric determination of arsenic by the Mayencon-Bergeret method. J. F. Reith (Pharm. Weekblad, 1933, **70**, 369—373).—The presence of Sb, Bi, and Fe makes the test described in the Dutch pharmacopœia less sensitive, but it is still satisfactory as a qual. test. In presence of these metals and Hg, Cu, and Se it is necessary to separate As before determination (cf. B., 1933, 90). S. C.

Qualitative analysis of the arsenic and iron groups by specific reactions. T. Grosset (Ann. Soc. Sci. Bruxelles, 1933, **B**, **53**, 16—40).—The following tests suffice for the detection of the metals of the As group in the presence of one another: Na_2HPO_2 in conc. HCl for As, $EtO{\cdot}CS_2K$ for Mo, cacothelin for Sn, rhodamin-*B* for Sb. Similar distinctive tests for the metals of the $(NH_4)_2S$ group are: $K_4Fe(CN)_6$ for Fe, dimethylglyoxime for Ni, NH_4CNS in Et_2O and $C_5H_{11}{\cdot}OH$ for Co, diphenylcarbazone for Cr, $(NH_4)_2S_2O_8$ and $AgNO_3$ for Mn, NEt_2Ph and $K_3Fe(CN)_6$ for Zn, alizarin-yellow for Al, H_2O_2 for Ti, and tetrahydroxyanthraquinone for Be. Analytical details are given. A. R. P.

Volumetric analysis of fluosilicic acid. V. Y. Anosov and S. K. Chirkov (J. Appl. Chem., Russia, 1932, **5**, 1097—1102).—Penfield's method is accurate if EtOH is added after the KCl solution. Sahlbom's method is satisfactory if the titration is carried out at room temp. Schucht's method is less satisfactory; Treadwell's is unsatisfactory. Ch. Abs.

Rapid semi-micro-determination of carbon dioxide in air. L. W. Winkler.—See B., 1933, 366.

Technique for determination of radioactive content of liquids. R. D. Evans (Rev. Sci. Instr., 1933, [ii], **4**, 216—222).—Methods for the removal of radon, and for the measurement of small quantities of radon or thoron, are described. N. M. B.

Picrolonic acid, a reagent for alkali metals. Y. Volmar and (Mlle.) M. Leber (J. Pharm. Chim., 1933, [viii], **17**, 366—372, 427—432).—Addition of *N*/50 picrolonic acid (I) to solutions of KCl or NaCl produces a ppt. of K or Na picrolonate, provided that the concns. of the chlorides exceed *N*/12 or *N*/9, respectively. NH_4, Ca, Sr, and Ba, but not Li, picrolonate likewise readily separate from solutions. (I) is a useful reagent for Na and K in qual. analysis. Methods of using (I) for the separation of Na and K are outlined. W. O. K.

Polarographic determination of the alkali metals. V. Majer (Z. anal. Chem., 1933, **92**, 321—351; cf. Heyrovsky, A., 1932, 1101).—Heyrovsky's polarographic method is applied, using a dropping Hg cathode and large Hg anode to fulfil the requirement of unpolarisability. Electrolysis is performed in presence of a large excess of another electrolyte. The use of NMe_4 salts (deposition potential for $NMe_4^{\cdot}$ —2·6 volts) permits simultaneous determination of Li (deposition potential —2·033 volts) and Na+K (—1·860 volts and —1·883 volts, respectively). The latter are not separable. Ions of other metals present are removed either by pptn. or by complex formation. Mg and Ti are pptd. as $Mg(OH)_2$ and $Ti(OH)_4$; Al is converted into aluminate. Ca and Fe are best removed by pptn. with $H_3PO_4+NMe_4OH$. J. S. A.

Precipitation of small amounts of potassium as potassium sodium cobaltinitrite. R. S. Hubbard (J. Biol. Chem., 1933, **100**, 557—559).—The technique of a method for the determination of 0·05—0·8 mg. of K giving a ppt., the composition of which corresponds exactly with the formula $K_3NaCo(NO_2)_6$, is described. A. L.

Colorimetric determination of small amounts of potassium. A. E. Sobel and B. Kramer (J. Biol. Chem., 1933, **100**, 561—571).—The intensity of colour of the yellow Co–cysteine–H_2O_2 complex at a ratio of cysteine $+0{\cdot}5H_2O_2$ to Co of $\pm$12 to 1 varies linearly with the Co concn. The technique of a method for the determination of K based on this fact is described, 10—40 mg.-% of K in 0·2 c.c. of solution being determined by colorimetric determination of the Co in the cobaltinitrite ppt. with an error of $\pm$1·9%. The at. ratio of K to Co in the cobaltinitrite ppt. obtained under the conditions specified is const. (1 : 0·6). A. L.

Microchemical contributions. VIII. L. Rosenthaler (Mikrochem., 1933, **13**, 83—84; cf. A., 1932, 1103).—(1) The uranyl acetate test for Na fails with $NaNO_3$. The type of ppt. observed is given also by KNO_3, but is not sp. for NO_3'. (2) "Hexamethyldiamino*iso*propanol di-iodide" (Iodisan) gives with $Cd^{\cdot\cdot}$ solutions a ppt. of clustered rod-like crystals. $Zn^{\cdot\cdot}$ (also $Fe^{\cdot\cdot\cdot}$) gives the reaction only on evaporation. J. S. A.

Determination of strontium as oxalate. K. N. Pochinok (J. Appl. Chem., Russia, 1932, **5**, 1078—1087).—Procedures are detailed for the determination of Sr alone and of Sr and Ca together. Ch. Abs.

Precipitation and separation of the cations of the third and fourth groups in qualitative analysis. C. PALMIERI (Officina, 1932, **5**, 136—141).—H_2S is removed, the solution oxidised, and Li, Ba, Sr, Mg, Ca, Fe, Al, Cr, Mn, Zn, Ni, and Cr are pptd. by addition of $(NH_4)_2HPO_4$ and aq. NH_3. The ppt. is dissolved in HCl, Ba, Sr, and Ca being pptd. with H_2SO_4 and EtOH. Otherwise the procedure is normal. CH. ABS.

Volumetric determination of barium. A. ROMEO (Annali Chim. Appl., 1933, **23**, 94).—The author acknowledges the priority of Garelli and Ravenna for the method described by him (this vol., 244). T. H. P.

Direct fusion method for determining the radium content of rocks. R. D. EVANS (Rev. Sci. Instr., 1933, [ii], **4**, 223—230).—Powdered rock specimens are boiled without flux in an evacuated graphite resistance furnace, the evolved gases being led to an ionisation chamber. Data for the % of radon removed from biotite granite as a function of temp., duration of heating, and fineness of grain indicate dependence on temp. only, radon removal being complete at 1800°. N. M. B.

Analysis of magnesium carbonates and hydrocarbonates. (MME.) L. WALTER-LEVY.—See B., 1933, 345.

Determination of lead in acid calcium phosphate. D. W. KENT-JONES and C. W. HERD.—See B., 1933, 384.

Rapid determination of copper in brass, aluminium alloys, etc. M. V. CHURAKOV.—See B., 1933, 431.

Determination of copper and lead in potable water. J. A. WIEGAND.—See B., 1933, 446.

Determination of indium and gallium with 8-hydroxyquinoline. W. GEILMANN and F. W. WRIGGE (Z. anorg. Chem., 1933, **212**, 32; cf. this vol., 43).—Priority is acknowledged. H. J. E.

Detection and determination of manganese in drinking water. L. W. WINKLER.—See B., 1933, 366.

Microchemical reactions of rhenium. E. KRONMANN and N. BERKMANN (Z. anorg. Chem., 1933, **211**, 277—280; cf. this vol., 138).—Characteristic cryst. ppts. are obtained by mixing a drop of dil. $KReO_4$ with conc. aq. HI and a sol. salt of K, Rb, Cs, Ag, Tl^I, or Hg-. The first three are the most suitable. MoO_3 and WO_3 should be absent. F. L. U.

Quantitative electrolytic reduction of iron. G. GALFAJAN and W. TARAJAN (Z. anal. Chem., 1933, **92**, 357—361; cf. this vol., 138).—Pb, Cu, and Zn may be used for cathodes. Hg and graphite proved unsuitable. Pr, Cu, Pb, or graphite may be used for the anode. J. S. A.

Potentiometric determination of iron and vanadium in ferrovanadium, and of iron and chromium in ferrochromium. P. DICKENS and G. THANHEISER.—See B., 1933, 430.

Volumetric determination of nitroprusside. O. TOMÍCEK and Z. REKTORIK (Coll. Czech. Chem. Comm., 1933, **5**, 129—135).—The ionic product of $Ag_2Fe[(CN)_5NO]$ is $7{\cdot}8\times10^{-13}$, *i.e.*, the solubility approximates to that of AgCl. $Fe[(CN)_5NO]''$ may be titrated potentiometrically with $AgNO_3$ in presence of Br′, I′, or CNS′; if Cl′ is present, it is pptd. simultaneously and quantitatively. Titration of $Fe[(CN)_5NO]''$ by Volhard's method is satisfactory, but with Mohr's method the end-point is less clear. H. F. G.

Application of 2 : 2′-dipyridyl to the determination of ferrous and total iron in natural waters. H. MÜLLER.—See B., 1933, 366.

Volumetric determination of cobalt. C. NIKOŁOW (Przemysł Chem., 1933, **17**, 46—48).—The solution of Co^{III} is made acid with AcOH, and Co is pptd. as $K_3Co(NO_2)_6$ by KNO_2. Pptn. is completed in about 18 hr., when the washed ppt. is dissolved in acid aq. $KMnO_4$, excess of KI added, and I is titrated with $Na_2S_2O_3$. The accuracy of this method compares favourably with that of other methods, and its simplicity and rapidity render it particularly useful for steel analysis, since it is not necessary to eliminate other metals. R. T.

Potentiometric determination of chromic anhydride in chromium-plating baths. N. I. CHLOPIN.—See B., 1933, 432.

Determination of chromium, manganese, and vanadium present together in special steels. W. HILTNER and C. MARWAN.—See B., 1933, 349.

Determination of tungsten by 8-hydroxyquinoline in a complex oxalate medium. A. JÍLEK and A. RYSANEK (Coll. Czech. Chem. Comm., 1933, **5**, 136—138).—Neither W^{VI} nor Sn^{IV} is pptd. by 8-hydroxyquinoline from a solution containing a mineral acid; from a neutral solution containing NH_4OAc the W is pptd., but the Sn^{IV} salt is hydrolysed and yields a ppt., whilst in presence of tartrate, only W^{VI} is pptd., but not quantitatively. Quant. pptn. of W^{VI} and separation from Sn^{IV} are obtained from $(NH_4)_2C_2O_4$ solution. In the method recommended, the solution (≯ 0·1 g. W^{VI}) is treated with 5 g. each of $H_2C_2O_4$ and NH_4OAc, neutralised with NH_3, and diluted to 150—200 c.c.; a 3—4-fold excess of the reagent is added to the solution at 60—80°, and after 1—2 hr. the ppt. is removed, washed first with a neutral solution containing $(NH_4)_2C_2O_4$, NH_4OAc, and the reagent, and then with H_2O, and ignited at 800°. Weighing after drying at 100—130° is not satisfactory. H. F. G.

Determination of the impurities in tin by means of the quartz spectrograph. C. S. HITCHEN.—See B., 1933, 351.

Tantalum and niobium cathodes *versus* platinum cathodes for electro-analysis. D. F. CALHANE and C. M. ALBER (Trans. Electrochem. Soc., 1933, **63**, 61—67).—In the electro-analytical determination of Cu a cathode of perforated Nb sheet gave results as accurate as the usual Pt gauze. A similar Ta cathode gave slightly low results, and inconsistent vals. were obtained if the cathode was not scratch-brushed before use. Both Nb and Ta cathodes are satisfactory in the determination of Zn, Ag, and Ni. Zn can be deposited directly on such cathodes. H. J. T. E.

Determination of niobium by 8-hydroxyquinoline. P. SUE (Compt. rend., 1933, **196**, 1022—1024).—About 40 mg. of Nb_2O_5 are brought into aq. solution (120—150 c.c.) as K niobate (in which case 0·2—0·5 g. of $H_2C_2O_4$ is added), or in aq. $H_2C_2O_4$, 5 c.c. of 10% aq. NH_4OAc are added, and the mixture is neutralised with aq. NH_3, heated at 70°, excess of 3% solution of 8-hydroxyquinoline in aq. EtOH (30 : 70) added, and the whole boiled for 30 min.; after 15 min. the cryst. ppt. is collected, washed, and dried for 2 hr. at 115°. Its composition is then $Nb_2O_5,5{\cdot}5C_9H_7ON,4H_2O$; the 8-hydroxyquinoline in the ppt. is determined volumetrically (cf. A., 1927, 847). The accuracy is about ±1%. Qualitatively, 0·01 mg. is detectable in 1 c.c. C. A. S.

Determination of palladium by means of ethylene. S. C. OGBURN, jun., and W. C. BRASTOW (J. Amer. Chem. Soc., 1933, **55**, 1307—1310).—C_2H_4 ppts. Pd quantitatively from aq. $PdCl_2$ and the separation from a mixture of the chlorides of the Pt metals is within 0·75% of theoretical. J. G. A. G.

Apparatus for recording the rate of cooling of a kata-thermometer. C. P. BLACK (J. Sci. Instr., 1933, **10**, 101—105).—A simple harmonic wave trace is made on an oscillating drum. C. W. G.

Crookes' radiometer and the intensity of radiation. G. RUSSELL (Phil. Mag., 1933, [vii], **15**, 997—1001).—The no. of r.p.m. of the vanes is proportional to the intensity of the radiation and to the cosine of the angle of its incidence, and inversely proportional to the square of the distance of the source. Infra-red radiation was most effective in producing rotation of the vanes. H. J. E.

Automatic apparatus assembly for thermal analysis. C. T. EDDY (Rev. Sci. Instr., 1933, [ii], **4**, 200—205).—Improved apparatus for determining thermal crit. temp., formation temp. of allotropic modifications, resistivity, and thermo-energy is described. N. M. B.

Elimination of error of parallax in thermometer readings. A. PERARD (Compt. rend., 1933, **196**, 1090—1091).—The thermometer is graduated on two diametrically opposite portions of the stem.

New model polarimeter. N. DEERR (Intern. Sugar J., 1933, **35**, 138—139).—The polarimeter moves in a vertical plane, so that it may be used in the "microscope position." An arrangement for protecting the polariser and analyser prisms against fungoid etching, whilst permitting easy access for cleaning, is described. In place of dichromate solution, a gelatin filter is recommended. The scales of the polarimeter are engraved in glass and mounted vertically for reading by transmitted light.

Chemical applications of the polarising microscope. N. H. HARTSHORNE (Chem. and Ind., 1933, 367).—Examples are given of the use of the polarising microscope for applying qual. tests to cryst. materials. D. R. D.

Optical activity. II. New type of polarimeter. C. H. JOHNSON (Trans. Faraday Soc., 1933, **29**, 618—625).—A cheap and easily constructed type of polarimeter, for the measurement of the variation of optical rotatory power with wave-length in the visible spectrum, is described. It is intended primarily for the examination of coloured optically active compounds undergoing racemisation in H_2O. Its range can probably be extended to the near ultra-violet. It is suitable for measuring small rotations and, although making use of white light, the application is in effect monochromatic. Rotatory power may be determined at any no. of wave-lengths. Although not so accurate as the ordinary polarimeter for the examination of transparent substances at sp. wave-lengths, it is remarkably trustworthy in regions of strong absorption. M. S. B.

Simple method of colour determination applied to fluorescence colours. E. HASCHEK and M. HAITINGER (Mikrochem., 1933, **13**, 55—82; cf. A., 1931, 928).—The light passing through red, green, and blue filters is compared photometrically with that reflected from a standard white body. The results are plotted on the triangular diagram of Konig and figures representing the colour-tone, saturation, and intensity of the fluorescence are derived. The method is illustrated by application to a no. of fluorescent compounds. J. S. A.

Laboratory modification of the Pulfrich refractometer. V. N. THATTE (J. Sci. Instr., 1933, **10**, 120—121).—By mounting two triangular glass cells on opposite sides of a rectangular glass block the use of a collimator can be avoided. C. W. G.

Sonic nephelometer. J. S. WILSON (J. Sci. Instr., 1933, **10**, 97—101).—The principle of the flicker photometer is applied to detect differences in the intensity of two beams of light which illuminate alternately a photo-electric cell after passing through the material under test. C. W. G.

Use of a simple Duboscq instrument for colorimetry, nephelometry, and the colorimetric determination of hydrogen-ion concentrations. J. GRANT and J. H. W. BOOTH (J. Sci. Instr., 1933, **10**, 106—110).—Side illumination is used for nephelometry. C. W. G.

Photographic method of measuring the relative intensities of spectral lines. K. B. THOMSON and O. S. DUFFENDACK (J. Opt. Soc. Amer., 1933, **23**, 101—104).—A step diaphragm is substituted for the slit of a spectrograph. N. M. B.

Multiple-prism glass spectrograph. D. H. RANK (J. Opt. Soc. Amer., 1933, **23**, 84—87).—A simple instrument is described giving resolving power and dispersion comparable with a 21-foot grating, with freedom from ghosts, and allowing many prism and lens combinations by simple adjustments. N. M. B.

Calibration of an infra-red spectrometer with a rock-salt prism. P. C. CROSS (Rev. Sci. Instr., 1933, [ii], **4**, 197—199).—Data for temp. correction of dispersion, and correction for prism angles between 59° and 61°, are tabulated. N. M. B.

Experiment bearing on Talbot's bands. A. C. G. BEACH (Proc. Physical Soc., 1933, **45**, 474—

481).—A form of spectroscopic diffraction pattern is discussed and is used to explain Talbot's bands. W. R. A.

Reference spectrum for spectrography in the visible spectrum. V. GAZZI (Annali Chim. Appl., 1933, **23**, 75—78).—As a reference spectrum, the Fe spark visible spectrum is open to the objections that the lines in some places are faint and in others are so close together that the blank spaces are small. Good results are obtained with a mixture prepared by heating $FeCl_3$ 5 g., $CuSO_4,5H_2O$ 1 g., $MnCl_2,4H_2O$ 0·1 g., $(NH_4)_6Mo_7O_{24},4H_2O$ 0·05 g., 0·5 c.c. of 0·1*N*-NaOH, and 10 c.c. of HNO_3 (*d* 1·11). T. H. P.

Photo-electric instrument for comparing the strengths of coloured solutions. E. W. H. SELWYN (J. Sci. Instr., 1933, **10**, 116—118).—A photo-electric cell and a wedge are used. C. W. G.

Apparatus for the measurement of high electrolytic conductivity. I. SORGATO (Annali Chim. Appl., 1933, **23**, 133—140).—This apparatus serves for measuring electrolytic resistances of the order 10^5 ohms with an accuracy of 0·1% and a sensitivity of 1 : 10,000. T. H. P.

Automatic apparatus for electrometric titration. H. VOGELS (Bull. Acad. roy. Belg., 1933, [v], **19**, 452—460).—Small equal vols. are run from an electrically operated burette, and potential measurements are made simultaneously. C. W. G.

New type of apparatus for experiments in secondary electron diffraction. W. T. SPROULL (Rev. Sci. Instr., 1933, [ii], **4**, 193—196).—Using a single W crystal, small-angle secondary beams can be analysed, and contact potential difficulties are eliminated. N. M. B.

Automatic Sprengel pump. R. CASTRO (Bull. Soc. d'Encour., 1933, **132**, 187—194).—Hg is raised to the upper reservoir by a filter pump and air-leak device. The upper reservoir feeds the Sprengel fall tube and also has an overflow tube through which excess Hg raised runs back to the collecting vessel. H. J. E.

Simple tapless microburette. K. SCHWARZ (Mikrochem., 1933, **13**, 1—5).—The liquid level is maintained by capillarity, liquid being expelled by pressure. Accuracy of 0·2% may be attained on a total vol. of a few cu. mm. J. S. A.

Automatic glass burette jet. D. R. PARANJPE and D. V. CHANDERKAR (J. Indian Chem. Soc., 1933, **10**, 33—34). A. S. C. L.

Fractionation column. J. ROSIN (Chem. Fabr., 1933, **6**, 174—175).—Ordinary columns are unsatisfactory in that they are effective only over a limited temp. range. The condenser described has an outer jacket in which a small quantity of a suitable liquid is placed; around the top of the jacket is a second jacket through which cold H_2O passes. The liquid should be such that it is kept at its b.p. by the vapour entering the condenser, and that the whole of the heavier fraction condenses; MeOH is suitable for the fractionation of EtOH–H_2O mixtures. Typical rectification curves for aq. EtOH, light petroleum, and di- and tri-chloroethylene mixtures, obtained with the new and with ordinary columns, are given. A special type of apparatus for use with liquids of b.p. >100° is described. H. F. G.

Measurement of small gas velocities. A. BAADER (Chem. Fabr., 1933, **6**, 171).—The principle of the apparatus described is that the stream of gas bubbles up through, and displaces, H_2O contained in a graduated tube; the time required for the H_2O level to fall a known distance is noted. The result is accurate to within 0·003 c.c. per sec. at moderate velocities. The apparatus does not require special calibration. H. F. G.

Simple device for regulating gas flow. F. G. GREGORY (Ann. Bot., 1933, **47**, 427—428).

Universal gas regulator, especially suited to the regulation of vacuum. V. JELÍNEK (Mitt. Kohlenforchungsinst. Prag, 1932, No. 3, 137—144).—The device consists of two chambers, an outer pressure chamber and an inner lenticular chamber, the sides of which are equipped with one or two flexible membranes. The two chambers are connected by a tube, capable of being closed by a valve. The inner chamber is connected between the pump and the experimental vessel. In use the two chambers are placed in communication and evacuation is commenced. On reaching the desired vac. the valve is closed. If now the pressure in the inner chamber falls, the membranes are forced together and the experimental vessel is isolated. The apparatus is unaffected by changes in barometric pressure. It can be adapted to regulate pressures > atm. or incorporated in a thermostat for controlling the temp. of gas-heated apparatus. A. H. E.

Wide-range variable gas flow-meter. B. W. BRADFORD (Chem. and Ind., 1933, 363—364).—With the flow-meter described, the rate of flow may be measured or kept const. within 1% over the range 100 c.c. to 10 litres per min. D. R. D.

Universal ebullioscope and its applications. W. SWIENTOSŁAWSKI (Rocz. Chem., 1933, **13**, 176—180).—A universal ebullioscope is described. R. T.

Beaker for quantitative analysis. G. P. BAXTER (J. Amer. Chem. Soc., 1933, **55**, 1462).—The beaker has two lips, one for pouring and the other for retaining the stirring rod. J. G. A. G.

Continuous extractor. R. J. BLOCK (J. Biol. Chem., 1933, **100**, 537—541).—The apparatus has an aq. layer of high *d*, a middle layer of H_2O-immiscible solvent, and an aq. layer of low *d*, a stirrer having blades in each layer being introduced. The material to be extracted is placed in the bottom and collects in the top layer. A. L.

Balance for the rapid determination of surface tension. H. V. HUGHES (Trans. Inst. Rubber Ind., 1933, **8**, 473—477).—A simple method applicable to liquids such as rubber latex employs a modified laboratory balance, one arm of which carries a Pt strip and the other supports a vertical metal rod which is partly immersed in paraffin. Small variations in load necessary to separate the Pt strip from the surface of the latex or other liquid are obtained by the movement, in the paraffin, of another uniform cylinder suspended in such a way that its movement

can be measured accurately. The results quoted include those for latex over a range of concns.
D. F. T.

Viscosity as a constant of materials and its measurement. L. UBBELOHDE (Chem. Fabr., 1933, **6**, 165—167).—Detailed criticisms of a paper by Fischer (this vol., 45). F. L. U.

Diameter of tube in the falling-sphere viscosimeter. O. MERZ (Farbe u. Lack, 1933, 201—202).—Experimental data are tabulated which show that the influence of the glass walls on the rate of fall of the sphere through low-η cellulose nitrate solutions can be neglected with tubes having much smaller diam. than that of the standardised apparatus. A smaler quantity of material can therefore be used. The dimensions of the English, American, and German instruments are compared. S. M.

Alarm clock operating at short intervals in a laboratory. M. HASSELBLATT (Chem.-Ztg., 1933, 57, 195).—The clock is used when readings have to be taken at regular intervals. C. I.

Universal dilatometer. R. HOLCOMB (Science, 1933, 77, 261—263).—An apparatus for measuring the change in vol. which occurs when liquids are mixed is described. L. S. T.

Vacuum evaporating plant for laboratory use. H. RISTRICK and G. SMITH (Biochem. J., 1933, **27**, 96—98).—The apparatus, consisting of six 5-litre flasks with a common central condenser and capable of distilling 2·5—4 litres per hr., is described.
F. O. H.

Vapur pressure of vacuum cements. R. M. ZABEL (Rev. Sci. Instr., 1933, [ii], **4**, 233—234).—Ion currens as a measure of pressure for 28 cements at a const. evacuation speed are tabulated. N. M. B

Molcular refraction in dilute solutions. I. Differntial buoyancy method for precision measurements of density. W. GEFFCKEN, C. BECKMNN, and A. KRUIS (Z. physikal. Chem., 1933, B, **20**, 398—419)—By a modification of Lamb and Lee's method (A., 1913, ii, 1026) the d of solutions relative to the solvent at concns. up to $1{\cdot}5N$ may be determined with a precision ranging from about $0{\cdot}0_52$ for the highest concns. to about $0{\cdot}0_62$ below $0{\cdot}1N$. Measurements with aq. NaCl and Na_2CO_3 solutions are described. R. C.

Simple method for accurate determinations of vapour pressures of solutions. D. A. SINCLAIR (J. Physical Chem., 1933, **37**, 495—504).—Bousfield's isopiestic method (A., 1923, ii, 460) has been modified so that equilibrium is reached within a few days, it being found that the time required in the original method was much longer than supposed by Bousfield. Data have been obtained for aq. sucrose, NaCl, and p-$C_6H_4Me{\cdot}SO_3K$, using aq. KCl as standard. All the curves show an irregularity at $0{\cdot}8$—$1{\cdot}3M$.
D. R. D.

Preparation of thin, free metallic membranes. C. MULLER (Physikal. Z., 1933, **34**, 340—341).—A method for preparing very thin membranes of Ni and Fe is given. A. J. M.

Apparatus for filtration at high temperatures. A. STADLER (Mitt. Kohlenforschungsinst. Prag, 1931, No. 2, 80—81).—The funnel is supported in an Al block which when heated electrically or by a gas burner serves as a heat reservoir. Even inflammable liquids may be filtered using a block pre-heated by a flame. E. S.

Apparatus for filtration at low temperatures, particularly for the determination of paraffin. B. G. ŠIMEK (Mitt. Kohlenforschungsinst. Prag, 1931, No. 2, 74—79).—Al blocks, shaped to hold filters etc., are cooled with liquid air and function as cold-accumulators. E. S.

Phosphoric anhydride as drying agent. H. W. THOMPSON (Chem. and Ind., 1933, 308).—A reply to criticism. E. S. H.

History of microchemistry. I. H. HARMS (Apoth.-Ztg., 1932, **46**, 1454—1458; **47**, 1274—1275, 1293—1294, 1307—1310, 1324—1325; Chem. Zentr., 1933, i, 1).

Geochemistry.

Ozone in the atmospheres of planets. D. J. EROPKI (Naturwiss., 1933, **21**, 221—222).—The quantit of O_3 in the atm. of the outer planets has been ca. In the atm. of Venus there is less O_3 than in the erth's atm., whilst in that of Neptune there is approx. 100 times as much as in air. That there is a high concn. of O_3 in the higher atm. of the planets is shown by comparison of wave-lengths of sp. bands in the spectra of the large planets with those of the weak O_3 absorption bands in the visible spectrum of air. There is no qual. difference between the atm. gases of the earth and other planets. A. J. M.

Ozone in the atmosphere of planets. R. WILDT (aturwiss., 1933, **21**, 286).—The contention of Eropki (preceding abstract) that there is no qual. difference between the gases of the earth's atm. and those of the atms. of other planets is disputed, reference to evidence being given. A. J. M.

Helium content of natural gas. E. VON ANGERER and H. FUNK (Z. physikal. Chem., 1933, B, **20**, 368—374).—The He content is determined by removing the other constituents of the gas with activated C, the purity of the residue being established by exciting it to spectral emission by electron bombardment. The gas from the Dürkheim spring is the only German natural gas which is comparable in He content with the He-bearing natural gases of North America.
R. C.

Iodine content of the atmosphere in Holland. J. F. REITH (Biochem. Z., 1933, **260**, 115—120; cf. A., 1930, 1628).—The I content (I) of the atm. is measured by determining (I) in rain. Although the first 0·2—0·3 mm. of rain following a dry period washes out most of the I from the atm., I continually returns to the atm., so that the rain is never free from I. No support is given to the view that the atm. near the sea contains more I than does the inland atm.,

except when the wind blows from the sea. The atm. in north Groningen (II) contains twice as much I as does that in the Rhine–Maas delta (III), probably because at (II) there is a greater evolution of I from the ground (which is rich in it) than at (III). W. McC.

Petroliferous waters. Means of fixation of hydrocarbons. D. A. Chahnazaroff (Ann. Guebhard-Séverine, 1932, **8**, 289—292).—Possible mechanisms whereby petroleum and H_2O may have been produced simultaneously are discussed. J. W. S.

Mud from Lake Dapkhur, Russia. V. I. Nikolaev, A. M. Solovov, and M. A. Frishmut (J. Appl. Chem., Russia, 1932, **5**, 809—814). Ch. Abs.

Radioactivity of well waters from Dumfries. J. Muir (J. Roy. Tech. Coll., 1933, **3**, 7—20).—H_2O from a well 450 ft. deep in a bed of red sandstone covered with 328 ft. of agglomerate igneous rock contained 60×10^{-12} curie of RaEm, whilst that from a well only 161 ft. deep in the igneous rock contained 150×10^{-12} curie. Neither H_2O contained permanent radioactivity. A. R. P.

Thermal history of the earth. A. Holmes (J. Washington Acad. Sci., 1933, 169—195).—A lecture. C. W. G.

Chemical composition of the earth. C. J. van Nieuwenburg (Chem. Weekblad, 1933, **30**, 278—280).—A lecture, dealing particularly with the frequency of occurrence of the elements as a function of the at. no. H. F. G.

Mineral deposits from Monte Rosso di Verra (Monte Rosa group). II. T. Carpanese (Atti R. Accad. Lincei, 1933, [vi], **17**, 192—196; cf. this vol., 482).—Mineralogical data for the titaniferous olivine and amphibolite deposits of this group are given. O. J. W.

Quartz-kyanite-rocks from Shetland Islands and their bearing on metamorphic differentiation. H. H. Read (Min. Mag., 1933, **23**, 317—328).—Quartz-kyanite-rocks occur as veins in kyanite-chloritoid-schist on the island of Unst. The latter rock is poorer in SiO_2 and relatively richer in Al_2O_3 than the surrounding argillaceous rocks of the Saxa Vord Group. It is suggested that here, as also in other types of quartz veins, there has been a segregation of SiO_2 in the veins in consequence of the metamorphism. L. J. S.

Stichtite from Shetland Islands. H. H. Read and B. E. Dixon (Min. Mag., 1933, **23**, 309—316).—Rose-pink stichtite, d 2·19, α' 1·543, γ 1·559, occurs as an alteration product of chromite in a serpentine-rock at Cunningsburgh. Deducting large amounts of intimately intermixed chromite and serpentine, analysis gave Cr_2O_3 17·75, Fe_2O_3 3·50, MgO 39·49, CO_2 6·83, H_2O 32·43. A discussion of this and previous analyses leads to the general formula $2(Cr,Fe)(OH)_3,5Mg(OH)_2,MgCO_3,Mg[CO_3,(OH)_2],4H_2O$. L. J. S.

Lapis lazuli and spinel in crystalline limestone in Afghanistan. J. Barthoux (Compt. rend., 1933, **196**, 1131—1134).—The lapis lazuli of Badakshan, containing fine crystals of lazurite the colour of which is sometimes intensified by the presence of pyrites, occurs in cryst. limestone, associated with phlogopite, humite, and forsterite. Spinel with almandine and rose corundum was found at Siz on the Oxus and at Jagdalik in cryst. limestone associated with humite, chondrodite, phlogopite, fuchsite, rutile, sphene, hæmatite, and pyrite. Diopside and pargasite occur in the limestone, the last-named with phlogopite in emerald-green crystals containing: SiO_2 53·08, Al_2O_3 5·04, Cr_2O_3 0·27, FeO 0·30, MgO 23·86, CaO 13·36, Na_2O 1·91, K_2O 0·69, TiO_2 0·78, MnO 0·07, $H_2O(+)$ 0·24, $H_2O(-)$ 0·22, total 99·62; d 3·028. C. A. S.

Zeolites. IV. Ashcroftine (kalithomsonite of S. G. Gordon). M. H. Hey and F. A. Bannister (Min. Mag., 1933, **23**, 305—308).—X-Ray and optical determinations made on the "kalithomsonite" of Gordon (A., 1924, ii, 868) show that it is not a K-bearing variety of thomsonite. It is tetragonal with a very large unit cell, a 34·04, c 17·49 Å., containing $40[NaK(Ca,Mg,Mn)Al_4Si_5O_{18},8H_2O]$; d 2·61. The refractive indices, n_ϵ 1·545, n_ω 1·536, are higher than those of artificial K-thomsonite and the optical orientation is different. Being a distinct species, it is named ashcroftine. L. J. S.

Origin of gold at Kivu. J. de la Vallée Poussin (Bull. Acad. roy. Belg., 1933, [v], **19**, 461—466).—The origin is considered to be granitic. C. W. G.

Trilobites and palæozoic phosphatic deposits. L. Cayeux (Compt. rend., 1933, **196**, 1179—1182; cf. A., 1932, 715).—Analyses of nine different species of trilobite show that seven contain only 0·077—0·353, average 0·138%, of P_2O_5, and two 1·108 and 2·162%, amounts insufficient to account for palæozoic phosphatic deposits, which must be due to some hitherto unrecognised organism. C. A. S.

Orientation of arsenolite and senarmontite on mica. R. Hocart (Compt. rend., 1933, **196**, 1234—1235).—When arsenolite or senarmonite is sublimed on to mica it is deposited in octahedra, respectively isotropic and birefringent, oriented so that similar dimensions of the crystal meshes coincide, *e.g.*, As_4O_6 13·54, Sb_4O_6 13·64, mica 13·66 Å. (cf. this vol., 214). C. A. S.

Composition of the magnetite contained in the basalt of Aci Trezza (Catania). F. Scafile (Annali Chim. Appl., 1933, **23**, 78—84).—This analcitic basalt contains 5% of titaniferous magnetite (d 4·45), in which 6 mols. of Fe_3O_4 are present per 5 mols. of $FeTiO_3$. The 8% of impurities include Mn, presumably as Mn_3O_4 (0·5%). T. H. P.

Geochemistry of noble metals. V. M. Goldschmidt and C. Peters (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1932, 377—401; Chem. Zentr., 1933, i, 38—39).—The concn. of Os, Ir, and Pt in rocks is too small to permit the use of a spectrographic method on the original material. The limits using an arc spectrum (admixture with SiO_2 or Al_2O_3) are: Ag 0·0001; Au, Ru, Rh, Pd 0·001; Pt 0·005; Ir, Os 0·01%. A concn. method employing Pb was therefore used; 0·5 g. of original material could then be employed and the following quantities ($\times 10^{-6}$ g.)

could be detected: Ag < 0·1; Rh, Pd, Pt, Au 0·1; Ru 0·25; Os 2·5, Ir 0·5. Fe meteorites were examined; all contained Pt metals and Au. Ni-rich Fe meteorites are frequently particularly rich in noble metals. Basaltic Fe, chromite, Mo- and Sn-minerals were examined. Pt metals and Au are: siderophile> chalkophile>lithophile; Ag is: chalkophile>siderophile. The distribution of noble metals in arsenides, antimonides, and sulphides, and their occurrence in Co and Ni minerals containing As and Sb, have been studied. A. A. E.

Geochemistry of beryllium. V. M. Goldschmidt and C. Peters (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1932, 360—376; Chem. Zentr., 1933, i, 37—38).—Probably the quantities of Li and Be in accessible rocks are ≮ the average vals. for the whole earth. Spectrographic determinations show Be to be markedly conc. in granites and nepheline syenites (average 0·001, 0·01% BeO, respectively). Be was not found in olivine and olivine rocks, but is present in alkali felspar, nepheline, pyroxene, amphibole, and mica. The average BeO content of rocks is determined as 0·0005%, and the average val. for meteorites is about the same; hence the Be content is held to be about 0·0002% and ≯0·0004%. A. A. E.

Altered pyrophysolite. I. D. Wallerius (Geol. For. Stockholm Forh., 1932, **54**, 279—280; Chem. Zentr., 1933, i, 200—201).—The purple material, *d* 2·76, contained no F, and consisted chiefly of SiO_2 and Al_2O_3 with a trace of Mn. A. A. E.

German ore deposits; rare elements present or suspected. H. Schneiderhohn (Metallwirt., 1932, **11**, 617—622; Chem. Zentr., 1933, i, 201).—Necessary investigations are discussed. A. A. E.

Non-transparent minerals in the lavas of Mt. Elgon, British E. Africa. O. H. Odman (Geol. For. Stockholm Forh., 1932, **54**, 285—304; Chem. Zentr., 1933, i, 200).—Magnetite is accompanied by perowskite, spinel, valleriite, pyrrhotine, chalcocite, covelline, bornite, chalcopyrite, proustite, and unidentified minerals, maghemite, hæmatite, ilmenite, ferric hydroxide, and pyrite. A. A. E.

Determination of chlorine and fluorine in Etna lava. A. Giammona (Annali Chim. Appl., 1933, **23**, 120—124).—A method is described. Most of the Cl in the lava is not ionic, but forms part of complex salts. The F is present partly as insol. fluoride and partly as complex ion. T. H. P.

Metamorphism of quartzite of Sarrabus. A. Cavinato (Atti R. Accad. Lincei, 1933, [vi], **17**, 236—241).—The mineral is described and its structure is discussed in some detail. H. F. G.

Artificial transformation of felspar into kaolin. R. Schwarz (Naturwiss., 1933, **21**, 252).—The theory that kaolin is formed by hydrolysis of felspar has been tested experimentally by treatment of felspar with dil. mineral acid in a pressure bomb at 300° for 250 hr., when kaolin was produced. Leucite can be converted into kaolin by a similar process. A. J. M.

Siwaliks and recent volcanic rocks in Afghanistan. J. Barthoux (Compt. rend., 1933, **196**, 944—947).—Several occurrences are described, and the following analysis of a dacitoid from Zardalu consisting of phenocrysts of oligoclase-andesine, albite, pericline, biotite, and hornblende in a vitreous ground mass is given: SiO_2 62·74, Al_2O_3 16·40, Fe_2O_3 1·60, FeO 2·67, MgO 1·90, CaO 4·82, Na_2O 4·53, K_2O 2·59, TiO_2 0·78, P_2O_5 0·15, MnO 0·10, H_2O 2·08, total 100·36. C. A. S.

Plasticity of rock-salt in water and in the dry state. L. Piatti (Nuovo Cim., 1932, **9**, 180—188; Chem. Zentr., 1932, ii, 3665—3666).

Habit and paragenesis of fluorspar. K. Obenauer (Neues Jahrb. Min., 1932, **A**, **66**, Bl-Bd., 89—119; Chem. Zentr., 1932, ii, 3693).

Salt deposit on Chelekeni Island. K. P. Kalitzki (Neft. Choz., 1931, **20**, 341—354). Ch. Abs.

New meteoric iron from Kyancutta, South Australia. L. J. Spencer [with M. H. Hey] (Min. Mag., 1933, **23**, 329—333).—A mass of 72 lb., ploughed up in 1932, has the structure of a medium octahedrite and contains Fe 90·57, Ni 7·30, Co 0·39, Cu trace, S 1·12, P nil, Cl trace, C 0·13, insol. 0·22=99·73, *d* 7·735. The spellings, Widmanstätten, Widmannstädten, etc. (14 variants are listed), commonly applied to the lamellar octahedral structure of meteoric irons, are all incorrect; the etched figures were first observed in 1808 by A. J. F. X. Beckh von Widmanstetter (1754—1849). L. J. S.

[Coal deposits in the Barzas district.] V. A. Orestov (Khim. Tverd. Topl., 1931, **2**, No. 11—12, 121—127). Ch. Abs.

Revised classification of soil types. E. B. Davies (New Zealand J. Sci. Tech., 1933, **14**, 255—256).—A modification is suggested of Grimmett's scheme of soil nomenclature (*ibid.*, 1926, **8**, 123) based on mechanical analyses. A. G. P.

Soil processes in volcanic ash-beds. Ash-beds of northern King-country and their secondary alumina minerals. N. H. Taylor (New Zealand J. Sci. Tech., 1933, **14**, 193—202).—The occurrence in these soils of minerals rich in Al is explained by a series of soil-forming processes resembling those taking place at the present time. Rhyolitic ash-beds are altered by podsolisation and andesitic beds by laterisation. When an acid humus layer is present, podsolic changes are superimposed on lateritic ones. A. G. P.

Deluvial soil processes. J. Żółciński (J. Landw., 1933, **81**, 45—66).—Analytical data and profile characteristics of deluvial soils are recorded and the manner of their formation is discussed. A. G. P.

Soil formation in southern Nigeria (the "Ilepa" profile). H. C. Doyne and W. A. Watson (J. Agric. Sci., 1933, **23**, 208—215).—Profile characteristics of these soils formed over acid igneous rocks subjected to alternating periods of percolation and surface evaporation are recorded. The mechanism of the formation of the soil and of the concretion layer is discussed. A. G. P.

Soil structure. II. P. Ehrenberg (Z. Pflanz. Düng., 1933, **29**, **A**, 25—37).—Current views are discussed. A. G. P.

Humus in [hollow] pollarded willows. P. HAGENE (Compt. rend., 1933, **196**, 1333—1335).—The humus accumulating in hollow pollarded willows, (*a*) old trees growing near water, (*b*) younger trees growing between a main road and large river, consists largely (37—77%) of particles < 2 mm. diam., losing on calcination (*a*) 71·38—94·2, (*b*) 44·1—47·3%; p_H 5·5—7·4; sol. in H_2O 6·5—8·48%; coeff. of hygroscopicity after drying in air (*a*) 34—39, (*b*) 20·3—24·8%. C. A. S.

Organic Chemistry.

Higher aliphatic compounds. III. Preparation of paraffins. (MISS) P. C. CAREY and J. C. SMITH (J.C.S., 1933, 346—347; cf. A., 1932, 468).—Hexadecyl (I) and octadecyl iodide with Zn dust and boiling AcOH give hexa- and octa-decane, trimorphous, m.p. 27·6° (transparent form), 28·02° (opaque form), and 29·7±0·1° (clearing of melt), respectively. Hexadecyl bromide is partly and the chloride entirely unaffected by this treatment; alternatively (I) is reduced by Zn–Cu in hot EtOH or is hydrogenated (Pd–$CaCO_3$) in PrOH. Hexadecyl formate, dimorphous, m.p. 22·7° (transparent) and 25° (26° in a capillary) (opaque), has b.p. 200°/20 mm., or 310° (slight decomp.)/760 mm. with or without addition of Fe or C. (I) is largely unaffected by hydrogenation (Pd–$BaSO_4$) in $C_6H_4Me_2$. R. S. C.

Chlorination of paraffins. II. E. WERTYPOROCH [with W. KWASNIEWSKI] (Ber., 1933, **66**, [*B*], 732—739; cf. A., 1932, 258).—Chlorination of *n*- (I) and *iso*-C_5H_{12} (II), *n*-C_6H_{14} (III), *n*-C_7H_{16} (IV), *cyclo*hexane (V), and petroleum fractions, b.p. 30—50° (VI), 50—60° (VII), and 60—70° (VIII) has been studied. Chlorination is not accelerated by $SbCl_5$, which is readily pptd. as an unstable double compound, the portion remaining in solution appearing to act restrictively. I has little action with (I) or (II), but increases in reaction through (III) and (V) to (IV). In absence of catalyst, moist Cl_2 is very advantageous for the production of Cl-compounds, its effect decreasing in the sequence (I) and (II), (III), (V), (IV). Tho ratio of mono- to poly-chloro is somewhat smaller with dry than with moist Cl_2. (I) yields mainly α- and δ-chloro-β-methylbutane and a little α-chloropentane. $SbCl_5$ yields much dichloride. Light scarcely accelerates the action of moist or dry Cl_2. In simultaneous presence of light and $SbCl_5$, the ratio Cl_1- : Cl_2-compounds is shifted from 1 : 1 to 9—11 : 1. (II) gives all four *iso*amyl chlorides. (III) affords mainly β- with little α-chlorohexane. Only α-chloroheptane is obtained from (III) with moist or dry Cl_2 or in presence of I or $SbCl_5$. Chlorination of (VI), (VII), and (VIII) gives equally good yields of Cl_1-derivatives with moist Cl_2 or in presence of $SbCl_5$ and sunlight. Moist has more action than dry Cl_2 on (V), but yields a greater proportion of dichlorides. H. W.

Addition to doubly-linked groups. A. BURAWOY (Z. physikal. Chem., 1933, **164**, 1—19).—In polymerisation, Br addition, and other reactions addition apparently occurs directly to the unsaturated atoms of the biradical mols. (cf. A., 1931, 144, 1052). The more saturated are these atoms, the more biradical mols. are present at equilibrium, and the smaller is the rate of addition. A mechanism is suggested for *trans* addition. The rate of addition of ketens and some other compounds increases with their polarity, suggesting that the first step is the relatively slow formation of a mol. compound, which rapidly changes into the normal additive product. In additive reactions yielding heteropolar compounds the decisive factor is the transfer of electrons. The energy content of biradical mols. is calc. to be 2·5—9·0 kg.-cal. > that of the mols. as ordinarily formulated. Reaction with biradical mols. probably requires activation. R. C.

Acetylene polymerides and their derivatives. VIII. α-Alkyl-β-vinylacetylenes. IX. New synthetic rubbers. IV. β-Chloro-α-alkyl-$\Delta^{\alpha\gamma}$-butadienes and their polymerides. R. A. JACOBSON and W. H. CAROTHERS. **X. Chlorination of the hydrochlorides of vinylacetylene.** W. H. CAROTHERS and G. J. BERCHET (J. Amer. Chem. Soc., 1933, **55**, 1622—1624, 1624—1627, 1628—1631).—VIII. Successive treatment of CH_2:CH·C:CH with $NaNH_2$ (in liquid NH_3) and Me_2SO_4 gives *α-methyl-β-vinylacetylene*, b.p. 59·2°/760 mm. *α-Ethyl-β-vinylacetylene*, b.p. 84·5—85·3°/758 mm., is similarly prepared using Et_2SO_4 or *p*-C_6H_4Me·SO_3Et (in Bu_2O), whilst α-n-*butyl*-, b.p. 62—63°/61 mm., and α-n-*heptyl*-, b.p. 74·5°/9 mm., -β-*vinylacetylenes* are obtained using BuBr and heptyl bromide, respectively. These hydrocarbons polymerise slowly to yellow syrups.

IX. *γ-Chloro-*$\Delta^{\alpha\gamma}$*-pentadiene*, b.p. 99·5—101·5°/759 mm., *-hexadiene*, b.p. 68·2—69°/117 mm., *-octadiene*, b.p. 64—65°/18 mm., and *-undecadiene*, b.p. 74—76°/1 mm., are prepared from the above CH_2:CH·C:C·Alk (1 mol.), conc. HCl (approx. 2·2 mols.), CuCl (0·25 mol.), and NH_4Cl (0·2 mol.). Condensation of these with α-naphthaquinone and subsequent oxidation with air in EtOH–NaOH gives 2-*chloro*-1-*methyl*-, m.p. 181°, -1-*ethyl*-, m.p. 151—152°, -1-n-*butyl*-, m.p. 129—130°, and -1-n-*heptyl*-, m.p. 112·5—113·5°, *-anthraquinone*, respectively. In the last case, the intermediate 2-*chloro*-1-*heptyl*-1 : 4 : 11 : 12-*tetrahydroanthraquinone*, m.p. 96—98°, is isolated. The above Cl-derivatives polymerise more slowly than chloroprene (B., 1932, 156) to rubber-like substances of inferior quality to polychloroprene.

X. δ-Chloro-$\Delta^{\alpha\beta}$-butadiene (I) (A., 1932, 1231) and Cl_2 (1 mol.) under various conditions give *βγδ-trichloro-*Δ^{α}*-butene* (II), b.p. 40—41°/10 mm. [oxidation (aq. $KMnO_4$) product, CH_2Cl·$CHCl$·CO_2H], and *αγδ-trichloro-*Δ^{β}*-butene* (III), b.p. 64—65°/10 mm. (oxidation product, CH_2Cl·CO_2H); (II) predominates at −70° to −60°, whilst (III) is the major product at 40—50°. Saturation of (I) with Cl_2 affords *αβγγδ-pentachlorobutane* (IV), b.p. 85°/10 mm. In all the above experiments about 20% of undistillable material is produced. β-Chloro-$\Delta^{\alpha\gamma}$-butadiene (1 mol.) and Cl_2 (1 mol.) give about 50% of undistillable material and a mixture of products [probably containing 25—30% of (III)].

βδ-Dichloro-Δ^{β}-butene and Cl_2 afford (II), (IV), and *αβγγ-tetrachlorobutane* (V), b.p. 90°/32 mm., 55—57°/10 mm.; (V) is the major product at 40—60°, whilst (II) or (IV) (according to the amount of Cl_2 used) predominates at —70° to —60°. H. B.

Reactions of substituted divinylacetylenes. A. T. Blomquist and C. S. Marvel (J. Amer. Chem. Soc., 1933, **55**, 1655—1662).—Stereoisomeric ζι-*dihydroxy-ζι-dimethyl-*Δ^{η}*-tetradecinenes*, b.p. 144—146°/2 mm. (I) and m.p. 86—87° (II), are prepared and dehydrated by Dupont's method (A., 1914, i, 134) to ζι-*dimethyltetradeca-*$\Delta^{\epsilon\iota}$*-diene-*Δ^{η}*-inene* (III), b.p. 95—98°/0·5 mm. (ozonolysis products, $AcCO_2H$ and *n*-valeric acid), which is reduced (H_2, PtO_2, Pt-black, AcOH) to ζι-*dimethyltetradecane*, b.p. 103—104°/1·5 mm. δη-Di-*n*-propyldeca-$\Delta^{\gamma\eta}$-diene-Δ^{ϵ}-inene (IV) (Dupont, *loc. cit.*) is similarly reduced to δη-di-*n*-propyldecane, b.p. 92—93°/1·5 mm. (cf. *loc. cit.*). (III) and (IV) are more stable to air than divinylacetylene; they add Br readily (but HBr is evolved even at 0°) and give amorphous adducts with maleic anhydride in xylene. (IV), conc. H_2SO_4, and AcOH at about 25° afford (probably) 4 : 5-*diethyl*-3 : 6-*di*-n-*propyl*-Δ^3-cyclo*hexenone*, b.p. 107—110°/0·7 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 97—98°), oxidised (O_3) to $PrCO_2H$, (probably) *γ-keto*-β-*ethyl*-α-n-*propylhexoic acid*, b.p. 110—112°/0·6—0·7 mm. (*semicarbazone*, m.p. 194—195°), and a neutral *compound*, b.p. 82—88°/0·1 mm., and reduced (as above) to a *hydrocarbon*, $C_{16}H_{32}$, b.p. 97—100°/1·5 mm. (III) is similarly converted into an unsaturated *ketone*, $C_{16}H_{28}O$, b.p. 128—131°/1·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 104—105°), reduced to a *hydrocarbon*, $C_{16}H_{32}$, b.p. 101—103°/1·5 mm. δη-Dihydroxy-δr-di-*n*-propyl-Δ^{ϵ}-decinene (V) and aq. $HgSO_4$ at 100° give 3-*keto*-2 : 2 : 5 : 5-*tetra*-n-*propyltetrahydrofuran*, b.p. 96—100°/0·9 mm., and not the cyclic acetylene described by Dupont (*loc. cit.*). (V) is reduced (H_2, PtO_2, EtOH) to δη-*dihydroxy-*δη-*di*-n-*propyl-*Δ^{ϵ}-*decene*, b.p. 136—138°/1·5 mm., which is dehydrated to 2 : 2 : 5 : 5-*tetra*-n-*propyl*-2 : 5-*dihydrofuran*, b.p. 92—94°/1·5 mm. 3-*Keto*-2 : 5-*dimethyl*-2 : 5-*di*-n-*amyltetrahydrofuran*, b.p. 112—113°/1 mm., is prepared from (I). ζι-*Dihydroxy-ζι-dimethyl-*Δ^{η}*-tetradecenes*, b.p. 128—130°/0·4 mm. and 149—151°/2 mm., are obtained by similar reduction of (I) and (II), respectively; both forms are dehydrated to 2 : 5-*dimethyl*-2 : 5-*di*-n-*amyl*-2 : 5-*dihydrofuran*, b.p. 100—101°/3 mm. H. B.

Hexafluoroethane. F. Swarts (Bull. Soc. chim. Belg., 1933, **42**, 114—118; cf. A., 1931, 601).—C_2F_6 has m.p. —106·3° and —94° (dimorphous). Vals. of *d* of the gaseous and liquid phases at —78° to 18·5° are represented graphically. When heated by a Pt spiral at 700° in presence of H_2O in a glass vessel, SiF_4, CO, CO_2, and (probably) CF_4 are formed. H. A. P.

Selenium dioxide, a new oxidising agent. III. Its reaction with alcohols and esters. S. Astin, A. C. C. Newman, and H. L. Riley (J.C.S., 1933, 391—394; cf. A., 1932, 1108).—In the following reactions the nature of the product depends largely on the temp., since the product is often sensitive to SeO_2. EtOH at 150—230° gives glyoxal (yield under optimum conditions 41%), Et_2SeO_3, and a *substance*, $(CH_2)_n$, m.p. 52°, according to the conditions. $Pr^{\alpha}OH$ gives $Pr^{\alpha}_2SeO_3$, b.p. 132—133°/25 mm., a *substance*, $(CH_2)_n$ (*n*=approx. 30), m.p. 60°, a trace of AcCHO, and polymerised products. $Bu^{\alpha}OH$ gives $Bu^{\alpha}_2SeO_3$, unstable, and a *hydrocarbon*. $CH_2Ph{\cdot}OH$ gives quantitatively PhCHO. Et_2 malonate at 120—130° gives Et_2 mesoxalate (32·3% yield; best known method of prep.). Et_2 succinate with an excess of SeO_2 at 170° gives Et_2 and Et H fumarate. Se is produced either in a grey "metallic" or a vitreous form; the latter is usually contaminated with org. matter and often explodes in O_2. SeO_2 is best recovered by HNO_3. R. S. C.

Preparation of the optically active forms of secondary butyl alcohol. F. Viditz (Biochem. Z., 1933, **259**, 294—300).—The method of Pickard and Kenyon (J.C.S., 1923, **123**, 1) is considerably simplified. The conditions for the separation of brucine (+) *sec.*-Bu phthalate, α_D^{20} +39·0°, are described and the existence of a second form is detected. Isolation of the (—)-isomeride is not so complete, the best sample having α^{20} —35·33° (95·2% pure). The dissociation const. of *r-sec.*-Bu H phthalate is determined. P. W. C.

Dehydration and rearrangement of pinacolyl alcohols and related compounds. F. C. Whitmore and P. A. Krueger (J. Amer. Chem. Soc., 1933, **55**, 1528—1535).—ζζ-*Dimethyldecan-*ε-*ol* (I), b.p. 112—113°/15 mm., and *γ-methyl-γ-butylheptan-*β-*ol* (II), b.p. 112—112·5°/14 mm., are obtained by reduction (Na and aq. Na_2CO_3 in presence of C_6H_6) of ζζ-dimethyldecan-ε-one, b.p. 63—63·5°/1·5 mm., 216—217°/735 mm., and γ-methyl-γ-butylheptan-β-one, b.p. 70—71°/2 mm. [semicarbazone, m.p. 107·2—107·7° (corr.)], which are prepared by Meerwein's method (A., 1920, i, 2), respectively. (I) and (II) are dehydrated by distillation with conc. H_2SO_4 to εζ-dimethyl-Δ^{δ}- (III) and -Δ^{ϵ}-decene (IV) and β-methyl-γ-butyl-Δ^{β}-heptene (V), the structures of which are proved by ozonolysis; relatively more of (III) and (IV) are obtained from (II) than from (I), indicating the greater mobility of the Bu group. None of the expected β-methyl-γ-butyl-Δ^{γ}-heptene (VI) is produced from (II), but (V) and (VI) are obtained by dehydration of ε-iso*propylnonan-*ε-*ol*, b.p. 75—75·5°/2 mm., which is prepared from $Pr^{\beta}CO_2Et$ and MgBuBr. Octyl alcohol and η-methylpentadecan-ι-ol (dicapryl alcohol), b.p. 130—132°/2 mm., are dehydrated by H_2SO_4 to olefines, b.p. 122—128°/733 mm., and 106—111°/mm., in approx. 90% yield. H. B.

Action of periodic acid on polyhydric alcohols and on hydroxy-acids. P. Fleury and J. Lange (J. Pharm. Chim., 1933, [viii], **17**, 313—326).—Oxidation of mannitol, dulcitol, volemitol, and inositol (I) by HIO_4 (II) proceeds in accordance with Malaprade's results. (I) gives slowly, but quantitatively, HCO_2H only. Pentaerythritol, glycollic, malic, and citric acids, which do not contain OH groups on adjacent C atoms, are unaffected by (II). Tartaric acid and (II) (1 mol.) give glyoxylic acid (III) (2 mols.). Gluconic acid and (II) (4 mols.) give CH_2O (1 mol.), HCO_2H (3 mols.), and (III) (1 mol.). Saccharic acid and (II) (3 mols.) give HCO_2H (2 mols.) and (III) (2 mols.). R. S. C.

Alkyl peroxides. X. Peroxides of formaldehyde. Pertrioxymethylene and tetraoxymethylene diperoxide. A. RIECHE and R. MEISTER (Ber., 1933, **66**, [*B*], 718—727).—Cryst. dihydroxymethyl peroxide (I) is obtained with certainty by extracting formalin and perhydrol with Et_2O, prolonged desiccation of the extracts over Na_2SO_4, and finally over P_2O_5, followed by preservation of the mixed solutions ($CH_2O : H_2O_2 = 2 : 1$) at room temp. (I) is converted by CH_2O (2 mols.) in Et_2O in presence of P_2O_5 at 0° into *dihyaroxymethyl peroxide dihydroxymethyl ether* (II) $(OH{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}O{\cdot})_2$, a moderately explosive liquid in which active O is much more accurately determined with HI than with $TiCl_3$. (I) becomes slowly transformed into a cryst. product which has a strong odour of CH_2O and sublimes partly at 140—145°, leaving a *residue* $C_6H_{12}O_7$ (possibly $-[CH_2{\cdot}O]_x{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}[O{\cdot}CH_2]_y-$), m.p. 152°. Prolonged action of P_2O_5 on (II) in Et_2O yields *pertrioxymethylene*, $CH_2<\begin{matrix}O{\cdot}CH_2{\cdot}O\\O{\cdot}CH_2{\cdot}O\end{matrix}$, b.p. 35—36°/12 mm., which very readily explodes with production of trioxymethylene and, possibly, *pertetraoxymethylene*, $O<\begin{matrix}CH_2{\cdot}O{\cdot}CH_2{\cdot}O\\CH_2{\cdot}O{\cdot}CH_2{\cdot}O\end{matrix}$ Intense action of P_2O_5 in Et_2O on (II) affords *tetraoxymethylene diperoxide* (III), $O<\begin{matrix}CH_2{\cdot}O{\cdot}O{\cdot}CH_2\\CH_2{\cdot}O{\cdot}O{\cdot}CH_2\end{matrix}>O$, which detonates at 94° (block) without previous melting. (III) is extraordinarily sensitive to pressure or friction. Its constitution is established by its conversion into HCO_2H and CH_2O when its solution in Et_2O is left in contact with aq. $FeSO_4$. H. W.

Nitrates of propylene glycol and the butylene glycols. C. MATIGNON, H. MOUREU, and M. DODÉ (Mem. Poudres, 1932—1933, **25**, 176—188).—The yield of αβ-propylene glycol dinitrate, b.p. 106°/27 mm., is unaffected by temp. between −10° and 10°, and only very slightly affected by the rate of addition of the glycol to the H_2SO_4–HNO_3. Esterification is markedly retarded by H_2O; the max. yield is obtained with 1·1 equiv. HNO_3 and sufficient H_2SO_4 to give a mass ratio $H_2SO_4 : H_2O$ at end of reaction = 2·43. The *dinitrates* of αβ-, b.p. 65°/1 mm., 109°/28 mm., βγ- (mixed stereoisomerides), b.p. 56—58°/1 mm., and αγ-n-*butylene glycol*, b.p. 90°/4 mm., and of αβ-iso-*butylene glycol*, b.p. 70°/6·5 mm., are similarly prepared. H. A. P.

Preparation of αγ-butylene glycol dinitrate. M. AUBRY (Mém. Poudres, 1932—1933, **25**, 194—196).—Details are given for the prep. of aldol in "almost quant." yield, its hydrogenation to $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and conversion of this into its dinitrate by HNO_3 (*d* 1·5) at −10° to 0°. H. A. P.

Nitro*iso*butanetriol [β-nitro-β-hydroxymethylpropane-αγ-diol] trinitrate. M. AUBRY (Mém. Poudres, 1932—1933, **25**, 197—204).—Improved processes are described for the prep. of nitromethane (I), its condensation with CH_2O (3 equivs.) to give $NO_2{\cdot}C(CH_2{\cdot}OH)_3$, and conversion of this into trinitrate (with HNO_3, *d* 1·52). The yield of (I) is increased to 70% (calc. on $CH_2Cl{\cdot}CO_2H$) by use of the Ca in place of the Na salt. H. A. P.

Electrolysis of trihalogenated aliphatic acids. Trifluoroacetic and chlorodifluoroacetic acids. F. SWARTS (Bull. Soc. chim. Belg., 1933, **42**, 102—113).—Electrolysis of aq. $CF_3{\cdot}CO_2H$ gives CO_2, O_2, HF, C_2F_6, CF_4, and *trifluoromethyl peroxide*, b.p. −40° to −32°, which reacts slowly with KI: $(CF_3)_2O_2 + 2KI + 2H_2O = 2I + 2CO_2 + 2KF + 4HF$. In presence of HF the main products are H_2 and O_2 (containing much O_3) in equiv. proportions, a little C_2F_6, and, apparently, no CF_4. Equimol. amounts of $CF_3{\cdot}CO_2H$ and $CF_3{\cdot}CO_2Na$ give much less O_2, and the anodic gases contain 30% by vol. of C_2F_6. $CClF_2{\cdot}CO_2H$ gives Cl_2, CO_2, O_2, HF, and CCl_2F_2 (possibly contaminated with $CClF_2{\cdot}CClF_2$). The results are difficult to reconcile with the oxidation theory of the Kolbe synthesis, and the anodic formation of the free radical $CHal_3$ is postulated. H. A. P.

Examination of certain azelao-glycerides obtained during the oxidation of some simple synthetic and natural glycerides. T. P. HILDITCH and S. A. SALETORE (J.S.C.I., 1933, **52**, 101—105T).—The separation of triazelain (I) or of diazelomonosaturated glycerides (II) from the products of oxidation of natural fats by $KMnO_4$ in $COMe_2$ solution is not practicable as an analytical means of determination of tri-unsaturated or of di-unsaturated-monosaturated glycerides. Monoazelao-disaturated glycerides (III), on the other hand, may often be isolated in a fairly pure state from the oxidation products if the corresponding mono-oleo-disaturated glycerides form a substantial proportion (50% or more) of the whole fat; but here, again, the amount isolable falls considerably below the total quantity present. The synthesis of some oleodistearins and oleodipalmitins is described, together with the corresponding azelao-derivatives obtained on oxidation of these and of a natural oleodistearin. Evidence is adduced which suggests that the β-oleo-αα′-distearin is the isomeride present in *Allanblackia* seed fat, cacao butter, Borneo tallow, and lard, thus pointing to a selected configuration in the natural oleodistearins. (II) (from dioleomonostearin or dioleomonopalmitin) and (I) (from triolein or from castor oil) have also been prepared, but (I) was not obtained in anything approaching purity. These products are sol. in aq. $KHCO_3$ and may thus be separated to a large extent from (III), when it is desired to isolate the latter. When azelaodistearin is treated in Et_2O with KOH–EtOH (2/3 that necessary for complete saponification) "alcoholysis" occurs and Et stearate is produced in some quantity.

Decarboxylation of unsaturated β-hydroxy-acids; synthesis of *allo*ocimene. F. G. FISCHER and K. LOWENBERG (Ber., 1933, **66**, [*B*], 669—674; cf. A., 1932, 600).—Aldehydes or ketones which contain one or more double linkings in conjugation with CO or belong to the aromatic series smoothly yield β-OH-esters when treated with $CH_2Br{\cdot}CO_2Et$ and Zn and then with H_2O (not mineral acid) at 0°. The β-OH-acids readily suffer thermal decomp.: $OH{\cdot}CR'R''{\cdot}CH_2{\cdot}CO_2H \longrightarrow$ (*a*) $CR'R'':CH_2 + CO_2 + H_2O$ or $\longrightarrow$ (*b*) $CR'R'':CH{\cdot}CO_2H + H_2O$, reaction (*a*) being facilitated by the accumulation of double linkings in the mol. Decarboxylation is not accelerated by

amines. The probable intermediate production of β-lactones is discussed. Crotonaldehyde is converted into Et β-hydroxy-Δ^{γ}-hexenoate, b.p. 75—77°/1 mm. The corresponding acid is decomposed at 145° into sorbic acid and $\Delta^{\beta\delta}$-pentadiene, b.p. 42—44° (37%). Cinnamaldehyde yields non-distillable Et β-hydroxy-δ-phenyl-Δ^{γ}-pentenoate, transformed into *β-hydroxy-δ-phenyl-Δ^{γ}-pentenoic acid*, m.p. 105—106° (decomp.), whence cinnamylideneacetic acid, m.p. 166—167°, and α-phenyl-$\Delta^{\alpha\gamma}$-butadiene, b.p. 83—84°/11 mm. *Et β-hydroxy-β-methyl-$\Delta^{\gamma\epsilon}$-octadienoate*, b.p. 82—83°/0·2 mm., affords non-cryst. *β-hydroxy-β-methyl-$\Delta^{\gamma\epsilon}$-octadienoic acid*, whence *β-methyl-$\Delta^{\alpha\gamma\epsilon}$-octatrienoic acid*, m.p. 160—161°, and *β-methyl-$\Delta^{\alpha\gamma\epsilon}$-heptatriene*, b.p. 42—44°/14 mm. From methylheptadienone (I) are obtained *Et β-hydroxy-βζ-dimethyl-$\Delta^{\gamma\epsilon}$-octadienoate*, b.p. 94—95°/0·2 mm., and βζ-dimethyl-$\Delta^{\beta\delta\zeta}$-heptatriene. (I) and CHMeBr·CO_2Et afford *Et β-hydroxy-αβζ-trimethyl-Δ^{γ}-octadienoate*, b.p. 99—104°/0·2 mm., hydrolysed with difficulty to the acid, which gives βζ-dimethyl-$\Delta^{\beta\delta\zeta}$-octatriene (*allo*ocimene) in 75% yield. Treatment of (I) with MgEtBr affords mainly *β-methyl-δ-ethyl-Δ^{β}-hepten-ζ-one* (II), b.p. 74—75°/13 mm. (*semicarbazone*, m.p. 127—128°), possibly accompanied by *tert.*-alcohol, which resinifies during distillation. (II) is hydrogenated to β-methyl-δ-ethylheptan-ζ-one (*semicarbazone*, m.p. 102°). H. W.

Ricinoleic acid and λ-hydroxystearic acid. F. Strauss, H. Heinze, and L. Salzmann (Ber., 1933, **66**, [*B*], 631—639).—The incorrectness of the lit. observation that optically inactive λ-hydroxystearic acid is obtained by reduction of ricinoleic acid (I) is established. The mixture of acids obtained by hydrolysis of castor oil is frozen from alcohol and crude (I) is converted into the Pb salt, which is extracted with Et_2O. The sol. salt is transformed into the Me ester (II) (b.p. 165—166°/0·1 mm., 153—155°/0·05 mm., $[\alpha]_D^{21}$ +5·17°, $[\alpha]_D^{21\cdot5}$ +3·52° in $CHCl_3$, $[\alpha]_D^{20}$ +10·30° in C_5H_5N), the b.p. of which is a poor criterion of purity. It is best purified through the *Bz* derivative, b.p. 195—196°/0·08 mm., $[\alpha]_D^{21}$ +15·99°, the Ac compound, b.p. 170—171°/0·1 mm., $[\alpha]_D^{20\cdot5}$ +24·20°, having a b.p. too close to that of (II). (I), $[\alpha]_D^{21}$ +7·86°, is dimorphous. When not too strongly cooled, it solidifies slowly and melts at 6—8° (III). When preserved at 7° it re-solidifies and then has m.p. 15—17° (IV). Molten (IV) when suddenly cooled to −30° or −40° retains its m.p.; if preserved at 4—5° for several hr. and then cooled to 0° or somewhat lower, it passes into (III). The purification of (I) from EtOAc at −45° to −50° is described. Hydrogenation of (II) in AcOH (Willstatter) is accompanied by absorption of an excess of about 10% of H_2 and production of Me stearate, which is readily removed. l-λ-*Hydroxystearic acid* has m.p. 80·5—81°, $[\alpha]_D^{19}$ −0·41° in C_5H_5N (*Me* ester, m.p. 35—37°, $[\alpha]_D^{9}$ −0·32° in C_5H_5N, −0·32° in $CHCl_3$, −0·34° in $C_2H_2Cl_4$; its *benzoate*, b.p. 198—199°/0·05 mm., $[\alpha]^{20}$ −1·25°; *acetate*, b.p. 158—160°/0·1 mm., 151—152°/0·01 mm., $[\alpha]_D^{21}$ +0·10°, and 3 : 5-*dinitrobenzoate*, m.p. 39—40°, $[\alpha]_D^{19}$ −1·04° in $CHCl_3$). H. W.

Acetoacetic ester condensation. V. Condensation of higher esters. R. R. Briese and S. M. McElvain (J. Amer. Chem. Soc., 1933, **55**, 1697—1700).—The following are prepared in 74—84% yield from the appropriate Alk·CO_2Et by the method previously described (A., 1929, 1424): *Et α-valeryl-valerate*, b.p. 109—110°/5 mm., *α-hexoylhexoate*, b.p. 132—133°/5 mm., α-heptoylheptoate, b.p. 147—148°/5 mm., *α-octoyloctoate*, b.p. 173—175°/5 mm., α-nonoylnonoate, b.p. 195—200°/5 mm., α-decoyldecoate, b.p. 220—225°/5 mm., *α-dodecoyldodecoate*, m.p. 28—29°, and *α-tetradecoyltetradecoate*, m.p. 37—38°. These are hydrolysed (KOH in 90% EtOH) to $COBu_2$, and diamyl, m.p. 14—15°, dihexyl, m.p. 30—31°, diheptyl, m.p. 41—42°, dioctyl, m.p. 52—53°, dinonyl, m.p. 58—59°, diundecyl, m.p. 68—69°, and ditridecyl, m.p. 78—79°, ketones, respectively, in yields of 72—98%. H. B.

Syntheses with "acetonised" glyceric ester. I. H. O. L. Fischer and E. Baer (Helv. Chim. Acta, 1933, **16**, 534—547).—*Me* αβ-iso*propylidenedioxypropionate* (I), b.p. 84—86°/15 mm. (the *Et* ester has b.p. 84—88°/9 mm.), prepared in 43·5% yield from Me glycerate, $COMe_2$, and $ZnCl_2$ (subsequently removed with quinoline), is hydrolysed [aq. $Ca(OH)_2$] to the *Ca* salt (+H_2O) of αβ-*iso*propylidenedioxypropionic acid [*amide*, m.p. 111—112°, from (I) and MeOH–NH_3; *hydrazide*, m.p. 78—79°; *piperidide* (II), b.p. 89—91°/0·4 mm.]. The *Me* ester, b.p. 81—83°/15 mm., of αβ-ethylidenedioxypropionic acid (*hydrazide*, m.p. 93—95°) is prepared from Me glycerate, MeCHO, and 84% H_3PO_4. (I), Na, and $COMe_2$ give *βδ-diketo-εζ-iso*propylidenedioxyhexane*, b.p. 107—109°/11 mm. [purified through its *Cu* salt, m.p. 184—185°; *γ-acetoxy*-derivative, b.p. 100—106°/0·8 mm., obtained by the action of $Pb(OAc)_4$ in C_6H_6]. *γε-Diketo-ζη-iso*propylidenedioxy-ββ-dimethylheptane*, b.p. 116—118°/8 mm. (*Cu* salt, m.p. 163°), *δζ-diketo-ηθ-iso*propylidenedioxy-β-methyl-Δ^{β}-octene*, b.p. 143—147°/10 mm. (*Cu* salt, m.p. 145—146°), *Ph -keto-γδ-iso*propylidenedioxybutyl ketone*, b.p. 135°/0·4 mm. (*Cu* salt, m.p. 190—191°), and 2-αβ-iso*propylidenedioxypropionyl*cyclo*hexanone*, m.p. 44—46° (*Cu* salt, m.p. 198°), are prepared from (I), Na, and $COMeBu^{\gamma}$, mesityl oxide, COPhMe, and *cyclo*hexanone, respectively. MgMeI and (II) give *Me* αβ-iso*propylidenedioxyethyl ketone*, b.p. 57—66°/10 mm., which with $Et_2C_2O_4$ and EtOH–NaOEt affords *Et αγ-diketo-δε-iso*propylidenedioxyhexoate*, b.p. 96—97°/0·1 mm. (*Cu* salt, m.p. about 175°) [the *Me* ester, b.p. 87—89°/0·1 mm. (*Cu* salt), is prepared using $Me_2C_2O_4$ and MeOH–NaOMe; its enol Me ether could not be obtained cryst.]; definite products were not obtained by hydrolysis (dil. AcOH; 0·1*N*-HCl) of these esters. H. B.

Refractometric determination of organic acids. (Mme.) G. Allard (Compt. rend., 1933, **196**, 1118—1119; cf. this vol., 621).—The Pb salts of glutaric (I), adipic (II), pimelic (III), and suberic acid (IV) are too sol. for determination of these acids by measuring *n* during pptn. by $Pb(OAc)_2$. AgOAc is suitable in determining (II) (0·01*M*) and (IV) (0·005*M*), but not for mixtures. Pptn. by $Hg(OAc)_2$ gives results within a few % for (I)—(IV) and their Na salts, and in a mixture of (I), (II), and azelaic acid the errors are 2%, 15%, and 4·5%, respectively. A. C.

Unsaturated αδ-dicarbonyl compounds. VIII. Derivatives of dimethylfumaric acid. R. E.

LUTZ and R. J. TAYLOR (J. Amer. Chem. Soc., 1933, **55**, 1585—1592).—Dimethylfumaric acid {*anilide*, m.p. 267° (all m.p. are corr.); *Me H* ester (I), m.p. 81° [chloride (II), b.p. 90—91° (corr.)/20 mm.; *anilide*, m.p. 74—75°, hydrolysed (aq. EtOH–KOH) to *dimethylfumaranilic acid*, m.p. 195°]; *Et H* ester (III), b.p. 118°/1 mm. (*chloride*, b.p. 90—91°/14 mm.; *anilide*, m.p. 121·5—122°)} and PCl_5 give *dimethylfumaryl chloride*, b.p. 79·5°/22 mm., which is rearranged by $AlCl_3$ at 100° into the *ψ*-dimethylmaleyl chloride of Otto and Holst (A., 1890, 1327). (I) is best prepared by partial hydrolysis of Me dimethylfumarate (IV) with KOH in 95% MeOH; hydrolysis with KOH in Et_2O–EtOH gives (III). (II) and $AlCl_3$ at 100° afford MeCl and dimethylmaleic anhydride (V). (IV) and MeOH–NaOMe in cold Et_2O give (mainly) a *Me H methoxydimethylsuccinate*, b.p. 130—131°/2 mm.; the free *acid*, m.p. 133·5°, when heated to 200°, yields (V). Et dimethylfumarate, (IV), and (I) undergo rearrangement during alkaline hydrolysis in EtOH containing min. amounts of H_2O; in dil. (40% H_2O) EtOH, dimethylfumaric acid results. Rearrangement must occur during hydrolysis, since the acid is stable under the conditions used. H. B.

Plant dyes. XLVII. Isomerism of the bixins. Theory of formation of carotenoid pigments in plants. P. KARRER and T. TAKAHASHI. **XLVIII. Violanin.** P. KARRER and G. DE MEURON. **XLIX. Synthesis of perhydrocrocetin.** P. KARRER, F. BENZ, and M. STOLL. **L. Conversion of perhydrocrocetin into perhydronorbixin.** P. KARRER and F. BENZ (Helv. Chim. Acta, 1933, **16**, 287—292, 292—296, 297—302, 337—338).—XLVII. Partial hydrolysis of methylbixin with 1 equiv. of NaOH in EtOH at 65° gives stable and labile bixins, and a mixture, m.p. 130°, of methylbixin and bixin, converted by CH_2N_2 into methylbixin. Hasselt's *iso*bixin (cf. A., 1911, i, 550) was not observed. In agreement with Herzig and Faltis (A., 1923, i, 477), methylation of norbixin with MeOH–HCl is found to give the Me_2 ester of stable norbixin. In reply to Kuhn and Grundmann (this vol., 145) it is claimed that the carotenoids are built up in the plant not necessarily from phytol alone, but from similar raw materials.

XLVIII. Violanin is separated by crystallisation of its picrate from H_2O into *violanin*-A (I) and *violanin*-B (II). (I) is very sparingly sol. in H_2O and gives on hydrolysis glucose (1 mol.), rhamnose (1 mol.), *p*-hydroxycinnamic acid (1 mol.), and delphinidin (1 mol.). Oxidation with H_2O_2 and treatment of the product with $NHPh{\cdot}NH_2$ gives an *osazone*, $C_{33}H_{38}O_{10}N_4$, containing both sugars and *p*-hydroxycinnamic acid. The acid must therefore be attached to the disaccharide part of the mol. (II) is a mixture of delphinidin-3-glucoside with a little pæonidin-3-glucoside, and gives phenylglucosazone only on treatment with H_2O_2 and $NHPh{\cdot}NH_2$.

XLIX. βζ-Dimethylheptane-αη-diol (this vol., 52) is converted by Na and EtI into its (mono)*Et ether*, b.p. 126°/12 mm. (and some *Et*, *ether*, b.p. 115°/12 mm.), which with PBr_3 gives the *bromide*. This with $CHNa(CO_2Et)_2$ in abs. EtOH gives, after hydrolysis, *θ-ethoxy-γη-dimethylnonoic acid*, b.p. 130°/0·2 mm., the Na salt of which is converted by electrolysis into *βζλξ-tetramethylhexadecane-απ-diol Et, ether*, b.p. 167°/0·5 mm. By successive treatment with HBr in AcOH at 100°, KOAc in EtOH, and hydrolysis with KOH, this yields *βζλξ-tetramethylhexadecane-απ-diol*, b.p. 165—167°/0·15 mm., which is oxidised by CrO_3 in AcOH+$KHSO_4$ to perhydrocrotecin, $(\cdot CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CO_2H)_2$ (diamide, m.p. 130°, identical with the product from natural sources).

L. βζλξ-Tetramethylhexadecane-απ-diol, prepared by reduction of perhydrocrocetin Me_2 ester, is converted into its dibromide, which is treated with $CHNa(CO_2Et)_2$, and the resulting tetracarboxylic ester hydrolysed and decarboxylated. Perhydronorbixin, m.p. 110·5—111°, identical with the natural product, is thus obtained. H. A. P.

Oxidation of citric acid. A. C. KUYPER (J. Amer. Chem. Soc., 1933, **55**, 1722—1727).—Oxidation of citric acid (I) with $KMnO_4$ and dil. H_2SO_4 is more complete (*i.e.*, more CO_2 is produced) at 20° than at 100°; the nature of the reaction changes at about 60°. Below 60°, (I) gives $CO(CH_2{\cdot}CO_2H)_2$ (II), which is oxidised to CH_2O, HCO_2H, and CO_2, and mol. O_2 takes part in the reaction; above 60°, (II) decomposes to $COMe_2$ before it can be oxidised. Small amounts of (I) in pure solution can be determined by oxidation with $KMnO_4$ in the Van Slyke const.-vol. apparatus by the use of proper conversion factors. H. B.

Reactions between citric and acetylsalicylic acids. A. J. DIETZLER and R. E. NELSON (J. Amer. Chem. Soc., 1933, **55**, 1605—1608).—Acetylcitric anhydride and PCl_5 in light petroleum at 25° give the *chloride*, $O<\begin{matrix}CO{\cdot}C(OAc){\cdot}CH_2{\cdot}COCl\\CO{\cdot}CH_2\end{matrix}$, m.p. 92—93°, which with *o*-$OH{\cdot}C_6H_4{\cdot}CO_2Na$ in cold $CHCl_3$ affords a *compound* (I), $C_{15}H_{12}O_9$, m.p. 162—163°, which could not be acetylated and does not contain a phenolic OH-group ($FeCl_3$); alternative structures are suggested. The rate of hydrolysis of (I) by 0·0987*N*-HCl at 38° is studied; the hydrolysis products are AcOH, *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, and citric and some aconitic acid. Unsuccessful attempts to combine citric and acetylsalicylic acids are outlined. H. B.

Synthesis of *d*-ascorbic acid (*d*-form of vitamin-*C*). T. REICHSTEIN, A. GRUSSNER, and R. OPPENAUER (Helv. Chim. Acta, 1933, **16**, 561—565).—*d*-Xylosone and aq. HCN at 45° give a product which is hydrolysed (7·5% HCl in CO_2) to 4-hydroxy-3-keto-5-hydroxymethyltetrahydrofuran-2-carboxylic acid (I), $[\alpha]_D$ −19·5° in MeOH [iso*propylidene* derivative, m.p. (vac.) 206—209° (corr.), which reduces I (in acid solution), $AgNO_3$, and 2 : 6-dichlorophenolindophenol (in neutral solution)]. The enolic form of (I) is considered to be ascorbic acid (cf. Micheel and Kraft, this vol., 489; Cox and Hirst, *ibid.*, 490). H. B.

Constitution of ascorbic acid. E. L. HIRST, E. G. V. PERCIVAL, and F. SMITH (Nature, 1933, **131**, 617; cf. A., 1932, 100).—Ascorbic acid Me_2 ether (I), $\begin{matrix}CO\\C(OMe)\end{matrix}>\begin{matrix}\text{———}O\text{———}\\:C(OMe)\end{matrix}>CH(OH){\cdot}CH_2{\cdot}OH$, from ascorbic acid and CH_2N_2, is neutral and reacts with 1 equiv. of warm 0·1*N*-alkali without elimination of MeOH. The lactone ring of (I) appears to be opened and

hence both OMe groups are enolic. Cone. alkali produces decomp. The cryst. substance, m.p. 123° (this vol., 325), obtained from (I) with MeOH–NH_3 is formed by the addition of NH_3 to the lactone group. The two OMe groups are retained in the product, $C_9H_{19}O_7N$, which behaves as an amide. The ring system in (I) has been elucidated by degradative oxidation of ascorbic acid Me_4 ether (II). O_3 gives a neutral substance, $CO_2Me{\cdot}CO{\cdot}O{\cdot}CH(CO_2Me){\cdot}CH(OMe){\cdot}CH_2{\cdot}OMe$, which with NH_3 gives $(CO{\cdot}NH_2)_2$ and α-hydroxy-βγ-dimethoxybutyramide quantitatively. The hydroxydimethoxybutyric acid consists of 80% of βγ-dimethylthreonic acid and βγ-dimethyl-*l*-erythronic acid. The isolation of the two epimeric acids suggests enolisation at C_4 at some stage and is important from the biological point of view. These results are incompatible with the furancarboxylic acid structure for ascorbic acid previously rejected on crystallographic grounds (this vol., 490), and require either the structure given above for (II) or an unlikely alternative which is discussed.

L. S. T.

Derivatives of glycuronic acid. I. Preparation of glycuronic acid from glycuron. Comparison of their reducing powers. W. F. Goebel and F. H. Babers (J. Biol. Chem., 1933, **100**, 573—581).—The prep. of glycuronic acid (I) from glycuron (II) (modified prep.) by $Ba(OH)_2$ is described. (I) is quantitatively oxidised by $NaIO_3$ to saccharic acid, but (II) is partly further oxidised. (I) and (II) have lower reducing vals. than glucose by Shaffer and Hartmann's method, particularly the micro-method; standardisation of each batch of reagent is advisable. (I) reduces Bertrand's reagent quantitatively, but (II) requires an excess of reagent. Pure (I) is about as stable as is glucose to Fehling's solution.

R. S. C.

Synthesis of hexuronic acids. II. Synthesis of *d*-mannuronic acid from *d*-mannosaccharic acid. C. Niemann and K. P. Link (J. Biol. Chem., 1933, **100**, 407—413).—*d*-Mannosaccharodilactone (modified prep.) with Na–Hg in dil. H_2SO_4 gives *d*-mannurolactone, m.p. 141·5—142°, $[\alpha]_D^0$ +92·8° (max.) in H_2O {Ba, $[\alpha]^{20}$ −4° in H_2O, brucine, m.p. 147·5—148° (decomp.), $[\alpha]_D^{20}$ −22·0° in H_2O, and cinchonine salts, m.p. 153—154° (decomp.), $[\alpha]_I^{20}$ +113·0° in H_2O}, identical with the lactone obtained from natural alginic acids. The method of drying affects the m.p. and [α] of the alkaloidal salts.

R. S. C.

Methylglucosides of naturally occurring hexuronic acids. I. Preparation of methyl-*d*-galacturonide. S. Morell and K. P. Link (J. Biol. Chem., 1933, **100**, 385—396).—The polygalacturonide (I), $[\alpha]^{25}$ +269·9° in 0·1*N*-NaOH, obtained by extraction of sol. substances from *Citrus* pectin by 70% EtOH, gives with hot, dry HCl–MeOH the *Me* ester (II), $+H_2O$, sinters at 136°, m.p. 138—140°, decomp. 140—141°, $[\alpha]_D^{28}$ +124·1° in H_2O, of *methyl*-d-*galacturonide* (yield, about 15%), the Me_4 ester of a Me glucoside of a tetragalacturonide (about 20%), depolymerised and unchanged (I), and possibly some reversion products. (II), also obtained in 56% yield from *d*-galacturonic acid, with dil. aq. $Ba(OH)_2$ gives *methyl*-d-*galacturonide*, $+2H_2O$, sinters at 109°, m.p. 112—114°, decomp. 120°, $[\alpha]_D^{28}$ +127·6° in H_2O [*Ba* salt, m.p. about 215° (darkens at 200°), $[\alpha]_D^{28}$ +99·1° in H_2O]. (II) is considered to be an α-glucoside.

R. S. C.

Isolation of α- and β-*d*-mannuronic acid. E. Schoeffel and K. P. Link (J. Biol. Chem., 1933, **100**, 397—405).—α- and β-d-*Mannuronic acid*, $+0{\cdot}5H_2O$, m.p. indef. (sinters at 110°; darkens at 120—130°) and 165—167°, $[\alpha]_D^{25}$ +33·51°⟶+31·51° (min. +26·81°), and −47·90°⟶−23·94° (in 24 hr.) in H_2O, respectively, are isolated from the Ba salt (A., 1932, 365). Both forms are hygroscopic and readily revert to the lactone, especially the α-form.

R. S. C.

Mucondialdehyde. F. G. Fischer and K. Löwenberg (Ber., 1933, **66**, [*B*], 665—669).—Ozonisation of *cyclo*hexene in AcOH at −50° to −70° followed by catalytic hydrogenation of the ozonide affords adipdialdehyde (I), b.p. 92—94°/12 mm., in 60—70% yield. Successive addition of Br in $CHCl_3$ and EtOH to (I) and treatment of the product with powdered KOH at 130°/12 mm. yields *mucondialdehyde tetraethylacetal*, b.p. 139—141°/12 mm., hydrolysed by tartaric acid in H_2O to *mucondialdehyde* (II), leaflets or needles, m.p. 121°. (II) remains unchanged when preserved as solid or in solution even in the presence of light, and is little altered when heated for a short period above its m.p. It is not autoxidised by atm. O_2. It is very slowly decomposed by mineral, but not by org., acids at room temp., but is immediately darkened by alkali. It could not be caused to react with $CH_2Br{\cdot}CO_2Et$ and Zn or with $CH_2(CO_2H)_2$. Reduction with Al–Hg in H_2O or Zn dust in AcOH gives dark, polymerised products. Oxidation to the dicarboxylic acid could not be effected. The *dihydrazone*, m.p. 192°, *diphenylhydrazone*, m.p. 228—229° (Berl; decomp.), *di*-p-*nitrophenylhydrazone*, m.p. 264° (Berl), *dioxime*, decomp. about 200°, and *disemicarbazone*, m.p. 264° (Berl), are described, several of which are very sensitive to mineral acids.

H. W.

Action of bleaching-powder on ketones and ethyl acetoacetate. C. D. Hurd and C. L. Thomas (J. Amer. Chem. Soc., 1933, **55**, 1646—1649).—COMeEt gives $CHCl_3$ (45%) and $EtCO_2H$ (40·7%); furfurylideneacetone (I) affords $CHCl_3$ (55·5%) and β-furylacrylic acid (89·5%); $CH_2Ac{\cdot}CO_2Et$ yields $CHCl_2{\cdot}CO_2H$ (60%) and no $CHCl_3$. Oxidation (dil. HNO_3) of (I) gives some $H_2C_2O_4$ and NH_4 tetroxalate.

H. B.

Preparation of dihydroxyacetone. A. I. Virtanen and M. Nordlund (Biochem. J., 1933, **27**, 442—444).—A culture of *A. suboxydans* is incubated with 4·55% glycerol in a 3% extract of yeast at 20° and p_H 5·2 for 14 days. Dihydroxyacetone is isolated through its compound with $NaHSO_3$.

H. D.

Products obtained by catalytic reduction of dioximes and acetoxime in acid medium. M. Krajčinović and D. Vranjican (Bull. Soc. chim., 1933, [iv], **53**, 145—150).—Reduction [H_2, Pt-black. aq. EtOH, HCl (2 mols.)] of dimethylglyoxime (I) gives βγ-diaminobutane hydrochloride (44%) and NH_4Cl (56%); acetylacetonedioxime similarly affords βδ-diaminopentane hydrochloride (62%) and NH_4Cl (38%). Reduction of acetonylacetonedioxime in

EtOH–$H_2C_2O_4$ gives $(NH_4)_2C_2O_4$ (8%) and the *oxalate* (+H_2O), m.p. 112°, of the *sec.*-hydroxylamine, $(CH_2)_2<^{CHMe\cdot N(OH)\cdot CHMe}_{CHMe\cdot N(OH)\cdot CHMe}>(CH_2)_2$ e' e arises by condensation of the intermediate εε-di(hydroxylamino)hexane with acetonylacetone and subsequent reduction. The difference in the behaviour of (I) and (II) is ascribed to the weaker acidity [as determined by the method of Pfeiffer *et al.* (A., 1925, i, 270)] and more ready hydrolysis (by aq. EtOH–HCl at 17°) of (II) than (I). Resinous products are formed by reduction of glyoxime and succinaldoxime (a little pyrrole is formed in this case); 16—17% of NH_4Cl is also produced. Reduction of acetoxime gives mainly NH_4Cl and a little *sec.*-hydroxylamine; $CEt_2{:}N\cdot OH$ and $CPr_2{:}N\cdot OH$ are more readily hydrolysed and afford much less NH_4Cl. H. B.

Pentose reactions. III. Xylan. C. D. Hurd and N. R. Currie (J. Amer. Chem. Soc., 1933, **55**, 1521—1523).—Oat hulls (I) are soaked in 2% aq. NH_3 for 2 days, extracted with hot 10% NaOH, the filtrate is treated with EtOH, and the pptd. material triturated with AcOH; xylan (II), $[\alpha]^{30}$ −71·2° in aq. NaOH, is thus obtained in 22—24% yield. (II) does not exist as such in (I), since initial extraction of (I) with PhOH [in which (II) is sol.] has little effect on the yield. (II) is hydrolysed (dil. H_2SO_4) to xylose and with Ac_2O and a little conc. HNO_3 at 70° gives diacetylxylan, *M* 298 (f.p. in $PhNO_2$), which is hydrolysed (10% KOH) to (II). Saturation of an emulsion of (II) in H_2O with C_2H_4 causes (after 3 weeks) 10% conversion into reducing sugar, none of which is formed in absence of C_2H_4. H. B.

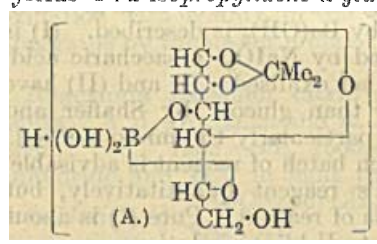
Highly reducing sugar derivative (reductone). H. von Euler and C. Martius (Svensk Kem. Tidskr., 1933, **45**, 73—74).—Short treatment of an aq. solution of glucose with aq. NaOH–KCN and $Pb(OAc)_2$ in N_2 at 90° and decomp. of the pptd. Pb salt with H_2S gives a highly reducing *substance* (gluco-reductone), $C_3H_4O_3$, m.p. 200—220° (*Na* salt). In reducing action and ultra-violet absorption spectrum (max. 268 mμ at p_H 2—4; max. 287 mμ at p_H 5·7—10) it closely resembles ascorbic acid (this vol., 490). Similar reducing compounds are obtained from xylose and $CO(CH_2\cdot OH)_2$. J. W. B.

Action of periodic acid on polyhydroxylic compounds. III. Action of periodic acid on sugars. P. Fleury and J. Lange (J. Pharm. Chim., 1933, [viii], **17**, 409—417).—A detailed account of the oxidation of $CO(CH_2\cdot OH)_2$ (I), glucose (II), and fructose (III) with HIO_4 (this vol., 376), the results of which show that the reactions are: (I)+HIO_4 HIO_3+CH_2O-OH·CH_2·CO_2H; (II)+5HIO_4⟶5HIO_3+CH_2O+5HCO_2H; and (III)+4[O]⟶either (*a*) CH O+3HCO_2H+OH·CH_2·CO_2H or (*b*) 2CH_2O+2HCO_2H+CHO·CO_2H+H_2O, the last two reactions occurring simultaneously, (*a*) being the more important. General conclusions relating to the effect of structure on the course of such oxidations are discussed. J. W. B.

Anhydride formation of 2 : 3 : 6-trimethylglucose. K. Hess and O. Littmann (Ber., 1933, **66**, [*B*], 774—779; cf. following abstract).—The action of Na powder in Et_2O on 1-chloro-2 : 3 : 6-trimethylglucose obtained by the action of HCl in Et_2O on trimethylcellulose (Freudenberg and Braun, A., 1928, 399) does not lead essentially to 2 : 3 : 6-trimethylglucose anhydride, but to a glucal-like compound (OMe=35·6%) containing a double linking and a free OH. A similar mixture is derived from the product of the action of HCl on 2 : 3 : 6-trimethylglucose (I) in Et_2O at 0°. Reaction is considered to consist in removal of Cl and OMe by Na and reduction by the liberated H. The non-volatile portion of the reaction mixtures gives (I) when hydrolysed with HCl–H_2O and may be the desired anhydride. H. W.

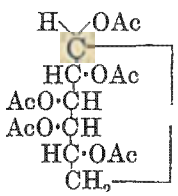
2 : 3 : 6-Trimethylglucose anhydride. K. Freudenberg and E. Braun (Ber., 1933, **66**, [*B*], 780—781).—The prep. of 2 : 3 : 6-trimethylglucose anhydride is invariably successful when the initial material is cellulose methylated in cold solution to a product which retains the fibrous structure. Lack of success of Hess and Littmann (preceding abstract) is ascribed to the use of powdered trimethylcellulose prepared in hot solution. H. W.

Partial acetonisation of sugars and sugar alcohols. I. 1 : 2-*iso*Propylidene-*d*-glucofuranose 3 : 5-monoborate. L. von Vargha (Ber., 1933, **66**, [*B*], 704—707).—Treatment of glucose with H_3BO_3 (1 mol.) and $COMe_2$ containing H_2SO_4 rapidly yields 1 : 2-*iso*propylidene-d-*glucofuranose* 3 : 5-*monoborate* H (I, *A*), m.p. (indef.) 90—110°, converted by distillation with MeOH into 1 : 2-*iso*propylideneglucose, from which (I) is derived by the action of H_3BO_3 in $COMe_2$, thus establishing the furanoid grouping. (I) is transformed by BzCl or *p*-$C_6H_4Me\cdot SO_2Cl$ in C_5H_5N into 1 : 2-*iso*propylideneglucose 6-benzoate and 6-*p*-toluenesulphonate, respectively; more highly acylated products cannot be obtained. With CPh_3Cl in C_5H_5N (I) gives 6-triphenylmethyl-1 : 2-*iso*propylideneglucose (Bz_2 derivative, m.p. 78—79°, $[\alpha]^{20}$ −4·2° in C_5H_5N). The presence of 2 OH groups attached to B is indicated by the necessity of using ≯ 3 mols. of reagent in the prep. of the above compounds. Oxidation of (I) with $KMnO_4$ in anhyd. $COMe_2$ gives K *iso*propylidenexyluronate. Reaction probably occurs in the sequence, ring transformation, esterification, acetonisation. With 2 mols. of H_3BO_3 acetonisation does not take place. Under similar conditions galactose yields di-*iso*propylidenegalactose. H. W.



New class of sugar derivatives. F. Micheel and F. Suckfull (Annalen, 1933, **502**, 85—98).—6-Iodo-1 : 2-3 : 4-di-*iso*propylidenegalactose is converted by hydrolysis (2*N*-HCl in dioxan) and subsequent condensation with EtSH into 6-*iodogalactose diethylmercaptal*, m.p. 123° (decomp.), $[\alpha]_D^{17}$ +6·9° in C_5H_5N, the *tetra-acetate* (I), m.p. 109—110°, $[\alpha]_D^{17}$ −2·3° in $CHCl_3$, of which with $HgCl_2$, $CdCO_3$, and aq. $COMe_2$ gives (under defined conditions) al-6-*iodogalactose* 2 : 3 : 4 : 5-*tetra-acetate*, m.p. 122° (previous sintering), $[\alpha]_D^{20}$ −3·7° in $CHCl_3$. (I) is also converted by the above reagents into al-*galactose* 2 : 3 : 4 : 5-*tetra-acetate hydrate* (II), m.p. 150° (previous sintering),

and a syrup (III). (III) consists largely of galactopyranose 2 : 3 : 4 : 6-tetra-acetate, since acetylation (Ac_2O–C_5H_5N) gives α- and β-galactopyranose penta-acetates, whilst *p*-nitrobenzoylation in $CHCl_3$–C_5H_5N affords *α-galactose* 1-p-*nitrobenzoate* 2 : 3 : 4 : 6-*tetra-acetate*, m.p. 108°, and a product which when distilled at 0·05 mm. yields *p*-NO_2·C_6H_4·CO_2H and the tetra-acetate, $C_{14}H_{18}O_9$, m.p. 110°, of Maurer and Mahn (A., 1927, 751). β-*Galactose* 1-p-*nitrobenzoate* 2 : 3 : 4 : 6-*tetra-acetate*, m.p. 123°, is prepared from *p*-NO_2·C_6H_4·CO_2Ag and acetobromogalactose in quinoline. A solution of (II) in C_5H_5N shows $[\alpha]_D$ +7·8° ⟶ −28°; acetylation of the resultant product gives α-, m.p. 128°, $[\alpha]_D^0$ −11° in $CHCl_3$, and β-, m.p. 101°, $[\alpha]_D^{18}$ −78·3° in $CHCl_3$, *-galactoseptanose penta-acetates* (as IV), which are interconvertible by treatment with a little $ZnCl_2$ in Ac_2O. H. B.


(IV.)

Distinction between aldo- and keto-hexoses by means of the resorcinol reaction. C. Sampietro and K. Taufel (Z. anal. Chem., 1933, **92**, 241—245).—Selivanov's reaction (A., 1887, 459) has been modified to render it suitable for the detection of keto-hexoses in coloured media, the 5-hydroxymethylfurfuraldehyde (I) being distilled in steam and the condensation with *o*-$C_6H_4(OH)_2$ effected in the colourless distillate. On heating for some time, (I) slowly undergoes some change, rendering it no longer volatile in steam. D. R. D.

Transformations of sugars in ammoniacal medium. J. Parrod (Ann. Chim., 1933, [x], **19**, 205—262, and Bull. Soc. chim., 1933, [iv], **53**, 196—200).—Partly an account of work previously reviewed (A., 1930, 480; 1931, 852; 1932, 45, 369; this vol., 260). The following is new. Prolonged interaction (60 days) of fructose and aq. NH_3 in absence or presence of Zn, Ca, Fe″, Fe‴, and Mn hydroxides in absence of air gives varying small amounts of 4-*methylglyoxaline* (I), b.p. 263°/760 mm., m.p. 55° (*oxalate*, m.p. 205—206°; *picrate*, m.p. 159—160°); 4-*methyl*-2-*hydroxymethylglyoxaline*, m.p. 129° (*picrate*, m.p. 82°), is also formed with $Mn(OH)_2$. When air is passed through the above reaction mixtures, small amounts of 4-hydroxymethylglyoxaline (II) are produced [except with $Ca(OH)_2$, when (I) results]. Passage of air through a mixture of fructose, methylene-blue, and aq. NH_3 for 1 month gives (II), *d*-arabinotetrahydroxybutylglyoxaline, and *glyoxaline*-4-*carboxylamide* (+H_2O), m.p. (anhyd.) 214° (*hydrochloride*, m.p. 220°; *picrate*, m.p. 208°). Work (lit.) on the synthesis of substances related to proteins is discussed. H. B.

Biological method for determination of different sugars in starch-degradation products. A. Schultz and G. W. Kirby (Cereal Chem., 1933, **10**, 149—155).—A selective method for the determination of glucose (I) or fructose (II), sucrose (III), and maltose (IV) in presence of each other has been devised. (I) or (II) was determined by measuring the vol. of CO_2 produced by complete fermentation with a mycoderma organism (a pure culture of an air-borne organism). A sugar- and maltase-free invertase prep. was then added to the reacting solution and the vol. of CO_2 then evolved measures the (III) present. The total fermentable sugar was determined with bakers' yeast and hence, by difference, the (IV). Details of the procedure and apparatus are given. It is advisable to control experiments with pure sugars. The method can also be used for detecting small amounts of invertase and maltase in plant materials. E. A. F.

Liquefaction of starch paste. H. Pringsheim, H. Borchardt, and R. Lewy (Naturwiss., 1933, **21**, 299—300).—No H_3PO_4 was formed when starch paste was liquefied, even when considerable conversion into sugar had taken place. This is contrary to expectations if the formation of starch paste is due to the esterification of the outer substance of the starch granules with H_3PO_4. A. J. M.

Starch nitrates. II. Starch nitrates from starches of different origin. J. Hackel and T. Urbański (Rocz. Chem., 1933, **13**, 221—225).—No marked differences were found in the N content or properties of the products of nitration of maize, wheat, rice, tapioca, potato, and sol. starch. R. T.

Action of solutions of orthophosphoric acid on cellulose. G. Champetier (Compt. rend., 1933, **196**, 930—933; cf. A., 1931, 941).—The action of aq. H_3PO_4 (1040 g. per litre) on cellulose (I) for 15 hr. gives $3C_6H_{10}O_5,H_3PO_4$. By washing with H_2O all H_3PO_4 is removed and (I) left unchanged. The *X*-ray diagram resembles that for cellulose save for being fainter. C. A. S.

[Attempted] preparation of polyatomic co-ordination rings. P. Pfeiffer and E. Lübbe (J. pr. Chem., 1933, [ii], **136**, 321—328).—Hexadecamethylene-απ-dicarboxylic acid [the Et ester is prepared by electrolysis of K Et sebacate (cf. Ruzicka *et al.*, A., 1929, 68)] is converted through the chloride into the *amide*, m.p. 179° (softens at 173°), and thence into the *nitrile*, m.p. 58° (softens at 54°); this is reduced (Na, EtOH) to *octadecamethylene-αα-diamine* (I), m.p. 93° (previous softening) [*dihydrochloride*, m.p. > 225°; Bz_2 derivative, m.p. 150° (softens at 145°)]. Complex formation is not observed with various metal salts and (I), tetra-, penta-, and decamethylenediamines, and 0-aminononoic acid. H. B.

New salts of quaternary ammonium bases. Q. Mingoia (Annali Chim. Appl., 1933, **23**, 104—114).—The following salts of therapeutic interest have been prepared: NMe_4, m.p. 80—82°, and NEt_4 *cacodylates*; NMe_4 and NEt_4 *methylarsinates*; NMe_4 and NEt_4 *camphorates*, m.p. 58—60°; NMe_4, m.p. 70—72°, and NEt_4 *glycerophosphates*. In each case, the p_H val. of the 1% aq. solution is unchanged by heating for 30 min. in an autoclave at 120°. T. H. P.

Preparation of the nitric ester of β-hydroxyethylamine nitrate. M. Aubry (Mém. Poudres, 1932—1933, **25**, 189—193).—Prepared from the free base, NH_2·CH_2·CH_2·O·NO_2,HNO_3, or its nitrate and HNO_3 (*d* 1·52), is too expensive and hygroscopic to be of val. as an explosive. H. A. P.

Resolution of β-ethoxyamines. W. R. Brode and I. J. Wernert (J. Amer. Chem. Soc., 1933, **55**,

1685—1689).—Details of the resolution of β-ethoxyhexylamine into *d*-, b.p. 70·8—71·2°/15 mm., $[\alpha]^{25}$ +8·6° in 95% EtOH, and *l*-, b.p. 70·5—70·7°/14 mm., $[\alpha]^{25}_{D}$ −24·6° in 95% EtOH, forms and of β-ethoxy-β-phenylethylamine into *d*-, $[\alpha]^{25}$ +104·5° in EtOH, and *l*-, $[\alpha]^{25}_{D}$ −104·2° in EtOH, forms by *d*-tartaric acid (I) are given. Partial resolution of β-ethoxy-butylamine and -amylamine could be effected only with (I) or *d*-camphorsulphonic acid. Salts of const. rotation (after about 20 recrystallisations) are often obtained, but these do not yield the fully resolved base. There is little difference in the solubility of the H tartrates or camphorsulphonates of the *d*- and *l*-amines. When the salts of the enantiomorphic forms have markedly different cryst. form, it is possible to crystallise either from a saturated solution of, *e.g.*, *dAdlB* by seeding with, *e.g.*, *dAdB* or *dAlB*. H. B.

Chitins, lichenins, and cellulose. G. von François (Diss., Zürich, 1930; Bied. Zentr., 1932, **3**, **A**, 51—52).—Both plant and animal chitin yield approx. 80% of *N*-acetylglucosamine (I). Enzymic decomp. of acetylchitosan yields (I), whilst chitosan yields polyglucosamine. Lichenin from *Cetraria islandica* is optically inactive. Its general properties and in particular the behaviour of its acetate indicate a close relationship to cellulose. The action of PBr_5 on cellulose acetates suggests a 1 : 6- in addition to a 1 : 4-linking of cellobiose. A. G. P.

Leucine and dileucine hydrochloride. Isolation of leucine. H. M. Barnett (J. Biol. Chem., 1933, **100**, 543—550).—Isolation of leucine (I) from casein and wheat gluten hydrolysates is based on its pptn. by NaCl. The salting out of (I) and of dileucine hydrochloride (II) at various p_H is described. (II) is possibly

$CH_2Pr^{\beta}\cdot CH(NH_2,HCl)\cdot CO_2NH_3\cdot CH(CO_2H)\cdot CH_2Pr^{\beta}$

R. S. C.

Oxidation of cystine in non-aqueous media. I. Solubility and stability of cystine in non-aqueous acid–base systems. G. Toennies and T. F. Lavine (J. Biol. Chem., 1933, **100**, 463—477).—Cystine is sol. in MeOH–HCl, but is esterified, whilst it is oxidised in solutions of $HClO_4$ (I) in AcOH; it is sol. and stable in a solution of (I) in MeCN. It is oxidised by free (I), but stable in the presence of ClO_4' ions. H. D.

Catalytic decomposition of nitroso-β-alkylaminoketones. I. Preparation of diazomethane. Evidence of the occurrence of diazotisation in the aliphatic series. E. C. S. Jones and J. Kenner (J.C.S., 1933, 363—368).—The additive products of mesityl oxide and the appropriate amine with HNO_2 at 0° give good yields of *nitroso-β-methyl-* (I), b.p. 111°/0·8 mm., *-ethyl-*, b.p. 114°/0·5 mm., *-n-propyl-* (II), b.p. 120°/1 mm., *-n-butyl-*, b.p. 127°/0·6 mm., and *-n-amyl-*, b.p. 127°/0·3 mm., *-aminoisobutyl Me ketone*; these compounds decompose to olefines when heated. The following aromatic analogues, which were prepared similarly in 25% yield, *nitroso-β-phenyl-*, m.p. 59—61°, *-m-*, m.p. 78°, and *-p-tolyl-aminoisobutyl Me ketones*, m.p. 105—108°, give the diazo-compound with aq. alcoholic NaOH. β-Benzylaminoisobutyl Me ketone (*hydrochloride*) gives the *NO*-derivative, m.p. 85—86°. The decomp. of (I) with various Na alkoxides gives varying yields of CH_2N_2, the max., 83·5%, being obtained with $NaOPr^{\beta}$. With 50% aq. KOH the aliphatic nitroso-ketones give varying yields of olefine; (II) gives propylene, $Pr^{\alpha}OH$, and $Pr^{\beta}OH$, whence the intermediate formation of propyldiazonium hydrate is inferred. The nitroso-ketones can be used for alkylation of phenolic compounds, but the requisite conditions vary with different phenols. With conc. mineral acids olefines are also formed, but the yield is poor owing to simultaneous production of amine, which is the sole product with HCl–Et_2O. R. S. C.

Alkylsemioxamazides. G. Tierie (Rec. trav. chim., 1933, **52**, 357—365).—The prep. of derivatives of the type X·CO·CO·NH·NH_2 (X = OR or NHR) and their use as reagents for carbonyl is investigated. With the appropriate aldehyde Et oxalhydrazinate (Curtius, A., 1915, i, 787) affords *Et oxal-*p*-methoxy-*, m.p. 161°, and *-3 : 4-methylenedioxy-*, m.p. 169°, *-benzylidene-hydrazinate*; and from the similarly prepared *Me oxalhydrazinate*, m.p. 116°, are obtained *Me oxalbenzylidene-*, m.p. 150°, *-p-methoxy-*, m.p. 147°, and *-3 : 4-methylenedioxy-*, m.p. 215°, *-benzylidene-hydrazinate*. Et *N*-methyloxamate, b.p. 120—124°/15 mm., m.p. 24° (improved prep. described), is converted by aq. NH_3 into semioxamazide and, by an improved method, the *semioxamazones* of anisaldehyde, m.p. 278° (decomp.), piperonal, m.p. 290° (decomp.), and vanillin, m.p. 265°, are prepared. *5-Methylsemioxamazide*, NHMe·CO·CO·NH·NH_2, m.p. 197° (prep. from N_2H_4 and NHMe·CO·CO_2Et or from CO_2R·CO·NH·NH_2 and NH_2Me), similarly affords the *5-methylsemioxamazones* of PhCHO, m.p. 245°, anisaldehyde, m.p. 247°, piperonal, m.p. 280°, vanillin, m.p. 270° (decomp.), furfuraldehyde, m.p. 252—258°, hydroxymethylfurfuraldehyde, m.p. 204—205°, $COMe_2$, m.p. 127°, and COPhMe, m.p. 179°. With the exception of the $COMe_2$ derivative all are tasteless. J. W. B.

Reduction of α-amino-nitriles. W. McMeeking and T. S. Stevens (J.C.S., 1933, 347—349).—Reduction of α-amino-nitriles, CRR′(CN)·NR″R‴, by powdered Na in moist Et_2O gives amines, CHRR′·NR″R‴ (30—50% yield) (R″ = R‴ = Me: R = H, R′ = Me; R = R′ = Me; R = Ph, R′ = H); however, with Na slices in Et_2O–aq. $KHCO_3$ the amine is formed in the yield stated if R or R′ is Ph (R = Ph, R′ = H: R″ = R‴ = H, 57; R″R‴ = C_5H_{10}, 85; R″ = Me, R‴ = H, 19; R″ = R‴ = H, 46; R″ = Ph, R‴ = Me, 50; and R = R″ = Ph, R′ = Me, R‴ = H, 55%), whereas the diamine, CRR′(NR″R‴)·CH_2·NH_2, is formed if R and R′ are aliphatic (R″ = R‴ = Me, R = Et, R′ = H, 39; R = R′ = R″ = R‴ = Me, 22; R = Me, R′ = H, R″ = Ph, R‴ = Et, 55%; R = R′ = Me, R″ = R‴ = H, entirely decomposed). The following are described: α-dimethylamino-*n*-butyronitrile, b.p. 156—158° [*picrate*, m.p. 148° (decomp.)]; *α-amino-β-dimethylaminobutane dihydrochloride*, m.p. 176° (decomp.); *α-amino-β-dimethylaminoisobutane dihydrochloride*, deliquescent, m.p. 256—258°; *α-ethylanilinopropionitrile*, b.p. 133—134°/10 mm.; *α-amino-β-ethylanilinopropane dihydrochloride*, m.p. 199—200°, and *picrate*, m.p. 164°; *benzylmethylamine picrate*, m.p. 117—118°; a neutral *substance*, m.p. 183°, as by-product in the prep. of α-methylaminophenylacetonitrile. R. S. C.

Preparation, toxicity, and absorption of bismuth compounds. IV. Bismuth compounds of thiolacetic acid. W. M. LAUTER, A. E. JURIST, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1933, **22**, 212—214).—*Na bismuthothiolacetate*, $(CO_2Na{\cdot}CH_2{\cdot}S)_2BiOH$ (32% absorbed in 27 days after intramuscular injection), and *bismuthotriothiolacetamide*, $Bi(S{\cdot}CH_2{\cdot}CO{\cdot}NH_2)_3$ (82% absorbed in 3 hr.), have the same order of toxicity (max. tolerated dose < 30 and < 50 mg./kg., respectively). The prep. of $SH{\cdot}CH_2{\cdot}CO_2Et$ and *Et bismuthothiolacetate* is described. E. H. S.

Preparation of silicon triethyl halides. E. A. FLOOD (J. Amer. Chem. Soc., 1933, **55**, 1735—1736).—*Si triethyl fluoride*, b.p. 110°, $SiEt_3Cl$, and $SiEt_3Br$ are obtained in almost quant. yield from $(SiEt_3)_2O$ and the appropriate Na or NH_4 halide in conc. H_2SO_4. H. B.

Oxidation of Grignard reagents. M. T. GOEBEL and C. S. MARVEL (J. Amer. Chem. Soc., 1933, **55**, 1693—1696).—The rates of absorption of O_2 by Et_2O solutions (0·0052—0·0162*M*) of MgEtBr, MgBuCl, $CH_2Ph{\cdot}MgBr$, MgPhBr, and Mg octyl (I) and cetyl (II) bromides at 0—29° are determined; oxidation proceeds rapidly at 0°, *i.e.*, when the v.p. of Et_2O is not high enough to prevent access of air. (I) and (II) are oxidised by O_2 giving good yields of octyl and cetyl alcohol, respectively. H. B.

Yields of aliphatic tertiary Grignard reagents and limits of their usefulness as synthetic reagents. F. C. WHITMORE and D. E. BADERTSCHER (J. Amer. Chem. Soc., 1933, **55**, 1559—1567).—$CMe_3{\cdot}MgCl$ (I), $CMe_2Et{\cdot}MgCl$ (II), $CMeEt_2{\cdot}MgCl$ (III), $CMeEtPr^{\alpha}{\cdot}MgCl$ (IV), $CMeEtBu^{\alpha}{\cdot}MgCl$ (V), $CMe_2Bu^{\alpha}{\cdot}MgCl$ (VI), $CEt_3{\cdot}MgCl$ (VII), and Mg dimethyl-*n*-amylcarbinyl chloride (VIII) are prepared in 58—80% yield. Of these, (I) only reacts with Et_2CO_3. (I), (II), and (VI) react with $ClCO_2Et$ to give the appropriate $CR_3{\cdot}CO_2Et$. (I) and AcCl give 40·7% of $COMeBu^{\gamma}$; small amounts of Me *tert.*-amyl ketone, γ-methyl-γ-ethylpentan-β-one, and γγ-dimethylheptan-β-one are similarly obtained from (II), (III), and (VI), respectively. ββ-*Dimethylheptyl*, b.p. 88—89°/15 mm., β-*methyl*-β-*ethylamyl*, b.p. 75·5—76°/15 mm., β-*methyl*-β-*ethylhexyl*, b.p. 85·5—86°/11 mm., and ββ-*diethylbutyl*, b.p. 75—78°/12 mm., *alcohols* are prepared in 10—41% yield from CH_2O and (VIII), (IV), (V), and (VII), respectively. (VI) and (VIII) react normally with CO_2. H. B.

Gallium trimethyl, gallium trimethyl etherate, and gallium trimethylammine. C. A. KRAUS and F. E. TOONDER (Proc. Nat. Acad. Sci., 1933, **19**, 292—298).—*Ga trimethyl* (I), b.p. 55·7±0·2°/762 mm., f.p. −19°, from $ZnMe_2$ and $GaCl_3$ (first at room temp. and then at 80—120°), is extremely reactive towards O_2. MgMeI and $GaCl_3$ in Et_2O and N_2 give *Ga Me*$_3$ *etherate* (II), b.p. 98·3°, f.p. −76°, which is oxidised slowly by atm. O_2, is hydrolysed by aq. KOH giving CH_4 (1 mol. at 35°; 2 mols. at 100°), and with liquid NH_3 affords *Ga trimethylammine*, m.p. 31°. (I) could not be obtained from (II) in a pure state. H. B.

Chlorination products of gallium trimethyl. C. A. KRAUS and F. E. TOONDER (Proc. Nat. Acad. Sci., 1933, **19**, 298—303).—Ga trimethylammine (I) and excess of HCl at room temp. to 160° give CH_4 (3 mols.) and NH_4 *tetrachlorogalliate*, not melted at 200°. (I) and HCl (2 mols.) in Et_2O afford *Ga dimethyl chloride monoammine*, m.p. 54° (a *diammine*, m.p. 112°, is also described), also obtained from NH_4Cl and $GaMe_3,Et_2O$ in Et_2O; the first-named reaction is $GaMe_3,NH_3 \xrightarrow{HCl} GaMe_3 + NH_4Cl \longrightarrow GaMe_2Cl,NH_3 + CH_4$. $GaMe_3$ and NH_4Cl do not react in liquid NH_3. *Ga methyl dichloride*, m.p. >75° (vac.) (monoammine, m.p. >80°; pentammine), is prepared from (I) and HCl (3 mols.) in Et_2O or from $GaMe_3,Et_2O$ and HCl (2 mols.) in Et_2O. H. B.

Carbon rings. XXIV. Twenty-three-membered carbon ring. L. RUZICKA and M. STOLL. XXV. Introduction of a triple linking in the fifteen- and seventeen-membered carbon rings. L. RUZICKA, M. HURBIN, and H. A. BOEKENOOGEN (Helv. Chim. Acta, 1933, **16**, 493—498, 498—505).—XXIV. Electrolysis of the Na salt of *Me H undecane*-αλ-*dicarboxylate*, m.p. 49—50° [obtained by partial hydrolysis (dil. HCl) of the Me_2 ester], in MeOH gives 60% of the *Me* ester, m.p. 68—70°, of *docosane*-αχ-*dicarboxylic acid*, m.p. 128—130°. Dry distillation of the Ce salt of this affords about 2% of cyclo*tricosanone* (I), b.p. 175—177°/0·02 mm., m.p. 38·5—39° (purified through its *semicarbazone*, m.p. 174—176°), (probably) Me docosyl ketone, and products of high b.p. (from which none of the expected C_{46}-diketone could be isolated). (I) is reduced (Clemmensen) to cyclo*tricosane* (II), b.p. about 177°/0·1 mm., m.p. 49—50°. The vals. of *M*/*d* for (I) and (II) agree with those calc. from similar rings; the m.p. and mol. refraction are not so regular.

XXV. Successive treatment of *cyclo*pentadecene (III) with Br (in cold CS_2) and EtOH–KOH (at 100°) gives impure 1-*bromo*-Δ^1-cyclo*pentadecene*, b.p. 128—132°/0·25 mm., converted by more conc. EtOH–KOH (at 150—175°) into cyclo*pentadecinene*, b.p. 158—159°/14 mm. (ozonolysis product, tridecane-αν-dicarboxylic acid), which is reduced (H_2, PtO_2, EtOAc) to *cyclo*pentadecane. 1-*Bromo*-Δ^1-cyclo*heptadecene*, b.p. 147—150°/0·5 mm., similarly gives cyclo*heptadecinene*, b.p. 127—128°/0·25 mm. (ozonolysis product, pentadecane-αο-dicarboxylic acid). *cyclo*Triacontadiene (IV) (A., 1932, 58) gives *mixtures*, m.p. 63—69° and 95—105°, of Br_2-derivatives when treated as above; these could not be freed from Br by EtOH–KOH at 180°/30 hr. Saturation of (III) with Br in CS_2, treatment of the resultant product with $NHMe_2$ in C_6H_6 at 140—150°, and addition of MeI to the resulting base gives cyclo*pentadecenyltrimethylammonium iodide*, m.p. about 230° (decomp.). *Tetramethyldiamino*cyclo*triacontadiene dimethiodide*, m.p. 256°, is similarly prepared in 6—10% yield from (IV). H. B.

Mechanism of the ionene synthesis. M. T. BOGERT (Science, 1933, **77**, 197—198; cf. this vol., 153).—Further evidence is given concerning the mechanism of this synthesis in so far as the transition from a monocyclic *tert.*-alcohol to a dicyclic hydrocarbon is involved. L. S. T.

Anodic oxidation of *cyclo*hexane and its derivatives. M. YOKOYAMA (Bull. Chem. Soc. Japan, 1933, **8**, 71—107).—The anodic oxidation of C_6H_6 in N-H_2SO_4 proceeds with a higher current yield (up to

95% at 70°) at a PbO_2 anode than at a Pt anode (> 55%), and with a lower temp. coeff.; the products include pyrocatechol, *p*-benzoquinone, maleic acid, HCO_2H, CO, and CO_2. *cyclo*Hexane (I) is very difficult to oxidise (< 10%) in *N*-H_2SO_4; in a mixture of 2*N*-H_2SO_4 and $COMe_2$ it yields adipic (II), succinic (III), malonic (IV), and, probably, glutaric acids. *cyclo*Hexanol yields on anodic oxidation *cyclo*hexanone (V), *cyclo*hexene (VI), and (I), (II), and (III), the current yield being up to 90%; (V) behaves in an analogous manner. (VI) yields similar products to those obtained from (I), but the yield diminishes continuously throughout the process (max. 93%). *cyclo*Hexanediol yields (II), (III), (IV), HCO_2H, and traces of (V). Details are given of the yield of each product. The mechanisms of the reactions are discussed, particularly in relation to the differences of behaviour of saturated cyclic and aromatic compounds. It appears probable that a persulphuric acid, formed at the anode, is the actual oxidising agent. H. F. G.

Slow combustion of benzene. J. Amiel (Compt. rend., 1933, **196**, 1122—1124).—Oxidation of mixtures of C_6H_6 (1 part) and O_2 (15 parts) at an initial pressure of 1 atm. heated in sealed tubes for 2 hr. commences at 420°, rapidly increasing between 435° and 485°. The CO_2 content of the gaseous products increases with rise of temp., whilst the CO content is max. (32—33%) at 477°. Oxidation is complete above 510°, the gaseous composition curve coinciding with that for the oxidation of CO. A. C.

Jacobsen reaction. III. Monobromo-derivatives of the three tetramethylbenzenes. L. I. Smith and C. L. Moyle (J. Amer. Chem. Soc., 1933, **55**, 1676—1682; cf. A., 1932, 607).—Bromodurene (I) and conc. H_2SO_4 at 25—30° give (after 10 days) dibromodurene (92—99%), prehnitenesulphonic acid (II) (max. yield 25%), and amorphous material (25—30%); much SO_2 is evolved and traces only of ψ-cumenesulphonic acids are produced. Similarly, bromo*iso*durene affords dibromo*iso*durene (80%) and (II) (35—40%), whilst bromoprehnitene furnishes (much more readily) dibromoprehnitene (99%) and (II) (81%). The first stage in the reaction is sulphonation; the sulphonic acid then rearranges (at 10—15° or 130—150°, hydrolysis and not rearrangement occurs). The Br_2-derivatives do not rearrange in contact with H_2SO_4. Little or no depression of the m.p. of mixtures of the Br- and Br_2-derivatives is observed; the latter are characterised by reduction (red P and HI at 225°) to the hydrocarbons and conversion of these into $(NO_2)_2$-derivatives. *Bromodurenesulphonic acid* (+1·5H_2O), m.p. 142—143° (decomp.) (*chloride*, m.p. 185°; *amide*, m.p. 194°), is prepared by short treatment of (I) with oleum at 0°. H. B.

Catalysis of polymerisation by ozonides. II. R. C. Houtz and H. Adkins (J. Amer. Chem. Soc., 1933, **55**, 1609—1617; cf. A., 1931, 597).—The course of the polymerisation of styrene (I) by ozonides and other catalysts is followed by determinations of the viscosity of a 10% solution of the reaction mixture in C_6H_6, the wt. of polystyrene (II) produced, and the sp. viscosity of a solution of 26 g. of (II) per litre of C_6H_6. The sp. viscosity of (II) reaches a max. and then decreases; it varies considerably with the experimental conditions and, contrary to Staudinger and Lautenschlager (A., 1931, 1031), is a max. with the (II) prepared at 100° in N_2 in absence of a catalyst. Contrary to these authors, Bz_2O_2 is a more active catalyst than O_2 for the polymerisation of (I); it is suggested that their specimen of (I) contained a catalyst. Di*iso*butylene ozonide (III) is a very active catalyst and also catalyses the polymerisation of Ph styryl, styryl Me, and Me $\Delta^{\alpha\gamma}$-pentadienyl ketones, $\Delta^{\beta\delta}$-hexadienal, Et sorbate, and $\Delta^{1\cdot3}$-*cyclo*hexadiene. *cyclo*Hexene and O_3 in AcOH give a liquid ozonide which is much less active for the polymerisation of (I) than (III); the solid ozonides (Harries, A., 1915, i, 966) are practically inactive. The mechanisms of catalysis and polymerisation of (I) are discussed. H. B.

Nitration of *p*-fluorotoluene. Y. Desirant (Bull. Acad. roy. Belg., 1933, [v], **19**, 325—345).—Nitration of *p*-C_6H_4MeF (I) in CCl_4 with HNO_3 in presence of P_2O_5 gives 25% yield of a mixture of 4-*fluoro*-3-*nitro*-, b.p. 241°/765 mm., m.p. 26·48°, and 4-*fluoro*-2-*nitro*-*toluene* (II), b.p. 213°/768 mm., m.p. 8·85°, identified by conversion into the nitrotoluidines. (II) has been synthesised by diazotisation of 2-nitro-*p*-toluidine in presence of HF. The nitration of (I) occurs 74·5% *m* to the Me group, showing that F>Cl>Me in orienting power. J. W. S.

Replacement of bromine by chlorine in organic halides. II. P. Pfeiffer and W. Praetorius (J. pr. Chem., 1933, [ii], **137**, 27—39; cf. A., 1930, 333).—Stilbene dibromide (I) and $HgCl_2$, slowly in boiling $COMe_2$–$CHCl_3$ but more rapidly in boiling AcOH, yield stilbene dichloride (II), m.p. 190·5—191°. As with $SnCl_4$ (*loc. cit.*), NO_2 has a protective action, so that 4-nitro- (III) and 2 : 4-dinitro-stilbene dibromide (IV) afford 7′-chloro-7-bromo-4-nitro-, m.p. 180—181°, and 2 : 4-dinitro-dibenzyl, α, m.p. 159·5—160·5°; β, m.p. 149—150·5°, respectively. 4 : 4′-Dinitrostilbene dibromide (V) does not react. In cold dioxan, $HgCl_2$ and 4-methoxystilbene dibromide (VI) give 7-*chloro*-7′-*bromo*-4-*methoxydibenzyl*, m.p. 168—169°; in the boiling solvent the second Br is attacked without production of homogeneous 4-*methoxystilbene dichloride*, m.p. 148—149° (obtained from 4-methoxystilbene and Cl_2 in CCl_4). αβ-Dibromo-β-phenylpropionic acid (VII), m.p. 195—196°, and $HgCl_2$ do not react in boiling $COMe_2$, but in boiling AcOH yield β-*chloro*-α-*bromo*-β-*phenylpropionic acid*, m.p. 183—184° (decomp.); in similar circumstances, no reaction occurs with αβ-dibromo-4-nitrophenylpropionic acid. αβ-Dibromo-4-methoxyphenylpropionic acid (VIII) and $HgCl_2$ at room temp. afford α-*bromo*-β-*ethoxy*-4-*methoxyphenylpropionic acid*, m.p. 118·5—119·5°; ill-defined results are obtained in dioxan. αβ-*Dichloro*-β-4-*methoxyphenylpropionic acid* has m.p. 133—134° (decomp.). In boiling EtOH or dioxan, respectively, meso- (IX) and *dl*-dibromosuccinic acids are not affected by $HgCl_2$. (II), m.p. 190—190·5°, in EtOH at 150° or $COMe_2$ at 200°, 4-nitrostilbene dichloride (X) in boiling EtOH, Bu$^\beta$OH, or *cyclo*hexanol, and 2 : 4-dinitrostilbene dichloride (XI) in boiling EtOH are indifferent towards LiBr. (II) is unchanged by LiI in boiling EtOH, but at 200° affords stilbene

(XII), also obtained from (I) in EtOH at 150° or AcOH at 100°. In boiling and cold $COMe_2$, respectively, (III) and (IV) yield the corresponding substituted stilbenes. (II) does not react with NaI in EtOH at 150°, but in AcOH at 200° gives (XII). At room temp. in $COMe_2$ (I) and NaI yield (XII). Under similar conditions (III) and (VI) give the corresponding stilbenes, (VII) yields $CHPh{:}CH{\cdot}CO_2H$, and (IX) affords fumaric acid. (X) and (XI) are indifferent towards $CaBr_2$ in EtOH. H. W.

Synthesis of homologous naphthalenes. E. DE B. BARNETT and F. G. SANDERS (J.C.S., 1933, 434—437).—Succinic anhydride, $AlCl_3$, and the appropriate hydrocarbon, best in $C_2H_2Cl_4$ (except with $C_{10}H_8$), give the following β-benzoylpropionic acids: 4-Me-, m.p. 129°, 4-Pr^{β}-, m.p. 142°, 3 : 4-, m.p. 129°, 2 : 4-, m.p. 114°, and 2 : 5-Me_2-, m.p. 86°, b.p. 215°/1 mm. Reduction by Clemmensen's method (Zn wool) (contrast lit.) readily afforded the following *n*-butyric acids: γ-*p*-tolyl-, m.p. 59°, -p-*cumyl*-, m.p. 50°, -o-, m.p. 53°, -*m*-, m.p. 79°, and -*p*-xylyl-, m.p. 70°, b.p. 175°/2 mm. Cyclisation by 80% H_2SO_4 at 100° led to the following 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalenes: 7-Me-, m.p. 35°, 7-Pr^{β}-, m.p. 36°, 6 : 7-, m.p. 49°, and 5 : 8-Me_2-, m.p. 33°, and 5 : 7-Me_2-. By the Grignard reaction these yielded the following 1 : 2 : 3 : 4-*tetrahydro*-1-*naphthols*: 1 : 7-Me_2-, m.p. 90°, 1-*Me*-7-Pr^{β}-, m.p. 83°, 7-Me-1-Pr^{β}- and 1 : 6 : 7-Me_3-, oils, and 1 : 5 : 8-Me_3-, m.p. 136°, whilst Clemmensen reduction gave 6 : 7-, b.p. 128°/7 mm., and 5 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 120°/1 mm. and 254°/760 mm. Dehydrogenation of the hydrocarbons or carbinols by Se at 300° (reaction in the vapour phase) led to the following substituted naphthalenes: 1 : 4-, b.p. 264° (picrate, m.p. 144°), 1 : 7-, b.p. 258° (picrate, m.p. 120°), and 2 : 3-Me_2-; 1 : 3-Me_2-, b.p. 107°/1 mm. (*picrate*, m.p. 118°); eudalene (picrate, m.p. 95°; styphnate, m.p. 122°); 1 : 4 : 5- and 1 : 6 : 7-Me_3-, m.p. 28° (picrate, m.p. 125°; styphnate, m.p. 149°). R. S. C.

Dichloronaphthalenes and related intermediates. R. W. BEATTIE and F. C. WHITMORE (J. Amer. Chem. Soc., 1933, **55**, 1546—1548).—Details are given of the prep. of nine naphthalenesulphonyl chlorides from $C_{10}H_6Cl{\cdot}SO_3Na$ (prepared from $NH_2{\cdot}C_{10}H_8{\cdot}SO_3H$ by the usual method) and PCl_5. $C_{10}H_6Cl{\cdot}SO_2Cl$ and PCl_5 at 160—165° give $C_{10}H_6Cl_2$ in 36—49% yield; 1 : 2-, b.p. 295—298°, m.p. 33—34°, 1 : 4-, m.p. 67·4—68°, 1 : 5-, m.p. 106—107°, and 2 : 6-, m.p. 136°, -$C_{10}H_6Cl_2$ are thus obtained. H. B.

[Regularity in the structure of the absorption spectra of aromatic hydrocarbons. IX.] H. CONRAD-BILLROTH (Ber., 1933, **66**, [*B*], 639—640).—A criticism of the work of Clar (this vol., 269) from a physical viewpoint. H. W.

Synthesis of phenanthrene and its derivatives. M. T. BOGERT (Science, 1933, **77**, 289).—1-Phenylethyl-*cyclo*hexan-1-ol, prepared from Mg phenylethyl bromide and *cyclo*hexanone, condenses (conc. H_2SO_4) to octahydrophenanthrene which yields phenanthrene by dehydrogenation with Se. L. S. T.

Isolation of a cancer-producing hydrocarbon from coal tar. I—III. J. W. COOK, C. L. HEWETT, I. HIEGER, and (in part) F. GOULDEN (J.C.S., 1933, 395—405).—Partly a detailed account of work previously reported (this vol., 85). Medium soft pitch, by fractional distillation, crystallisation of the picrates, etc., gives 2 : 3-benzcarbazole [2 : 7-*dinitroanthraquinone* compound, m.p. 291—294° (decomp.)], chrysene, 4 : 5-*benzpyrene* (I), m.p. 181—187° (*picrate*, m.p. 235°) (probably not carcinogenic), 1 : 2-*benzpyrene* (II), m.p. 175·5—176·5° (*picrate*, m.p. 188—192°) (highly carcinogenic; gives the characteristic fluorescence spectrum of the carcinogenic fractions of tar), perylene, and 1 : 2-benzanthracene (isolated by dissociation of the maleic anhydride adduct when sublimed at 300°/5 mm.). Succinic anhydride, pyrene (III), and $AlCl_3$ in $PhNO_2$ at room temp. give β-1-*pyrenoylpropionic acid*, m.p. 183° (*semicarbazone*, m.p. 203—205°, unchanged by NaOEt at 200°; *Et* ester, m.p. 90—91°), giving pyrene with $ZnCl_2$ at 160—170° or hot AcOH–H_2SO_4, and reduced by Zn dust–NaOH–aq. NH_3 (but not by Zn and HCl–AcOH, or by Clemmensen's method) to γ-1-*pyrenyl*-γ-*butyrolactone*, m.p. 178°, and γ-1-1-*pyrenylbutyric acid*, m.p. 185—186°, also obtained by reduction of the lactone. This acid with $ZnCl_2$ at 180°, or, much better, $SnCl_4$ at 115—120°, gives 4′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzpyrene*, m.p. 171·5—173·5° [*oxime*, m.p. 222—224° (decomp.)], whence by Se at 300—340° (II) (*NO*$_2$-derivative, m.p. 233—236°; *quinone*, m.p. 242—244°) was obtained. *o*-$C_6H_4(CO)_2O$, (III), and $AlCl_3$ in C_6H_6 give 1-*pyrenoyl*-o-*benzoic acid*, m.p. 224·5—225·5°, reduced (Zn dust–Cu–aq. NaOH) to 1-o-*carboxybenzylpyrene*, m.p. 217—218°, which is cyclised by $ZnCl_2$ at 200° to a ketone [also obtained from *o*-toluoyl chloride, (III), and $AlCl_3$ in CS_2 or $PhNO_2$], not obtained pure, but reduced (Zn dust–hot aq. NaOH) to 2′ : 3′-*naphtha*-1 : 2-*pyrene*, orange, m.p. 273° (probably not carcinogenic), which with maleic anhydride in hot xylene gives 2′ : 3′-*naphtha*-1 : 2-*pyrene*-1′ : 4′-endo-αβ-*succinic anhydride*, decomp. 270—280°. 4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene and MgPhBr or $Mg(C_6H_{11})Cl$ give 4-*hydroxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 140—141° (not completely dehydrated by picric acid in boiling EtOH), and an oil, whence by Se phenanthrene and a *substance*, $C_{28}H_{16}O$, m.p. 312°, possibly a *diphenanthrafuran*, were obtained. Triphenylene, $AlCl_3$, and $(COCl)_2$ in CS_2 at room temp. give *triphenylenecarboxylic acid*, m.p. 325—326° (decomp.) (*Na* salt; *Me* ester, m.p. 122—124°). Reduction of pyrene with Na and amyl alcohol gives *s*-hexahydropyrene (IV), m.p. 132—133° (lit. 129—130°), also prepared by hydrogenation with Ni in tetrahydronaphthalene (cf. A., 1907, i, 310), and as-*hexahydropyrene* (V), m.p. 105—105·5° (*picrate*, m.p. 147·5—148°). The constitution of (IV) is proved by oxidation with $KMnO_4$ in KOH–aq. $COMe_2$ to naphthalene-1 : 4 : 5 : 8-tetracarboxylic dianhydride, whereas (V) was more resistant and did not give a $C_{10}H_5(CO_2H)_3$. (IV), succinic anhydride, and $AlCl_3$ in $PhNO_2$ give β-1 : 2 : 3 : 6 : 7 : 8-*hexahydro*-4-*pyrenoylpropionic acid*, m.p. 173·5°, reduced by Na–Hg in NaOH to γ-1 : 2 : 3 : 6 : 7 : 8-*hexahydro*-4-*pyrenyl*-γ-*butyrolactone*, m.p. 150—154°, whilst the *semicarbazone*, m.p. 221—222°, with NaOEt–EtOH at 180—190° gives γ-1 : 2 : 3 : 6 : 7 : 8-*hexahydro*-4-*pyrenylbutyric acid*, m.p. 133—134°; with 80% H_2SO_4 at 100° this affords

1′-*keto*-1 : 2 : 3 : 6 : 7 : 8 : 1′ : 2′ : 3′ : 4′-*decahydro*-4 : 5-*benzpyrene*, m.p. 147—148°, dehydrated by Se at 320—340° to (I) (*picrate*, m.p. 229—230°), believed to be identical also with the substance, m.p. 183°, stated to be $C_{17}H_{12}$ or $C_{17}H_{10}$ by Meyer *et al.* (A., 1920, i, 589). R. S. C.

Chemical reactions induced by light. IV. L. Vecchiotti and C. Piccinini (Gazzetta, 1933, **63**, 112—115; cf. A., 1932, 130).—The action of sunlight for 6 months on a mixture of *o*-$C_6H_4Me{\cdot}NO_2$ and NH_2Ph gave a product containing *p*-$OH{\cdot}C_6H_4{\cdot}NH_2$, 2′-*methylazoxybenzene*, $Ph{\cdot}NO{:}N{\cdot}C_6H_4Me$, m.p. 70°, and an isomeride of the latter, probably a *benzeneazocresol*, m.p. 88—89°. O. J. W.

Preparation of anils of simple aliphatic ketones. (Mlles.) M. Montagne and G. Rousseau (Compt. rend., 1933, **196**, 1165—1167).—Butyranilide and excess of MgEtBr form the complex $CPrEt(OMgBr){\cdot}NPh{\cdot}MgBr$, which is hydrolysed to COEtPr, but is converted by heating in presence of C_6H_6 or PhMe followed by hydrolysis into *Et Pr ketanil* (I), b.p. 114—115°/11 mm. (*picrate*, m.p. 102°), and an anil of a higher unsaturated *ketone*, b.p. 99—103°/14 mm. (*oxime*, b.p. 138—142°/14 mm.). (I) is reduced by Na–EtOH to *γ-anilinohexane*, b.p. 123—125°/13 mm. (*phenylurethane*, m.p. 55°; *acetate*, b.p. 154—155°/13 mm.). Butyro-*p*-toluidide gives *Et Pr ketotolil*, b.p. 130—133°/13 mm., reduced to *γ*-p-*toluidinohexane*, b.p. 138—139°/15 mm. Propionanilide gives, in addition to the unsaturated *ketone*, b.p. 90—93°/20 mm., *Et*$_2$ *ketanil*, b.p. 110—111°/18 mm. (*picrate*, m.p. 143°), which is reduced to *γ-anilinopentane*, b.p. 114°/13 mm. (*acetate*, b.p. 153°/18 mm.). *Butyrophenoneanil* has b.p. 150°/3 mm. A. C.

Modified Curtius degradation. VII. Degradation of aromatic acids. C. Naegeli and A. Tyabji (Helv. Chim. Acta, 1933, **16**, 349—366; cf. A., 1929, 540).—Reactive Ar·COCl are heated with NaN_3 in C_6H_6 until evolution of N_2 ceases and the resulting Ar·NCO (isolated or in solution) is warmed with conc. HCl [sometimes with 60% (vol.) H_2SO_4], 1—50% alkali hydroxide, or AcOH–Ac_2O, thus giving $Ar{\cdot}NH_2$,HCl, NH_2Ar, or NHArAc, respectively, together with varying amounts (0—98%) of $CO(NHAr)_2$. The products thus obtained from the azide or carbimide from BzOH, *m*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, 3 : 5-$(NO_2)_2C_6H_3{\cdot}CO_2H$, and azobenzene-*m*-carboxylic acid [*chloride*, m.p. 72°; *azide* (I), m.p. 76—77° (decomp.)], are studied in detail. *p*-$NO_2{\cdot}C_6H_4{\cdot}CON_3$ is hydrolysed only with difficulty. Relatively large amounts of $(p\text{-}NO_2{\cdot}C_6H_4{\cdot}NH)_2CO$ are usually formed during the above treatments. (I) decomposes in C_6H_6 at 90—100° to m-*benzeneazophenylcarbimide*, m.p. 45—46°, which with H_2O or *m*-aminoazobenzene (II) gives s-*di*-(m-*benzeneazophenyl*)*carbamide* (III), m.p. 275—276°, with EtOH yields *Et* m-*benzeneazophenylcarbamate*, m.p. 102—103°, and with Ac_2O at 90° affords 32% of (III) and 29 and 21%, respectively, of the Ac and Ac_2, m.p. 60—61°, derivatives of (II). *m*-$NO_2{\cdot}C_6H_4{\cdot}NCO$ and $CCl_3{\cdot}CO_2H$ in C_6H_6 give 17% of $(m\text{-}NO_2{\cdot}C_6H_4{\cdot}NH)_2CO$ and 68% of m-*nitrotrichloroacetanilide*, m.p. 104° (also prepared from *m*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and $CCl_3{\cdot}COCl$). 3 : 5-*Dinitrophenylcarbimide*, m.p. 91°, passes into a polymeride, m.p. about 330° (decomp.), when heated to 94—95°, *m*-$C_6H_4Br{\cdot}NCO$ (in C_6H_6) is hydrolysed by 10% KOH to *m*-$C_6H_4Br{\cdot}NH_2$ (90% yield). H. B.

Action of aromatic sulphur compounds on fungi. T. Hachiya and J. Nishimura.—See this vol., 638.

Fluorene derivatives. I. 3-Aminofluorene. M. Hayashi and A. Nakayama (J. Soc. Chem. Ind. Japan, 1933, **36**, 127—130B).—The ultra-violet absorptions of a no. of fluorene derivatives are determined. The following are described: 3-*nitro*-2-*acetamido*-, m.p. 200—201° (1-NO_2-?; prepared from "3-nitro-2-aminofluorene" from 2-acetamidofluorene; cf. A., 1902, i, 758); 7-nitro-2-acetamido-, m.p. 256—257° (+1H_2O); 3-(or ? 1)*amino*-2-*acetamido*-, m.p. 194·5—195·5°, and 3-*amino*-*fluorene*, m.p. 151—152° (*Ac* derivative, m.p. 189—190°). H. A. P.

Isatogens. XI. Reduction products of di- and tri-nitrodistyrylbenzene. P. Ruggli, A. Zimmermann, and W. Heitz (Helv. Chim. Acta, 1933, **16**, 454—468).—4 : 6-Dinitro-1 : 3-distyrylbenzene is reduced by EtOH–NH_4HS to 5-*nitro*-2 : 4-*distyrylaniline*, m.p. 111° (*Ac* derivative, m.p. 235°), and by $SnCl_2$ and AcOH–HCl, or, better, H_2, Ni, and aq. EtOH–EtOAc, to 4 : 6-distyryl-*m*-phenylenediamine, m.p. 201° (lit. 204°) (*Ac*$_2$, m.p. 284—285°, and *di*-p-*toluenesulphonyl*, m.p. 233°, derivatives). 2 : 4 : 6-Trinitro-1 : 3-distyrylbenzene (I) is reduced (EtOH–NH_4HS) to 3 : 5-*dinitro*-2 : 4-*distyrylaniline*, m.p. 171—172° (*Ac*, m.p. 208°, and *Ac*$_2$, m.p. 175°, derivatives), or a mixture of this and 5-*nitro*-4 : 6-*distyryl*-m-*phenylenediamine* (II), m.p. 175·5° [*Ac*$_2$ derivative (III), m.p. 276°], according to the conditions used. (II) is also obtained by catalytic reduction (as above) of (I). Reduction (Zn dust, AcOH) of (III) affords 3 : 5-*diacetamido*-2 : 6-*distyrylaniline*, m.p. 230°, acetylated (Ac_2O) to the *Ac*$_3$ derivative, m.p. about 334° (becomes brown > 290° and black at 320°), of 2 : 4 : 6-*triamino*-1 : 3-*distyrylbenzene*, m.p. 161°. All the above amines are purified through their Ac derivatives. Further acetylation of (III) gives *Ac*$_3$ (+AcOH), m.p. 224°, and *Ac*$_4$, m.p. 150°, derivatives; these are readily hydrolysed (dil. EtOH–NaOH) to (III). H. B.

Reactions of s-di-(9-phenyl-9-fluorenyl)hydrazine. L. A. Pinck (J. Amer. Chem. Soc., 1933, **55**, 1711—1716).—9-Bromo-9-phenylfluorene and N_2H_4,H_2O in xylene at 100° give s-*di*-(9-*phenyl*-9-*fluorenyl*)*hydrazine* (I), m.p. 195—196° (decomp.), and 9-phenylfluorenyl peroxide (II), m.p. 194°, and a little 9-phenylfluorene (III); at room temp., (III) is the main product. (I) reacts with Na in liquid NH_3 to give a Na-derivative [hydrolysed to (III)], is unaffected by "active" Ag_2O, and is oxidised ($KMnO_4$–$COMe_2$; Bz_2O_2–$CHCl_3$) to (II). (I) and Pd-black (IV) in C_6H_6 give N_2, (III), and a little diphenyldi(diphenylene)ethane (V), indicating the intermediate formation of azo-9-phenyl-9-fluorene. Air bubbled through (I) and (IV) in C_6H_6 gives (II) and 9-hydroxy-9-phenylfluorene. (II) and (V) are reduced [H_2, (IV), C_6H_6] to (III). Wieland's results (A., 1909, i, 836) on the probable transitory existence of $(\text{:}N{\cdot}CPh_3)_2$ are confirmed. s-Di(triphenylmethyl)hydrazine and HCl

do not give the hydrochloride (cf. Wieland, *loc. cit.*), but afford $N_2H_4,2HCl$ and CPh_3Cl. H. B.

Interaction of acetonephenylhydrazone and phenylcarbimide. F. J. Wilson, W. A. Caldwell, J. Chapman, and H. W. Goodwin (J. Roy. Tech. Coll., 1933, **3**, 24—25).—$NHPh{\cdot}N{:}CMe_2$ and PhNCO (I) in boiling C_6H_6 or at 100° (no solvent) give acetone-βδ-diphenylsemicarbazone, m.p. 141° (also prepared from $COMe_2$ and βδ-diphenylsemicarbazide), αβ-di(phenylcarbamyl)phenylhydrazine, m.p. 208° [also obtained from $NHPh{\cdot}NH_2$ and (I) (2 mols.) or from (I) and αδ- or βδ-diphenylsemicarbazide], and tarry products (cf. Whyburn and Bailey, A., 1928, 516). H. B.

Action of chlorosulphonic acid on phenol and *p*-cresol at low temperatures. G. N. Burkhardt (J.C.S., 1933, 337—338).—Interaction of $ClSO_3H$ (I) (added in 20 min.) with PhOH in CS_2 at −15° during 2 hr. affords approx. equimol. proportions of $PhHSO_4$ and p-$OH{\cdot}C_6H_4{\cdot}SO_3H$. Slow addition of (I) or long period for reaction favour sulphonate formation. Similarly *p*-cresol affords a product containing > 90% *p*-tolyl H sulphate. J. L. D.

Thermal decomposition of phenyl vinyl ether. W. M. Lauer and M. A. Spielman (J. Amer. Chem. Soc., 1933, **55**, 1572—1574).—Ph vinyl ether (I) heated at 295—300°/3 hr. in a sealed tube gives PhOH, $CHMe(OPh)_2$ [prepared by slow addition of PhOH to boiling (I) in CO_2], and a residue of high mol. wt. H. B.

Basis for the physiological activity of -onium compounds. XII. Aryl ethers of choline. R. R. Renshaw and C. Y. Hopkins (J. Amer. Chem. Soc., 1933, **55**, 1524—1528).—The following are prepared from the appropriate $C_6H_4R{\cdot}O{\cdot}CH_2{\cdot}CH_2Br$ and NMe_3: β-p-*hydroxy*-, m.p. 254°, -p-*methoxy*-, m.p. 144°, -o-*methoxy*-, m.p. 139°, -p-*benzoyloxy*-, m.p. 208—209°, -p-*acetoxy*-, m.p. 152°, -p-*amino*-, m.p. 195° (*hydrochloride*, m.p. 265°), -p-*acetamido*-, m.p. 248°, -2-*methoxy*-4-*allyl*-, m.p. 147°, and -2-*methoxy*-4-*propenyl*-, m.p. 158°, *-phenoxyethyltrimethylammonium bromides*; none of these is as active as $OPh{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br$ (A., 1929, 1487) in stimulating respiration and blood pressure. p-*Hydroxy*- (I), m.p. 107°, p-*acetoxy*-, m.p. 76·5—77°, p-*benzoyloxy*-, m.p. 119°, p-*methoxy*-, m.p. 49—50°, 2-*methoxy*-4-*propenyl*-, b.p. 190°/12 mm., and 2-*methoxy*-4-*allyl*-, b.p. 182°/13 mm., m.p. 23° (all m.p. except this are corr.), *-phenyl β-bromoethyl ethers* are prepared from $C_6H_4R{\cdot}OH$, s-$C_2H_4Br_2$, and MeOH–KOH. *Quinol di-β-bromoethyl ether*, m.p. 115°, is formed with (I). αβ-*Di*-m-*hydroxyphenoxy*-, m.p. 165°, and αβ-*dianisyloxy*- (described as αβ-dianisyl-), m.p. 147·5°, *-ethanes* are also prepared. H. B.

Stereochemistry of dicyclic ring systems. VII. Stereoisomerism of decahydronaphthalene and its derivatives. III. Stereoisomeric 1-substituted decahydronaphthalenes. W. Huckel, R. Danneel, A. Gross, and H. Naab. **IV. 9-Substituted decahydronaphthalenes.** W. Huckel and M. Blohm (Annalen, 1933, **502**, 99—114, —136).—VI. Reduction (H_2, colloidal Pt, H_2O) (the effect of pressure, amount of catalyst, and temp. are studied) of *ar*-tetrahydro-α-naphthol (1) gives decahydronaphthalene, liquid decalols, and (mainly) *cis*-α-decalol (*cis*-decahydro-α-naphthol) (II), b.p. 245° (corr.)/745 mm., m.p. 93° (A., 1925, i, 258) [*acetate*, b.p. 129°/15 mm.; *H phthalate*, m.p. 176°; *H succinate*, m.p. 66°; *succinate*, m.p. 150°; *oxalates*, m.p. 98—100° and 139°; p-*nitrobenzoate*, m.p. 83°; p-*toluenesulphonate*, m.p. 96—98° (decomp.)], also obtained in small amount (together with a compound, $C_{20}H_{22}O$, m.p. 113—114°, and other products) by similar reduction of α-$C_{10}H_7{\cdot}OH$. *cis*-α-Decalol, m.p. 55° (*H phthalate*, m.p. 142°), is prepared from (V) (below) and HNO_2. Reduction (Ni ?) of α-$C_{10}H_7{\cdot}OH$ at 180—210°/60—80 atm. gives tetra- and deca-hydronaphthalenes, (I), 1-ketodecahydronaphthalene, *trans*-α-decalol (III), m.p. 49° (A., 1930, 206) [*acetate*, b.p. 115°/10 mm., m.p. 30°; *H phthalate*, m.p. 121°; *H succinate*, m.p. 107°; *oxalates*, m.p. 77—78° (dimorphous; also with m.p. 85°) and 143°; p-*nitrobenzoate*, m.p. 116°], and *trans*-α-decalol, m.p. 63° [*acetate*, b.p. 121°/12 mm.; *H phthalate*, m.p. 168°; *H succinate*, m.p. 85°; *oxalate*, m.p. 111°; p-*nitrobenzoate*, m.p. 86°; phenylurethane, m.p. 114 (lit. 172°)]. Some (III) is also produced during Adams reduction of (I). The above pairs (*r*- and meso-forms) of oxalates are obtained by the action of $(COCl)_2$ in C_5H_5N and are separable through their differing solubilities in light petroleum; the use of $H_2C_2O_4$ (A., 1926, 238) gives unsatisfactory results. *cis*-β-Decalol, m.p. 105° (*acetate*, b.p. 122°/9 mm., m.p. 32°), yields *oxalates*, m.p. 64—65° and 120°, whilst *trans*-β-decalol, m.p. 75° (*acetate*, b.p. 118°/9 mm.), affords *oxalates*, m.p. 148° and 90—102°. The *acetate* of *trans*-β-decalol, m.p. 53°, has b.p. 110°/9 mm.

Reduction (H_2, colloidal Pt, AcOH) of *ar*-tetrahydroacet-α-naphthalide gives the *Ac* derivative, m.p. 181°, of *cis*-α-decalylamine (*cis*-decahydro-α-naphthylamine) (IV), b.p. 98°/10 mm., m.p. 8° (*Bz* derivative, m.p. 206°), whilst reduction (Na, EtOH) of *cis*-α-decaloneoxime affords a mixture of (IV) and *cis*-α-decalylamine (V), b.p. 100°/12 mm., m.p. −2° (*Ac*, m.p. 141°, and *Bz*, m.p. 193°, derivatives), separable through their hydrochlorides. Whilst alkaline reduction of *trans*-α-decaloneoxime gives *trans*-α-decalylamine (VI), b.p. 106°/16 mm., m.p. −1° (Leroux, Ann. chim., 1910, [viii], **21**, 458), reduction with H_2 and Pt-black in AcOH affords (VI), *trans*-α-decalylamine (VII), b.p. 99°/11 mm., m.p. −18° [*Ac*, m.p. 130° (lit. 127°), and Bz, m.p. 112°, derivatives], and trans-α-*decahydronaphthylhydroxylamine*, m.p. 113°. Reduction (H_2, Pt-black, AcOH) of α-tetraloneoxime gives (IV) (65%), (V) (25%), (VII) (10%), and (VI) (trace only).

VII. trans-9-*Nitrodecahydronaphthalene* (VIII), m.p. 24°, is separable from the mixture of NO_2-derivatives obtained by Nametkin and Madaev-Sitschev (A., 1926, 508), and is obtained directly by nitration of *trans*-decahydronaphthalene. Reduction (Al–Hg, moist Et_2O) of (VIII) gives trans-9-*hydroxylamino*-(IX), m.p. 121—123° (*Bz* derivative, m.p. 67—68°), and trans-9-*nitroso-decahydronaphthalene*, blue (unimol.), b.p. 87°/18 mm., m.p. −16°, and colourless (bimol.), m.p. 100°, forms [also prepared by oxidation (H_2O_2) of (IX)]. More prolonged reduction affords trans-9-*aminodecahydronaphthalene* (X), b.p. 222·6° (corr.)/757 mm., 90°/13 mm., m.p. −25° [*Ac*, m.p. 183°, and *Bz*, m.p. 148—149° (cf. *loc. cit.*), derivatives;

formate, m.p. 172° (decomp.)]. The non-cryst. fractions obtained during the separation (above) of (VIII) are similarly reduced to (IX), (X), and cis-9-*amino*-*decahydronaphthalene* (XI), b.p. 111°/18 mm., m.p. —13° [*Ac*, m.p. 127°, and *Bz*, m.p. 147°, derivatives; *formate*, m.p. 165—166° (decomp.)]. The 9-NO_2- and -NH_2-compounds of Nametkin and Madaev-Sitschov (*loc. cit.*) are mixtures of the *cis*- and *trans*-isomerides. Reduction (Al–Hg, moist Et_2O) of 10-chloro-9-nitroso-decahydronaphthalene (XII) (A., 1930, 76) gives 10-*chloro*-9-*hydroxylaminodecahydronaphthalene* (XIII), m.p. 116—120° (decomp.) (*hydrochloride*, decomp. 172—174°; *Ac* derivative, m.p. 81—83°), whilst Zn dust and Et_2O–conc. HCl afford (XIII) and (XV) (below). Reduction (Al–Hg, moist Et_2O, conc. HCl) of (XII) yields 9-*hydroxylamino*-10-*hydroxydecahydro*-*naphthalene* (XIV), m.p. 115—119° (*Bz* derivative, m.p. 99°). (XIII) is converted by boiling 2*N*-NaOH into 9-*hydroxylamino*-*octahydronaphthalene*, m.p. 138—143° (decomp.) (*Bz* derivative, m.p. 48—50°), and an unsaturated by-product, b.p. 45°/2 mm. Reduction (Zn dust, Et_2O–conc. HCl, or Al–Hg and moist Et_2O for 10 days) of (XII) also affords 9-*amino*-$\Delta^{4:10}$-*octahydro*-*naphthalene* (XV), b.p. 95°/11 mm., m.p. —11·5° [*Ac* (XVI), m.p. 141°, and *Bz*, m.p. 119—120°, derivatives; *formate*, m.p. 138—141°], reduced (H_2, PtO_2, dil. HCl) to (XI) and a little (X). Rapid reduction (H_2, PtO_2, Et_2O) of (XVI) gives the Ac derivative of (XI), whilst slow reduction (H_2, Pd–C, MeOH) also affords about 25% of the Ac derivative of (X). Reduction (Zn dust, Et_2O–conc. HCl) of (XII) also gives 9-*amino*-10-*hydroxydecahydronaphthalene*, m.p. 103° [*Ac*, m.p. 171—172°, and *Bz* (+H_2O), m.p. 150—152°, derivatives; O-*formyl* derivative *formate*, m.p. 185—187°], also obtained as a by-product in the prep. of (XV), by reduction (H_2, PtO_2, dil. HCl) of (XIV), and from $\Delta^{9:10}$-octahydronaphthalene oxide and conc. aq. NH_3 at 100°, which with HNO_2 affords *trans*-9 : 10-dihydroxydecahydronaphthalene and (as the result of a pinacolin rearrangement) a little *cyclo*hexanone-2-*spirocyclo*pentane (A., 1930, 76). (X) and HNO_2 give some trans-9-*hydroxydecahydronaphthalene*, m.p. 54° (which with aq. CrO_3 in light petroleum affords a chromate), and cis-9-*hydroxydecahydronaphthalene*, m.p. 65° [also formed from (XI) and HNO_2]; these alcohols are accompanied by mixtures of $\Delta^{1:9}$- and $\Delta^{9:10}$-octahydronaphthalenes. (XV) and HNO_2 give an unsaturated alcohol, oxidised (CrO_3, aq. AcOH) to (probably) 1-*keto*-$\Delta^{9:10}$-*octahydronaphthalene* [*semi*-*carbazone*, m.p. 244° (decomp.); *oxime*, m.p. 148° (*Bz* derivative, m.p. 134°)], which is reduced (H_2, Pd–C, Et_2O) to *trans*-1-ketodecahydronaphthalene.

H. B.

Antiseptics and anthelmintics. I. 1-Alkyl-β-naphthols. K. C. Gulatt, S. R. Seth, and K. Venkataraman (J. pr. Chem., 1933, [ii], **137**, 47—52).—β-Naphthyl esters are isomerised by $AlCl_3$ to 1-acyl-β-naphthols, the ketonic nature of which is established by transformation by Bz_2O and NaOBz into 2-alkylnaphthaflavones, and these are reduced (Clemmensen) to 1-alkyl-β-naphthols. The following transformations are described: β-naphthyl propionate into 1-*propionyl*-, m.p. 70—71° (2-*methyl*-β-*naphthaflavone*, m.p. 110°), and 1-*propyl*-β-*naphthol*, b.p. 143—145°/3 mm.; β-*naphthyl* n-*butyrate*, b.p. 164—165°/3 mm., into 1-*butyryl*-β-*naphthol*, b.p. 167—168°/1—2 mm., 2-*ethyl*-β-*naphthaflavone*, m.p. 112°, and 1-n-*butyl*-β-*naphthol*, b.p. 190°/3 mm., m.p. 80—81°; β-*naphthyl* n-*valerate*, b.p. 166°/4 mm., into 1-*valeryl*-β-*naphthol*, b.p. 165—166°/1 mm., 2-*propyl*-β-*naphthaflavone*, m.p. 103°, and 1-n-*amyl*-β-*naphthol*, m.p. 84°; β-*naphthyl* n-*hexoate*, b.p. 174—176°/1—2 mm., into 1-*hexyl*-β-*naphthol*, b.p. 188—190°/4 mm., 2-*butyl*-β-*naphthaflavone*, m.p. 103°, and 1-n-*hexyl*-β-*naphthol*, m.p. 123°.

H. W.

Walden inversion reactions of the *p*-toluenesulphonic and -sulphinic esters of *l*-phenylmethylcarbinol. J. Kenyon, H. Phillips, and F. M. H. Taylor (J.C.S., 1933, 173—178; cf. A., 1930, 1177).—*l*-CHPhMe·OH (I) [Ac derivative (II), b.p. 109°/18 mm., $[\alpha]_{5893}$ −58·4°] with *p*-toluenesulphinyl chloride in C_5H_5N gives the *l*-*p*-toluenesulphinate (III) without inversion, since (III) gives (I) with EtOH and K_2CO_3. (III) with EtOH alone gives *d*-α-phenyldiethyl ether (IV), also obtained (with a little di-*p*-tolylsulphoxide) when (I) is heated in anhyd. EtOH with *p*-toluenesulphinic acid. A similar reaction with *p*-toluenesulphonic acid on the *d*-alcohol gives *l*-α-phenyldiethyl ether (V), inversion occurring in both cases. The *p*-toluenesulphonate (VI) of (I) could not be isolated. Measurements of the relative rates of formation of (VI) and *p*-tolyl-α-phenylethyl-sulphone from (III) in EtOH with air in presence and absence of K_2CO_3 are recorded. Action of EtOH and K_2CO_3 on (VI) [prepared *in situ* in this and the following reactions by the action of H_2O_2 on (III)] also gives (IV) with inversion, and a similar reaction with *n*-BuOH gives d-n-*butyl* α-*phenylethyl ether*, b.p. 102°/23 mm. [*l*-isomeride, $[\alpha]_{5893}$ −53·8° in EtOH, from BuI and the K derivative of (I)]. (VI) with LiCl in Ac_2O gives *d*-α-chloroethylbenzene (VII), and the *d*-form of (II). The latter is produced from (VI), since (VII) with Ac_2O alone gives only a little acetate. (III) and (VI) in EtOH with LiCl and K_2CO_3 give (V), the reaction with (III) in presence of air giving a product of lower rotation than when air is absent. Reasons are given for assuming that (VII) is produced with inversion as an intermediate in this reaction. (VI) with AcOH gives the *d*-form of (II), whilst similar treatment of (III) gives unusually the *dl*-form. When the entering group forms an anion, (VI) undergoes replacement reactions with inversions similar to *p*-toluenesulphonates in which the asymmetric C atom is not directly attached to Ph. (III) differs from purely aliphatic and hydroaromatic *p*-toluenesulphinates in undergoing inversion reactions, particularly in acid solution.

A. A. L.

Catalytic hydrogenation of esters to alcohols. III. H. Adkins, B. Wojcik, and L. W. Covert (J. Amer. Chem. Soc., 1933, **55**, 1669—1676; cf. A., 1932, 599; this vol., 143).—Pure $CH_2Ph·CO_2Et$ (I) is obtained by heating the commercial product with catalytic Ni and H_2 at 175°/100 atm. for 3 hr. and subsequent distillation; $CH_2Ph·CN$ (the chief impurity) is eliminated partly as NN-*di*-β-*phenylethyl*-*phenylacetamide*, m.p. 143·5°. The best yields of $CH_2Ph·CH_2·OH$ (II) from (I) and a Cu–Cr oxide catalyst (*A*) are obtained when reduction is interrupted [5—10% of (I) remaining]. $OH·CHPh·CO_2Et$

is reduced [(*A*); practically all experiments using (*A*) are at 250°] to (II) and a little PhEt; Ni at 175° gives 95% of (I). (I) is reduced (Ni at 200°) to Et *cyclo*hexylacetate (77%) and thence (*A*) to β-*cyclo*hexylethyl alcohol (94%). *o*-$C_6H_4Bz{\cdot}CO_2Et$ gives (*A*) *o*-$C_6H_4Me{\cdot}CH_2Ph$ (93%); with Ni at 150°, *o*-benzylbenzoic acid (III) results (by way of the lactone of benzhydrol-*o*-carboxylic acid). The Et ester of (III) is reduced (Ni at 150°) to *Et o-hexahydrobenzylhexahydrobenzoate*, b.p. 155—158°/12 mm., converted further (*A*) into *o-hexahydrobenzylcyclohexylcarbinol*, b.p. 148—152°/10 mm., and a little *2-hexahydrobenzyl-1-methylcyclohexane*, b.p. 125—131°/10 mm. *o*-$C_6H_4(CO)_2O$ is reduced (Ni at 150°) to phthalide (34%), *o*-$C_6H_4Me{\cdot}CO_2H$ (36%), and hexahydro-*o*-toluic acid (23%); *o*-$C_6H_4(CO_2Et)_2$ (IV) gives (*A*) *o*-$C_6H_4(CH_2{\cdot}OH)_2$ (0—9%), *o*-$C_6H_4Me{\cdot}CH_2{\cdot}OH$ (0—14%), and *o*-xylene (67—84%), whilst Et hexahydrophthalate [from (VI) using Ni at 200°] similarly affords the corresponding hexahydro-derivatives (0—40%, 70—94%, and 6%, respectively). Et benzilate is reduced (*A*) rapidly at 125° to αα-diphenylethylene glycol (77%), probably through the tautomeric form, $CPh_2{<}\overset{O}{\underset{}{}}C(OH){\cdot}OEt$; $CHPh_2{\cdot}CO_2Et$ similarly gives (at 200°) $CHPh_2{\cdot}CH_2{\cdot}OH$ (58%) and $CHPh_2Me$ (38%). Attempts to modify (*A*) so that reduction of (I) gave increased amounts of (II) were unsuccessful. H. B.

Rearrangements of polyinenes. IV. s-Tetraphenyldi-(γ-methyl-γ-ethyl-Δ$^{\alpha}$-pentinyl)ethane. J. Harmon and C. S. Marvel (J. Amer. Chem. Soc., 1933, **55**, 1716—1722; cf. this vol., 56, 57).—*Me diphenyl-(γ-methyl-γ-ethyl-Δ$^{\alpha}$-pentinyl)methyl ether*, b.p. 143—147°/0·32 mm., prepared from the corresponding carbinol (A., 1932, 496) by the method of Moureu *et al.* (A., 1925, i, 136), and 40% Na–Hg in Et_2O and N_2 give Na diphenyl-(γ-methyl-γ-ethyl-Δ$^{\alpha}$-pentinyl)methyl (I), which with CO_2 affords *diphenyl-(γ-methyl-γ-ethyl-Δ$^{\alpha}$-pentinyl)acetic acid* (II), m.p. (block) 141—142°, (tube) 153—154° (softens at 140°). (II) is oxidised (CrO_3, AcOH) to BzOH, $COPh_2$ (57%), *o*-$C_6H_4Bz{\cdot}CO_2H$, and anthraquinone; $COPh_2$ (57%) and BzOH result from $KMnO_4$ and 1% KOH. (I) is converted by *s*-$C_2Me_4Br_2$ in Et_2O into the unstable (not isolated) *s*-tetraphenyldi-(γ-methyl-γ-ethyl-Δ$^{\alpha}$-pentinyl)ethane (ζζηη-tetraphenyl-γκ-dimethyl-γκ-diethyl-Δ$^{\delta\theta}$-dodecadi-inene), which is cleaved by 40% Na–Hg to (I), is readily oxidised (air; CrO_3) to $COPh_2$, and rearranges to the hydrocarbon, $C_{42}H_{46}$ (III), m.p. 105·6—108° (cf. *loc. cit.*). (III) is not oxidised by O_2, but with $K_2Cr_2O_7$ and AcOH gives a neutral *compound*, $C_{36}H_{30}O_2$, m.p. 137—138° [*tetrahydro*-derivative, m.p. 226·5—228° (corr.)], and a little *o*-$C_6H_4Bz{\cdot}CO_2H$. (III) and 40% Na–Hg in Et_2O give a Na alkyl which with CO_2 affords (II) in a max. yield of 36% [thus indicating that half of the mol. of (III) has retained the original structure]. H. B.

Action of selenium dioxide on sterols and bile acids. I. Ergosterol and dihydroergosterol. R. K. Callow and O. Rosenheim (J.C.S., 1933, 387—390).—Ergosterol, dihydroergosterol (I), lumisterol, calciferol, and *apo*cholic acid in EtOH–H_2O at room temp. react with SeO_2 and deposit Se (cf. A., 1932, 487). Many other ergosterol derivatives react when heated, those containing an ethenoid or bridge linking resistant to catalytic hydrogenation being the more reactive (cf. A., 1932, 736, 845). Some cholesterol derivatives react only in AcOH at 100°. Ergosterol reacts with SeO_2 in EtOH–C_6H_6 at 18° during 19 hr. to give dehydroergosterol (3 : 5-*dinitrobenzoate*, m.p. 185—189°). (I) (3 : 5-*dinitrobenzoate*, m.p. 206·5—207·5°, $[\alpha]_D^{20°}$ −1·8° in C_6H_6), prepared by hydrogenating ergosterol (Pd–C), gives with SeO_2 in EtOH–C_6H_6 *dihydroergosterol oxide* (II), m.p. 110—111°, $[\alpha]_D^{20°}$ −44·3° in $CHCl_3$ [+5*MeOH*, m.p. 99°; *Ac* derivative (III), m.p. 107—109°, $[\alpha]_D^{20°}$ −47° in $CHCl_3$; *Bz* derivative, m.p. 118—120°, $[\alpha]_D^{20}$ −36° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 198° (decomp.)]. Crude (I) with Ac_2O during 10 min. affords a product (m.p. 170—173°) which with NaOH–EtOH gives ergosterol-*D*. (II) on prolonged boiling with Ac_2O containing H_2SO_4 affords ergosterol-B_3 acetate, which is formed rapidly at room temp. from (III) in AcOH containing 1 drop of H_2SO_4. Ergosterol-*D* acetate is not isomerised under these conditions. J. L. D.

Synthesis of perhydrovitamin-*A*. P. Karrer, R. Morf, and K. Schopp (Helv. Chim. Acta, 1933, **16**, 557—561).—Et δ-2 : 6 : 6-trimethyl-Δ^1-*cyclo*hexenyl-β-methyl-Δ$^{\alpha\gamma}$-butadiene-α-carboxylate (A., 1932, 852) is reduced (H_2, Pt) to the fully saturated ester, which is then reduced (Na, EtOH) to ε-2 : 6 : 6-trimethyl-*cyclo*hexyl-γ-methyl-*n*-amyl alcohol. The bromide is converted (malonic ester method) into ζ-2 : 6 : 6-trimethyl*cyclo*hexyl-δ-methylheptoic acid, and thence into the chloride, which with ZnMeI gives ζ-2 : 6 : 6-trimethyl*cyclo*hexyl-δ-methylhexyl Me ketone (semicarbazone, m.p. 114°). This with Zn and $CH_2Br{\cdot}CO_2Et$ affords Et β-hydroxy-θ-2 : 6 : 6-trimethyl*cyclo*hexyl βζ-dimethylnonoate; replacement of the OH by Br and then H and subsequent reduction (Na, EtOH) gives ι-2 : 6 : 6-*trimethyl*cyclo*hexyl-γη-dimethyl*-n-*nonyl alcohol* (I), b.p. 148—149°/0·15 mm., which is identical with perhydrovitamin-*A* (II), b.p. 148—150°/0·15 mm. (A., 1932, 200). The bromides from (I) and (II) are converted (malonic ester method) into κ-2 : 6 : 6-*trimethyl*cyclo*hexyl-δθ-dimethylundecoic acid*, b.p. 186°/0·4 mm., the chloride of which with ZnMeI gives κ-2 : 6 : 6-trimethyl*cyclo*hexyl-δθ-dimethyldecyl Me ketone (*semicarbazone*, m.p. 67°). No details are given. H. B.

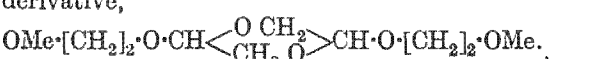
Surface films of œstrin derivatives and of pregnandiol. J. F. Danielli, G. F. Marrian, and G. A. D. Haslewood (Biochem. J., 1933, **27**, 311—320).—Measurements of surface pressure and surface potential indicate that the products of reduction of ketohydroxyœstrin (I) by Clemmensen's method and of its semicarbazone by NaOEt are identical; this is supported by direct comparison (mixed m.p.). Similar measurements on other derivatives of œstrin and pregnandiol, and on calciferol and ψ-cholesterol, support Butenandt's formulæ for pregnan-diol and -dione (A., 1932, 54) and for (I) and trihydroxyœstrin (Z. angew. Chem, 1932, **45**, 655), but do not fix the positions of the Me and OH or :O groups in the latter cases. Hydrogenation of (I) (PtO_2) in EtOH gives *dihydroxyœstrin*, m.p. 174—176° (*diacetate*, m.p. 120—122°; *Me ether*, m.p. 91—94°), and *hexahydrodihydroxy-*

œstrin, m.p. 209—211°, which is obtained in better yield in AcOH. H. A. P.

[Polyterpenes and polyterpenoids. XXIX.] Dehydrogenation of cholesterol and cholic acid. O. DIELS (Ber., 1933, **66**, [*B*], 487—488).—A reply to Ruzicka and Thomann (this vol., 278). H. W.

Properties of ergosterol and calciferol. A. L. BACHARACH, E. L. SMITH, and S. G. STEVENSON.—See this vol., 542.

Reactions relating to carbohydrates and polysaccharides. XLV. Polymerisation, under the influence of heat, of compounds containing the ethylene oxide ring. E. C. JAHN and H. HIBBERT (Canad. J. Res., 1933, **8**, 199—209).—Phenylglycide (I), m.p. 26·5°, b.p. 134—135°/4—5 mm. (*phenylurethane*, m.p. 87°), prepared from cinnamyl alcohol and BzO_2H in $CHCl_3$ at 0°, is converted by heating at 140—155° (29 hr.) into a *dimeride*. This gives a *Me*$_2$ *ether*, b.p. 180—185°/0·03 mm., with MeI and Ag_2O, but a *monotrityl* derivative, and therefore has only one primary OH group. With NH_3 the Me$_2$ ether gives a *monoammine*, $C_{20}H_{24}O_4,NH_3$, and therefore contains only a single ethylene oxide ring. Polymerisation occurs therefore by addition of the ethylene oxide ring to the OH group (cf. Nef, A., 1905, i, 3 *et seq.*). When heated for a much longer period (32 days) at 105°, colourless resinous polymerides, which still combine with NH_3, and coloured by-products are formed. Methylglycide, b.p. 93—97°/44 mm. (*phenylurethane*, m.p 66·5°), similarly prepared from crotyl alcohol, when heated at 105° for 22 days gives a liquid dimeride (*diphenylurethane*, m.p. 78—80°). Oxidation of *s*-dipropenylethylene glycol with BzO_2H gives δε-*dihydroxy*-βγ-ζη-*dioxido-octane*, b.p. 125—128°/4 mm., which is partly converted into a *trimeride* during fractional distillation at 4 mm. The *acetate* of (I), b.p. 129—133°/3 mm. (from CHPh:CH·CH$_2$·OAc), is slowly converted at 140° into a mixture of polymerides from which a *dimeride*, b.p. 140—145°/0·1 mm., and a solid resin were isolated. The *Me ether* of (I), b.p. 130—137°/21—23 mm. (from *cinnamyl Me ether*, b.p. 92°/5 mm.), is not polymerised by heating alone or with moist KOH or $ZnCl_2$, but undergoes complex decomp. with formation of resins. The *Me ether*, b.p. 107—110°, of β-hydroxyethyl vinyl ether is oxidised by BzO_2H to *dimeric glycide* β-*methoxyethyl ether*, b.p. 118—119°/0·1 mm., which absorbs only 0·16 mol. NH_3 and is therefore regarded as the stable dioxan derivative,



A

Chemical structure and optical rotation. IV. Configurative relationship of disubstituted acetic and propionic acids containing a phenyl group. P. A. LEVENE, R. E. MARKER, and A. ROTHEN (J. Biol. Chem., 1933, **100**, 589—602; cf. A., 1932, 1028).—The substances previously (A., 1930, 1287) described as (*a*) β-phenyl-butyric and (*b*) -valeric acids contained (*a*) mostly and (*b*) much α-phenylbutyric and -valeric acid, respectively, formed by rearrangement during the decomp. of the amine. Since, however, the *sec.* halides give inactive substituted acetic acids, the correlations previously established are still valid. They are confirmed by the present observations. α-Phenylethyl bromide and chloride give β-phenylpropionic acid with the same *M*[α], the same amount of racemisation having taken place in each case. The esters of disubstituted phenylacetic acids are racemised by reduction in PhMe, but not in C_6H_6 solution. The rotation of α-*cyclo*hexylbutyric acid previously (*loc. cit.*) given should be reversed. All rotations (which are not max.) given below are for the homogeneous liquid, unless otherwise stated. α-Phenylpropionic acid, $[M]_D^{25}$ +35·1°, is hydrogenated (PtO_2) in AcOH to α-cyclo*hexylpropionic acid*, b.p. 103°/3 mm., $[\alpha]_D^{25}$ +5·2°. α-Phenylbutyric acid, $[M]^{25}$ +46·7°, gives α-cyclo*hexylbutyric acid*, b.p. 120°/3 mm., $[\alpha]_D^{25}$ −0·15°, and α-phenylvaleric acid, $[M]_D^{25}$ +16·0°, α-cyclo*hexylvaleric acid*, b.p. 140°/3 mm., $[\alpha]^{25}$ −0·64°. β-Phenyl-*n*-propyl alcohol is resolved by the brucine salt of the 3-nitrophthalate, giving the d-*form*, b.p. 92°/4 mm., $[\alpha]_D^{27}$ +9·07°, hydrogenated to β-cyclo*hexyl*-n-*propyl alcohol*, b.p. 84°/2 mm., $[\alpha]_D^{25}$ 0°, giving with PBr_3 β-*phenyl*-n-*propyl bromide*, b.p. 78°/1 mm., $[\alpha]_D^{23}$ −2·56°, and with PCl_3 the corresponding *chloride*, b.p. 72°/1 mm., $[\alpha]_D^{25}$ −2·00°; the halides yield (Grignard) β-*phenylbutyric acid*, b.p. 127°/1 mm., $[\alpha]_D^{25}$ −10·39° and −10·35°, respectively. β-Phenyl-*n*-butyl alcohol, resolved by the strychnine salt of the 3-nitrophthalate, gives the l-*form*, b.p. 86°/1 mm., $[\alpha]_D^{25}$ −1·93°, which led to β-*phenyl*-n-*butyl bromide*, b.p. 87°/1 mm., $[\alpha]_D^{25}$ +0·84°, β-*phenyl*-n-*valeric acid*, b.p. 124°/1 mm., $[\alpha]^{25}$ +7·04° (homogeneous), +4·46° in C_6H_6, and β-*phenyl*-n-*butane*, b.p. 68°/20 mm., $[\alpha]^{25}$ −2·13°. Et α-phenylpropionate, $[\alpha]_D^{25}$ −59·6° (from the acid, $[M]^{25}$ −111·6°), gives β-*phenyl*-n-*propyl alcohol*, b.p. 92°/4 mm., $[\alpha]_D^{25}$ +3·35°, and Et α-phenylbutyrate, $[\alpha]^{25}$ −66·8° (from the acid, $[M]_D^{25}$ −140·0°), gives β-*phenyl*-n-*butyl alcohol*, b.p. 95°/2 mm., $[\alpha]^{25}$ −2·69°. R. S. C.

Molecular rearrangements involving optically active radicals. III. Lossen rearrangement of optically active hydroxamic acids. E. S. WALLIS and R. D. DRIPPS (J. Amer. Chem. Soc., 1933, 55, 1701—1705).—The *O*-Bz derivative, m.p. 115·5—116·5°, $[\alpha]^{20}_{5461}$ +92·1° in 95% EtOH, of *d*-benzylmethylacethydroxamic acid is converted by the method previously described (A., 1926, 279) into the K salt, which when heated in C_6H_6 gives a *d*-carbimide. This and dry NH_3 afford *d*-α-benzylethylcarbamide (I), m.p. 136·5—137°, $[\alpha]^{20}_{5461}$ +12·1° in $COMe_2$. Possible causes of the previous failure (*loc. cit.*) to obtain (I) are discussed. These results support the conclusion (cf. A., 1931, 1053) that the asymmetric radical retains its configuration or undergoes complete inversion during its migration from C to N. H. B.

Theory of metal hydrate ions. II. P. PFEIFFER and S. VON MÜLLENHEIM (J. pr. Chem., 1933, [ii], **137**, 9—26; cf. A., 1930, 1390).—Salts of aromatic carboxylic acids are much less suited to the investigation of co-ordination theory than are those of naphthalenesulphonic acids (*loc. cit.*). Hexa-aquo-salts have not been obtained, the cryst. salts from H_2O being anhyd. or containing too little H_2O. Salts of the "six type" containing $C_2H_4(NH_2)_2$ are de-

scribed which frequently contain "excessive" H_2O mols. The following salts are described :
Ni$(CO_2C_{10}H_7$-α$)_2$, *tetrahydrate* and *hexa-ammoniate*; [*Ni en*$_2(OH_2)_2$]$(CO_2C_{10}H_7$-α$)_2$; [*Ni en*$_3$]$(CO_2$·$C_{10}H_7$-α$)_2$,2H_2O and anhyd.; *Ni*$(CO_2$·$C_{10}H_7$-β$)_2$, *tetrahydrate* and *hexa-ammoniate*; [*Ni en*$_2(OH_2)_2$]$(CO_2$·$C_{10}H_7$-β$)_2$; [*Ni en*$_3$]$(CO_2$·$C_{10}H_7$-β$)_2$,2H_2O; Ni$(OBz)_2$,3H_2O; [*Ni en*$_2(OH_2)_2$]$(OBz)_2$; [*Ni en*$_3$]$(OBz)_2$,2H_2O; Ni$(CO_2$·C_6H_4·OMe-*p*$)_2$,3H_2O; [*Ni en*$_2(OH_2)_2$]$(CO_2$·C_6H_4·*OMe*-p$)_2$,2H_2O; [*Ni en*$_3$]$(CO_2$·C_6H_4·*OMe*-p$)_2$,2H_2O; *Cu*$(CO_2$·$C_{10}H_7$-α$)_2$,H_2O; [*Cu en*$_2(OH_2)_2$]$(CO_2$·$C_{10}H_7$-α$)_2$; *Cu*$(CO_2$·$C_{10}H_7$-β$)_2$; [*Cu en*$_2(OH_2)_2$]$(CO_2$·$C_{10}H_7$-β$)_2$ (+1H_2O and 3H_2O); Cu$(OBz)_2$,3H_2O; [*Cu en*$_2(OH_2)_2$]$(OBz)_2$,2H_2O; Cu$(CO_2$·C_6H_4·OMe$)_2$,3H_2O; [*Cu en*$_2(OH_2)_2$]$(CO_2$·C_6H_4·*OMe*-p$)_2$; *Zn*$(CO_2$·$C_{10}H_7$-α$)_2$,2H_2O (also *tetra-ammoniate*); [*Zn en*$_3$]$(CO_2$·$C_{10}H_7$-α$)_2$; *Zn*$(CO_2$·$C_{10}H_7$-β$)_2$; [*Zn en*$_3$]$(CO_2$·$C_{10}H_7$-β$)_2$,2H_2O; [*Zn en*$_3$]$(OBz_2)_2$,2H_2O; *Zn*$(CO_2$·C_6H_4·*OMe*-p$)_2$,3H_2O; [*Zn en*$_2(OH_2)_2$]$(CO_2$·C_6H_4·*OMe*-p$)_2$; *Cd*$(CO_2$·$C_{10}H_7$-α$)_2$,3H_2O; *Cd*$(CO_2$·$C_{10}H_7$-β$)_2$; [*Cd en*$_3$]$(CO_2$·$C_{10}H_7$-β$)_2$ (also 2H_2O); [*Cd en*$_3$]$(OBz)_2$,2H_2O; 3Cd$(CO_2$·C_6H_4·OMe-*p*$)_2$,4H_2O; [*Cd en*$_2(OH_2)_2$]$(CO_2$·C_6H_4·*OMe*-p$)_2$,0·5H_2O. H. W.

Colour and chemical reactivity in the cinnamic series. (Mme.) Ramart-Lucas and R. Trivedi (Bull. Soc. chim., 1933, [iv], **53**, 178—190).—A more detailed account of work previously reviewed (this vol., 63). H. B.

Reformatsky reaction with compounds of the ethylene oxide type. G. R. Clemo and J. Ormston (J.C.S., 1933, 362; cf. A., 1932, 848).—*cyclo*Pentanealdehyde, CH_2Br·CO_2Et, and Zn in boiling C_6H_6 during 3 hr. affords *Et* β-*hydroxy*-β-cyclo*pentylpropionate*, b.p. 117°/14 mm. (*hydrazide*, m.p. 154°, identical with the hydrazide of the product of the Reformatsky reaction on *cyclo*hexene oxide). Similarly, *cyclo*pentene oxide or *cyclo*pentanone yields *Et* cyclo*pentan*-1-*ol*-1-*acetate*, b.p. 108°/18 mm. (*hydrazide*, m.p. 143°), indicating that reaction is preceded by isomerisation. J. L. D.

Salicylic acid. IV. 4-Sulphosalicylic acid. N. W. Hirwe and M. R. Jambhekar (J. Indian Chem. Soc., 1933, **10**, 47—51).—2-Nitrotoluene-4-sulphonic acid, m.p. 92°, decomp. 245° (*K* salt), is prepared both from *p*-C_6H_4Me·SO_3H and HNO_3 (*d* 1·41) in Ac_2O at room temp. (cf. A., 1910, i, 20) and from *o*-C_6H_4Me·NO_2 and H_2SO_4 (cf. Annalen, 1870, **155**, 27). It is oxidised by alkaline $KMnO_4$ at room temp. to 2-*nitro*-4-*sulphobenzoic acid* (+2·5H_2O), m.p. 111° [*dichloride*, m.p. 160° (softens at 145°); *diamide*, m.p. 226°; *sulphonyl chloride*, decomp. 202° (softens at 192°) (partial hydrolysis of dichloride); *sulphonamide* (I), m.p. 192°] (cf. A., 1881, 1144). This is reduced by Sn and HCl to 4-*sulphoanthranilic acid* (+1H_2O) {*Ba* salt; *sulphonamide*, m.p. 227—228° [from (I) and $(NH_4)_2S$ in EtOH]}, which with HNO_2 gives 4-*sulpho*-2-*diazobenzoic acid*, decomp. 163—164°, converted by boiling dil. HCl into 4-*sulphosalicylic acid* (II) (+3H_2O), m.p. 82°, (+2H_2O), m.p. 133°. [*Na H* (+2H_2O), *K H*, *Ba* (+4H_2O), and *Ca* salts]. The structure of (I) is confirmed by fusion of its *K H* salt with KOH at 230—240°, which gives β-resorcylic acid. No evidence is given for the structures assigned to the half-chlorides and -amides. H. A. P.

Pyrolysis of mandelic acid and related compounds. C. D. Hurd and H. R. Raterink (J. Amer. Chem. Soc., 1933, **55**, 1541—1546).—Mandelic acid heated at 200° gives OH·CHPh·CO·O[·CHPh·CO·O]$_n$·CHPh·CO_2H (n=1—2 according to time of heating), probably some cyclic ester (lactide type), but practically no gaseous products. At 250°, CO, CO_2, PhCHO, CH_2Ph·CO_2H (I), and diphenylmaleic anhydride (II) result; *dimandelic anhydride* (III), O<CHPh·CO / CHPh·CO>O, m.p. 152—154°, which gives the same products at 250°, is probably an intermediate which decomposes thus: (III)⟶ H_2O+(II); (II)⟶ CHPh:C:O $\xrightarrow{H_2O}$ (I). ONa·CHPh·CO_2Et and CHBrPh·CO_2Et in Et_2O afford 30% of *Et dimandelate*, O(CHPh·$CO_2Et)_2$, b.p. 215—216°/8 mm.; the free *acid* (+H_2O), softens 120—130°, is dehydrated by Ac_2O to (III). Hexahydromandelic acid decomposes at 250° to CO, CO_2 (trace), and hexahydrobenzaldehyde, whilst dilactic anhydride similarly gives CO, CO_2, and MeCHO. H. B.

Unsaturated αδ-dicarbonyl compounds. IX. Unsaturated aryl-αδ-diketones and -ketonic acids derived from dimethyl-maleic and -fumaric acids. R. E. Lutz and R. J. Taylor (J. Amer. Chem. Soc., 1933, **55**, 1593—1601).—Dimethylmaleic anhydride (I), C_6H_6, and $AlCl_3$ give cis-β-*benzoyl*-α-*methylcrotonic acid* (II), m.p. 94° (all m.p. are corr.) (*Me* ester, b.p. 163—164°/9 mm., m.p. 53°), whilst the chloride (III) of Et H dimethylfumarate, C_6H_6, and $AlCl_3$ afford *Et* trans-β-*benzoyl*-α-*methylcrotonate*, b.p. 120° (corr.)/2 mm. [*Me* ester (IV), b.p. 141° (corr.)/5 mm., prepared similarly], which is hydrolysed (aq. EtOH–NaOH) to the trans-*acid* (V), m.p. 119°. (II) could not be converted into (V) by exposure of a solution in $CHCl_3$ containing I or Br to sunlight, but hydrolysis of (IV) with MeOH–NaOMe gives a poor yield of (II); possible mechanisms are discussed. Mesitylene, (I), and $AlCl_3$ afford trans-β-2 : 4 : 6-*trimethylbenzoyl*-α-*methylcrotonic acid*, m.p. 169·5° (*Me* ester, m.p. 83°), the *Et* ester, b.p. 131—133° (corr.)/2 mm., of which is similarly prepared from (III). Dimethylfumaryl chloride, C_6H_6, and $AlCl_3$ give trans-βγ-*dibenzoyl*-Δ^{β}-*butene*, m.p. 139·5° (also prepared similarly in poor yield from *trans*-β-benzoyl-β-methylcrotonyl chloride), which could not be converted into the *cis*-form and is reduced (Zn dust, AcOH) to 2 : 5-*diphenyl*-3 : 4-*dimethylfuran*, m.p. 116°. trans-βγ-*Di*-2 : 4 : 6-*trimethylbenzoyl*-Δ^{β}-*butene*, m.p. 174·5°, is converted partly into the cis-*form*, m.p. 149°, by exposure of a solution in C_6H_6 to sunlight; both forms are reduced (Zn dust, AcOH) to 2 : 5-*di*-2 : 4 : 6-*trimethylphenyl*-3 : 4-*dimethylfuran* (VI), m.p. 144°, and a little βγ-*di*-2 : 4 : 6-*trimethylbenzoylbutane*, m.p. 191·5—192° [convertible into (VI) by Ac_2O–conc. H_2SO_4]. H. B.

Synthesis of tyrosinephosphoric acid. P. A. Levene and A. Schormuller (J. Biol. Chem., 1933, **100**, 583—587).—*N*-Formyltyrosine, MgO, and $POCl_3$ in CCl_4 give N-*formyltyrosine*-O-*phosphoric acid*, hydro-

lysed by hot 2*N*-HCl to *tyrosine-O-phosphoric acid*, m.p. 253° (decomp.), $[\alpha]_D^{20}$ −2·0° (*Ba* and *Pb* salts). The method failed with serine. R. S. C.

Preparation of substituted vanillic acids. L. C. Raiford and D. J. Potter (J. Amer. Chem. Soc., 1933, **55**, 1682—1685).—6-*Chloro*-5-*bromo*-4-*hydroxy*-3-*methoxybenzaldoxime*, m.p. 203—204° (decomp.), and boiling Ac_2O give 6-*chloro*-5-*bromo*-4-*acetoxy*-3-*methoxybenzonitrile*, m.p. 165°, which is hydrolysed (6*N*-KOH) to 6-*chloro*-5-*bromovanillic acid* (+0·5H_2O), m.p. 196—197°. The following are prepared similarly: 5-*chloro*-6-*bromo*-4-*hydroxy*-3-*methoxybenzaldoxime*, m.p. 203—204° (decomp.); 2-*bromo*-, m.p. 71—72°, 2 : 6-*dibromo*-, m.p. 143—144° (which could not be hydrolysed), 2 : 5 : 6-*tribromo*-, m.p. 174—175°, 5-*chloro*-, m.p. 133—134°, 6-*chloro*-, m.p. 131—132°, 5 : 6-*dichloro*-, m.p. 143—144°, and 5-*chloro*-6-*bromo*-, m.p. 176°, -4-*acetoxy*-3-*methoxybenzonitriles*; 2-*bromo*-, m.p. 163—164°, 5-bromo-, m.p. 231—232° (lit. 221°), 5 : 6-*dibromo*- (+0·5H_2O), m.p. 199—200°, 2 : 5 : 6-*tribromo*-, m.p. 231—232° (decomp.), 5-*chloro*-, m.p. 244—245°, 6-*chloro*-, m.p. 207°, 5 : 6-*dichloro*- (+0·5H_2O), m.p. 184—185°, and 5-*chloro*-6-*bromo*- (+0·5H_2O), m.p. 187—188°, *-vanillic acids*. Vanillic acid is prepared from 4-acetoxy-3-methoxybenzonitrile. H. B.

Stereochemistry of diphenyls. XXX. Preparation and resolution of 2 : 2′-di-iododiphenyl-4 : 4′-dicarboxylic acid. N. E. Searle and R. Adams (J. Amer. Chem. Soc., 1933, **55**, 1649—1654).—Et 4-iodo-3-nitrobenzoate and Cu-bronze in $PhNO_2$ give *Et* 2 : 2′-*dinitrodiphenyl*-4 : 4′-*dicarboxylate*, m.p. 95—96°, reduced (H_2, PtO_2, EtOH) to the 2 : 2′-*diamino*-ester, m.p. 99—100°, which is converted by Mascarelli's method (A., 1909, i, 94) into the *Et* ester, m.p. 118°, of 2 : 2′-*di-iododiphenyl*-4 : 4′-*dicarboxylic acid*, m.p. 339—341°. This is resolved by brucine into *d*-, m.p. 339—341°, $[\alpha]_D$ (in dioxan) +51·3°⟶0°, and *l*-forms (I), m.p. 339—341°, $[\alpha]_D$ (in dioxan) −47·5°⟶0° (*brucine* salts, m.p. 212—224° and 201—212°, respectively, which exhibit mutarotation). The Na salt of (I) racemises more slowly in H_2O than (I) in org. solvents. H. B.

Oxidation of 3 : 4-dihydroxyphenyl-*N*-methylalanine with reference to its possible function as a precursor of adrenaline. R. D. H. Heard and H. S. Raper (Biochem. J., 1933, **27**, 36—53).—3 : 4-Dihydroxyphenylalanine (I) and its *N*-Me derivative (II) are oxidised in presence of tyrosinase to small amounts of pressor bases (probably aminoacetopyrocatechol and adrenalone), the activity of which is greatly increased by subsequent catalytic reduction [adrenaline (III) probably being formed]. With Ag_2O, Fe, or H_2O_2 pressor bases [probably noradrenaline and (III)] are produced, subsequent catalytic reduction not affecting the activity. Formation of (III) is one of three possible methods of oxidation of (II), and is considered to take place by this route *in vivo*, although it does not occur when (II) is perfused through the surviving adrenal gland. Side-chain oxidation does not take place when the CO_2H group is absent. R. S. C.

Synthesis of *dl*-3 : 4-dihydroxyphenyl-*N*-methylalanine. R. D. H. Heard (Biochem. J., 1933, **27**, 54—57).—Piperonylideneacetylglycine with Me_2SO_4 gives *piperonylideneacetmethylamidoacetic acid*, m.p. 196°, which with red P, I, and boiling HI (*d* 1·7) in CO_2 yields dl-3 : 4-*dihydroxyphenyl*-N-*methylalanine*, m.p. variable, about 280°. Methylation of piperonylhydantoin is difficult, and produces mainly the Me_2 compound. Piperonylidenedimethylhydantoin is hydrolysed by $Ba(OH)_2$ at the ethylenic linking. Piperonal condenses with acetylglycine or hippuric acid, but not with benzenesulphonylglycine, sarcosine, or acylsarcosines. R. S. C.

Preparation of nitrophthalic anhydrides. M. Hayashi and K. Kawasaki (J. Soc. Chem. Ind. Japan, 1933, **36**, 121—123B).—A detailed account of the nitration of *o*-$C_6H_4(CO)_2O$, separation of the 3-, m.p. 211° (decomp.) (44·1% of theory), and 4-, m.p. 164—165° (39·2% of theory), -nitrophthalic acids, and their conversion into anhydrides by standard methods. H. A. P.

Course of addition of sodium enolates of malonic and methylmalonic esters to phenyl styryl ketone and crotonic ester. A. Michael and J. Ross (J. Amer. Chem. Soc., 1933, **55**, 1632—1646; cf. A., 1932, 252).—Ph styryl ketone (I) and $CHMe(CO_2Et)_2$ in Et_2O containing a little piperidine or NaOEt (0·1 mol.) give 80% of *Et* δ-*benzoyl*-γ-*phenylbutane*-ββ-*dicarboxylate* (II), m.p. 95° (*phenylhydrazone*, m.p. 130°), which with Na (1 mol.) or NaOEt (1 mol.) in cold Et_2O undergoes almost complete retrogression to (I), $CNaMe(CO_2Et)_2$ (as enolate) (III), and (probably) a trace of $CH_2Bz{\cdot}CO_2Et$, thus rendering Holden and Lapworth's (A., 1931, 1272) mechanism of the reaction between (I) and (III) untenable. (III), (I) [or (II)], and NaOEt in Et_2O give Et α-methylcinnamate and $CH_2Bz{\cdot}CO_2Et$; contrary to Holden and Lapworth (*loc. cit.*), the production of these has no connexion with the formation of the Na-enolate of Et γ-carbethoxy-αβ-dimethylglutarate from (III) and $CHMe{:}CH{\cdot}CO_2Et$, during which additive process migration of Me must occur.

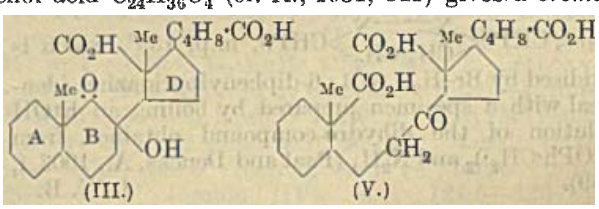
(I) and $CH_2(CO_2Et)_2$ in Et_2O containing a little piperidine or NaOEt give the Et ester (IV), m.p. 71°, of γ-*benzoyl*-β-*phenylpropane*-αα-*dicarboxylic acid*, m.p. 165° (decomp.), whilst $CHNa(CO_2Et)_2$ (1 mol.) and (I) (2 mols.) in Et_2O afford *Et* 2-*benzoyl*-1 : 3 : 5 *triphenyl*-Δ^1-cyclo*hexene*-4 : 4-*dicarboxylate* (V), m.p. 235° (which arises by loss of H_2O from Et αε-dibenzoyl-ββδ-diphenylpentane-γγ-dicarboxylate), *Et* γε-*dibenzoyl*-ββδ-*diphenylpentane*-αα-*dicarboxylate* (VI), m.p. 197°, *Et* 4 : 6-*dibenzoyl*-3 : 5-*diphenyl*cyclo*hexanone*-2-*carboxylate* (VII), m.p. 187° [formed by loss of EtOH from (VI)], and (IV). The production of (V) is favoured by an excess of NaOEt and prolonged reaction time; the enolate of (VII) is formed from (I) and (IV) in presence of < 1 equiv. of NaOEt. (VI) and (VII) are interconvertible (as enolates) by NaOEt; in these reactions a little (V) is produced. Methylation (MeI, EtOH–NaOEt, EtOAc) of (VII) or (VI) gives *Et* 4 : 6-*dibenzoyl*-3 : 5-*diphenyl*-2- (VIII), m.p. 170°, and -6-, m.p. 175°, *-methyl*cyclo*hexanone*-2-*carboxylates*, *Et* γε-*dibenzoyl*-βδ-*diphenylhexane*-αα-*dicarboxylate*, m.p. 237°, and *Et* δζ-*dibenzoyl*-γε-*diphenylheptane*-ββ-*dicarboxylate*, m.p. 210°; the open-chain compounds predominate. (VIII) and EtOH–NaOEt in cold Et_2O

give *Et* αγ-*dibenzoyl*-ββ′-*diphenyl*-α′-*methylpimelate*, m.p. 188°, and a *stereoisomeride*, m.p. 210°; in the hot, EtOBz and *Et* γ-*benzoyl*-ββ′-*diphenyl*-α-*methylpimelate*, m.p. 154°, result. H. B.

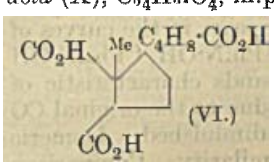
Usnic acid. I. Derivatives of methylphloroglucinol. F. H. Curd and A. Robertson (J.C.S., 1933, 437—444).—Interaction of $CHMe(CO_2Et)\cdot COCl$ (I) and $CO(CH_2\cdot CO_2Et)_2$ (II) (Na derivative) in Et_2O during 1 hr. affords *Et hexane*-2 : 4-*dione*-1 : 3 : 5-*tricarboxylate*, b.p. 165—168°/1 mm., which cyclises with NaOEt to *Et methylphloroglucinoldicarboxylate* (III), m.p. 92—93° (*Ac*$_3$ derivative, m.p. 99°), hydrolysed and decarboxylated to methylphloroglucinol. $CHMe(CO_2Et)_2$, (II), and NaOEt at 160° during 1 hr. afford some (III), but mainly Et 4 : 5 : 7-trihydroxycoumarin-6(or 8)-carboxylate (A., 1917, i, 277). (I) with Et sodioacetoacetate affords a dione which does not cyclise to (III). The diazonium compound of 2 : 6-dinitro-*p*-toluidine and boiling aq. $CuSO_4$ afford 2 : 6-*dinitro*-p-*cresol*, m.p. 154—155° [*Me ether* (IV), m.p. 103—104°]. Reduction of (IV) with Sn and hot HCl, followed by prolonged boiling of the reduction product with H_2O, affords methylphloroglucinol α-Me ether (cf. A., 1898, i, 578). The orientation of the β-Me ether (Herzig and Wenzel, A., 1902, i, 463) follows. (IV) with H_2S in EtOH–NH_3, Na_2S_2, or $SnCl_2$ affords 6-*nitro*-4-*methoxy*-o-*toluidine*, m.p. 82—83° (*Ac* derivative, m.p. 171—172°), which when diazotised and treated with boiling H_2SO_4 yields 6-*nitro*-4-*methoxy*-o-*cresol*, m.p. 126° [*Me ether* (V), m.p. 93°]. (V) is reduced by Na_2S, and the amine (*Ac* derivative, m.p. 146°) isolated as the sulphate when diazotised and treated with boiling H_2SO_4 affords methylphloroglucinol α-Me_2 ether (VI) (cf. A., 1898, i, 578), thus confirming the structure of the latter. Phloroglucinaldehyde and MeI in $COMe_2$ containing K_2CO_3 during 3 hr. afford 2-*hydroxy*-4 : 6-*dimethoxy*-m-*tolualdehyde*, m.p. 168—169° [*Ac* derivative (VII), m.p. 123—124°] [also formed by methylating methylphloroglucinaldehyde, and from (VI) and HCN according to the Hoesch procedure], converted by acetylanisole and HCl in EtOAc into 5 : 7 : 4′-trimethoxy-8-methylflavylium chloride (*ferrichloride*, m.p. 196—197°). Similarly, Me phloroglucinolcarboxylate with MeI affords *Me* 2-*hydroxy*-4 : 6-*dimethoxy*-m-*toluate* (VIII), m.p. 144—145° (and some Me 2 : 4 : 6-trimethoxybenzoate), also obtained from Me 2 : 4-dihydroxy-6-methoxy-*m*-toluate and MeI. Me 2 : 4 : 6-trihydroxy-*m*-toluate with MeI and $COMe_2$ affords (VIII) and *Me* 2 : 4 : 6-*trimethoxy*-m-*toluate*, m.p. 80—82°, hydrolysed and decarboxylated to methylphloroglucinol Me_3 ether (*Br*$_2$-derivative, m.p. 102—103°) or gently hydrolysed to the *acid*, m.p. 182° [also obtained by oxidising (VII) followed by hydrolysis], decarboxylated to (VI). Methylphloroglucinol and MeCN with $ZnCl_2$ and HCl in Et_2O affords *methylphloracetophenone*, m.p. 211—212° (*Ac*$_3$ derivative, m.p. 111°), methylated to 2-*hydroxy*-4 : 6-*dimethoxy*-3-*methylacetophenone* (IX), m.p. 141—142° (*Ac* derivative, m.p. 86—87°) [also obtained from phloracetophenone and MeI, or from (VI) with MeCN, $ZnCl_2$, and HCl], which condenses with anisaldehyde to give 2-*hydroxy*-4 : 6 : 4′-*trimethoxy*-3-*methylchalkone*, m.p. 134—135° (*Ac* derivative, m.p. 148°), cyclised by H_2SO_4–EtOH in 15 hr. to 5 : 7 : 4′-*trimethoxy*-8-*methylflavanone*, m.p. 144°. (IX) with *p*-hydroxybenzaldehyde affords 2 : 4′-*dihydroxy*-4 : 6-*dimethoxy*-3-*methylchalkone*, m.p. 199—200° (*Ac*$_2$ derivative, m.p. 135°), and with $CH_2Br\cdot CO_2Et$, $COMe_2$, and K_2CO_3 affords *Et* 2-*acetyl*-3 : 5-*dimethoxy*-6-*methylphenoxyacetate*, m.p. 70°. J. L. D.

Bile acids. XXXVIII. Can the Van Slyke method of amino-nitrogen determination be applied to derivatives of bile acids? M. Schenck and J. Reschke (Z. physiol. Chem., 1933, **216**, 81—90; cf. this vol., 274).—The Van Slyke method gives untrustworthy results with NH_2-acids of the bile acid group. Thus the aminoketotetracarboxylic acid $C_{27}H_{37}O_9N$ gives vals. for N 230 and 290% of theoretical after 3 and 21 hr., respectively. High N vals. are probably due to liberation of N_2 from HNO_2. Inversion products *A* and *B* from the oximinoamino-acid $C_{24}H_{38}O_9N_2$ give larger amounts of NH_2-N than corresponds with one NH_2 group, but titration with and without CH_2O indicates that *A* is a lactam-amino-acid. The substance obtained by boiling *A* for 6 hr. with 20% HCl gives low Van Slyke N; the lactam ring probably remains intact. J. H. B.

Bile acids. L. Complete structure and nature of ring D. H. Wieland and E. Dane (Z. physiol. Chem., 1933, **216**, 91—104; cf. A., 1931, 841).—The ketodicarboxylic acid (I), $C_{23}H_{36}O_5$, with Br in AcOH gives a *bromoketodicarboxylic acid* (II), m.p. 182° (decomp.), which with 0·1*N*-KOH affords a *hydroxyketodicarboxylic acid* (III), $C_{23}H_{36}O_6$, m.p. 204—206°, and the unsaturated *ketodicarboxylic acid* (IV), $C_{23}H_{34}O_5$, m.p. 214—217°. With KOH in MeOH, (II) gives the *Me ether*, m.p. 158—162°, of (III). Oxidation of (III) with CrO_3 in AcOH yields the *ketotricarboxylic acid* (V), $C_{23}H_{36}O_7$, m.p. 196°. With HNO_3, (V) affords a trans-*tricarboxylic acid* (VI), $C_{13}H_{20}O_6$, m.p. 187°, $[\alpha]_D$ −27·3° [*anhydride* (VII), m.p. 145—146°]. Hydrolysis of (VII) gives the cis-*tricarboxylic acid* (VIII), m.p. 136°, $[\alpha]_D$ +36·4°, which regenerates (VII) on distillation. Bromination of the enol acid $C_{24}H_{36}O_4$ (cf. A., 1931, 841) gives a *bromo-*



diketocholanic acid (IX), m.p. 130—133° (decomp.), which in boiling C_5H_5N gives the unsaturated *enol acid* (X), $C_{24}H_{34}O_4$, m.p. 160°.



The C and D rings of the sterols and bile acids are thus connected in the *trans*-position. The present evidence supports the most probable constitution of the bile acids, particularly as to the 5-membered ring D and the positions of the Me groups and side-chain. J. H. B.

Condensation of certain γ-ketonic esters with aromatic aldehydes. II. C. F. H. Allen, G. F.

FRAME, J. B. NORMINGTON, and C. V. WILSON (Canad. J. Res., 1933, **8**, 137—141).—*Me*, m.p. 103°, and *Et* α-*phenyl*-, m.p. 41°, and Et α-*p*-anisyl-β-benzoylpropionate condense with PhCHO in presence of alkali to give α*γ*-*diphenyl*- (I), m.p. 145° (yield 85%) [*oxime*, m.p. 181°; *chloride* (II), m.p. 79°], oxidised to Ph CH_2Ph diketone, and *γ*-*phenyl*-α-p-*anisyl*-β-*benzoylcrotonic acid* (III), m.p. 136° (cf. A., 1932, 1030). (I) at 230—240° yields α-*benzylidene*-β-*phenylpropiophenone* (IV), m.p. 48° (2 : 4-*dinitrophenylhydrazone*, m.p. 189°), oxidised by $KMnO_4$ to BzOH, by CrO_3 to CH_2Ph·COPh, and gives PhCHO with O_3. The similar product (oily) produced from (III) gives *p*-OMe·C_6H_4·CHO with O_3. (IV) with HCl in MeOH gives isomerides of β-*chloro*-β-*phenyl*-α-*benzylpropiophenone*, m.p. 126° and 132°, also obtained from the interaction of benzylacetophenone, PhCHO, and HCl. (I) reacts with 2 mols. of Grignard reagent giving 1 mol. of CH_4, whilst (IV) reacts with 1 mol. without evolution of gas. (II) with AgOAc gives the *acetanhydride*, m.p. 126° [also obtained from (I) with Ac_2O and H_2SO_4], and with the appropriate aniline the *p*-bromo-, m.p. 179°, and p-*iodoanilide*, m.p. 200° (also with 1 mol. of C_6H_6), of (I). A. A. L.

Structural changes produced in the selenium dehydrogenation method. I. Ring changes in *spiro*-compounds. G. R. CLEMO and J. ORMSTON (J.C.S., 1933, 352—353).—2-Keto*cyclo*hexane*spirocyclo*pentane (I), b.p. 102—103°/20 mm. (modified prep.; semicarbazone, m.p. 189—190°), and *cyclo*hexane*spirocyclo*pentane, b.p. 75°/20 mm. [prepared from (I) by Clemmensen reduction], with excess of Se at 280—320° give $C_{10}H_8$ (poor yield). R. S. C.

Decomposition of ω-chloroacetophenonesemicarbazone. A. P. J. HOOGEVEEN and C. W. VAN HOOGSTRATEN (Rec. trav. chim., 1933, **52**, 378—384).—CH_2Cl·CPh:N·NH·CO·NH_2 (I), m.p. 149° (lit. m.p. 156°), is converted by H_2S in EtOH into the *disemicarbazone*, m.p. 228°, of $(COPh·CH_2·)_2S$. When boiled with $NaHCO_3$ in aq. EtOH, (I) affords a *substance*, $C_{17}H_{17}ON_3$, m.p. 221·5°, converted by heating with NaOEt in EtOH at 160° into 3 : 6-*diphenyl*-3 : 4 : 5 : 6-*tetrahydropyridazine*, CHPh<N—N / CH_2·CH_2>CHPh, m.p. 159°, which is oxidised by Br–H_2O to 3 : 6-diphenylpyridazine, identical with a specimen prepared by boiling an EtOH solution of the dihydro-compound obtained from $(COPh·CH_2·)_2$ and N_2H_4 (Paal and Dencks, A., 1903, i, 289). J. W. B.

Absorption spectra of oximes. J. MEISENHEIMER and O. DORNER (Annalen, 1933, **502**, 156—174).—The characteristic band of the CO group in $COMe_2$ and *cyclo*hexanone disappears in the curves of the corresponding oximes. CHPh:N·OH, CPh_2:N·OH (I), and CPhMe:N·OH show bands characteristic of the C_6H_6 nuclei, but the band due to the original CO again disappears or is markedly diminished. Isomeric oximes generally show great similarity. Comparison of the spectra of (I) and its *p*-Cl-, *p*-OMe-, and *p*-OH-derivatives confirms Wolf and Herold's (A., 1931, 996) rule regarding displacement towards the red; the *p*-NO_2 group has, however, the max. effect. The hydrochlorides of aromatic oximes show stronger absorption than the oximes themselves, whilst the curves of the *O*-Me ethers are either identical or parallel (displaced somewhat towards the red) with those of the corresponding oximes, thus indicating that the free oxime exists mainly in the C:N·OH and not the C<NH / O form; the absorption of the ethers is unaffected by HCl. The *N*-Me ethers show stronger absorption than their hydrochlorides or the original oximes; the curves resemble those of the alkali salts of the related oximes. Differentiation of the stable and labile forms of oximes is possible, since the latter show stronger absorption in the region of longer wavelengths. The following data are reported: α-, m.p. 129° (lit. 133°), and β-, m.p. 177° (lit. 184°), -*p*-nitrobenzaldoximes; α-, m.p. 158—159° (lit. 156°), and β-, m.p. 97° (lit. 95°), -*p*-chlorobenzophenoneoximes; α-, m.p. 146° (lit. 138°), and β-, m.p. 118° (lit. 116°), -*p*-methoxybenzophenoneoximes; α-, m.p. 159° (lit. 152°), and β-, m.p. 83° (lit. 81°), -*p*-hydroxybenzophenoneoximes. H. B.

Preparation of 4-fluoro- and 4 : 4′-difluorobenzophenone. R. D. DUNLOP [with J. H. GARDNER] (J. Amer. Chem. Soc., 1933, **55**, 1665—1666).—PhF, BzCl, and $AlCl_3$ give 66% of 4-fluorobenzophenone, m.p. 48·2—48·7° (lit. 52°). 4 : 4′-*Difluorobenzophenone*, m.p. 107·5—108·5° (*oxime*, m.p. 137—138°, rearranged by PCl_5 in Et_2O to *p*-fluorobenz-*p*-fluoroanilide, m.p. 183·5—184·2°), is prepared in 52% yield from *p*-C_6H_4F·COCl, PhF, and $AlCl_3$; a little of the 4 : 2′-isomeride is also formed. H. B.

Grignard reaction in the synthesis of ketones. II. Preparation of mono- and di-chlorodeoxybenzoins. S. S. JENKINS and E. M. RICHARDSON (J. Amer. Chem. Soc., 1933, **55**, 1618—1621; cf. this vol., 394).—$CH_2Ph·MgCl$ (I) and *o*-C_6H_4Cl·CO·NH_2 (II) in Et_2O and H_2 give o-*chlorophenyl benzyl ketone*, b.p. 176—178°/5 mm. [anti-*oxime*, m.p. 131·5—132·5° (all m.p. are corr.), rearranged by PCl_5 in Et_2O to *phenylacet*-o-*chloroanilide*, m.p. 120°]; *o*-$C_6H_4Cl·CH_2·MgBr$ (III) and NH_2Bz afford *Ph* o-*chlorobenzyl ketone*, m.p. 70·5° (anti-*oxime*, m.p. 85—86°, rearranged to *o*-$C_6H_4Cl·CH_2·CO·NHPh$); (III) and (II) yield o-*chlorophenyl* o-*chlorobenzyl ketone*, b.p. 195—210°/6 mm. (anti-*oxime*, m.p. 103—104°, rearranged to o-*chlorophenylacet*-o-*chloroanilide*, m.p. 159·5°; syn-*oxime*, m.p. 145—146°, rearranged to N-o-*chlorobenzoyl*-o-*chlorobenzylamine*, m.p. 111°); (I) and *p*-C_6H_4Cl·CO·NH_2 (IV) furnish p-*chlorophenyl benzyl ketone*, m.p. 107·5° (anti-*oxime*, m.p. 122·5—123·5°, rearranged to *phenylacet*-p-*chloroanilide*, m.p. 168°); *p*-$C_6H_4Cl·CH_2·MgBr$ (V) and NH_2Bz give *Ph* p-*chlorobenzyl ketone*, m.p. 138° (anti-*oxime*, m.p. 95—96°, rearranged to *p*-$C_6H_4Cl·CH_2·CO·NHPh$); (V) and (IV) afford p-*chlorophenyl* p-*chlorobenzyl ketone*, m.p. 114° (anti-*oxime*, m.p. 124·5—125·5°, rearranged to p-*chlorophenylacet*-p-*chloroanilide*, m.p. 190°); (III) and (IV) yield p-*chlorophenyl*-o-*chlorobenzyl ketone*, m.p. 108·5° (anti-*oxime*, m.p. 105—106°, rearranged to o-*chlorophenylacet*-p-*chloroanilide*, m.p. 184°); (V) and (II) furnish o-*chlorophenyl* p-*chlorobenzyl ketone*, m.p. 65° (anti-*oxime*, m.p. 88—89°, rearranged to p-*chlorophenylacet*-o-*chloroanilide*, m.p. 171°). The above

anilides are also prepared by the usual method. The yields of ketones are 70—80%. H. B.

Dehydration of the α-forms of *r*- and (+)-*o*- and -*m*-tolylhydrobenzoins. R. ROGER and W. B. MCKAY (J.C.S., 1933, 332—336; cf. A., 1932, 1251).—*r*-*m*-Tolylhydrobenzoin (α-form) with boiling dil. H_2SO_4 in 3 hr. affords r-m-*tolyldeoxybenzoin* (I), m.p. 83—84°, whilst cold conc. H_2SO_4 affords a mixture of (I) and m-*tolyl CHPh$_2$ ketone* (III), m.p. 97°. Further action of H_2SO_4 on (I) affords a *product*, m.p. 173—174°, which contains S. Similarly, (+)-*m*-tolylhydrobenzoin (α-form) with dil. H_2SO_4 as well as with boiling $H_2C_2O_4,2H_2O$ during 8 hr. affords (I). (I) is prepared from r-*phenyl*-m-*tolylacetonitrile*, m.p. 38·5—39°, and MgPhBr in Et_2O. Interaction of *m*-C_6H_4MeBr, Mg, and $CHPh_2$·CN in Et_2O during 4 hr. affords (III). *r*-*o*-Tolylhydrobenzoin (α-form) (II) with boiling dil. H_2SO_4 affords *diphenyl*-o-*tolylacetaldehyde* (IV), m.p. 163—164° (which with KOH–EtOH gives *diphenyl*-o-*tolylmethane*, m.p. 82—83°), and r-o-*tolyldeoxybenzoin* (?) (V), m.p. 56—57°. (II) with cold conc. H_2SO_4 affords o-*tolyl CHPh$_2$ ketone* (?) (VI), m.p. 47—48°, and (V). (IV) is further acted on by cold conc. H_2SO_4 to give (VI) and (V). (+)-*o*-Tolylhydrobenzoin (α-form) with boiling dil. H_2SO_4 affords (IV) and (+)-o-*tolyldeoxybenzoin* (?), m.p. 79·5—80·5°, $[\alpha]_{5893}$ +202·5° in $CHCl_3$, rapidly racemised by 0·5*N*-KOH–EtOH to (V). The significance of the preceding reactions is discussed. J. L. D.

Nitration of chalkone. R. J. W. LE FEVRE, P. J. MARKHAM, and J. PEARSON (J.C.S., 1933, 344—346).—4-Nitrochalkone (I) (A., 1902, i, 379) and 3′-nitrochalkone are both converted by HNO_3 (*d* 1·5) below 0° into 3 : 4-dinitrochalkone (II), m.p. 204—205° (lit., about 225°). Chalkone (III), contrary to Goldschmidt (A., 1895, i, 422), is dinitrated by HNO_3–H_2SO_4 to (II). Goldschmidt's "*o*-nitrobenzylideneacetophenone" is mainly an oxidation product, as it affords only traces of 2-phenylquinoline on reduction. Interaction of (III) and KNO_3–H_2SO_4 at −10° affords (I). J. L. D.

Constitution of the chlorination products of benzanthrone. R. S. CAHN, W. O. JONES, and J. L. SIMONSEN (J.C.S., 1933, 444—449).—Chlorination of benzanthrone (I) by dichloroamine-*T* in AcOH affords 13-chlorobenzanthrone (II), m.p. 182—183° (cf. A., 1929, 1304). Interaction of 5 : 8-dichloro-1-naphthoyl chloride, C_6H_6, and $AlCl_3$ during 8·5 hr. affords *Ph* 5 : 8-*dichloro*-α-*naphthyl ketone*, m.p. 93°, which failed to cyclise to (II). Further chlorination of (I) or (II) affords 6 : 13- and 8 : 13-dichlorobenzanthrone, oxidised [as is 6-chlorobenzanthrone (III)] to 6-chloro-[*Me* ester, m.p. 190—191°; *acid chloride*, m.p. 234—236° (decomp.)] and 8-chloro-anthraquinone-1-carboxylic acid (*Me* ester, m.p. 124—125°), respectively, the latter acid being synthesised from 8-*chloro*-1-*aminoanthraquinone*, m.p. 225—227° (*Ac* derivative, m.p. 223—225°), through the nitrile. Similarly, 5-chloro-1-aminoanthraquinone (*Ac* derivative, m.p. 218—220°) is converted into 5-*chloroanthraquinone*-1-*carboxylic acid*, m.p. 306° (decomp.) [*Me* ester, m.p. 181°, identical with the ester prepared from Butescu's α-chloroanthraquinone-1-carboxylic acid (cf. A., 1913, i, 273)]. 7-Chlorobenzanthrone (IV) is oxidised to 7-*chloroanthraquinone*-1-*carboxylic acid*, m.p. 262—264° (*Me* ester, m.p. 193—194°), previously obtained, although not oriented, by Butescu. Interaction of *m*-C_6H_4Cl·COCl and $C_{10}H_8$ (cf. A., 1922, i, 258) affords m-*chlorophenyl* β-*naphthyl ketone*, m.p. 143° [*dinitrophenylhydrazone*, m.p. 264—265° (decomp.)], and *m*-C_6H_4Cl α-$C_{10}H_7$ ketone, m.p. 86° (lit., 77—79°) (*dinitrophenylhydrazone* isolable in two forms, m.p. 247° and 198—200°), which readily cyclises to (III). Similarly, *p*-C_6H_4Cl·COCl and $C_{10}H_8$ afford a mixture of α- and β-$C_{10}H_7$ derivatives (α-ketone purified) which cyclises to (IV), further chlorinated to 7 : 13-*dichlorobenzanthrone*, m.p. 251—252°. J. L. D.

Hydroxylamine derivatives of phenyl styryl ketone and dibenzoylmethane. K. VON AUWERS and H. MÜLLER (J. pr. Chem., 1933, [ii], **137**, 57—80).—Treatment of CHPh:CH·COPh (I) with NH_2OH,HCl (2 mols.) in EtOH containing 1 drop of conc. HCl or in anhyd. EtOH without HCl gives the normal oxime (II), m.p. 115—116°. Free NH_2OH (III) in absence of other alkali and in cold solution gives primarily β-hydroxylamino-β-phenylpropiophenone (IV) (not isolated), which in presence of excess of (I) yields the compound, $(CH_2Bz·CHPh)_2N·OH$, m.p. 190°. If excess of (III) is present, (IV) yields γ-hydroxylamino-αγ-diphenylpropanoneoxime (V), m.p. 147°. A third possible transformation is the oxidation of (IV) to $CH_2Bz·CPh{:}N·OH$, m.p. 165°. Correspondingly, (IV) is oxidised to $CH_2(CPh{:}N·OH)_2$, m.p. 209°. Production of (II) is subsidiary. In hot solution the amount of (II) increases as, to a still greater extent, does that of diphenyl*iso*oxazoline, m.p. 75°, particularly when free alkali is present. The extent of its oxidation to diphenyl*iso*oxazole depends on experimental conditions. H. W.

Oxidative processes. VII. Preparation, racemisation, and autoxidation of the optically active 2 : 2′-diethoxybenzoins. A. WEISSBERGER and E. DYM (Annalen, 1933, **502**, 74—85; cf. this vol., 161).—*o*-OEt·C_6H_4·CHO (in Et_2O) and KCN+NH_4Cl (in H_2O) give o-*ethoxymandelonitrile*, m.p. 86—89°, hydrolysed (Et_2O–EtOH–HCl and then H_2O) to dl-o-*ethoxymandelic acid* (I), m.p. 102·5—103·5° [*Me* ester, m.p. 71—72°; *amide* (II), m.p. 102·5—103·5°]. (II) and *o*-OEt·C_6H_4·MgBr afford *dl*-2 : 2′-diethoxybenzoin. (I) is resolved by cinchonine into (−)-, m.p. 126·5—127·5° (corr.), $[\alpha]_D^{20}$ −144·9° in EtOH [Me ester, b.p. 84—86°/0·02 mm., m.p. 30—31°; amide (III) m.p. 125·5—126·5° (corr.)], and (+)-forms, m.p., 125·5—126·5° [amide (IV), m.p. 124·5—125·5°]. (−)-*d*- and (+)-*l*-2 : 2′-Diethoxybenzoins, m.p. 58·5—59·5°, $[\alpha]_D$ −30° and +30° in EtOH, respectively, are prepared (as above) from (III) and (IV), respectively. Racemisation and autoxidation of these under the conditions previously described (A., 1931, 844) occur at almost identical rates; steric hindrance by the OEt groups involves ionisation or enolisation (and subsequent dissociation) but not oxidation of the ion R·CO·CO·R. H. B.

Potentiometric studies on semiquinones. L. MICHAELIS and E. S. HILL (J. Amer. Chem. Soc., 1933, **55**, 1481—1494; cf. A., 1931, 1130, 1309).—Analysis of the oxidation or reduction curves of *p*-$NH_2·C_6H_4·NMe_2$, *p*-$C_6H_4(NMe_2)_2$, *p*-$NH_2·C_6H_4·NEt_2$,

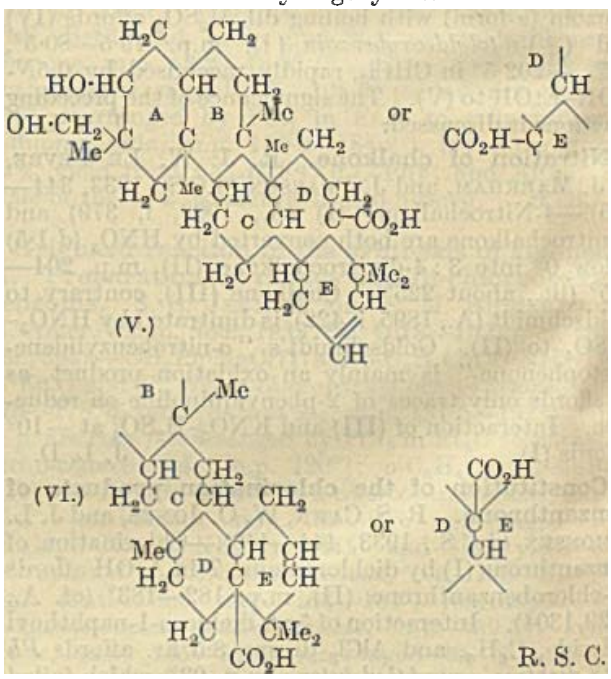
p-$C_6H_4(NEt_2)_2$, p-$C_6H_4(NHPh)_2$, 4 : 4′-dipyridyl and its *dimethochloride*, and phenazine shows that the semiquinonoid form differs from the holoquinonoid by one electron without change of mol. size. Semiquinonoid compounds are radicals in which one electron is shared by two atoms each possessing a septet. H. B.

Anthraquinone derivatives. I. Chloroaminoanthraquinone. M. Hayashi, K. Kawasaki, and A. Nakayama (J. Soc. Chem. Ind. Japan, 1933, **36**, 123—127B).—Interaction of 4-nitrophthalic anhydride, PhCl in excess, and $AlCl_3$ at 120—130° gives 4′-*chloro*-4(or 5)-*nitro*-, m.p. 198° [*Me* ester, m.p. 150—150·5°; NH_2-compound, m.p. 192° (decomp.) (*Ac* derivative, m.p. 222·5—223°)] (38% of theory), and 4′-*chloro*-5(or 4)-*nitro*-2-*benzoylbenzoic acid*, m.p. 194—194·5° [*Me* ester, m.p. 109—109·5°; NH_2-compound, m.p. 225·5—226° (decomp.) [*Ac* derivative, m.p. 224·5—225°)] (16·5% of theory). Both NH_2-compounds with H_2SO_4 at 150—155° give 2-*chloro*-6(or 7)-, m.p. 284—284·5°, and -7(or 6)-*aminoanthraquinone*, m.p. 295—296°, and an unidentified compound, m.p. 300°. H. A. P.

Structure of simple nucleic acids. III. Yeast- and muscle-adenylic acid. H. Steudel (Z. physiol. Chem., 1933, **216**, 77—80; cf. A., 1931, 1317).—Yeast- and muscle-adenylic acids differ in α during acid hydrolysis and in their pentose content. The Cu salts do not differentiate the two forms. J. H. B.

Plant-growth substances. V. Phytohormone of cell elongation. Chemistry of crystalline auxin. F. Kögl, H. Erxleben, and A. J. Haagen-Smit (Z. physiol. Chem., 1933, **216**, 31—44; cf. this vol., 435).—Auxin (I), $C_{18}H_{32}O_5$, and its lactone show mutarotation, final vals. $[\alpha]_D$ −3·19° and −3·44° in EtOH, respectively. (I) forms a *Me* ester, m.p. 148°, $[\alpha]_D^{20}$ −3·77°, *tri*-m-*dinitrobenzoyl* derivative, m.p. 168°, p-*phenylphenacyl* ester, m.p. 166°, *dihydro*-derivative, m.p. 199°, final $[\alpha]_D^{20}$ −3·14° in EtOH, and *dihydrolactone*, m.p. 191°. On keeping, (I) gives a mixture of various physiologically inactive isomerides differing in α but not showing mutarotation. The mixture on hydrogenation gave a *product*, m.p. 198°. (I) is a monocyclic singly unsaturated tricarboxylic acid. J. H. B.

Constitution of hederagenin and oleanolic acid. IV. Z. Kitisato and C. Sone (Acta Phytochim., 1933, **7**, 1—26; cf. A., 1932, 1035).—Bromohedragone lactone, prepared by Beckmann's mixture (5O) from bromohederagenin lactone in cold AcOH, is accompanied by *bromohedragenonedi-acid lactone*, $C_{29}H_{43}O_5Br$, m.p. 192—193° (decomp.) [*oxime*, m.p. 258° (decomp.)], the *Me* ester, m.p. 195° (decomp.) [*oxime*, m.p. 236—237° (decomp.)], of which with Br in MeOH gives the *Me* ester, m.p. 183° (decomp.), of *dibromohedragenonedi-acid lactone*, and with Zn dust and AcOH yields the *Me* ester (I), m.p. 181—182° (decomp.), of *hedragenonedi-acid* (II), the Me_2 ester, m.p. 159—160°, of which is obtained from (I) by CH_2N_2. Hedragenetri-acid has m.p. above 300° (*Me* ester, m.p. 149°). (II) and KOBr give a product which with Br in MeOH yields bromohedratri-acid lactone and its *Me* ester (III), +0·66MeOH, m.p. about 200° (also +AcOH) [Me_2 ester, $C_{30}H_{45}O_6Br$, m.p. 187° (decomp.)]. (III), Zn dust, and hot AcOH afford *hedratri-acid*, $C_{28}H_{42}O_6$, m.p. 240° (decomp.), and its *Me* ester, m.p. 122—124°. (III) and KOH–EtOH give *γ-ketohedratri-acid*, $C_{28}H_{42}O_7$,+H_2O, m.p. 255° (decomp. 272°) (*Me* ester, m.p. 164°). Ketohedragone lactone and KOBr led to *ε-ketohedragenetri-acid*, m.p. 288—289° (decomp.) (*Me* ester, m.p. 164°). Ketohederagenin lactone [*Br* derivative, m.p. 235° (decomp.)] and KOH–EtOH give *ε-ketohederagenin* (IV), $C_{30}H_{46}O_5$, m.p. 290° (decomp.), which by Me_2SO_4 and subsequent acetylation gives the *Me* ester, m.p. 237°, of the Ac_2 derivative of (IV), which yields the *Me* ester, m.p. 220°, of (IV) by hydrolysis. Keto-oleanolic acid lactone and KOH–EtOH give *ε-keto-oleanolic acid*, $C_{30}H_{46}O_4$,+0·5H_2O, m.p. 268—269° (decomp.), giving similarly the *Me* ester, m.p. 200° (Ac_2 derivative, m.p. 236—238°). The above and previous results are held to prove formula (V) for hederagenin and formulæ are assigned to many of its degradation products. (VI) is, however, also possible; further, all these compounds may contain one C atom more than given above. Hedragonedi-acid is re-named hedragenetri-acid and deoxydehydrohedrabetulin becomes hydragenylene.



Oleanolic acid (guagenin). III. Oxidation of acetyloleanolic acid and oleanolic acid with chromic acid. W. Schicke and E. Wedekind (Z. physiol. Chem., 1933, **215**, 199—206; cf. A., 1931, 1100).—Oxidation of acetyloleanolic acid with CrO_3 in AcOH at 80° gives, in addition to δ-ketoacetyloleanolic acid lactone (Kitasato and Sone, A., 1932, 1035), a *dicarboxylic acid*. $C_{27}H_{40}O_7$, m.p. 293—294°, which was deacetylated to an *acid*, $C_{25}H_{38}O_6$, m.p. 292°. Oxidation in boiling AcOH afforded a keto-acid $C_{30}H_{46}O_3$, m.p. 187° (*oxime*, m.p. 299°), identical with Prelog's product (A., 1930, 1044). J. H. B.

Active principle of *Atractylis gummifera*. T. Ajello (Gazzetta, 1933, **63**, 99—102).—For K

atractylate the new formula $C_{30}H_{48}O_{18}S_2K_2$ is suggested (cf. A., 1924, i, 195). E. W. W.

Pyrolysis of menthoglycol and *iso*pulegyl acetate. J. DŒUVRE (Bull. Soc. chim., 1933, [iv], 53, 170—177).—When menthoglycol is passed over glass wool in a Pyrex glass tube at 540°/30—40 mm. at the rate of 10 g. per hr., $COMe_2$ and 3-methyl*cyclo*hexanone (I) are the main products; some dehydration to *iso*pulegol [which is then largely transformed into citronellal (cf. A., 1930, 893)] also occurs. 3-Methyl*cyclo*hexanol (p-*diphenylylcarbamate*, m.p. 106—107°) and *cyclo*hexanol similarly give (I) and *cyclo*hexanone, respectively. *iso*Pulegyl acetate at 540—550°/50 mm. affords AcOH and approx. equal amounts of $\Delta^{2:8(9)}$- and $\Delta^{3:8(9)}$-p-*menthadienes*, b.p. 171—173° (corr.)/750 mm., $[\alpha]^{20}_{5461}$ +133·5°, and b.p. 182—184° (corr.)/750 mm., $[\alpha]^{20}_{5461}$ +118·33°, respectively. H. B.

Camphor and terpenes. IX. Transformation of camphor and optically active systems of the camphor series into their spatial antipodes. J. HOUBEN and E. PFANKUCH (Annalen, 1933, 501, 219—246; cf. A., 1932, 62).—*D*-Camphor, PCl_3, and PCl_5 give (cf. Meerwein and Wortmann, A., 1924, i, 188) a lævorotatory mixture of (mainly) *D-l*-2 : 2-dichlorocamphane (α-*D*-camphor dichloride) (I), varying smaller amounts of 2 : 4-dichlorocamphane (*L-d*-4-chloro*iso*bornyl chloride) (II), and probably a little *D*-1-chlorocamphene hydrochloride (III). Treatment of the mixture with KOAc and PhOH gives (cf. *loc. cit.*) 1-chlorocamphene [from (I) and (III)], 4-chlorocamphene [from (III)], and a little chlorotricyclene [from (II)]. The production of (II) is considered to occur thus: (I)⟶(III)⟶*L*-4-chlorocamphene hydrochloride (IV)⟶(II). The changes (I)⟶(III) and (IV)⟶(II) involve ring isomerisation, whilst the change (III)⟶(IV) occurs through migration of Cl and Me (cf. A., 1931, 1300; Nametkin and Brüssov, A., 1928, 182) and effects a transformation of the *D*- into the *L*-series. Related transformations are studied.

Impure *L*-camphor, PCl_3, and PCl_5 give a 2 : 2-dichlorocamphane, $[\alpha]^{20}$ +15·2° in Et_2O, convertible into *L-d*-α-chlorocamphene, $[\alpha]^{18}_{5461}$ +18·8° in EtOH, which is reduced (Na, EtOH) to a camphene, $[\alpha]^{19}$ −68° in EtOH. Rearrangement of (I) with $SnCl_4$ in PhMe (cf. *loc. cit.*) affords *L*-4-chloro*iso*bornyl chloride (β-camphor dichloride), $[\alpha]^{19}_{5461}$ +18·25° in Et_2O, convertible into *L-l*-β-chlorocamphene, $[\alpha]^{17}_{5461}$ −53° in EtOH. *D*-α-Chlorocamphene (V) and HBr–AcOH at 5—10 °give *D-l*-1-chlorocamphene hydrobromide (VI), m.p. 140—145° (decomp.), $[\alpha]^{19}_{5461}$ −11·2° in Et_2O, converted by dry Ag_2O in Et_2O+Na_2SO_4 into D-l-1-*chlorocamphene*, b.p. 72—73°/12 mm., m.p. 3—5°, $[\alpha]^{20}_{5461}$ −12·9° in EtOH, which is reduced (Na, EtOH) to *D*-camphene, m.p. 45—46°, $[\alpha]^{20}$ +97·5° in EtOH. (VI) rearranges in *m*-cresol into L-d-4-*chloroisobornyl bromide*, m.p. 156—158°, $[\alpha]^{19}_{5461}$ +51·5° in EtOH [a small amount of which is formed with (VI) (above)]; treatment of the solution (in *m*-cresol) with C_5H_5N gives L-l-4-*chlorocamphene*, m.p. 132—133°, $[\alpha]^{18}_{5461}$ −108° in EtOH, which is reduced (Na, EtOH) to *L-l*-camphene (VII), m.p. 51° (sinters at 48°), $[\alpha]^{19}_{5461}$ −104·7° in EtOH. (VII) and HCl in Et_2O give *L-d-iso*bornyl chloride, $[\alpha]^{20}_{5461}$ +60° in EtOH. (V), AcOH, and 50% H_2SO_4 afford 4-*chloroisobornyl acetate*, b.p. 129—130°/13 mm., $[\alpha]^{20}$ +51·5° in EtOH; the yield and rotation of the acetate vary considerably. (V) and $CCl_3{\cdot}CO_2H$ at 50—60° give 4-*chloroisobornyl trichloroacetate*, m.p. 67—68°, $[\alpha]^{19}_{5461}$ +41·5° in EtOH (which is partly racemised by $CCl_3{\cdot}CO_2H$), hydrolysed (MeOH–KOH) to a partly racemised alcohol; pure *L-d*-4-chloro*iso*borneol, $[\alpha]^{21}_{5461}$ +32·8° in EtOH, is more sol. than the *r*-form in light petroleum and is thus separable. *D-l*-4-Chloro*iso*borneol, $[\alpha]_D$ −23·1°, prepared from *L*-camphor by way of *L*-α-chlorocamphene, is reduced (Na, EtOH) to *D-l-iso*borneol, $[\alpha]^{20}$ −23·7° in EtOH, which is oxidised (CrO_3, AcOH) to *D*-camphor, $[\alpha]^{1}_{5461}$ +31·8° in EtOH. L-4-*Chlorocamphorhydrazone*, m.p. about 120° [hydrochloride, m.p. 230—235°; *Ac* derivative, m.p. about 250° (decomp.)], and HgO in EtOH give 4-chlorotricyclene, m.p. 135—136°. H. B.

Resin. II. Extension of the Liebermann colour reaction for abietic acid. W. A. LA LANDE, jun. (J. Amer. Chem. Soc., 1933, 55, 1536—1540).—Factors influencing the colour produced in the Liebermann test are discussed. The use of anhydrides (other than Ac_2O) and acyl chlorides is investigated; the most brilliant colorations (greenish-brown⟶green-ish-blue⟶indigo-blue⟶purple⟶dull brown) are observed with BzCl and conc. H_2SO_4. Most of the compounds of known structure which give blue or violet colorations with Ac_2O and conc. H_2SO_4 are *m*-menthadienes containing the ·CMe:CH_2 group (I) or *m*-menthenols which can give (I) by dehydration. Abietic acid may contain the $\Delta^{x:8(9)}$-*m*-menthadiene grouping. H. B.

Preparation of 5-methylfurfuraldehyde. I. J. RINKES (Rec. trav. chim., 1933, 52, 337—338).—Details of the prep. of 5-methylfurfuraldehyde (70 g.) by the action of HCl (*d* 1·163) at 50°, rising to 72°, on crude sucrose (1 kg.) are given (cf. A., 1931, 95). J. W. B.

Preparation of 5-bromofuroic acid. R. M. WHITTAKER (Rec. trav. chim., 1933, 52, 352—356).—The yields of 5-bromofuroic acid (I) obtained by bromination of furoic acid (II) in various solvents and with different catalysts are tabulated. The best yield (41%) is obtained by slowly adding Br to (II) in $CHCl_3$ (+red P). Any dibromofuroic acid is removed by purification of the Ba salt. An improvement of the method of Shepard *et al.* (A., 1930, 923) for decarboxylation of (I) is described. J. W. B.

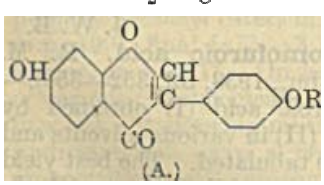
Anthoxanthins. XIV. ω-Hydroxyphloracetophenone and certain derivatives. Synthesis of galangin under milder conditions than those used heretofore. J. J. CHAVAN and R. ROBINSON (J.C.S., 1933, 368—370).—ω : 2 : 4 : 6-Tetrabenzoyloxyacetophenone (I), m.p. 142·5°, prepared from ω-benzoyloxyphloracetophenone, is dehydrated by KOAc–EtOH to O-*tribenzoylgalangin*, m.p. 177°, or by Ac_2O–NaOAc to galangin. Acetoxyacetonitrile and phloroglucinol yield ω-*hydroxyphloracetophenone*, m.p. 224°, which is benzoylated to (I), and is acetylated to ω : 2 : 4 : 6-*tetra-acetoxyacetophenone*, m.p. 106·5°. F. R. S.

Synthesis of pyrylium salts of anthocyanidin type. XX. Morindin chloride. Cyanomac-

lurin. E. H. CHARLESWORTH, J. J. CHAVAN, and R. ROBINSON (J.C.S., 1933. 370—374).—Resorcinol and acetoxyacetonitrile form *ω-acetoxyresacetophenone*, m.p. 164·5° (*phenylhydrazone*, m.p. 152°; *ω-acetoxy-2 : 4-dibenzoyloxy-*, m.p. 151·5°, and *ω : 2 : 4-triacetoxyacetophenone*, m.p. 93·5°), hydrolysed to ω : 2 : 4-trihydroxyacetophenone (fisetol) (*osazone*, m.p. 204·5°; *Bz*- derivative, m.p. 140°). Fisetol and 2-*O*-benzoylphloroglucinaldehyde afford mainly 5-*O*-benzoylmorinidin chloride, hydrolysed to morinidin chloride (colour reactions described), of which the reduction products (Pt–MeOH) do not closely resemble cyanomaclurin (I). The constitution of (I) is discussed (cf. Kuhn and Winterstein, this vol., 72). F. R. S.

Synthetical experiments in the *iso*flavone group. VIII. Limitations of the phenacyl aryl ether cyanohydrin method. W. BAKER, W. M. MORGANS, and R. ROBINSON (J.C.S., 1933, 374—375).—*ω-Diazo-p-acetylanisole*, m.p. 83—84°, is obtained from anisoyl chloride and CH_2N_2. 3 : 4 : 5-*Trimethoxyphenyl* p-*methoxyphenacyl ether*, m.p. 110—111°, prepared from *p*-methoxyphenacyl bromide and antiarol, forms with difficulty a *cyanohydrin*, m.p. 126—127° (which does not undergo ring closure), and is dehydrated by P_2O_5 to 4 : 5 : 6 : 4′-*tetramethoxy-3-phenylcoumarone*, m.p. 104—105°. *ω-Diazo-3 : 4 : 5-trimethoxyacetophenone*, m.p. 97—98°, gives with HBr 3 : 4 : 5-*trimethoxyphenacyl bromide*, m.p. 51—52°, which with antiarol and NaOH forms 3 : 4 : 5-*trimethoxyphenyl* 3 : 4 : 5-*trimethoxyphenacyl ether*, m.p. 135—136°, dehydrated by P_2O_5 to 4 : 5 : 6 : 3′ : 4′ : 5′-*hexamethoxy-3 : 3-diphenylcoumarin*, m.p. 112—113°. F. R. S.

Synthesis of daidzein and of 7-hydroxy-4′-methoxy*iso*flavone. F. WESSELY, L. KORNFELD, and F. LECHNER (Ber., 1933, **66**, [*B*], 685—687).—4-Methoxybenzyl 2 : 4-dihydroxyphenyl ketone with Na in HCO_2Et gives formononetin (I; A, R=Me), m.p. 257°. Analogously, 4-hydroxybenzyl 2 : 4-dihydroxyphenyl ketone affords daidzein (II; A, R=H), m.p. 323° after darkening at 300° (cf. Baker *et al.*, this vol., 510). (I) or (II) with CH_2N_2 or MeI yields methylformononetin, m.p. 162—164°. H. W.

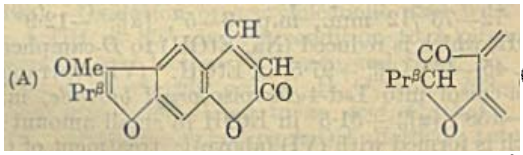


(A.)

Colouring matter of "Awobana." II. C. KURODA (Proc. Imp. Acad. Tokyo, 1933, **9**, 94—96).—A co-pigment (*A*, pale yellow) was isolated, which gave *p*-OH·C_6H_4·CO_2H and *p*-OH·C_6H_4·COMe. Details are given of the isolation of the pure pigment (*B*) from *Awobana* paper; alkali fusion gives phloroglucinol and gallic acid, and *B* is considered to be a monoglucoside of delphinidin. (Cf. A., 1931, 777.) P. G. M.

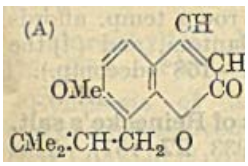
Styrylpyrylium salts. XIV. Colour phenomenon associated with benzonaphtha- and dinaphtha-*spiro*pyrans. I. M. HEILBRON, R. N. HESLOP, and F. IRVING (J.C.S., 1933, 430—434).—7-*Methoxy-2-ethylchromone*, m.p. 141—142° (from 2-hydroxy-4-methoxyacetophenone, Pr_2O, and NaOPr) and PhMgBr form 7-*methoxy-4-phenyl-2-ethylbenzopyrylium ferrichloride*, m.p. 110—111°; from the corresponding carbinol base, β-naphthol-1-aldehyde, and HCl, 7-*methoxy-3′-methylbenzo-β-naphtha*spiro*pyran*, m.p. 165—166°, is obtained. 2-*Ethylchromone*, m.p. 116°, gives 4-*phenyl-3′-methylbenzo-β-naphtha*spiro*pyran*, m.p. 153—154°, through 4-*phenyl-2-ethylbenzopyrylium perchlorate*, m.p. 207—209° (decomp.); 7-*methoxy-3-methyl-2-ethylchromone*, m.p. 85—86°, 7-*methoxy-4-phenyl-3-methyl-2-ethylbenzopyrylium perchlorate*, m.p. 203—205° (decomp.), and 7-*methoxy-4-phenyl-3-methylbenzo-β-naphtha*spiro*pyran*, m.p. 198—199°, are similarly prepared. 4-*Phenyl-*, m.p. 193—194° [4-phenyl-2-methyl α-naphthapyrylium perchlorate, m.p. 197—199° (decomp.)], 4-*phenyl-3′-methyl-*, m.p. 188—190° [2-*ethyl-α-naphthachromone*, m.p. 199—200°, and 4-phenyl-2-ethyl-α-naphthapyrylium perchlorate, m.p. 221° (decomp.)], 4-*phenyl-3-methyl-*, m.p. 181—182° [4-phenyl-2 : 3-dimethyl-α-naphthapyrylium perchlorate, m.p. 223—224° (decomp.)], and 4-*phenyl-3 : 3′-dimethyl-αβ-dinaphtha*spiro*pyran*, m.p. 181—182° [3-*methyl-2-ethyl-α-naphthachromone*, m.p. 102—103°; 4-phenyl-3-methyl-2-ethyl-α-naphthylpyrylium perchlorate, m.p. 228—230° (decomp.)]; 4′-*phenyl-3′-methylbenzo-α-naphtha*spiro*pyran*, m.p. 115—116°; 3 : 3′-*dimethylenedi-*, m.p. 245—246°, and 3 : 3′-(β-*methyltrimethylene*)*di*-β-*naphtha*spiro*pyran*, m.p. 253—254°, are also described. The colour reactions described are not accounted for by the "chelate" hypothesis of Dickinson and Heilbron (A., 1927, 884). F. R. S.

Vegetable fish poisons. II. Constitution of peucedanine and oreoselone (from *Peucedanum officinale*). E. SPATH and K. KLAGER. III. Constitution of osthol (from *Imperatoria ostruthium*). E. SPATH and O. PESTA (Ber., 1933, **66**, [*B*], 749—754, 754—760; cf. A., 1931, 1298).—II. Treatment of oreoselone (I) with NaOH–KOH at 220° yields resorcinol and β-resorcylic acid. Similar treatment of dihydro-oreoselone affords 7-hydrodihydrocoumarin, m.p. 134°, thus establishing the coumarin structure of (I). Oxidation of (I) by H_2O_2 in alkaline solution smoothly yields *iso*butyric acid. Tetrahydropeucedanine loses MeOH when distilled in high vac. and the product is hydrogenated to *deoxydihydro-oreoselone*, $C_{14}H_{16}O_3$, m.p. 117·5°, reduced by P and HI probably with opening of the hydrogenated furan ring to a phenol, converted by H_2O_2 in alkaline solution into *iso*hexoic acid. (I) when dissolved in conc. H_2SO_4, poured into H_2O, and oxidised with $KMnO_4$ yields α-hydroxy*iso*valeric acid, m.p. 81—83°. iso*Dihydro-oreoselone*, $C_{14}H_{14}O_4$, m.p. 178·5—180°, is prepared from dihydro-oreoselonic acid by Cu powder in quinoline at 240—245°. The formulæ A and B are thus established for peucedanine and (I).



III. Oxidation of osthol (I) by $KMnO_4$ in $COMe_2$ gives 2-hydroxy-4-methoxybenzoic acid, m.p. 154—155°. (I) is hydrogenated (Pd–C) in AcOH to *tetrahydro-osthol*, b.p. 145—150° (bath)/0·006 mm., which is not immediately sol. in 20% NaOH, is oxidised by

conc. HNO_3 at room temp. to succinic acid and by H_2O_2 in alkaline solution to *iso*hexoic acid (phenylhydrazide, m.p. 144—145°). $COMe_2$ is obtained from (I) and CrO_3–AcOH. Ostholic acid (Butenandt and Marten, A., 1932, 751) is decarboxylated by Cu powder in boiling quinoline to *7-methoxy-8-methylcoumarin*, m.p. 136—137·5°, the constitution of which follows from its oxidation to 2-hydroxy-4-methoxy-3-methylbenzoic acid, m.p. 214·5—215·5°, which is transformed by PH_4I and HI (*d* 1·7) into 2 : 6-$C_6H_3Me(OH)_2$, m.p. 119—121° (Bz_2 derivative, m.p. 106—107·5°). (I) has therefore the constitution A. H. W.



Crystalline colouring compounds in redwood extract. E. C. Sherrard and E. F. Kurth (J. Amer. Chem. Soc., 1933, **55**, 1728—1732).—Details are given for the isolation of *sequoyin* (I), $C_{30}H_{38}O_{10}$, m.p. 214° (*octa-acetate*, m.p. 104—106°), from the heartwood of *Sequoia sempervirens*. *iso*Sequein, red, m.p. 188°, has also been isolated from two specimens of the green wood; it is apparently present in most redwood liquors. (I) is hydrolysed (5% H_2SO_4) to *sequeinol*, $C_{16}H_{18}O_4$, m.p. 242° (decomp.) (*tetra-acetate*, m.p. 176—177°), which is unaffected by fusion with KOH at 220°, and *sequein* (II), $C_{20}H_{20}O_6$, m.p. 190°. (II) gives a bright red colour with alkalis, is phenolic, affords *hexa-acetates*, m.p. 114° and 124° [which are not hydrolysed to (II)], and is considered to contain the 2-hydroxypyran grouping (which undergoes fission during acetylation). H. B.

Action of erepsin and trypsin-kinase on prolyl polypeptides. E. Abderhalden and H. Nienburg (Fermentforsch., 1933, **13**, 573—596).—The following were prepared from the corresponding αδ-dibromovaleryl (I) compounds (A., 1932, 1064): dl-*prolylleucine*, m.p. 207°, from (I)-dl-*leucine*, m.p. 100—130°; l- (II), m.p. 217°, $[\alpha]_D^{20}$ —2·9°, and d-*prolyl*-l-*tyrosine* (III), $[\alpha]_D^{20}$ +1·92°, from (I)-l-*tyrosine*; l- (IV), m.p. 247°, $[\alpha]^{20}$ —57·02°, and d-*prolyl*-l-*leucine* (V), m.p. 207°, $[\alpha]_D^{20}$ +9·59°, from (I)-l-*leucine*. Tyrosine Et ester hydrochloride with benzylamine at 37° for 70 hr. yields l-*tyrosylbenzylamine*, m.p. 172°, which with $CH_2Cl·COCl$ affords N-*chloroacetyl*-, m.p. 175—177°, and NO-*dichloroacetyl*-l-*tyrosylbenzylamine*, m.p. 208°. N-*Benzylcarbonato*-l-*proline*, from *l*-proline in aq. NaOH with benzyloxycarbonyl chloride (A., 1932, 935), is converted into the corresponding *chloride* by PCl_5 and treated with glycine in aq. NaOH to give N-*benzylcarbonato*-l-*prolylglycine*, which with Pd–H_2 yields l-*prolylglycine*, m.p. 236°, $[\alpha]^{20}$ —22·77°. Similarly are prepared N-*benzylcarbonato*-l-*prolyl*-l-*tyrosine* and its *Et* ester, N-*benzylcarbonato*-l-*prolyl*-l-*proline* (VI), m.p. 186—187°, N-*benzylcarbonato*-l-*prolyl*-l-*leucine*, and NO-*benzylcarbonato*-l-*tyrosine Et ester*, m.p. 103—104°. Erepsin (VII) hydrolyses *dl*- and *l*-prolylglycine, (II), (IV), and *dl*-prolylglycylglycine, but not (III), (V), (VI), and *l*-proline anhydride. Trypsin (VIII) hydrolyses only (II). This confirms the presence in preps. of (VII) of a sp. enzyme, prolinase, which attacks the prolyl group probably at the NH linking. Chloroacetyl-*l*-tyrosine on condensation of the CO_2H and OH groups or of the CO_2H group alone with benzylamine is no longer hydrolysed by (VIII). (VII) is far more readily inactivated by H_2S than is (VIII). F. O. H.

Catalytic dehydrogenation of pyrroline, and conversion of pyrroline into a mixture of pyrrole and pyrrolidine in presence of a platinum catalyst. J. P. Wibaut and W. Proost (Rec. trav. chim., 1933, **52**, 333—336).—Pyrroline (I) is converted by passage over Pt-asbestos at 160° into pyrrole (II) and H, some of which further reduces (I) to pyrrolidine (III). At 200° (II) can be detected, but secondary reactions occur. In the presence of freshly-reduced Pt in N_2 boiling (I) is converted into a mixture of (II) and (III), but at 50° only (II) and unchanged (I) can be detected. J. W. B.

Cinchomeron[hydr]azide. G. Gheorghiu (Bull. Soc. chim., 1933, [iv], **53**, 151—157).—Cinchomeronhydrazide (I) (Meyer and Mally, A., 1912, i, 514) [Ag_2 salt (+$2H_2O$); Ac_2 derivative, m.p. 146—147°] titrates as a monobasic acid and does not condense with aldehydes; Me derivatives could not be prepared. The extinction curve of (I) is analogous to those of phthal- and quinolin-hydrazides (A., 1930, 1191) and does not differ appreciably from those of 4-aminophthalhydrazide and the Na salt of 4-nitrophthalhydrazide (cf. *loc. cit.*). H. B.

Anhydro-bases from phenacylpyridinium halides. F. Krollpfeiffer and A. Müller (Ber., 1933, **66**, [*B*], 739—743).—3-*Bromoacetyl*-4-*ethylthioltoluene*, m.p. 69—70°, which gradually passes when preserved into 5 : 5′-dimethylthioindigotin and yields 3-hydroxy-5-methylthionaphthen when distilled with steam, is readily converted by C_5H_5N into 3-*ethylthiol*-5-*methylphenacylpyridinium bromide* (I), m.p. 201—203° (decomp.). Treatment with 2*N*-NaOH at 100° converts (I) into methylpyridinium salt and 2-*ethylthiol*-5-*methylbenzoic acid* (II), m.p. 136·5—137·5° (the 2-methylthiol acid, m.p. 140—141°, is obtained analogously from 2-*methylthiol*-5-*methylphenacylpyridinium bromide*, decomp. 220°). Treatment of an aq. solution of (I) with excess of 2*N*-NaOH yields the *anhydro-base* (III), $C_{16}H_{17}ONS$, m.p. 129—131° after darkening, immediately converted by dil. acid into the pyridinium salt. Boiling H_2O rapidly transforms (III) into the methylpyridinium salt of (II). With MeOH and EtOH, respectively, (III) yields the *Me*, m.p. 36—37°, and *Et*, m.p. 20—22°, ester of (II). (III) and CS_2 almost immediately yield a yellowish-red, cryst. *product*. H. W.

Reaction between indoles and Schiff's bases. M. Passerini and T. Bonciani (Gazzetta, 1933, **63**, 138—144).—This reaction occurs readily to give the following: 3-α-*anilino*-, m.p. 154°, 3-α-p-*toluidino*-, m.p. 147—148°, 3-α-β′-*naphthylamino*-, m.p. 80—82°, and 3-α-*anilino*-p-*methoxy*-, m.p. 85—87°, -*benzyl*-2-*methylindole*; and 2-α-*anilinobenzyl*-3-*methylindole*, m.p. 155—156°. These are hydrolysed by HCl to amine, aldehyde, and benzylidenedi-indole; for 2 : 2′-benzylidene-3 : 3′-dimethyldi-indole the new m.p. 160—161° is given. Indole and NPh:CHPh form a *product*, m.p. 75—85°. E. W. W.

Doebner reaction. XI. R. Ciusa and L. Musajo (Gazzetta, 1933, **63**, 116—119; cf. A., 1930, 222).—Polemical against Carrara (A., 1931, 1429). E. W. W.

Condensation of anthranilic acid with 4-chloroquinaldine and with 2-chlorolepidine. O. G. Backeberg (J.C.S., 1933, 390—391).—4-Chloroquinaldine and anthranilic acid afford 4-o-*carboxyphenylaminoquinaldine*, m.p. 309—310° (decomp.), which with H_2SO_4 gives 7-*keto*-6-*methyl*-7 : 10-*dihydro*-8 : 9-*benzquinoquinoline*, m.p. 295—296° (decomp.) (*sulphate*), converted by distillation with Zn into 6-*methyl*-8 : 9-*benzquinoquinoline*, m.p. 137° (*chloroplatinate*, m.p. >325°). *N*-(2-lepidyl)anthranil [*hydrochloride*, m.p. 222° (decomp.)], obtained by Ephraim (A., 1892, 1488), with NaOH gives 2-o-*carboxyphenylaminolepidine*, m.p. 202°, which does not form the acridone. F. R. S.

Preparation of 5-aminouracil and derivatives. M. T. Bogert and D. Davidson (J. Amer. Chem. Soc., 1933, **55**, 1667—1668).—Addition of HNO_3 (*d* 1·5) to the hot solution of uracil obtained by Davidson and Baudisch's procedure (A., 1926, 1154) gives 5-nitrouracil (47—51%), which is reduced ($Na_2S_2O_4$, aq. NH_3) to 5-aminouracil. 5-Nitro-6-methyluracil and K 5-nitrouracil-6-carboxylate are similarly reduced. 5:6-Diaminouracil is prepared from 5-nitroso-6-aminouracil. H. B.

Substituted dialuric and hydurilic acids. I. H. Aspelund (J. pr. Chem., 1933, [ii], **136**, 329—344).—5-Ethylbarbituric acid (I) [5-*Br*-derivative (II), m.p. 202°] is oxidised (3% H_2O_2; 0·5*N*-$K_2Cr_2O_7$ and AcOH) to 5-*ethyldialuric acid* (III), m.p. 216—217° [a small amount of which is formed during the prep. of (I) by (essentially) von Merkatz's method (A., 1919, i, 355)] (O-*Ac* derivative, m.p. 177°), which is hydrolysed (aq. NaOH) to *ethyltartronic acid*, m.p. 115—116°. Oxidation ($KMnO_4$, aq. H_2SO_4) of (I) gives (III) and some 5 : 5′-*diethylhydurilic acid* (+H_2O) (IV), m.p. >310° (decomp.), also formed from (II) and the Na salt of (I) in $CHCl_3$, which is hydrolysed by conc. KOH to a substance, m.p. 261—262°, and by conc. HCl at 210—240° to the *s*-diethylsuccinic acids. Oxidation (aq. $KMnO_4$) of (I) affords (IV) and a *substance*, $C_{12}H_{14}O_6N_4,3H_2O$, m.p. about 200° (decomp.) (according to rate of heating), m.p. (anhyd.) 165—170° (becoming yellow) (decomp. about 200°), which is a strong acid and is oxidised ($KMnO_4$, dil. H_2SO_4) to (III) and (IV). A substance, m.p. 175—178°, is formed from the Na salt of (I) and aq. $KMnO_4$. 5-*Benzyldialuric acid* (+$2H_2O$), m.p. 214—215° (O-*Ac* derivative, m.p. 202°) (hydrolysed to *benzyltartronic acid*, m.p. 145—146°), and 5 : 5′-*dibenzylhydurilic acid* (+$2H_2O$), m.p. about 315° (decomp.), are obtained by similar oxidation of 5-benzylbarbituric acid (5-*Br*-derivative, m.p. 168°); a by-product in the oxidation with aq. $KMnO_4$ is a N compound, m.p. 87—88°, hydrolysed (conc. KOH) to α-hydroxy-β-phenylpropionic acid. H. B.

Hydro-orotic acid. M. Bachstez and G. Cavallini (Ber., 1933, **66**, [*B*], 681—683; cf. A., 1930, 781).—Condensation of maleic acid with $CO(NH_2)_2$ at 132° affords *hydro-orotic acid* (I), $NH<^{CO\cdot CH_2}_{CO-NH}>CH\cdot CO_2H$, m.p. 247—249° (corr.) (*K*, *Ag*$_2$, *Pb*, and *Cu* salts), which could not be esterified by HCl and EtOH or dehydrogenated to orotic [uracil-4-carboxylic] acid. Oxidation of (I) by $KMnO_4$ at room temp. affords $CO(NH_2)_2$, $H_2C_2O_4$, γ-methylhydantoin, and (?) the *oxime* of *oxalmonoamide*, m.p. 157—158° (decomp.). H. W.

[Isolation of] bases by means of Reinecke's salt. H. W. Dudley (Biochem. J., 1933, **27**, 157).—This salt with $COMe_2$ gives di- and tri-acetonamine under the conditions used for the isolation of bases from natural sources. R. S. C.

Production of amines from amino-acids. M. Wada (Biochem. Z., 1933, **260**, 47—51).—Hydantoins prepared from NH_2-acids yield the corresponding amines (*e.g.*, $CH_2Ph\cdot NH_2$, tyramine, NH_2Me, *iso*amylamine, histamine, putrescine, cadaverine, indolethylamine, aminoethyl disulphide, pyrrolidine, β-alanine, γ-aminobutyric acid) in good yield (usually 70—84%) when treated with acid (H_2SO_4, HCl) or alkali [$Ba(OH)_2$, NaOH]. W. McC.

Pyrimidines. CXXXII. Synthesis of thymine. W. Bergmann and T. B. Johnson (J. Amer. Chem. Soc., 1933, **55**, 1733—1735).—α-*Cyanopropionylcarbamide* (I), m.p. 192°, from $CO(NH_2)_2$, $CN\cdot CHMe\cdot CO_2H$, and Ac_2O at 100°, gives NH_3 and thymine when reduced (H_2, Pt-black, H_2O). (I) is converted by cold aq. 20% NaOH or MgO in boiling aq. solution into 4-*aminothymine* (4-*amino*-2 : 6-*dihydroxy*-5-*methylpyrimidine*), m.p. 355°. H. B.

Behaviour of aspartic acid when heated in glycerol; supposed *cyclo*dipeptides of asparagine. C. Ravenna and R. Nuccorini (Gazzetta, 1933, **63**, 103—109).—Previous work (A., 1930, 627; 1931, 1430) is confirmed. Aspartic acid in glycerol at 160—170° remains largely unaltered; by use of $Pb(OAc)_4$ a *substance*, $C_{11}H_{18}O_9N_2$ (?), is obtained, regarded as a diaspartic ester of glycerol, whilst on prolonged heating a *substance*, $C_{11}H_{16}O_8N_2$, results. The former is also obtained from NH_4 aspartate. The view of Shibata (A., 1927, 891) that *cyclo*dipeptide condensation occurs through the CO_2H group is thus not confirmed. E. W. W.

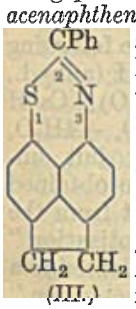
2-Phenyl-1′ : 2′-naphthiminazole. F. Galimberti (Gazzetta, 1933, **63**, 96—99).—Benzoyl-*o*-phenylenediamine is dehydrated when heated to 2-phenylbenziminazole. 1-Nitro-2-benzoylnaphthalide is reduced (Zn+HCl in EtOH) to 2-*phenyl*-1′ : 2′-*naphthiminazole*, m.p. 296°. A modified method of prep. of the 1-Ph isomeride is described. E. W. W.

4-Nitro-5-(3-pyridyl)pyrazole, a new oxidation product of nicotine. III. Confirmatory synthetical experiments. G. A. C. Gough and H. King (J.C.S., 1933, 350—351).—4-Amino-5-(3-pyridyl)pyrazole (cf. A., 1932, 68; this vol., 76) is deaminated to 5-(3-*pyridyl*)*pyrazole* (I) [*picrate* (+H_2O), m.p. 194—195°; *flavianate* (+$2H_2O$), m.p. 229° (decomp.); *methiodide*, m.p. 217·5°; *methopicrate*, m.p. 185°]. Et nicotinate, $COMe_2$, and Na afford β-pyridoylacetate, which with N_2H_4,H_2SO_4 forms 3-*methyl*-5-(3-*pyridyl*)-*pyrazole* (+1·5H_2O), m.p. 81—83°, and 137—138° (*monopicrate*, m.p. 202—203°; *hydrochloride*, m.p.

214—216°), oxidised with $KMnO_4$ to 5-(3-*pyridyl*)-*pyrazole*-3-*carboxylic acid*, m.p. 308—310° (efferv.) (*picrate*, m.p. 242—245°). The acid is decarboxylated to (I). F. R. S.

Chlorophyll *a*. H. FISCHER (Annalen, 1933, **502**, 175—200).—A lecture. H. B.

Synthesis of acenaphthene-*peri*-*m*-thiazines and of dyes derived therefrom. M. T. BOGERT and R. B. CONKLIN (J. Amer. Chem. Soc., 1933, **55**, 1705—1710).—4-Nitroacenaphthene-3-sulphonyl chloride is reduced ($SnCl_2$, AcOH–HCl) to 3-*amino*-4-*thiolacenaphthene chlorostannate*, which when treated successively with NaOAc–AcOH at 90° and *m*-NO_2·C_6H_4·COCl gives the NS-*di*-m-*nitrobenzoyl* derivative (I), decomp. about 235·5° (all m.p. and decomp. are corr.), of 3-amino-4-thiolacenaphthene (II). The N-p-*nitrobenzoyl* derivative, decomp. 246—247° (turning dark red), of (II) and 2-p-*nitrophenyl*-peri-m-*thiazine*, decomp. 253·7°, are obtained similarly using *p*-NO_2·C_6H_4·COCl, whilst with BzCl, 2-*phenyl*-*acenaphthene*-peri-m-*thiazine* (III), m.p. 142·3° (shrinks and softens at about 128°), results. (I) heated with NaOAc–AcOH gives 2-m-*nitrophenylacenaphthene*-peri-m-*thiazine*, m.p. 190·3—191·3° (decomp.) (shrinks at about 189°). Dyes of the Columbia-yellow type are prepared from 2-m-, m.p. 176·7—177·7° (decomp.), and 2-p-, m.p. 214·8—215·8° (decomp.), -*aminophenylacenaphthene*-peri-m-*thiazines*; their dyeing properties are compared with those from the analogous *peri*naphtho-*m*-thiazines (A., 1932, 176). H. B.

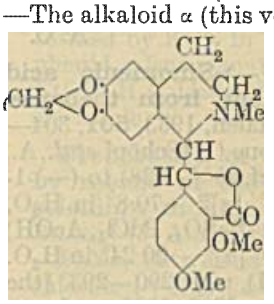


(III.)

***Sophora* alkaloids. I. Alkaloids of the foliage of *S. pachycarpa*.** A. OREKHOV, M. RABINOVITSCH, and R. KONOVALOVA. **II. Alkaloids of *Thermopsis lanceolata*.** A. OREKHOV, S. NORKINA, and H. GUREVITSCH (Ber., 1933, **66**, [*B*], 621—625, 625—630).—I. Percolation of the finely-divided foliage of *S. pachycarpa* with EtOH containing 2% of AcOH removes about 3% of total alkaloid, divisible into portions sol. in Et_2O and $CHCl_3$, respectively. The Et_2O extract yields an alkaloid $C_{15}H_{2c}N_2$, b.p. 138°/2 mm., $[\alpha]_D^{20}$ +5·54° or +16·3° in EtOH, provisionally named *pachycarpine*, but probably *d*-sparteine. The following derivatives are described: *mono*-, m.p. 234—235°, $[\alpha]_9$ +9·8° in EtOH, and *di*-, m.p. 255—257° after softening at 250°, -*hydriodide*; *picrate*, m.p. 199—200°; *chloroplatinate*, m.p. 240—241° (decomp.) after darkening at 235°; *chloroaurate*, m.p. 192—193° (decomp.); *methiodide*, m.p. 236—238°, $[\alpha]_D$ +24·5° in H_2O, and its *hydriodide*, m.p. 223—224° (decomp.) and, after re-solidification, m.p. 234—235°.

II. The foliage of *T. lanceolata*, R. B. (syn. *S. lupinoides*, Pall), is percolated with EtOH containing 2% of AcOH, the percolate evaporated to dryness, and the residue treated with 3% HCl. The acid solution is rendered strongly alkaline with NH_3 and extracted with Et_2O, to which it yields 0·53% of crude alkaloids (I) (calc. on dried material). The aq. solution is treated with NaOH and extracted successively with Et_2O and $CHCl_3$, to which it yields 0·34% and 0·23% of alkaloid, respectively. From (I) are isolated: (A) *thermopsine*, $C_{15}H_{20}ON_2$, m.p. 205—206°, $[\alpha]_D^0$ −159·6° in EtOH, highly unsaturated but not hydrolysed by acid or alkali. It yields a *picrate*, m.p. 208—209°, *chloroplatinate*, decomp. 254—256° after darkening at 250°, *hydriodide*, m.p. 306—308° (decomp.), and *methiodide*, m.p. 241—242° (decomp.). The second N atom and the O atom are indifferent. Catalytic hydrogenation (PtO_2 in *N*-HCl) yields *tetrahydrothermopsine*, m.p. 75·5—76·5°, $[\alpha]_D$ −52·23° in EtOH [*dihydriodide* (+3MeOH), m.p. 296—298° (decomp.) after softening at 290°; *picrate*, m.p. 143—144°; *chloroplatinate*, m.p. 241—242° (decomp.)]; (B) pachycarpine, identified with that described above by direct comparison of hydriodides and methiodide hydriodides; (C) *alkaloid* III, a pale yellow, very viscous liquid which yields a very hygroscopic *hydrochloride*, *picrate*, m.p. 217—218°, and *methiodide*, m.p. 226—229° (decomp.). H. W.

Alkaloids of fumaraceous plants. III. A new alkaloid, bicuculline, and its constitution. R. H. F. MANSKE (Canad. J. Res., 1933, **8**, 142—146).—The alkaloid α (this vol., 105), now called *bicuculline* (annexed formula), m.p. 177°, and 196° (two forms) [*hydrochloride*, m.p. 259° (slight decomp.)], is found in *Corydalis sempervirens* and *Adlumia fungosa*, Greene, and has probably been isolated from other sources. Hydrolysis gives hydrastinine and 2-*carboxy*-3:4-*methylenedioxybenzaldehyde*, m.p. 155°, which gives an *imide*, m.p. 270° (sublimes), with NH_2OH,AcOH, is reduced to 3:4-methylenedioxyphthalide, m.p. 227°, and after oxidation gives 3:4-methylenedioxyphthalethylimide. Bicuculline methiodide after conversion into the hydroxide gives N-*methylbicuculleine*, m.p. 246°, with hot H_2O.



A. A. L.

***Strychnos* alkaloids. LXXIII. Oxidation by chromic acid of brucine- and strychnine-sulphonic acids I and II and fission by hydrogenaton of the ether groups in the acids $C_{16}H_{20}O_7N_2S$ I and II.** H. LEUCHS, G. SCHLEMPP, and A. DORNOV (Ber., 1933, **66**, [*B*], 743—749; cf. A., 1932, 953).—Strychninesulphonic acid I (*CHPh* derivative, $[\alpha]_D^{20}$ −250°/*d* in 0·05*N*-NaOH) could not be satisfactorily hydrogenated (PtO_2) in H_2O, H_2O–NH_3, H_2O–alkali, or H_2O–AcOH. Brucinesulphonic acid I (purification described) behaves similarly. The acid $C_{17}H_{20}O_8N_2S$ (*A*) (*semicarbazone*, $[\alpha]_D^{20}$ −192°/*d* in H_2O) is reduced by Na–Hg to the *acid* $C_{17}H_{22}O_8N_2S$ (*B*), $[\alpha]_D^{20}$ −107·6°/*d* in H_2O, which could not be catalytically hydrogenated. *A* in presence of PtO_2 yields the *substance* $C_{17}H_{22}O_8N_2S$, $[\alpha]_D^{20}$ −74°/*d*, with minor amounts of *B*. The acids $C_{16}H_{20}O_7N_2S$ I (*C*) and II are hydrogenated (PtO_2) to the isomeric *acids* $C_{16}H_{23}O_4N_2SO_3H$ I, $[\alpha]_D^{20}$ −25°/*d* in H_2O, and II, $[\alpha]^{20}$ −62·6°/*d*, reaction being considered to be accompanied by fission of the ether groups. Oxidation of *C* with Br–HBr in H_2O gives the *products* $C_{16}H_{20}O_8N_2S$, $[\alpha]^{20}$ −136·4°/*d* in H_2O, and $C_{16}H_{20}O_8N_2S$,HBr, $[\alpha]_D^{20}$ −130°/*d*. Brucinesulphonic acid II (*D*) is hydrogenated to the *acid* $C_{23}H_{28}O_7N_2S$, $[\alpha]_D^{20}$ +140°/*d* in 0·05*N*-NaOH. *D* is

oxidised with less CrO_3 to the *acid* $C_{19}H_{21}O_6N_2{\cdot}SO_3H$, $[\alpha]^{20}$ $-90{\cdot}5°/d$ in NaOH, analogous to the Hannsen C_{19} acid, and by more CrO_3 to the *acid* $C_{16}H_{19}O_4N_2{\cdot}SO_3H$ II (*E*), $[\alpha]_D^{20}$ $+192°/d$ in H_2O. *E* is obtained in larger yield from strychninesulphonic acid II through the NO_2-compound $C_{21}H_{21}O_7N_3S$, $[\alpha]_D^{20}$ $-28{\cdot}9°$, and the NH_2-compound, $C_{21}H_{23}O_5N_3S$, which is oxidised with CrO_3–H_2SO_4. H. W.

Lupinine. K. KRIEG (Diss., Marburg, 1928; Bied. Zentr., 1932, **3**, *A*, 51).—Oxidation of anhydrolupinine and of lupinine (I) and the Hofmann decomp. of lupinan indicate the generally accepted formula of (I) to be untenable. The side-chain is not in the α-position with respect to N. A. G. P.

Rotatory power of quinine salts in aqueous solution. C. LAPP (Compt. rend., 1933, **196**, 970—971).—The [α] of quinine increases with acidity, the [α]–p_H curves showing inflexions at p_H 4·6—6·5 and < 2, corresponding with the neutral and acid salts, respectively. Vals. of [α] for different λ are given, on which is based a polarimetric method of determining quinine at p_H 5·5. A. C.

Sinomenine. XXXV. (−)-Sinomenic acid and (−)-1-bromosinomenilone from thebaine. K. GOTO and H. SHISHIDO (Annalen, 1933, **501**, 304—308).—(−)-1-Bromosinomeninone (I) (Schopf *et al.*, A., 1932, 290) is oxidised (H_2O_2) (cf. *ibid.*, 628) to (−)-1-*bromosinomenic acid*, m.p. 251°, $[\alpha]_D^{22}$ $-70{\cdot}8°$ in H_2O, which is debrominated (H_2, Pd–$BaSO_4$, $PdCl_4$, AcOH) to (−)-*sinomenic acid*, m.p. 289° $[\alpha]_D^{22}$ $-90{\cdot}24°$ in H_2O. (−)-1-*Bromosinomenilic acid* (II), m.p. 290—293° [the (+)-acid (*ibid.*, 760) has m.p. 290—293°, and not 285°], $[\alpha]_D^{20}$ $-91{\cdot}4°$ in dil. NaOH (*Ac* derivative, m.p. 165°), best prepared by reduction (Na–Hg in H_2O and CO_2) of (−)-1 : 7-*dibromosinomenilic acid*, m.p. 226°, $[\alpha]_D$ $-79{\cdot}5°$ in dil. NaOH [obtained with a little (II) from (I) and Br in AcOH], is converted by oleum (cf. *ibid.*, 720) into (−)-1-*bromosinomenilone*, m.p. 182°, $[\alpha]_D^{19}$ $-246{\cdot}04°$ in EtOH. The following *dl*-compounds are prepared from their (+)- and (−)-forms: 1-bromosinomenic acid, blackens at 251° (sinters at 190°, decomp. at 200°); sinomenic acid, m.p. 286°; 1-bromosinomenilic acid, m.p. 293°; 1 : 7-dibromosinomenilic acid; 1-bromosinomenilone, m.p. 155—158°. H. B.

Aldehyde oxidation of tolylarsinic acids. H. M. PARMELEE and C. S. HAMILTON (J. Amer. Chem. Soc., 1933, **55**, 1463—1469).—Oxidation of the appropriate $C_6H_4Me{\cdot}AsO_3H_2$ with Mn_2O_3 (or MnO_2) and H_2SO_4 (40—96%) at 80—100° and treatment of the diluted solutions with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$,HCl give *benzaldehyde*-p-*nitrophenylhydrazone*-2- (I), m.p. 201·5° (corr.), -3-, m.p. > 250°, and -4- (II), m.p. > 250°, *-arsinic acids*. (I) and (II) are also prepared by oxidation with CrO_3, AcOH, Ac_2O, and H_2SO_4 (cf. A., 1930, 1601). *Benzaldehydephenylhydrazone*-o-*arsinic acid* has decomp. 130—137° (according to rate of heating) (darkens at 105°). 4 : 6-*Dinitro*-o-*tolylarsinic acid*, m.p. 201—203° (NH_4 salt), from the 4-NO_2-acid, HNO_3 (*d* 1·6), and oleum (20% SO_3), is reduced [$Fe(OH)_2$] to 4 : 6-*diamino*-o-*tolylarsinic acid* (*Na* salt), and with *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and Na_2CO_3 in MeOH+EtOH gives the p-*dimethylaminoanil* of 4 : 6-dinitrobenzaldehyde-2-arsinic acid. A modification of the method (B., 1930, 348) of determining As is given. H. B.

Action of chlorine on *p*-tolylarsinic acid under the influence of ultra-violet light and its chlorination with hypochlorous acid. C. S. HAMILTON and W. N. KING (J. Amer. Chem. Soc., 1933, **55**, 1689—1692).—Chlorination of *p*-$C_6H_4Me{\cdot}AsO_3H_2$ (I) in C_2Cl_6 at 185—190° or of *p*-$C_6H_4Me{\cdot}AsCl_4$ (II) in C_2Cl_6 at 140° gives (after treatment with 6*N*-NaOH) *p*-$C_6H_4Cl{\cdot}CO_2H$ (III). Chlorination of (II) at 90—100° under the influence of ultra-violet light affords $AsCl_3$ and *p*-C_6H_4MeCl and then (III). (I) and HOCl give 2-*chloro*-p-*tolylarsinic acid*, m.p. >250°, which is oxidised (alkaline $KMnO_4$) to 3-*chloro*-4-*carboxyphenylarsinic acid*, m.p. 233°. Dichloro-2-chloro-*p*-tolylarsine and Cl at 100° in ultra-violet light yield (as above) 2 : 4-$C_6H_3Cl_2{\cdot}CO_2H$. H. B.

Isomerism of hydroxyphenylarsinic acids. G. GILTA (Bull. Soc. chim. Belg., 1933, **42**, 119—126; cf. A., 1928, 1146).—*p*-$OH{\cdot}C_6H_4{\cdot}AsO_3H_2$ prepared from diazotised *p*-$OH{\cdot}C_6H_4{\cdot}NH_2$ is identical with that prepared by arsenical fusion of PhOH. The following *salts* are described: Na H (+5H_2O); K H (anhyd., +2H_2O, +3H_2O); Rb H (anhyd., +2H_2O); Cs H (+2H_2O); NH_4 H (+3H_2O); Na_2 (+3H_2O, +4H_2O, +5H_2O); $ONa{\cdot}C_6H_4{\cdot}AsO_3Na_2$ (hydrated, but unstable). With a few exceptions these were obtained from both forms of the acid. The *Ba* salt from the "fusion" acid is anhyd., but the "diazotisation" acid gives a *Ba* salt (+2H_2O), readily dehydrated to a new anhyd. salt, and converted into the "fusion" isomeride by heating in aq. EtOH. H. A. P.

Arylarsinites of thiophenols [phenylthiolarsines] and their complex mercuric salts. G. SCHUSTER (J. Pharm. Chim., 1933, [viii], **17**, 331—334).—PhSH and the appropriate chloroarsine in EtOH afford *aryldi*(*phenylthiol*)*arsines*, $AsAr(SPh)_2$, in which Ar is 4-*chloro*-3-*nitrophenyl*-, an oil, o-, m.p. 83° (220°), m-, an oil (200°), and p-*nitrophenyl*-, m.p. 26—27° (m.p. 196°), p-*chlorophenyl*-, an oil, p-*aminophenyl*-, m.p. 127° (230°), o-, an oil (140°), and p-*tolyl*-, an oil (200°), and *diphenyl*-, an oil (260—270°). The temp. in parentheses are the approx. temp. at which the complex *salts* with $4HgCl_2$ sublime. The arsines and their Hg salts are quantitatively oxidised by I to arylarsinic acids and Ph_2S_2. R. S. C.

Derivatives of benzaldehyde-*p*-arsinic acid. C. S. GIBSON and B. LEVIN (J.C.S., 1933, 352).—Benzaldehyde-*p*-arsinic acid gives the following: with $CH_2(CO_2H)_2$ p-*arsonobenzylidenemalonic acid*, m.p. > 300°; with $CN{\cdot}CH_2{\cdot}CO_2H$, *cinnamonitrile*-p-*arsinic acid*, m.p. > 300°; *benzaldehyde*-p-*dichloroarsine*, m.p. 105°, -p-*arsenious oxide*, m.p. 232°, and 4 : 4′-*dialdehydoarsenobenzene*, decomp. 240°. F. R. S.

Additive compounds of phenylboric acid with bases. D. L. YABROFF and G. E. K. BRANCH (J. Amer. Chem. Soc., 1933, **55**, 1663—1665; cf. A., 1932, 836).—*Compounds* of the type $NR_3{\cdot}BPh(O{\cdot}BPh{\cdot}OH)_2$, derived from 3 mols. of $PhB(OH)_2$ and 1 mol. of base by elimination of $2H_2O$, are prepared from $NHEt_2$, NEt_3, NH_2Pr, C_5H_5N, and piperidine; they have m.p. 85°, 39°, 140—143°, 148—149°, and 213°, respectively.

NH_2Ph, $NHPh_2$, MeCN, PhCN, $CH_2Ph{\cdot}CN$, and CH_2Ac_2 and its Na salt do not form stable additive compounds. H. B.

Interconversion of arylmercuric halides and mercury diaryls. II. R. W. Beattie and F. C. Whitmore (J. Amer. Chem. Soc., 1933, **55**, 1567—1571).—1-*Chloronaphthalene*-4-, m.p. 111°, -5-, m.p. 121°, -6-, m.p. 127—128°, -7-, m.p. 128·5—129°, and -8-, m.p. 105°, and 2-*chloronaphthalene*-1-, m.p. 87°, -6-, m.p. > 300°, -7-, m.p. 134°, and -8-, m.p. 127°, *-sulphinic acids* are prepared by reduction (Na_2SO_3, aq. NaOH) of $C_{10}H_6Cl{\cdot}SO_2Cl$; in many cases the m.p. increases > 100° when the acids are kept. These are converted by aq. $HgCl_2$ into 4-*chloro*-1-*naphthylmercuric chloride*, m.p. 252° (*bromide*, m.p. 251°; *iodide*, m.p. 233°), 5-*chloro*-1-*naphthylmercuric chloride*, m.p. 244° (*bromide*, m.p. 231·5°; *iodide*, m.p. 221·5°), 5-*chloro*-2-*naphthylmercuric chloride*, m.p. 307° (*bromide*, m.p. 316°; *iodide*, m.p. 276·5°), 8-*chloro*-2-*naphthylmercuric chloride*, m.p. 223° (*bromide*, m.p. 247°; *iodide*, m.p. 257°), 8-*chloro*-1-*naphthylmercuric chloride*, m.p. 214° (*bromide*, m.p. 195·5°; *iodide*, m.p. 156·5—157·5°), 2-*chloro*-1-*naphthylmercuric chloride*, m.p. 215° (*bromide*, m.p. 204°), 6-*chloro*-2-*naphthylmercuric chloride*, m.p. 260° (*bromide*, m.p. 260°; *iodide*, m.p. 298°), 7-*chloro*-2-*naphthylmercuric chloride*, m.p. 295° (*bromide*, m.p. 288°; *iodide*, m.p. 272°), and 7-*chloro*-1-*naphthylmercuric chloride*, m.p. 232·5° (*bromide*, m.p. 226°; *iodide*, m.p. 192·5°), respectively. The chlorides are converted into $HgAr_2$ by EtOH–NaI; the following are described: *Hg di*-4-, m.p. 275·5°, -5-, m.p. 223·5°, -8-, m.p. 215·5—216·5°, -2-, m.p. 293·5°, and -7-, m.p. 273·5°, *-chloro*-1-*naphthyls*; *Hg di*-5-, m.p. 246°, -6-, m.p. 260°, -7-, m.p. 299°, and -8-, m.p. 230·5°, *-chloro*-2-*naphthyls*. HgPhCl and EtOH–NaCN (1 mol.) give $HgPh{\cdot}CN$, but with excess of NaCN, $HgPh_2$ results; Hg di-*p*-tolyl (I), $Hg(C_{10}H_7\text{-}\beta)_2$, m.p. 247—248° (II), and the above $HgAr_2$ are similarly prepared. HgArCl is also converted into $HgAr_2$ by EtOH–KOH or Alk·OH–NaOAlk; $HgPh_2$, (I), and (II) are thus prepared. H. B.

Formation of a heterocyclic ring closed through mercury atoms. III. L. Vecchiotti and C. Silvestrini (Gazzetta, 1933, **63**, 110—111).—*o*-$C_6H_4(CH_2Br)_2$ treated in petroleum (b.p. 150—160°) with Na_xHg_y gives a *compound*, $C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}Hg$ (?). E. W. W.

Arylselenium halides. II. O. Behaghel and H. Siebert (Ber., 1933, **66**, [*B*], 708—717; cf. A., 1932, 762).—m-*Chlorophenyl selenocyanate*, b.p. 150—152°/13 mm., m.p. 53°, is obtained from *m*-$C_6H_4Cl{\cdot}NH_2$ through the diazo-compound. 2 : 2′-*Dinitrodiphenyl diselenide* is derived from NaOMe and *o*-nitrophenyl selenocyanide in MeOH in 98·2% yield. The following *Se aryl bromides* have been prepared: o-$C_6H_4{\cdot}NO_2$, m.p. 64—65°, which does not add Br, is very stable to H_2O, and converted by alkali into the diselenide; p-$C_6H_4{\cdot}NO_2$, m.p. 92°, converted by H_2O or Na_2CO_3 into 4 : 4′-*dinitrodiphenyl diselenide*, m.p. 177°. The following *Se aryl tribromides* have been prepared: m-, decomp. 114°, and p-$C_6H_4{\cdot}NO_2$, decomp. 107—108°; o-, decomp. 107°, m-, decomp. 107—108°, and p-, decomp. 123—124°, *-*C_6H_4Cl; *p*-C_6H_4Me, m.p. 115—116°. *Se Ph chloride*, m.p. 59—60°, and *Se o-nitrophenyl chloride*, m.p. 64°, are derived from the diselenides and SO_2Cl_2 or $SOCl_2$, respectively. Treatment of the requisite selenocyanates or diselenides in $CHCl_3$ with Cl_2 or with SO_2Cl_2 in slight excess leads to the following *Se aryl trichlorides*; m-, decomp. 132° (indef.), and p-$C_6H_4{\cdot}NO_2$, decomp. 183—184°; o-, decomp. 162°, m-, decomp. 150°, and p-C_6H_4Cl, decomp. 172°. Hydrolysis of the trichlorides or tribromides with H_2O yields the following arylseleninic acids: Ph, m.p. 122°; *o*-, m.p. 184°, *m*-, m.p. 156° and p-$C_6H_4{\cdot}NO_2$, m.p. 214—215°; *p*-C_6H_4Me, m.p. 169—170°; o-, m.p. 160°, m-, m.p. 155°, and *p*-C_6H_4Cl, m.p. 179—180°. SePhBr is transformed by MgEtBr in Et_2O into Ph Et selenide, b.p. 102—104°/20 mm. Se *o*-nitrophenyl bromide (chloride, trichloride) and $NPhMe_2$ in boiling Et_2O afford 2-*nitro*-4′-*dimethylaminodiphenyl selenide*, m.p. 169° (*hydrochloride*, decomp. 180° after blackening at 174°). 4-*Nitro*-4′-*dimethylaminodiphenyl selenide*, m.p. 180°, yields a hydrochloride and (?) *tribromide*, decomp. (indef.) 97°. Se *o*-nitrophenyl bromide (I) is transformed by KCN in boiling $CHCl_3$–AcOH into *o*-nitrophenyl selenocyanate. Hydrolysis of (I) by KOH in EtOH–H_2O leads through a violet compound to the diselenide. H. W.

Preparation of tri-*p*-tolylselenonium chloride by means of the Friedel–Crafts reaction with selenium dioxide. J. H. Crowell [with W. E. Bradt] (J. Amer. Chem. Soc., 1933, **55**, 1500—1502).—PhMe, SeO_2, and $AlCl_3$ give tri-*p*-tolylselenonium chloride (+H_2O), m.p. 160° (corr.) [isolated in 77% yield as its additive 2 : 1-*compound*, m.p. 235°, with $ZnCl_2$], which when heated to 200—235° affords *p*-C_6H_4MeCl and $Se(C_6H_4Me\text{-}p)_2$. The *compound*, $2SePh_3Cl,ZnCl_2$, has m.p. 273·5—274°. H. B.

Isolation of methionine and ergothioneine. N. W. Pirie (Biochem. J., 1933, **27**, 202—205).—Methionine is best obtained from the enzymic hydrolysate of caseinogen (or ovalbumin) by pptn. with $Hg(OAc)_2$ and phosphotungstic acid, followed by fractionation with EtOH and pptn. with $HgCl_2$. Ergothioneine is best obtained from aq. ergot extract by forming the Cu^I derivative and dissolving the ppt. in H_2O. R. S. C.

Preparation and fractionation of the α-naphthylcarbimide compound of plastein. S. J. Folly (Biochem. J., 1933, **27**, 151—152).—Pptn. of a feebly alkaline solution of the *compound* of purified plastein and α-naphthylcarbimide first by CO_2 and then by AcOH gives fractions of different basicity, further subdivided by extraction with hot and cold EtOH. R. S. C.

Polarographic studies with the dropping mercury cathode. XXXI. Test for proteins in presence of cobalt in ammoniacal ammonium chloride solutions. R. Brdicka (Coll. Czech. Chem. Comm., 1933, **5**, 112—128).—When protein (I) is added to an ammoniacal solution of a cobaltammine salt the max. in the current–voltage curve due to the deposition of Co vanishes and two new waves appear; their form, magnitude, and position depend on the (I) content and the Co, NH_4^+, and NH_3 concns.

In all cases the waves rise to a limiting height with increase of the (I) concn. Their appearance is related to the presence of cystine (II) in the (I) mol., since no wave is produced by other NH_2-acids or by gelatin and silk. (II) itself at low concns. ($2\times10^{-6}M$) produces a wave 500 times > would be expected from simple reduction, and it therefore appears that the effect is due to catalysis by (II) of the H deposition. H. F. G.

Primary and secondary reactions of proteins with acids and bases. G. V. SCHULZ and G. ETTISCH (Z. physikal. Chem., 1933, **164**, 97—120; cf. A., 1932, 465).—The reaction of casein and serum-albumin and globulin with acid or alkali consists of an instantaneous ionic reaction followed by a secondary reaction which continues for about 20 hr. In the primary reaction, which may be represented as $R\cdot CO_2'+H^{\cdot}=R\cdot CO_2H$, or $R\cdot NH_3^{\cdot}+OH'=R\cdot NH_2+H_2O$, the amount of alkali fixed rises and tends to a saturation val. with rise in the equilibrium alkali concn., and the amount of acid or alkali taken up by 1 g. of protein is independent of the protein concn. The acid and alkali titration curves of albumin can be successfully calc. by applying the mass law to the above equations and assuming that between p_H 1·2 and 12·8 three alkali-binding and two acid-binding groups are active. The dissociation consts. of these groups have been calc. and identified with those of certain amino-acids. In the secondary reaction, which for acids is only feeble, the amount of alkali taken up increases continually with the alkali concn. Above p_H 11 this reaction consists principally in an irreversible breaking up of protein mols. with release of new active groups: $R\cdot CO\cdot NHR'+NaOH=R\cdot CO_2Na+R'\cdot NH_2$, $R\cdot CO\cdot NHR'+HCl+H_2O=R\cdot CO_2H+R'\cdot NH_3Cl$. Below p_H 11 similar, but reversible, changes occur. R. C.

Barley-husk protein. H. LUERS and W. HUTTINGER (Woch. Brau., 1933, **50**, 97—102).—Extraction of Moufang's "testinic acid" (B., 1931, 217), with $COMe_2$ removes the tannin (*A*), leaving the protein (*B*). The cystine, tryptophan, tyrosine, and histidine in *B* were determined colorimetrically. *B* resembles the albumins: acid hydrolysis reveals a high proportion of NH_3-, proline-, cystine-, asparagine-, histidine-, and arginine-*N*. *A* contains gallic and ellagic acid and glucosidically bound sugar. It may be separated into a H_2O-, Et_2O-, and $COMe_2$-sol. group. The tannin isolated by another method (A., 1931, 777) contains phloroglucinol and *p*-hydroxybenzoic acid, but no ellagic or gallic acid. R. H. H.

Action of alkali on collagen. I. Water- and alkali-soluble non-collagen proteins and collagen degradation products. II. Influence of nature and concentration of alkali and state of the collagen on solubility of non-collagen proteins. III. Effect of alkali treatment on insoluble collagen residue. A. KUNTZEL and J. PHILIPS (Collegium, 1933, 193—206, 207—212, 213—229).—I. Only 6·7% of the total N of a H_2O extract of collagen (I) is protein-N (pptd. by $CCl_3\cdot CO_2H$), as compared with 47% for a NaOH extract and 66·5% for a $Ca(OH)_2$ extract. A concn. of 5% $CCl_3\cdot CO_2H$ ppts. some protein degradation products as well as protein itself. The (I)-protein contains 17·6% N, that from the H_2O extract 10·6%, and the alkali extract 12·3%. Purified (I) contains 18% of arginine (gelatin, 14·7%).

II. $Ca(OH)_2$ is a better solvent for the non-(I) proteins of fresh (I) than Na_2S or NaOH, but the last two are more effective on the dried product.

III. The conversion: (I) ⟶ gelatin is promoted more by $Ca(OH)_2$ than by NaOH and Na_2S; the reverse is true for (I) degradation. Degradation is aided by an increased temp. (1 day at 40°) and conversion into gelatin by increased time (30 days at 20°). P. G. M.

Phosphorus-containing amino-acid from caseinogen. F. LIPMANN (Naturwiss., 1933, **21**, 236—237).—When caseinogen is hydrolysed with 2·5*N*-HCl, 60% of the total P is in org. combination in the hydrolysate. This gives a Ba salt, sol. in H_2O but insol. in 40% EtOH, from which, by further hydrolysis, an NH_2-acid is obtained with N : P ratio 1 : 1 (Ag salt, 61·2% Ag; serinephosphoric acid salt requires 63·8% Ag). P. G. M.

Prolysin, α-amino-δ-hydantoinvaleric acid, a new decomposition product of protein. I. M. WADA (Proc. Imp. Acad. Tokyo, 1933, **9**, 43—46).—*Prolysin*, $C_8H_{13}O_4N_3$ (I), has m.p. 222° (decomp.) (*Cu* salt, m.p. 260°; *picrate*, m.p. 122°). The isolation of (I) from the products of tryptic digestion of caseinogen and by hydrolysis of gelatin with HCl-saturated 60% aq. EtOH as the xanthyl derivative and the Ag salt, respectively, is described. (I) on hydrolysis with conc. HCl or NaOH gives lysine; with aq. HI, α-aminopimelic acid; with $Ba(OH)_2$, α-uramino-α'-aminopimelic acid (II); with H_2SO_4 and $BaCO_3$, (II), and with HNO_3, parabanic acid. Condensed with $CO(NH_2)_2$, (I) gives αγ-dihydantoinpropane, which with $Ba(OH)_2$ is converted into cadaverine. From these observations (I) is believed to be *α-amino-δ-hydantoinvaleric acid*. Colour reactions of (I) are described. A. L.

Internal structural changes of ovalbumin during denaturation. A. VON KÚTHY (Biochem. Z., 1933, **259**, 432—435).—Tables show the total-, amide-, basic, humin-, NH_2-, and non-NH_2-N of native albumin and after denaturation with KCNS, $CO(NH_2)_2$, urethane, EtOH, PrOH, $COMe_2$, and by heat. Considerable increase in humin-, basic, and non-NH_2-N and decrease of NH_2- and amide-N are recorded. The results show that heat- and EtOH-denaturation are analogous processes and are explained in terms of ring closure and the formation of inner anhydrides. P. W. C.

Action of ether and alcohol on solid protein. G. ETTISCH and G. V. SCHULZ (Biochem. Z., 1933, **259**, 418—419).—Whereas EtOH denatures solid protein in the same way as protein in solution, Et_2O has little effect. P. W. C.

Interaction of caseinogen and nicotine. I. S. JAITSCHNIKOV (Biochem. Z., 1933, **259**, 381—383).—1 g.-mol. of nicotine unites with 2000 g. of caseinogen, or, assuming that the mol. wt. of the latter is 12,000, with 1/6 mol. of caseinogen. This corresponds with the figure 2000 which is usually given as the equiv.

Electrolyte-free proteins. XI. Electrochemical composition of highly purified protein solutions. D. VON KLOBUSITZKY and W. PAULI (Biochem. Z., 1933, **260**, 201—212).—Further support is provided for the view that in solutions of highly purified proteins [ovalbumin (I), seralbumin (II)] the dissociated protons are distributed over the whole protein mol., this distribution giving rise to the production of positively and negatively over-charged, together with neutral hybrid ions. With electropositive pseudoglobulin no such distribution occurs and it is less pronounced with (II) than with (I). W. McC.

Acropeptide from caseinogen. Structure of polypeptide chains in relation to enzymic hydrolysis. A. FODOR and S. KUK (Biochem. Z., 1933, **259**, 331—339).—The octapeptide D_1 (mol. wt. 913) obtained by the degradation of caseinogen in glycerol (A., 1931, 1436) on treatment with α*N*-lactic acid at 37° for several days gives a quant. yield of a product mol. wt. 467, total N (Kjeldahl) 13·53% (D_1 13·80%), the same NH_2-N as D_1, half the CO_2H titration, and $-65·19°$ (D_1 $-63·38°$). The results are discussed in relation to the structural changes. P. W. C.

Comparative fission of triglycylglycine by normal sodium hydroxide and erepsin at 37°. E. ABDERHALDEN and A. NEUMANN (Fermentforsch., 1933, **13**, 459—466).—When triglycylglycine (I) is hydrolysed by *N*-NaOH at 37° a terminal glycyl group is first eliminated yielding diglycylglycine; no fission occurs at the middle of the mol. (cf. A., 1932, 935). The action of erepsin on (I) is similar but less rapid; the p_H optimum is 7·8 at the beginning, but changes during the course of hydrolysis. F. O. H.

Action of crystalline trypsin on pentaglycylglycine, tri-*l*-alanyl-*l*-alanine, and tetra-*dl*-alanyl-*dl*-alanine. J. H. NORTHROP and M. KUNITZ (Fermentforsch., 1933, **13**, 597—600).—The polypeptides are not hydrolysed to any significant extent. F. O. H.

General applicability of the micro-Kjeldahl determination. A. FRIEDRICH (Z. physiol. Chem., 1933, **216**, 68—76).—N_2 loss in Kjeldahl determinations on hydrazine, NO_2-, NO-, and azo-derivatives is obviated by preliminary reduction with HI. Volatile substances or those yielding volatile N compounds must be heated in a sealed tube with HI. Antipyrine under these conditions gives trustworthy figures. Diazo-compounds must first be coupled with a phenol. The process is generally applicable to all compounds containing organically bound N, but not to NO_3'. J. H. B.

Determination of arsenic in organic compounds by the calorimetric bomb. F. GARELLI and B. CARLI (Annali Chim. Appl., 1933, **23**, 129—132).—Use was made of a Kroeker type bomb of V2A steel. With cacodylic acid and therapeutic arsenicals good results were obtained. T. H. P.

Determination of phosphorus in organic compounds by the calorimetric bomb. F. GARELLI and B. CARLI (Annali Chim. Appl., 1933, **23**, 124—128).—The substance, mixed with PhMe or decahydronaphthalene, is burnt in a quartz crucible in the bomb, which contains 10 c.c. of H_2O. After 30 min., the P_2O_5 is determined as $Mg_2P_2O_7$. T. H. P.

Colorimetric determination of small quantities of lead in organic matter in presence of tin. M. A. MACHEBŒUF, H. CHEFTEL, and J. BLASS (Bull. Soc. chim., 1933, [iv], **53**, 190—196).—Org. matter is destroyed by heating with H_2SO_4 and HNO_3, a paste of $CaSO_4$ is added followed by a large quantity of H_2O containing H_2SO_4 and EtOH, and the whole is washed by centrifuging and filtered. The process is repeated and the residue washed with EtOH and dissolved in hot aq. NH_4OAc. The vol. is reduced by evaporation and Pb pptd. as PbS in presence of gelatin and determined colorimetrically. 0·2 mg. of Pb may be determined with an accuracy of approx. 6%. The error may be reduced to 1% by using a photo-electric cell and suitable coloured screens. The accuracy is unaffected when 0·1—0·5 mg. of Pb is determined in presence of 5 mg. of Sn, 0·5 g. of sugar, or 1 g. of meat. Bi and Hg have no effect, but Ag gives too high a val. when present in excess of 0·1 mg. M. S. B.

Duclaux method [for determination of volatile acids]. J. B. MCNAIR (J. Amer. Chem. Soc., 1933, **55**, 1470—1474).—Mixtures of four volatile aliphatic acids are analysed by determining one (or more) by chemical methods and the remainder by Gillespie and Walters' graphic method (A., 1917, ii, 549; cf. Duclaux, A., 1875, 188). H. B.

Refractometric determination of organic acids. (MME.) G. ALLARD (Compt. rend., 1933, **196**, 937—938).—This method (A., 1932, 632) has been extended to the higher aliphatic dibasic acids. The errors in determining azelaic acid, its Na salt, and Na sebacate in dil. solution are −5, +2·5, and +2·5%, respectively. The total acidity of mixtures of these with $H_2C_2O_4$ and $CH_2(CO_2H)_2$ is determined with similar accuracy, but the individual vals. show greater errors. A. C.

Volumetric analysis of anthranilic acid and its salts. H. FUNK and M. DITT (Chem.-Ztg., 1933, **57**, 334; cf. this vol., 244).—Anthranilic acid and its salts are tetrabrominated by direct titration with bromide–bromate solution in about 4*N*-HCl to the yellow change with an indigocarmine–styphnic acid indicator, the slight excess of Br being determined by addition of a few c.c. of 0·2*N*-KI and titration of the I with $Na_2S_2O_3$. E. A. F.

New reagent for identification of alkaloids. M. S. MOKRAGNATZ (Bull. Soc. Chim. Yougoslav, 1932, **3**, 171—177).—A solution of 0·05 g. of $KReO_4$ in 5 c.c. of H_2O, diluted to 100 c.c. with conc. H_2SO_4, gives characteristic colour reactions with morphine, codeine, brucine, cryptopine, hydrastine, hydrastinine, narcotine, quebrachamine, stypticine, yohimbine, boldine, chelidonine, *apo*morphine, and bulbocapnine. Many other alkaloids either give identical colour reactions with H_2SO_4 alone, or give no reaction. R. T.

Determination of morphine. B. KLJATSCHKINA and E. STUBER (Arch. Pharm., 1933, **271**, 217—219).—A method of determining morphine (I) (in small or large quantities) is based on the extraction of its

hydrochloride from approx. 2% aq. HCl by PhOH–$CHCl_3$ (1 : 4). The base can be recovered by extraction of the $CHCl_3$ solution with H_2O, concn., and pptn. by NH_3. Aq. NH_3 (p_H 9·1) dissolves 1·3 mg. of (I) per c.c., this figure being confirmed by the above method of determination. R. S. C.

Biochemistry.

Apparatus for determination of oxygen uptake of small animals. F. Rappaport and F. Gottdenker (Biochem. Z., 1933, **258**, 460—466).—An apparatus is described which differs from the usual self-registering one in that the O_2 uptake is determined not by the vol. decrease of an O_2 reservoir serving as spirometer, but by the vol. decrease of the whole system, which is sealed and provides for the absorption of CO_2. In this way the experiment is finished in 6—8 min. and many of the usual errors (change of H_2O vapour tension etc.) are avoided or may be disregarded. P. W. C.

Micro-respiration apparatus. E. T. Nielsen (Biochem. Z., 1933, **260**, 226—229).—The apparatus, which is fixed in a paraffin-oil bath, consists of a 1 c.c. pipette (graduations 0·002 c.c.) to which are sealed, in T-form, two glass-stoppered vessels (capacity < 2 c.c. each) containing respectively anhyd. Na_2SO_4 and soda-lime. A second apparatus is used for control. Measurements are made at const. vol. and at const. H_2O v.p., absorption of O_2 being recorded. W. McC.

Oxygen consumption of fasting white mice. J. E. Davis and H. B. Van Dyke (J. Biol. Chem., 1933, **100**, 455—462).

Pigment of *Halla parthenopea*, an accessory respiration catalyst. E. A. H. Friedheim (Biochem. Z., 1933, **259**, 257—268).—Electrometric titration shows that the pigment of *H. parthenopea* (hallochrome) forms a reversible two-stage oxido-reduction system. The pigment in *M*/90,000 solution increases by several hundred % the respiration of unfertilised sea urchin's eggs, of fertilised eggs of *Ascaris suis*, and of rabbit's red blood-corpuscles. The properties of hallochrome as to range of potential and consts. of the two-stage oxidation agree fairly closely with those of pyocyanin. P. W. C.

Elementary composition of various hæmocyanins. F. Hernler and E. Philippi (Z. physiol. Chem., 1933, **216**, 110—119).—Hæmocyanins from *Helix pomatia*, *Busycon canaliculatum*, *Octopus vulgaris*, *Loligo pealei*, *Limulus polyphemus*, and *Homarus americanus* isolated by various methods were analysed after drying at 105°. They showed close agreement in elementary composition. The mollusc product contained 0·25% and the arthropod product 0·18% of Cu. J. H. B.

Do hæmocyanins contain other metals besides copper? A. Gatterer and E. Philippi (Z. physiol. Chem., 1933, **216**, 120—122).—All hæmocyanins examined contain no metal in the mol. other than Cu. Traces of other metals found are due to impurity. J. H. B.

Iron-containing component of blood-pigment. Its combination with globin to give hæmoglobin. A. Herzog (Biochem. Z., 1933, **260**, 213—214).—A cryst. compound (hæmatin), $C_{34}H_{33}O_5N_4Fe$, obtained from coagulated blood yields a cryst. "reduced hæmatin," $C_{34}H_{33}O_4N_4Fe$. These substances and also chlorohæmin (I), oxyhæmoglobin, and CO-hæmoglobin (II) yield a cryst. compound (III), $C_{33}H_{30}$(or H_{31})O_4N_4Fe, which can be reconverted into the precursors. (III), which is probably the prosthetic group of hæmoglobin, combines with globin to give a product convertible into methæmoglobin and (II). It follows that the 34th C of (I) is introduced during its prep. and that ætioporphyrin has 31 C. W. McC.

Equilibrium between carbon monoxide-hæmoglobin and potassium ferricyanide. H. Schuler (Biochem. Z., 1933, **259**, 475).—Acknowledgment of Conant's earlier work (A., 1926, 1050; 1928, 315). P. W. C.

Detection of a complex compound of carbon dioxide and hæmoglobin in blood. O. M. Henriques (Biochem. Z., 1933, **260**, 58—71; cf. A., 1928, 1389, and Margaria, J. Physiol., 1931, **73**, 311).—Theoretical considerations and further experimental evidence confirm previous results pointing to the existence in blood of a complex CO_2–hæmoglobin compound (I). The extent of combination is 2%, 40%, and 0% at p_H 6·5, 7·2, and 8·0, respectively. As regards the Donnan equilibrium in blood, the predominating factor is the concn. of basic compounds of metals. In (I) the CO_2 is probably attached to an OH or NH_2 group giving a complex acid stronger than H_2CO_3. W. McC.

Absorption of light by carbon monoxide-hæmoglobin. V. Sebesta (Biochem. Z., 1933, **260**, 187—191; cf. A., 1926, 314).—The absorption of light by CO-hæmoglobin (horse, ox) as shown on a curve (I) where sp. extinction coeffs. are plotted against λ exhibits max. at 566 and 537·5 mμ and a min. at 551 mμ. As compared with the corresponding curve for oxyhæmoglobin (I) shows less absorption at the max. (but not at the min.) and lies nearer to the violet for the most part of its course, the shift for the 566 mμ max. being > for the other. W. McC.

Relative value of clinical blood-tests. T. F. Bloem (Biochem. J., 1933, **27**, 121—131).—The min. concns. of oxyhæmoglobin and its derivatives detectable by a given spectroscopic technique (I) were investigated and the results applied to the quant. determination of these substances in urine, fæces, and dil. blood. (I) is more sensitive than tests dependent on the benzidine reaction (A., 1932, 1151) and is comparable with the acid hæmatin method. F. O. H.

Generic and specific identification of blood by the Ganassini reaction. D. Ganassini (Arch. Ist.

Biochim. Ital., 1933, 5, 11—20).—A reply to criticism. The reaction depends on the catalytic action of hæmoglobin and Fe. Differences in the reaction of fœtal blood observed by Nicoletti are within the experimental error. R. K. C.

Spectrum analysis of the mitogenetic radiation from the blood of living animals. K. P. GOLISCHEVA (Biochem. Z., 1933, **260**, 52—57).—The complete (1900—2500 Å.) spectrum of the mitogenetic radiation from the blood circulating in the vena saphena of the rabbit has been examined and the various bands observed have been referred to processes (glycolysis, hydrolysis of peptides and of creatine phosphate, phosphatase action, oxidation) which give rise to them. W. McC.

Perinuclear granules and reticulum. III. Chemical nature of the granules. G. VAGI (Trans. Japan. Path. Soc., 1931, **21**, 248—251).—The substance in the granules and reticulum of white and red blood-cells is a basic nucleoprotein. CH. ABS.

Permeability of erythrocytes to chloride. M. MAIZELS (Biochem. J., 1933, **27**, 33—35).—When erythrocytes (I) are placed in solutions containing permeating anions (II) (*e.g.*, Cl′) and other anions or non-electrolytes (III) which permeate less easily (*e.g.*, PO_4''' or glucose), the amount of (II) diffusing across the positively-charged membrane of (I) depends on the external p_H and on the total osmotic pressure of (III), provided that a certain abs. quantity and min. concn. of (II) is exceeded. The concn. of (II) in the cell may greatly exceed the equilibrium concn. in the external phase. F. O. H.

Iron. VI. Determination and properties of the "easily eliminated" iron in blood. VII. Behaviour of inorganic iron on addition to blood. G. BARKAN (Z. physiol. Chem., 1933, **216**, 1—16, 17—25; cf. A., 1930, 1304).—VI. The determination of the readily eliminated Fe is modified by the use of Et_2O containing peroxide. Previous results are confirmed.

VII. Inorg. Fe^{II} salt added to blood differs from fraction *E* of the readily eliminated Fe in not showing inhibition by CO and in occurring only in blood fluid. It has, in common with *E*, a relatively high rate of dissolution in dil. acid. J. H. B.

Pancreatic ammoniophaneresis. M. POLONOVSKI, P. BOULANGER, and G. BIZARD (Compt. rend., 1933, **196**, 1147—1149).—The NH_3 content of pancreatic venous blood (I) is > that of arterial blood in dogs. Intravenous injection of $(NH_4)_2CO_3$ causes a further increase in (I) to vals. > those for the renal and femoral veins. A. C.

Blood-sugar content as an index of condition of cattle. H. VON TEICHMAN (Arch. Tierernahr. Tierzucht, 1932, **7**, 532—570).—The blood-sugar content of cattle is influenced by age, body-wt., period of lactation, milk yield, and pregnancy. Vals. obtained showed considerable variation in the individual during a 12-hr. period. To produce definite increases in sugar level, glucose must be given in solution at the rate of 1 pt. per 250 pts. body-wt. No correlation between blood-sugar curves and the condition of the animals was observed. A. G. P.

Analysis of serum with the ultra-centrifuge. P. VON MUTZENBECHER and T. SVEDBERG (Naturwiss., 1933, **21**, 331).—Ultra-centrifuge measurements made on dil. horse serum show the presence of mols. of four species with sedimentation consts. respectively $4{\cdot}4\times10^{-13}$, $6{\cdot}6\times10^{-13}$, 9×10^{-13}, and 18×10^{-13}, the first representing the albumin, the last three the globulin. Paraglobulin prepared by electrodialysis contains all three species, whilst eu- and para-globulin prepared by salt pptn. both contain the type with sedimentation const. 18×10^{-13}, but neither of them that with const. 9×10^{-13}. W. O. K.

Union of colloids. I. Supposed albumin–globulin compound in serum. State of combination of calcium in serum. W. M. BENDIEN and I. SNAPPER (Biochem. Z., 1933, **260**, 105—114; cf. A., 1929, 110).—The proteins of blood-serum (I) can be subjected to fractional ultra-filtration (II) by means of membranes (III) prepared by a modification of MacBain's method. Since the ratio of albumin (IV) to globulin (V) in the ultra-filtrates (VI) differs, in some cases greatly, from that in (I), it is probable that (IV) and (V) are not united in complex combination in (I). (II) probably takes place also through the membranes of the body in diseases (*e.g.*, albuminuria) where body-fluids (*e.g.*, urine) have a high (IV) to (V) ratio. Analyses of (VI) and of the residue which does not pass through the (III) indicates that all the combined Ca of (I) is united to the (IV). W. McC.

State of combination of calcium in the blood-plasma of the hen. M. LASKOVSKI (Biochem. Z., 1933, **260**, 230—240).—During the laying period the Ca and inorg. P contents of the blood-plasma of hens increase (average Ca and P per c.c.: laying, 0·208 and 0·045 mg.; not laying, 0·135 and 0·029 mg.). In non-laying hens (I) almost all the inorg. P in the plasma is ultra-filterable, in laying hens (II) only half, but the concn. (III) of ultra-filterable Ca in the plasma is the same in (I) and (II). All the additional Ca in the plasma of (II) most probably forms part of a colloidal Ca–P-complex and cannot be ultra-filtered. When $CaCl_2$ is added to plasma of (I) or (II), (III) increases to the same extent as does that (IV) of the total Ca, and intravenous injection of $CaCl_2$ into (II) results in increase in (III) in the blood. In the normal hen (III) is independent of the sexual state and of the changes in (IV) related to it. Only in the healthy living hen does regulation of (III) occur. W. McC.

Variations in the concentrations of magnesium, calcium, and inorganic phosphorus in rabbit's serum. R. W. BROOKFIELD (Biochem. J., 1933, **27**, 173—182).—With rabbits on a mixed diet, and especially during the period of intestinal absorption, the serum-Ca level (I) fluctuates in a manner directly opposed to that of the Mg level (II), the actual vals. of both (I) and (II) being influenced by the composition of the diet. The existence of an inverse relationship between (I) and the inorg. PO_4 level (III) is confirmed. Hence (II) follows a course parallel with that of (III). Mg does not diffuse from erythrocytes into the serum unless the time of keeping is > 4 hr. The balance of bivalent cations in the blood is discussed. F. O. H.

Serum-albumin and heparin. P. VON MUTZENBECHER (Naturwiss., 1933, **21**, 331).—The mol. wt. of serum-albumin is not altered by treatment with highly active heparin, which it has been suggested changes it into globulin (cf. Fischer, A., 1932, 73). Serum treated with heparin shows no increase in its albumin fraction. W. O. K.

Antiprothrombin and globulins. I. P. EARLE and P. E. HOWE (Science, 1933, **77**, 213—214).—Fischer's observation that heparin produces in serum a combination pptd. at approx. p_H 5·0, but not the conclusion that this combination is eu- or pseudo-globulin, is confirmed (cf. A., 1932, 636, 870; this vol., 296). L. S. T.

Fractional specificity of serum-albumin. T. ASABA (Arb. Med. Univ. Okayama, 1932, **3**, 314—346).—The different fractions of bovine serum manifest a definite fractional specificity. The behaviour of the various fractions is described. Globulin *E* obtained by electrodialysis contains chiefly eu- and pseudo-globulin and little albumin. In immunisation with bovine serum the globulin antibody appears prior to the albumin antibody. CH. ABS.

Combining and inhibition zones in immuno-reactions and colloidal reactions. K. OHTAHARA (Arb. Med. Univ. Okayama, 1932, **3**, 255—278).—The immuno-reactions, particularly the pptn. reaction, behave with regard to optimal flocculation and inhibition of flocculation similarly to oppositely charged dyes. CH. ABS.

Role of lipins in Forssman antigens. M. ARMANGUE, P. GONZALEZ, and S. ROMERO (Amer. J. Hyg., 1933, **17**, 277—286).—In sheep cells, horse and guinea-pig kidneys the common antigenic factor appears to be the EtOH-sol. lipin. The proteins in the Forssman antigen appear to act as carriers. The lipins have better antigenic qualities when united with adsorbents. Proteins present in Forssman antigens produce strictly sp. antibodies. Sp. antisera acting on the proteins of the kidney of the guinea-pig prove toxic for this animal; the same holds for sera produced against the heterophile lipins. CH. ABS.

Effects of various non-specific adsorbents on the hæmagglutinins of the rabbit immunised with goat red-blood cells. M. HOMMA (Japan. Z. Mikrobiol. Path., 1932, **26**, 1033—1062).—The hæmagglutinins are adsorbed by kaolin or $Al(OH)_3$. CH. ABS.

Components of hæmolytic complements. B. MITSUSE (Japan. Z. Mikrobiol. Path., 1932, **26**, 1702—1751).—A component stable on boiling at 100° for 2 hr. was obtained by extraction with petroleum benzine. CH. ABS.

The crystals of the living body. (SIR) W. BRAGG (Proc. Roy. Inst., 1933, **27**, 606—624).—A lecture.

Composition of some fatty materials found in ancient Egyptian tombs. A. BANKS and T. P. HILDITCH (Analyst, 1933, **58**, 265—269).—Analyses of four fats (1350—3000 B.C.) are given, and the general conclusions of Chapman and Plenderleith (B., 1926, 986) are confirmed. Glycerides and small amounts of oleic acid (together with its normal oxidation scission products, azelaic and nonoic acids) were present. The saturated acids were mainly intact, and large quantities of palmitic and stearic acids were obtained in proportions which, in at least two cases, indicate that the origin of the specimens was the body-fat of an animal (probably an ox). The unsaponifiable matter, however, provided no confirmation of this. J. G.

Chemical composition of cerumen. S. NAKASHIMA (Z. physiol. Chem., 1933, **216**, 105—109).—Cerumen contains fatty acids 0·85%; fats 12·4%; cholesterol 2·5%; cerotic acid (?) 1·9%; neurostearic acid (?) 0·35%; a bitter *substance*, m.p. 123°, trace; a *substance* $C_8H_{14}O_5N$, m.p. 204°, 0·8%; protein (of high lysine and low cystine content) 43·2%; ash (mainly Na_2SO_4) 3·45%. J. H. B.

Micro-determination of cholesterol and phosphatides in tissue and blood. W. MILBRADT (Z. physiol. Chem., 1933, **216**, 181—188).—The cholesterol is determined colorimetrically by the Tschugaev–Bernoulli reaction (A., 1932, 510) in the hydrolysed extract of 0·1 c.c. of hæmolysed blood, phosphatides by the method of Fiske and Subbarow (A., 1926, 443). Tissue (0·1—0·2 g.) is extracted with Et_2O–EtOH. J. H. B.

Examination of cholesterol by ultra-violet rays. H. MARCELET (Bull. Soc. Chim. biol. 1933, **15**, 379—384).—The liver oil of *Orthagoriscus mola* is very rich in cholesterol (I); the purified (I) gives a homogeneous mauve fluorescence (II) with filtered ultra-violet rays. Specimens from placentæ, ovaries, and calculi gave similar (II), whilst older samples from different sources stored in the dark gave impure (II); recrystallisation of one gave an improved (II). The m.p. of (I) varies with time. H. D.

Glutathione content and reductive power towards cystine of desiccated organs. L. WURMSER (J. Pharm. Chim., 1933, [viii], **17**, 327—331).—Various desiccated animal organs contain small amounts of compounds possessing the SH group (always < the fresh organ), have autoreductive power, and reduce cystine. R. S. C.

Preparation of lactacidogen and adenylic acid from muscle-juice. A. HAHN and M. DÜRR (Z. Biol., 1933, **93**, 490).—The statement by Steudel (A., 1932, 1273) that ox-flesh (I) is not a suitable source of adenylic acid is refuted. From 1 kg. of (I) 0·7 g. of crude Ba salt was obtained, whilst 10 kg. yielded 1·6 g. of the pure acid (cf. A., 1931, 860). The efficiency of the method is shown by its application to the prep. of the pure acid from blood (A., 1931, 1080). F. O. H.

Colloidal behaviour of muscle-proteins. IV. Mol. wt. of muscle-protein and the active volume (van der Waals) of myogen particles. H. H. WEBER and R. STOVER (Biochem. Z., 1933, **259**, 269—284).—The mean mol. wt. of dialysed myogen is 81,000, the hydrate vol. of 1 g. is 1·98 c.c. With myosin in Edsal's solution, the mol. wt. is 0·6—1·2 × 10^6. The hydrate vol. of myogen agrees with the viscosity vol. when calc. by Einstein's formula. Conc. solutions of urea decrease the mol. wt. of myogen to 34,000 and of myosin to 100,000, whilst conc. NH_4CNS

increases that of myogen to > 300,000. Muscle press-juice contains about 7% of muscle-protein which is almost exclusively myogen. The myogen of the purified solution appears to be identical with that of the muscle press-juice. P. W. C.

Calcium content of muscle. C. M. BURNS (Biochem. J., 1933, **27**, 22—32).—The normal muscle-Ca (I) of rats, cats, and rabbits varies considerably (cf. A., 1926, 431). With diets containing normal amounts of Ca, (I) does not increase with increased content of vitamin-*D* or of Ca. A state of hyper-excitability or active tetany induced by injection of guanidine, by feeding of phosphates or irradiated ergosterol to rachitic animals (A., 1931, 254), or by parathyroidectomy (A., 1929, 1332; 1931, 1327) is not accompanied by any appreciable change in (I). F. O. H.

Composition of bones of vegetarian and omnivorous rats. S. WAN (Chinese J. Physiol., 1933, **7**, 23—34).—No significant differences were found in the contents of ash, org. matter, Ca, P, and CO_2. F. O. H.

Phosphorus content of *Crustacea* of the Belgian coast. M. L. COMPERNOLLE (Natuurwetensch. Tijds., 1933, **15**, 83—84).—The PO_4''' content of eight varieties, calc. as P, ranged from 0·005% to 0·016%; it varied considerably from one specimen to another and with the season and locality. H. F. G.

Determination of inorganic iodine in desiccated thyroid gland. W. LAWSON (Biochem. J., 1933, **27**, 112—115).—Aq. extraction of the gland extracts I compounds other than inorg. to an extent dependent on the protein denaturation which has occurred in the gland during treatment for analysis. Exhaustive extraction with EtOH or MeOH removes only dialysable I, together with a trace of I combined with fat. For rapid determinations, 0·2—0·3 g. of the powdered gland is shaken with 20 c.c. MeOH at room temp. for 2·5 hr., the extract filtered and evaporated, and I determined in the residue. F. O. H.

Detection of chitin in the wing residues of *Coleoptera* of the upper middle eocene (found at Geiseltal). E. ABDERHALDEN and K. HEYNS (Biochem. Z., 1933, **259**, 320—321).—The wing residues of *Coleoptera* (age 25×10^6 years) contain chitosamine isolated as the phenylhydantoin, m.p. 210°, $[\alpha]_D^{20}$ +72·4° (synthetic, m.p. 210°, $[\alpha]_D^{20}$ +76°). P. W. C.

Acetylcholine in the human placenta. P. HAUPSTEIN (Arch. Gyn., 1932, **151**, 262—280; Chem. Zentr., 1933, i, 246).—Placentas at various periods of pregnancy contain 59—280 mg. of acetylcholine per kg. Relatively large amounts were found in immature placentas. A. A. E.

Determination of glycogen. C. A. GOOD, H. KRAMER, and M. SOMOGYI (J. Biol. Chem., 1933, **100**, 485—491).—A modification of the Pflüger method permits the determination to be made in a few hr. For the initial hydrolysis, treatment with 30% aq. KOH is sufficient. The glycogen is then pptd. at the b.p. with 1 vol. of 95% EtOH, and after centrifuging is hydrolysed for 2 hr. with 0·6*N*-HCl or *N*-H_2SO_4. A. L.

Celluloid impressions of the surface structure of animal fibres. J. MANBY (J. Roy. Micros. Soc., 1933, **53**, 9—12).—Modifications of Hardy's method of studying the surface structure of animal fibres are described. H. G. R.

Practice of fixation for animal tissues. P. GRAY (J. Roy. Micros. Soc., 1933, **53**, 13—19).—A guide to the choice of the most suitable fixative. The use of ten aq. and two alcoholic "basal fixative solutions" is recommended, as many fixatives are unstable. H. G. R.

Histological applications of triphenylmethane and diphenylnaphthylmethane dyes. I—III. S. HASHIMOTO (Japan. Z. Mikrobiol. Path., 1932, **26**, 1075—1100, 1101—1114, 1115—1128).—The electric charge, diffusibility, colouring, lipin-solubility, carbinol reaction, and toxicity were studied. In general, basic dyes have lipin-solubility, whilst acid dyes have not. The basic dyes are the more toxic. The vital staining of protoplasmic granules is closely related to the electric charge and diffusibility. CH. ABS.

Application of triphenylmethane and diphenylnaphthylmethane dyes in morphological studies. IV—VI. S. HASHIMOTO (Japan. Z. Mikrobiol. Path., 1932, **26**, 1527—1533, 1631—1641, 1642—1650).—Chromazurol S (G) is adsorbed electrically and is chemically combined with NH_2-acids or proteins in the staining of tissues. CH. ABS.

Vital staining with diamine dyes. K. FUJITA (Trans. Japan. Path. Soc., 1931, **21**, 206—208).—Most of the effective dyes are acid dyes. CH. ABS.

Relation between the intensity of the staining reaction of cell granules and the composition of the fixing solution. Y. KON and K. TAKEDA (Trans. Japan. Path. Soc., 1931, **21**, 233—235). CH. ABS.

Relationship between the chemical reaction of fixative solution and the basophilic granules in stained tissue. K. KATOH (Trans. Japan. Path. Soc., 1931, **21**, 236—237).—Diffuse staining was usually accentuated by fixation in alkaline solution. CH. ABS.

Reticulo-endothelial system. II. Secretion of specific substances. G. OBO (Trans. Japan. Path. Soc., 1931, **21**, 324—328).—A non-protein substance, not a true lipin, which stimulates the reticulo-endothelial system and accelerates the detoxication of morphine, is present shortly after the injection of India ink into rabbits. CH. ABS.

Chemistry of the liquor amnii. J. F. D. SHREWSBURY (Lancet, 1933, **224**, 415—416).—Data are recorded. Cholesterol is absent and the Ca level is slightly lower than for normal serum-Ca. L. S. T.

Fractionation of Australian snake venoms. II. Venoms of the tiger snake (*Notechis scutatis*), black tiger snake (*Notechis scutatis niger*), and black snake (*Pseudechis porphyriacus*). H. F. HOLDEN (Austral. J. Exp. Biol., 1933, **11**, 1—7).—Ultra-filtration through pyroxylin or gelatin membranes was not satisfactory for the separation of the constituents of snake venoms. Of various adsorbents,

freshly prepared $BaCO_3$ was most efficient. It adsorbs thrombin, but not "neurotoxin." W. O. K.

Secretion and oxygen consumption in isolated salivary glands of *Aplysia*. T. Ni (Chinese J. Physiol., 1933, **7**, 71—78).—Electrical stimulation of the salivary glands of *A. punctata* and *A. limacina* increases the flow of saliva (I) and the O_2 consumption (II) (from 1·2 to 2·5 c.mm. per min.) of the glands. NaCN inhibits (II), but does not always inhibit (I) or depress the secretory excitability (III). Following treatment with NaCN, methylene-blue restores (II) without affecting (III). From the concn. equivs. of the saliva (1·61*M*) and hæmolymph (1·08*M*) it follows that the osmotic work performed during the secretion of 1 litre of saliva is 24·3 kg.-m. F. O. H.

Influence of bile salts on salt excretion in liver-bile. II. Elimination of phosphoric acid through bile acids after administration of glucose. Y. Kawada (Arb. Med. Univ. Okayama, 1932, **3**, 163—171).—The ash and total solid content of fistula bile from dogs is decreased after administration of glucose; after that of bile salts it is unaltered or only slightly lowered. The elimination of PO_4 is decreased after oral administration of glucose, but unaltered or only slightly lowered when bile salts are given simultaneously. Ch. Abs.

Bilirubin. VIII. Determination of bilirubin in body-fluids. Quantitative extraction process. W. Kerppola and E. Leikola (Acta Med. Scand., 1932, **78**, 24—41; Chem. Zentr., 1933, i, 94).—The bilirubin is extracted with $CHCl_3$ before and after acidification and determined colorimetrically. The diazo-method is subject to interference by substances present in body-fluids. The colour of 0·0075 mg. of bilirubin in 1 c.c. corresponds with that of 0·05% aq. $K_2Cr_2O_7$. Methods for the determination of bilirubin in urine, bile, and serum are described. A. A. E.

Sugars of human milk. M. Polonovski and A. Lespagnol (Bull. Soc. Chim. biol., 1933, **15**, 320—349).—40 litres of 95% EtOH are added to 7 litres of human milk; after concn. and removal of fats the solution is filtered. At 0° crystals separate. By recrystallisation of the latter from MeOH, *allo*lactose, $[\alpha]_D$ +25°, is obtained pure. The reducing group of this disaccharide is aldehydic. It gives an osazone (I); on hydrolysis it gives glucose (II) and galactose and it is hydrolysed by emulsin. On oxidation with I and subsequent hydrolysis (II) is obtained. Hydrolysis of (I) and treatment of the product with phenylhydrazine gives galactosazone. Hence it is assumed that *allo*lactose is a β-*d*-galactosido-*d*-glucose. The possibility of its identity with the synthetic 6-β-galactosidoglucose is discussed. The mother-liquors from the original crystals are separated into two fractions by pptn. with MeOH. The ppts. obtained by repeating the process show decreasing reducing powers, whilst the fractions more sol. in MeOH have consts. closer to those of gynolactose. H. D.

Endocrine glands and excretion of milk. Q. Calabro and F. Fantozzi (Arch. Ist. Biochim. Ital., 1933, **5**, 79—96).—A study of the effect of injection of thyroid, parathyroid, and ovarian extracts on the quantity, *d*, f.p., dry residue, and fat content of goat's milk. R. K. C.

Influence of copper on the peroxidase reaction of milk. K. Jeschki (Milch. Forsch., 1933, **15**, 110—114).—The presence of Cu in milk produces a positive peroxidase reaction although the milk has been heated. If the peroxidase reaction be positive after the test sample has been boiled the presence of Cu or other metal may be deduced. E. B. H.

Effect of light on the oxidation-reduction potential of milk. E. Martini (Biochem. Z., 1933, **260**, 153—160).—A rapid fall of potential is produced by the action of light on milk in which the enzymes have been destroyed by heat. H. W. D.

Specific influence of sugar-beet leaves and tops on the quality of milk. G. Zwagermann (Intern. Mejerikongr., 1931, 274—284; Bied. Zentr., 1932, **3**, A, 99).—The feeding of sugar-beet tops and leaves does not increase the fat content of milk and it produces therein an unpleasant taste and odour. The latter is ascribed to the presence of NMe_3 derived from the betaine of the leaves. The odour can be removed from butter by washing with H_2O acidified with lactic, citric, or tartaric acids. Butter is less affected if the cream is pasteurised. Use of fresh sugar-beet tops produces a hard, crumbly butter. Appropriate stall feeding minimises the odour. A. G. P.

Influence of feeding and the condition of milking animals on the vitamin content of their milk. M. Schieblich (Tierarztl. Rundschau, 1931, **37**, 860; Bied. Zentr., 1932, **3**, A, 88).—The vitamin-*A* content of milk is affected by the amount supplied in the ration. Vitamin-*B* is synthesised internally by bacteria and is independent of external supplies. This is not the case with non-ruminants. Although the vitamin-*C* content of milk is closely related to that of the ration, some internal synthesis must be assumed. The low vitamin-*C* content of winter milk is attributed to the customary shortage of green food, but may be remedied by the use of silage. Pasture grazing and ultra-violet radiation increase the vitamin-*D* content of milk. The latter is maintained during winter by the use of silage and hay or of irradiated foodstuffs, *e.g.*, yeast. Cod-liver oil has little effect on plant-eating animals owing to its poor digestibility.

Destruction of citric acid in milk by bacteria. J. Mussill (Milch. Forsch., 1933, **15**, 42—49).—A micro-centrifugal method is suitable for the determination of citric acid in milk. The citric acid content is unaltered by sterilisation or by keeping after sterilisation and decreases only under the influence of bacteria. Proteolysis and citric acid breakdown have no relationship; thus *B. coli* rapidly destroys citric acid, scarcely affecting proteins. Acid formation does not necessarily follow citric acid destruction. E. B. H.

Calculations relating to transport of material in the organism. R. Fürth (Kolloid-Z., 1933, **63**, 215—220).—The energy required for electro-osmotic transport of liquid in the organism is calc. to be only 0·00001 of that actually furnished by the observed bio-electric currents. The osmotic work done in the

kidney during secretion of urine is about 0·1 of that corresponding with the local e.m.f. In general, bioelectric sources of energy are more than adequate to account both for transport of material and for the maintenance of differences of concn. across membranes. F. L. U.

Intracellular hydrogen-ion concentration studies. VII. Secreting cells of the mesonephros in the chick. R. CHAMBERS and G. CAMERON (J. Cell. Comp. Physiol., 1932, **3**, 99—103).—Columnar cells of the walls of the proximal convoluted tubule in the chick have the property of favouring unidirectional passage of sulphonephthalein indicators through the cytoplasm. Intracellular p_H for healthy cells is 6·8+0·2 and in certain unhealthy tubules 5·2 (approx.). A. G. P.

Micro-analysis of urine and blood by the step photometer. IX. Determination of ammonia in urine. C. URBACH (Biochem. Z., 1933, **259**, 351—357). P. W. C.

Is blood-protein amide-nitrogen a source of urinary ammonia? III. Question of the synthesis of protein amides from ammonia. E. F. WILLIAMS, jun., and T. P. NASH, jun. (J. Biol. Chem., 1933, **100**, 515—524).—After injection of aq. $(NH_4)_2CO_3$ into the femoral artery of dogs there is no significant change in the protein amide vals. of the plasma and whole blood. A. L.

Secretion of urea in the frog. E. K. MARSHALL, jun. (J. Cell. Comp. Physiol., 1932, **2**, 349—353).—The amount of urea excreted by the frog's kidney is much in excess of that accounted for by the glomerular filtrate as measured by xylose. Urea is largely excreted by tubular secretion. A. G. P.

Unknown nitrogenous substances in urine. V. Occurrence of γ-butyrobetaine in dog's urine. H. REINWEIN (Z. physiol. Chem., 1933, **216**, 26—30).—γ-Butyrobetaine was isolated from normal dog's urine and is therefore not necessarily a symptom of metabolic disturbance. J. H. B.

Relationship of urinary composition to acid-base equilibrium. VI. Mechanism of the origin of acid and alkaline urine. S. M. NEUSCHLOSZ (Biochem. Z., 1933, **259**, 322—330).—Mathematical treatment of the usual Cushny theory of filtration at the glomerulus and back absorption in the kidney tubules leads to a formula permitting the calculation of the $NaHCO_3$ concn. of the reabsorbed fluid ($-B_0$) and experiments with 24 healthy men gave a practically const. val. for B_0 (mean deviation 4·8%). The excreted urine is more acid or alkaline than the blood as the $NaHCO_3$ concn. in the blood-plasma is lower or higher than B_0. P. W. C.

Composition of the urine of white mice. I. A. PARFENTJEV and W. A. PERLZWEIG (J. Biol. Chem., 1933, **100**, 551—555).—The average composition of normal mouse urine as determined using pooled samples from 20—100 animals is as follows: total N 4·15, urea 5·70, protein 1·52, allantoin 0·92, NH_3 0·36, creatinine 0·10, creatine 0·09, hippuric acid 0·28, NH_2-acid (as glycine) 0·09, uric acid 0·04, purine bases (as guanine) 0·01, indican 0·005, total S 0·27, total SO_4-S 0·20, inorg. SO_4-S 0·15, inorg. P 0·43, Cl 0·62%; d 1·059, p_H 5·3; total base 3810, total acidity 1820 mol. equiv. per litre. The protein probably belongs to the chondromucoid group. A. L.

Composition of the urine of cows. A. T. DANN (Austral. J. Exp. Biol., 1933, **11**, 53—58).—Analyses are given. Acid diet (brewer's grains) reduces the p_H and increases the total N, NH_3-N, and creatinine contents. W. O. K.

Copper content of urine of normal individuals. I. M. RABINOWITCH (J. Biol. Chem., 1933, **100**, 479—483).—Cu was found in human urine ranging in amounts from traces to 0·4 mg. per litre. H. D.

Biological chlorophyll degradation. III. Isolation of chlorophyll derivatives from elephant and human fæces. H. FISCHER and A. HENDSCHEL (Z. physiol. Chem., 1933, **216**, 57—67; cf. A., 1932, 659).—Elephant fæces contain principally phyllocerythrin, and, in small amounts, two green pigments with higher HCl val., one of which has an *Et* ester, m.p. 222°. Human (vegetarian) fæces contain protophorbide *a*; sheep fæces contain rhodoporphyrin-γ-carboxylic acid. J. H. B.

Nature of the calcium and phosphorus combination in the excreta of the non-laying pullet. F. KNOWLES, J. E. WATKIN, and F. W. F. HENDRY (J. Agric. Sci., 1933, **23**, 196—203).—Normal excretion of Ca is not in the form of $Ca_3(PO_4)_2$, but conforms closely in composition with a mixture of $CaCO_3$ and $CaHPO_4$. A. G. P.

[Optical] rotation of blood-serum before and after hydrolysis and its clinical significance. G. SANT (Pharm. Weekblad, 1933, **70**, 425—433, 443—449).—Serum (2 c.c.) is diluted with 16 c.c. of physiological saline and α determined. Hydrolysis is effected by adding 2 c.c. of serum to 16 c.c. of 28% HCl and observing α as rapidly as possible before reflocculation and decomp. commence. The difference in α $\times 100$ divided by the original α is the hydrolysis no. (I) and is a measure of the serum-albumin. (I) for healthy persons is >100. In cases of sickness (eclampsia) it falls as low as 26. There is no relationship between (I) and the urea content or the CH_2O titration. S. C.

Etiology of beri-beri. H. Y. OH (Korean Med. J., 1932, **2**, 113).—Blood-Ca was diminished in Korean patients, who improved on administration of Ca preps. CH. ABS.

Rabbit carcinoma produced by nicotine. S. KATSUNUMA (Trans. Japan. Path. Soc., 1931, **21**, 244—247). CH. ABS.

Independence of growth and type of metabolism in malignant cells. F. EICHHOLTZ, W. KEIL, and L. KLUGE (Biochem. Z., 1933, **260**, 139—142).—In white rats inhibition by *X*-ray irradiation of the growth of tumour cells is not accompanied by any change in their lactic acid content (I). Administration of prolan has no effect on (I) or on other properties of the sarcoma. From these and previous results it follows that the growth of such cells is independent of the type of metabolism which occurs in them. W. McC.

Glutathione content of the blood in cancer. R. Willheim and K. Stern (Biochem. Z., 1933, **260**, 180—186; cf. A., 1930, 493).—Blood from cancerous persons contains less glutathione than does that of healthy persons. The difference is more pronounced when related to the no. of erythrocytes. W. McC.

Phosphatases of human uterine tumours. M. Morii and Y. Takabatake (Arb. III Abt. anat. Inst. Univ. Kyoto, 1932, C, No. 3, 46—51).—Carcinoma: In lymphoglandular metastases a very active phosphatase was present. No phosphatase was present in normal lymph glands or in myoma. Ch. Abs.

Cathepsin and peptidases in carcinomatous and sarcomatous animals. E. Maschmann and E. Helmert (Z. physiol. Chem., 1933, **216**, 161—172).—The cells of liver, spleen, and kidney of normal and carcinomatous or sarcomatous animals contain much more cathepsin than those of mouse carcinoma or mouse and fowl sarcoma. Muscle tissue and embryonic cells contain even less. In necrotic material from mouse carcinoma, catheptic proteinase is almost absent, and the dipeptidase content is reduced to 1/3. The peptidase content of organ and tissue extracts is about the same. Dipeptidase is absent from serum and fowl muscle. The liver-cathepsin of normal is < that of carcinomatous animals; the enzyme seems to accumulate in the spleen of the diseased animals. J. H. B.

Butyric acid in the treatment of cancer. J. Watson (Lancet, 1933, **224**, 746—748).—$PrCO_2H$ has a destructive action on cancerous but not on normal tissue. L. S. T.

Treatment of coccidiosis in rabbits by injection of oil–thymol–carbon tetrachloride mixtures. Moussu (Compt. rend. Acad. Agric. France, 1933, **19**, 133—136).—Successful results of subcutaneous injection of preps. of olive oil, thymol, and CCl_4 are recorded. A. G. P.

Calcæmia in dermatoses. J. L. Carrera (Rev. sudamer. endocrinol., 1932, **15**, 893—928).—In dermatoses only slight deviations from normal vals. were found. Ch. Abs.

High carbohydrate diets in diabetes. J. Eason and D. M. Lyon (Lancet, 1933, **224**, 743—745).—Considerable reduction of fat in the diet makes possible an increase in carbohydrate without an increase in insulin requirement, but a lower calorific intake generally results. Fat appears to make demands on the supply of natural or administered insulin. L. S. T.

Effect of galactose feeding on depancreatised dogs. J. H. Roe and R. F. Cahoon (Science, 1933, **77**, 331—333).—Galactose is not converted into glucose by depancreatised dogs. About one half of the administered galactose is retained and apparently utilised. Galactose is used preferentially to glucose by the depancreatised dog. Galactose feeding prevents or suppresses some of the consequences of pancreatectomy. L. S. T.

Changes in the distribution of muscle-phosphorus and -glycogen in fasting cats and in cats with experimental diabetes mellitus with or without administration of insulin. V. M. Vesselkina (Z. ges. exp. Med., 1932, **85**, 463—476; Chem. Zentr., 1933, i, 449—450).—In hunger the total, lipin, and acid-sol. P are unchanged, but in the acid-sol. P the hexose-phosphoric (I) and creatine-phosphoric acid (II) are diminished. In diabetes the total P is unchanged, and the lipin-P is increased at the expense of the acid-sol. P; the (I) is diminished and (II) is increased. When insulin is given to depancreatised cats with normal blood-sugar (sugar being administered) all P fractions become normal; in insulin hypoglycæmia (I) rises; in all cases the glycogen remains low. A. A. E.

Glucose equivalent of insulin. W. Falta and R. Boller (Wien. med. Woch., 1932, **82**, 1296—1300; Chem. Zentr., 1933, i, 449).—In the diabetic individual the glucose equiv. is not const. A. A. E.

Influence of callikrein (padutin) on blood-sugar in diabetes mellitus. A. W. Elmer and M. Scheps (Klin. Woch., 1932, **11**, 1993—1994; Chem. Zentr., 1933, i, 450).—Large doses (35—70 units) given perorally have practically no effect. A. A. E.

Emotional glycosuria in Chinese students. W. H. Adolph, T. Y. Wang, and P. C. Wang (Chinese J. Physiol., 1933, **7**, 1—4).—Glycosuria, accompanied by hyperglycæmia, was detected in only one amongst 76 students sitting for examinations. F. O. H.

Intermediary carbohydrate metabolism during experimental fever. K. Adachi and S. Kasai (Tohoku J. Exp. Med., 1932, **20**, 191—210).—Prolonged tying down of rabbits causes a fall in body temp., prolonged hypoglycæmia, and a temporary increase in blood-lactic acid. During naphthylamine fever the blood-sugar shows irregular variation, and blood-lactic acid rises after the max. temp. has been attained. During fever induced by medullary puncture the blood-glucose and -lactic acid rise after the max. temp. has been attained. Ch. Abs.

Intermediary metabolism of muscle in fever. I. Gas and carbohydrate. II. Phosphoric and uric acids. K. Adachi (Tohoku J. Exp. Med., 1932, **20**, 93—106, 107—122).—I. Experimental fever in dogs causes a transient increase in O_2 consumption by muscle. Blood-sugar falls temporarily, and sugar utilisation by muscle usually increases. In very high fever the blood-lactic acid at first rises and then rapidly becomes normal. Blood-CO_2 is considerably decreased, and CO_2 formation in muscle is accelerated.

II. Dogs' arterial and venous blood normally contain, respectively, 3·81 and 3·92 mg. inorg. P per 100 c.c. In fever the blood-inorg. P usually increases, and the amount formed in the muscle decreases. Normal uric acid vals. are 0·76 and 0·79 mg. per 100 c.c. In fever, blood-uric acid increases considerably, partly due to leucocytosis, and formation in muscle is also increased. Ch. Abs.

Grass-pollen antigen for hay-fever desensitisation. J. Freeman (Lancet, 1933, **224**, 573—574). Extracts from all the various grass-pollens yield the same antigen for desensitisation to hay-fever. L. S. T.

Brain-cholesterol and -lipins of mental deficients. P. Laurie (Bull. Soc. Chim. biol., 1933, **15**, 418—425).—No significant difference between the

normal and mentally deficient is observed with regard to the brain-total-P, -fatty acids, and -cholesterol either in the grey or in white matter. H. D.

Gastric secretion during high intestinal obstruction. S. KIM (Korean Med. J., 1932, 2, 86—92).—In dogs the acidity, [Cl], and amount of the gastric juice increased. Similar changes follow the injection of histamine. CH. ABS.

Oxygen consumption and nitrogen metabolism. II. In leucæmia. C. W. BALDRIDGE and A. BARER (Arch. Int. Med., 1933, **51**, 589—615).—Increased O consumption following *X*-ray treatment of the spleen in leucæmia is accompanied by an increase in protein catabolism (increased uric acid excretion). A secondary phase follows in which O consumption is decreased and is accompanied by N retention. P. G. M.

Kidney-phosphatase in experimental nephritis. S. TOMIKAWA (Arb. III Abt. anat. Inst. Univ. Kyoto, 1932, **C**, No. 3, 62—67).—The quantity is greatly decreased. Most of the phosphatase is present in the cortex. CH. ABS.

Factors in the development of deforming leg weakness in chickens. R. T. PARKHURST and M. R. MCMURRAY (J. Agric. Sci., 1933, **23**, 311—327).—Perosis in chickens is associated with the feeding of excessive amounts of meat and bone meal. The level of protein feeding and rate of growth were without influence on the appearance of the deformation. Feeding of ground limestone did not produce slipped tendons. A. G. P.

I. Cause of mottled enamel in human teeth. M. C. SMITH, E. M. LANTZ, and H. V. SMITH. **II. Mottled enamel in Arizona and its correlation with the concentration of fluorides in water supplies.** H. V. SMITH and M. C. SMITH. **III. Experimental production of mottled enamel.** M. C. SMITH and E. M. LANTZ (Arizona Agric. Exp. Sta. Tech. Bulls., 1931, No. 32; 1932, No. 43; 1933, No. 45).—I. Mottled enamel of human teeth is associated with a relatively high F content in drinking-H_2O supplies.

II. Observations in a no. of areas indicate that no injury results from H_2O containing < 2 p.p.m. of F. No relationship was apparent between the F content of H_2O and the nature of the source of supply. Sensitiveness to F injury is probably affected by dietary factors.

III. Mottling of rats' teeth is induced by ingestion of NaF in H_2O or foodstuffs and by subcutaneous or intramuscular injection. A return to normal conditions followed the cessation of F administration. A. G. P.

Blood-bromine in psychomotor excitation. W. KLIMKE and B. HOLTHAUS (Deut. med. Woch., 1932, 58, 1558—1560; Chem. Zentr., 1933, i, 450—451).—Blood-Br is diminished. A. A. E.

Glycuronic acid in scurvy. A. J. QUICK (J. Biol. Chem., 1933, **100**, 441—444).—The scorbutic guinea-pig synthesises glycuronic acid. H. D.

Phosphorus content of the blood, muscles, and urine during scurvy. A. MICHAUX (Compt. rend., 1933, **196**, 1341—1344).—The P content of the urine and blood of guinea-pigs decreases during scurvy; that of the striated muscles decreases during chronic, but not during acute, scurvy. R. S. C.

Chemotherapy of infections of *Trypanosoma congolense*. Elective action of organic polyarsenicals. E. FOURNEAU, J. TREFOUEL, (MME.) J. TREFOUEL, D. BOVET, and P. KŒTSCHET (Compt. rend., 1933, **196**, 1173—1175).—Toxicities towards mice and chemotherapeutic indices are recorded for a large no. of derivatives of C_6H_6, Ph_2, $CO(NHPh)_2$, $[NHPh{\cdot}CH_2{\cdot}]_2$, benzidine, and azobenzene containing two $\cdot AsO_3H_2$ groups, which have a more favourable action on experimental infections of *T. congolense* than have monoarsinic acids, but are inactive towards *T. brucei*. A. C.

Chloride content of urine of diseased and healthy cattle with special reference to tuberculous cattle. M. VESPER (Diss., Leipzig, 1931; Bied. Zentr., 1932, **3**, **A**, 86).—Reduced Cl' in urine of diseased cattle is not a sp. result of disease, but is due to disturbed digestive conditions. In tuberculous cows no reduction was observed. A. G. P.

Influence of aliphatic hydroxy-acids on the solubility of rare-earth salts of vital dyes. G. CANNERI (Annali Chim. Appl., 1933, **23**, 58—61).—The low solubility of these salts, used in the chemotherapy of tuberculosis, may be increased by addition of Na citrate. T. H. P.

Basal metabolism of American-born Chinese girls. F. G. BENEDICT and M. H. MEYER (Chinese J. Physiol., 1933, **7**, 45—59).—Data from 18 subjects indicate a basal metabolism 6—9% lower than that of American girls. F. O. H.

Catalytic oxidising action of body fluids on tissue metabolism. L. KARCZAG (Biochem. Z., 1933, **260**, 44—46).—Ultra-filtrates (I) from human blood-serum, cerebrospinal fluid, and the aq. humor of the pig's eye, used alone as nutrient media, increase, often very greatly, the respiration of guinea-pig kidney and mouse brain, aerobic and anaerobic glycolysis being at the same time inhibited. The metabolism of mouse carcinoma proceeds aerobically in (I) instead of anaerobically as in Ringer's solution, no glycolysis taking place. W. McC.

Effect of muscular work on the oxidations in the body. I. KANAI (Biochem. Z., 1933, **260**, 129—138).—In healthy rats biological oxidations (I) become more complete as a result of muscular exercise (II). When great fatigue (III) begins, (I) becomes less complete, especially in untrained rats. The N metabolism remains unchanged during (II) until it becomes severe with subsequent (III), when increase occurs. W. McC.

Measurement of tissue respiration. M. DIXON and D. KEILIN (Biochem. J., 1933, **27**, 86—95).—The method of Dickens and Simer (A., 1931, 1182) has been modified. A new type of flask, which necessitates the use of only one manometer and two readings for each experiment, allows the O_2 or CO_2 of respiration of a tissue or cell suspension to be determined, using as medium either phosphate buffer, HCO_3'–Ringer solution (I), or serum in equilibrium

with the physiological tension of CO_2. With (I), a third reading gives the aerobic glycolysis. F. O. H.

Growth and reproduction on synthetic diets. III. Fats. G. A. HARTWELL (Biochem. J., 1933, **27**, 146—150).—Rats fed on a basal diet of caseinogen, potato starch, salt mixture, marmite, and cod-liver oil show better growth with addition of bacon-fat (I), lard (II), or margarine than with that of butter, beef or mutton suet, or olive oil. With (I) or (II), reproduction does not occur, whilst with any of the above synthetic diets, reproduction, growth, and condition of the fur are inferior to those of rats fed on kitchen scraps. F. O. H.

Nutritive value of sperm- and finback-whale oils. Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 245—253).—The oils have no growth-promoting effect in young rats. The cetyl and oleyl alcohols derived from them are definitely toxic, although neither they nor the pure waxes produce seborrhœa in young rats either by oral administration or intraperitoneal injection. A daily dose of 50—100 mg. of linoleic acid *per os* has a beneficial effect on the seborrhœa of rats supplied with whale oils. P. G. M.

Physiological actions of the ether-soluble substances of polished rice. Y. SAHASHI (J. Agric. Chem. Soc. Japan, 1932, **8**, 1093—1103).—Higher unsaturated fatty acids (clupanodonic, hiragonic) hindered the growth of rats. The linoleic acid of rice is necessary for normal nutrition. No difference was observed between the nutritive vals. of Et_2O-extracted polished rice and wheat flour. CH. ABS.

Role of the liver in cholesterol metabolism. A. L. MJASSNIKOV (Klin. Woch., 1932, **11**, 1910; Chem. Zentr., 1933, i, 79).—In dogs poisoned with P or salvarsan the blood-cholesterol rapidly rises, and then slowly falls. The liver has the power of producing as well as of excreting cholesterol. A. A. E.

Degradation of cholesterol. H. BEUMER and H. FASOLD (Biochem. Z., 1933, **259**, 471—474).—In infants receiving cholesterol, and in rats either starving or on an ordinary diet, no degradation of cholesterol could be detected. On feeding cholesterol or sitosterol to rats considerable destruction occurred, but is regarded as entirely due to intestinal bacterial action. P. W. C.

Nutritive value of pentosan. III. Glycogen accumulation in the body of rats on xylan feeding. IV. Methods of treatment and the kinds of animal for the digestibility of pentosan. H. IWATA (J. Agric. Chem. Soc. Japan, 1932, **8**, 1175—1179, 1252—1258).—III. Glycogen accumulation is slightly less when xylan is fed than when starch is fed, but the val. calc. on the digestible substance is practically const.

IV. When straw of rice, barley, wheat, *Panicum crus-galli*, L., var. *frumentaceum*, Hook., or coarse hay of *Muscanthus sinensis*, Anders., was treated with cold 0·75—1·5% NaOH for 4 hr. or 1% $Ca(OH)_2$ for 2 days, or was boiled with 1% $Ca(OH)_2$ for 1·5—3 hr. the digestibility of the pentosan was 1·4—2·1 times that of the untreated material. When rice straw was treated with 0·25% NaOH for 4 hr., or with wood-ash solution for 2 days, or was boiled with H_2O for 3 hr., no increase in digestibility was observed. Rabbits digest 78·9, rats 33·1, and guinea-pigs 62·9% of xylan. CH. ABS.

Glycogen changes of the organisation centre in amphibian gastrula. M. W. WORDEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 189—194).—A method of following the changes in the glycogen content during the development of the egg and embryo of the Mexican axolotl is described. The probability of a genetic connexion between plasma and glycogen is discussed. M. S. B.

Effect of bile acids on carbohydrate metabolism. XX. Glycogen synthesis by bile salts on administration of different amino-acids. S. FUZITA (Arb. med. Univ. Okayama, 1932, **3**, 192—200).—Glycogen synthesis in starving dogs is increased by administration of bile salts. *d*-Alanine and *l*-leucine increase, whilst glycine decreases, the synthesis of liver-glycogen after administration of bile salts. CH. ABS.

Factors influencing the metabolism of glucose ingested by fasting dogs. M. DANN and W. H. CHAMBERS (J. Biol. Chem., 1933, **100**, 493—514).—Determinations of the R.Q. after administration of varying amounts of glucose to dogs fasted for about 3 weeks showed that the inhibition of carbohydrate oxidation was complete for about 4 hr. following the ingestion. 400 g. of glucose administered over a period of 4 days did not restore normal metabolism. The recovery val. of other foods tested decreased in the order cracker meal, wheat-germ extract, yeast concentrate, and maltose, the first three being in the reverse order to that of their vitamin content. The effectiveness of insulin (2—6 units per kg.) was < that of yeast concentrate, but the combined effect exceeded that of either alone. A. L.

Cause of selective absorption of sugar from the intestine. W. WILBRANDT and L. LASZT (Biochem. Z., 1933, **259**, 398—417).—Galactose is most quickly and glucose, fructose, mannose, xylose, and arabinose with decreasing velocity absorbed from the rat's small intestine. Absorption of glucose but not of xylose is accelerated by PO_4''' and it is suggested that phosphorylation precedes absorption. Under the action of $CH_2I{\cdot}CO_2H$ absorption of hexoses is, but of pentoses is not, inhibited. Phosphorylation of glucose in presence of intestinal mucosa extract is inhibited by $CH_2I{\cdot}CO_2H$ but is unaffected by NaF, NaCN, and urethane. The action of $CH_2I{\cdot}CO_2H$ is a direct action on the absorption of sugar and is not brought about indirectly by increasing blood-sugar. Increased hexose phosphate content in the intestinal wall during absorption of glucose could not be detected. P. W. C.

Physiology of the surviving mammalian heart. VII. Consumption of sugars by the cat's heart. R. VON POMÓTHY (Biochem. Z., 1933, **260**, 192—200; cf. A., 1929, 467).—Results of previous workers concerning the glucose consumption (I) of the surviving heart are confirmed. Mannose, fructose, and galactose are consumed to the extent of

two thirds, one fifth, and one sixth of (I), respectively, whilst lactose and maltose are not consumed. W. McC.

Metabolism of silkworms. II. Methylglyoxal as an intermediate product in the carbohydrate metabolism of *Bombix mori*, L. A. SMOLIN (Biochem. Z., 1933, **260**, 34—38; cf. A., 1932, 638).—Pulped silkworms (deprived of intestines and of contents of the digestive system), extracts of such worms and pupæ produce AcCHO from Na hexose diphosphate. W. McC.

Sexual variation in carbohydrate metabolism. II. Acetoacetic acid in fasting rats and guinea-pigs. J. S. BUTTS and H. J. DEUEL, jun. (J. Biol. Chem., 1933, **100**, 415—428).—No sexual variation in the excretion of ketonic substances (I) is observed with fasting rats. Doses of Na acetoacetate which were toxic for female rats had no deleterious effects on males; with a daily dose of 1·5 mg. per sq. cm. body-surface the excretion of (I) in females is > in males. The same is true for guinea-pigs. The ketosis is reduced by feeding carbohydrate. H. D.

Intervention of liver in fixation and synthesis of peptides. R. MARTENS (Bull. Soc. Chim. biol., 1933, **15**, 369—378).—Administration to a dog of 5 g. of peptone (I) per kg. body-wt. is followed after 25—30 min. by an increase in portal blood-polypeptide-N (II) from 4·57 to 5·20 mg. per 100 c.c. in the portal vein, whilst no change is observed in the peripheral veins. With man an increase in (II) occurs after 1 hr., and (II) becomes const. after 2 hr. In dogs injected with ThO_2 or with ligatured bile-ducts a similar increase in (II) occurs 30 min. after absorption of (I). Men suffering from hepatic lesions show the same effect 90 min. after injection of (I). The subsequent increases of (II) observed are due to the synthetic action of the liver which is unimpaired by the lesions. H. D.

Dependence of the structure of tissue-proteins on the metabolism of the organs. I. E. G. SCHENCK and H. WOLLSCHITT (Arch. exp. Path. Pharm., 1933, **170**, 151—165).—The amounts of free and combined tryptophan (I) in various tissues (liver, kidney, muscle, heart) and body-fluids of rats depend on the state of the organism. Thus variations occur with differences in diet. The utilisation of orally administered (I) also depends on the condition and diet of the animal. Inclusion of protein in the diet produces formation of body-protein, and differentiation between exogenous and endogenous protein metabolism no longer holds. Plasma-proteins are probably derived from organ-proteins. F. O. H.

Cow's milk or human milk? W. SCHARFNAGEL (Süddeut. Apoth-Ztg., 1932, **72**, 379; Chem. Zentr., 1933, i, 79).—The advantage of mother's milk in the nutrition of infants is attributed to sp. protein groups and particularly to the diastase content. The saliva of new-born infants contains little diastase. A. A. E.

Creatinuria and muscular contraction. L. HÉDON (Bull. Soc. Chim. biol., 1933, **15**, 407—409).

Nitrogen metabolism after blood transfusion. W. KI (Tôhoku J. Exp. Med., 1932, **20**, 123—147). CH. ABS.

Growth retardation by the partly oxidised sulphydryl of cysteine. F. S. HAMMETT (Science, 1933, **77**, 190—191).—A partly oxidised S derivative of cysteine retards the growth of *Hydra hydranths* and the embryonic development of *Crepidula* eggs and larvæ. This establishes the postulate that growth by increase in cell no. is regulated by the naturally-occurring chemical equilibrium between SH and its partly oxidised derivatives. L. S. T.

Variations in the growth-accelerating power of chicken embryo juice on cultivated tissues *in vitro*. J. SHIMIZU (Japan. Z. Mikrobiol. Path., 1932, **26**, 1174—1182).—The juice is inactive after 24 days at 0°, 10 days at room temp., or 48 hr. at 37°. CH. ABS.

Effects of various organ preparations on the growth of tissue *in vitro*. I, II. M. OMMYOJI (Japan. Z. Mikrobiol. Path., 1932, **26**, 999—1014, 1183—1194).—I. Thyroid, parathyroid, ovary, pituitary, testes, and prostate preps. accelerate the growth of fibroblasts of chick embryo in dil., and inhibit it in conc., solutions.

II. Corpus luteum, lung, spleen, kidney parenchyma, and pancreas extracts accelerate the growth in dil., but these, except lung and liver parenchyma, inhibit it in conc., solutions. CH. ABS.

Law of maximum normal nutritive value [of foodstuffs]. E. B. FORBES (Science, 1933, **77**, 306—307). L. S. T.

Digestibility of foodstuffs. H. MOSER (Z. Unters. Lebensm., 1933, **65**, 257—274).—Curves are given relating the p_H with (1) the Hirsch buffer val. (θ), and (2) the sp. digestibility ($s=\theta$/calorific val. per g.) for the digestive juices and milks of various animals, and for egg, cheese, wines, fruits, and carbohydrate foods. An attempt is made to deduce from these curves the digestibility of the various foods in the presence of digestive juices. Ox bile shows a more rapid change in θ with p_H than human saliva or canine gastric juice, and wheat bread a greater change in s with p_H than the other carbohydrate foods. Between p_H 2 and 3 there is a rapid rise in θ and s, for human milk, which is absent from cow or goat milk. J. G.

Effect of diet on egg composition. I. Partial chemical analyses of eggs produced by pullets on different diets. H. W. TITUS, T. C. BYERLY, and N. R. ELLIS (J. Nutrition, 1933, **6**, 127—138).—The composition of yolks was influenced > that of the whites by dietary differences. A. G. P.

Mineral and nitrogen metabolism of hens receiving varied diets. W. SCHMIDT (Arch. Tierernahr. Tierzucht, 1932, **7**, 436—464).—Comparison of artificially adjusted physiologically-acid and -alkaline diets showed the former to favour Ca and P retention and the utilisation of ingested minerals. Max. mineral retention by laying hens was produced by addition of $CaCO_3$ to physiologically acid, or $CaCl_2$ to alkaline, diets. The Ca : P ratio of the ration had no direct influence on the ratio Ca : P retained. Low physiological acidity in the diet caused greater retention of minerals than high acidity or alkalinity. A. G. P.

Lime and phosphoric acid requirement for chicks. R. M. SHERWOOD (Texas Agric. Exp. Sta. Bull., 1932, No. 462, 14 pp.).—Data for chicks of various ages are recorded and discussed in comparison with other workers' results. A. G. P.

Suitability of the mineral composition of young meadow grass and stall rations, especially for milch cows. B. SJOLLEMA (Landbowk. Tijdschr., 1931, **43**, 793; Bied. Zentr., 1932, **3**, **A**, 106).—The Ca balance of cows was, in general, negative during winter, remaining so in the grazing season as a result of increased milk production and becoming positive only in late summer. Young grass contains a relative excess of K and N and insufficient Na for a normal ration. During stall feeding, negative Na and Cl balances occur. Mg and S supplied in grass and stall feeds are normally sufficient. Heavy manuring of grassland with N and K may produce grass of very unsuitable composition. More rational manuring increases the growth of clovers and improves the mineral composition of the herbage. A. G. P.

Nutritive value of high and low calcium-carrying wheat. E. O. GREAVES and J. E. GREAVES (J. Nutrition, 1933, **6**, 113—125).—In rats receiving rations consisting of 90% wheat the % of total ash, Ca and P in the bones and the Ca and P of serum was higher in all cases where high-Ca wheat was used. A. G. P.

Nutritive value of various types of phosphoric acids. K. TAKAHASHI (J. Agric. Chem. Soc. Japan, 1932, **8**, 515—518).—No growth (of rats) took place with H_3PO_2 in absence of H_3PO_4; with the other PO_4-acids normal growth was observed. CH. ABS.

Influence of iodine feeding on the development of ewes and lambs and on the yield and quality of wool. E. VÉGHELYI (Mezogaz. Kutatasok, 1931, **4**, 349; Bied. Zentr., 1932, **3**, **A**, 105).—Rations supplemented with 2% of $CaCO_3$ containing 0·15% KI produced greater live-wt. increases in ewes and lambs and also raised the yield and I content of wool. The quality of the wool was not affected. The yield and I content of the ewes' milk were increased. A. G. P.

Is fluorine an indispensable element in the diet? G. R. SHARPLES and E. V. MCCOLLUM (J. Nutrition, 1933, **6**, 163—178).—Determination of F is based on its bleaching action on the yellow colour produced by treatment of Ti compounds with H_2O_2. The F content of teeth and bones in rats increases (within certain limits) with age and varies with the diet. Young rats contain very little F. A low-F diet does not affect growth or reproduction, nor produce any change in the Ca : P ratio of bones. A. G. P.

[Pharmacology of] *Ammi Visnaga*. K. SAMAAN (Quart. J. Pharm., 1933, **6**, 13—22; cf. A., 1931, 885).—A study of visnagan. W. S.

Experimental variation of the toxicity of *Digitalis*. II. Combination of *Digitalis* with purine derivatives. R. KOHN and B. C. COSTOPANAGIOTIS (Arch. exp. Path. Pharm., 1933, **170**, 226—238; cf. this vol., 422).—The min. lethal dose to cats of a *Digitalis* prep. was increased by 20—30% by simultaneous administration of caffeine (I) and decreased 20—40% by that of theobromine or theophylline (II). The action of (I) could not be eliminated or reversed by admixture with (II). The effects are probably due to changes in the circulation and in cell-permeability. F. O. H.

Effect of strong ultra-violet irradiation on the toxicity of pure nicotine. G. WAKEHAM and C. B. JOHNSTON (J. Amer. Chem. Soc., 1933, **55**, 1601—1604; cf. A., 1932, 540).—Intense irradiation, even for long periods, does not destroy the toxicity. The observation (*loc. cit.*) that the partial detoxication obtained by controlled irradiation is restored by over-irradiation is confirmed. H. B.

Pharmacology of "atebrin." G. HECHT (Arch. exp. Path. Pharm., 1933, **170**, 328—338).—Small doses of "atebrin" (I) (an alkylated diaminoacridine used in malaria) produce a local cell irritation and some disturbance of the central nervous system. Larger doses paralyse the intestine and affect the higher nervous centres leading to respiratory failure and death. Elimination of (I) from the body is very slow, little being excreted in the fæces. A part appears in the bile and is re-absorbed in the intestine. F. O. H.

Excretion of "atebrin" in urine and fæces. C. TROPP and W. WEISE (Arch. exp. Path. Pharm., 1933, **170**, 339—346).—"Atebrin" (cf. preceding abstract) is excreted unchanged in the urine and fæces (of man) in approx. equal amounts. Following administration, the excretion is rapid for a short period and then rapidly falls to a low level, at which it remains for a comparatively long period. The total amount excreted is only a fraction of that injected. F. O. H.

Pharmacological application of azoxy-compounds. G. CARRARA (Annali Chim. Appl., 1933, **23**, 140—144).—Acetamidoazoxytoluene (Erba-azoform) is superior in cicatrising action to diacetamidoazotoluene. T. H. P.

Comparative pharmacology of some condensation products of phenols with aliphatic aldehydes. D. I. MACHT and W. C. HARDEN (J. Pharm. Exp. Ther., 1933, **47**, 377—390).—The actions of compounds of the series $CHR(p\text{-}C_6H_4\cdot OH)_2$, $CHR(3:4\text{-}C_6H_3Me\cdot OH)_2$, and $CHR[2:4\text{-}C_6H_3(OH)_2]_2$ (R=Me, Et, Pr, Bu, n-C_5H_{11}, n-C_6H_{13}, and n-C_7H_{15}) have been investigated on *Lupinus albus* seedlings, *Staphylococcus aureus*, *Carassius auratus* (toxic effect), cats (blood-pressure and respiration), and rabbits (kidney function). The order of activity is peculiar for each test and for each of the three series of compounds, so that no positive generalisation as to the relation between chemotherapeutic effect and pharmacological action can be found. W. O. K.

Influence of sympathetic poisons and narcotics on muscle metabolism. O. RIESSER and K. YAMADA (Arch. exp. Path. Pharm., 1933, **170**, 208—225).—Continuous intravenous injection of acetylcholine (I) into normal rabbits produces changes in the muscle-glycogen (II), -phosphagen (III), and -lactic acid (IV) closely resembling those due to adrenaline (V). That the effect is not due to (V) is shown by the same changes occurring when (I) is injected into ergotaminised rabbits. With nephrectomised rabbits, (I) produces a marked rise in (II), a

slight rise in (III), and a fall in (IV). Atropine produces a rise in (II), (III), and (IV), a result due to a process more complicated than that of sympathetic stimulation. Aq. $MgSO_4$ produces a rise in (II) and (III) and a marked fall in (IV). Urethane has a similar action, whilst with veronal (II) is unchanged, (III) is increased, and (IV) is decreased. The mechanism of these changes is discussed. F. O. H.

Action of quaternary ammonium salts on nerve. S. L. Cowan (Nature, 1933, **131**, 658).—Quaternary NH_4 salts have a curare-like action in preventing transmission of excitation from nerve to muscle. They do not affect muscle or medullated nerve directly in the concn. required for paralysis (cf. this vol., 527). L. S. T.

Excretion of morphine by normal and tolerant dogs. W. A. Wolff, C. Riegel, and E. G. Fry (J. Pharm. Exp. Ther., 1933, **47**, 391—410).—Both in normal dogs and in dogs tolerant to morphine, about 17—20% of the morphine injected (2—200 mg.) is excreted, approx. $\frac{2}{3}$ in the urine, and $\frac{1}{3}$ in the fæces. No significant difference could be detected in the rates of excretion by the two types of animals. W. O. K.

Pharmacology of cocaine. II. Fate in the animal body. H. A. Oelkers and W. Raetz. **III. Action in the organism.** H. A. Oelkers (Arch. exp. Path. Pharm., 1933, **170**, 246—264, 265—270).—II. Cocaine (I) injected into rabbits, guinea-pigs, and dogs is excreted in the urine only to the extent of approx. 1% (cf. A., 1913, i, 1135; 1925, i, 736) and not at all in the fæces. The level of (I) in the blood reaches a max. in 10—15 min. after subcutaneous injection and then falls so that only traces are detectable after 1 hr. (I) also appears rapidly in the organs, the brain having a max. val. (equal to that of the blood) in 15—25 min., whilst (I) is also found in the liver, kidney, and muscles within 48 hr. of injection. The decomp. of (I) *in vivo* appears to be chemical rather than enzymic. Polarised light does not decompose (I) (cf. A., 1930, 111).

III. The influence of heavy dosage of (I) on metabolism appears not to depend to any appreciable extent on its action on enzymes. Thus (I) has practically no action *in vitro* on pepsin, trypsin, erepsin, cathepsin, pig's liver-esterase, or pancreatic diastase. Potato-tyrosinase, however, is accelerated, whilst soya-bean urease, serum-lipase, and the reducing action of frog's muscle are inhibited. Damage of the liver- and kidney-tissues occurs. F. O. H.

Determination of percaine in urine. K. O. Möller (Biochem. Z., 1933, **259**, 458—464).—Pptn. reactions of percaine, the results of its electrometric titration, and methods for its determination in H_2O and urine are given. The formation of a ppt. with Reinecke's salt which after recrystallisation from EtOH had m.p. 120° is regarded as characteristic. P. W. C.

Factors influencing the susceptibility of albino rats to injections of sodium amytal. D. H. Barron (Science, 1933, **77**, 372—373).—The sex difference in the reaction to Na amytal is confirmed. The resistance to the drug appears to be related to the H_2O metabolism and in the adult rat the testes seem to influence the H_2O metabolism control. Injection of Ringer's solution into the blood reduces the effectiveness of the drug. L. S. T.

Relation between the speed of passage of local anæsthetics through lipin membranes and their anæsthetic value. J. Sivadjian (J. Pharm. Chim., [viii], **17**, 361—365).—The hydrochlorides of local anæsthetics of the quinoline and piperazine series (cf. A., 1930, 1597) dissolved in aq. NaOAc have been dialysed through an oil–collodion membrane. The quantity of base which passes through is related to the local anæsthetic activity, especially in the quinoline series, but there is not, in general, complete parallelism. The experiments broadly confirm the lipin-solubility theory of anæsthetics. W. O. K.

Maximal limits of alcohol consumption. E. M. P. Widmark (Biochem. Z., 1933, **259**, 285—293).—Assuming that the lethal concn. of EtOH in blood is 0·5%, a table shows the mean calc. lethal doses for persons of both sexes of varying body-wt. and gives some indication of normal variation. The results agree fairly well with clinical observations. The max. consumption of EtOH per day in a 70-kg. man is 170 g. and of MeOH 34 g. There is no evidence to support the view that the max. consumption is different in people who habitually drink from that of people who abstain from drinking EtOH. P. W. C.

Effect of muscular exercise on the metabolism of ethyl alcohol. T. M. Carpenter (J. Nutrition, 1933, **6**, 205—224).—A review. A. G. P.

Uptake of ethyl alcohol by the isolated tortoise's heart. J. Robertson and A. J. Clark (Biochem. J., 1933, **27**, 83—85).—The amounts of EtOH taken up by the isolated heart of *Testudo graeca* from perfusion liquids containing 0·35—3·5% of EtOH were determined. With these concns. no arrest of the heart occurred and both the taking up and release (by washing out) of EtOH were rapid. The results indicate that the uptake of EtOH does not depend on differential solubility, but is due to adsorption on surfaces in the heart-cells. F. O. H.

Co-existence in barley radicles of substances producing hyperglycæmia and hypoglycæmia. E. Donard and H. Labbé (Compt. rend., 1933, **196**, 1047—1050).—Fermentation of an extract of the radicles which has a hyperglycæmic action on rabbits yields an EtOH-sol. fraction which causes a hyperglycæmia of 36% in doses of 0·07 g. per kg., and is identified as mannitol. The fraction insol. in 95% EtOH causes a hypoglycæmia of 37·9% in doses of 0·065 g. per kg. A second hyperglycæmia-producing substance, probably hordenine, was isolated. A. C.

Dependence of cytoplasmic structures in the egg of the sea-urchin on the ionic balance of the environment. A. R. Moore (J. Cell. Comp. Physiol., 1932, **2**, 41—51).—The hyaline layer of the egg acts as an ion–protein compound and cannot be maintained intact by $Ca^{\cdot\cdot}$ in acid solutions. The structural elements of the cytoplasm are maintained by alkali or alkaline-earth cations even under acid conditions and under alkaline conditions are unimpaired in the absence of these ions. The membrane system is stable

in acid conditions in the absence of inorg. cations and is destroyed by alkalinity unless inorg. cations are present in the surrounding solution. In this and similar biological systems alkali and alkaline-earth cations act additively and $Ca^{\cdot\cdot}$ is approx. 100 times as effective as $Na^{\cdot}$ in this respect. A. G. P.

Intracellular hydrogen-ion concentration studies. IX. p_H of the sea-urchin egg. C. G. PANDIT and R. CHAMBERS (J. Cell. Comp. Physiol., 1932, **2**, 243—249).—The normal cytoplasmic p_H is $6{\cdot}8\pm0{\cdot}2$ and that of injured tissues $5{\cdot}3\pm0{\cdot}2$. Development of the same p_H outside the egg occurs prior to visible signs of cytolysis within the egg. A. G. P.

Permeability of the *Arbacia* egg to ethylene glycol at different temperatures. D. R. STEWART and M. H. JACOBS (J. Cell. Comp. Physiol., 1932, **2**, 275—283).—Data covering a temp. range of 5—32° are given. A. G. P.

Permeability of human skin to electrolytes. A. G. R. WHITEHOUSE and H. RAMAGE (Proc. Roy. Soc., 1933, **B**, **113**, 42—48).—Immersion of the arm in aq. LiCl or KI is not followed by any increase in the Li or I content of the urine or blood. Intact skin is therefore impermeable to dissolved electrolytes. The skin absorbs I from I ointment. A. C.

Increase in blood-lactic acid due to undercooling. E. GEIGER (Arch. exp. Path. Pharm., 1933, **170**, 296—302).—Exposure of rabbits to cold produces a marked increase in the blood-lactic acid, the effect being greatly diminished by splanchnicotomy. This increase, together with the hyperglycæmia resulting from subnormal temp., is therefore due to an increased liberation of adrenaline. F. O. H.

Chromatic inclusions in the cytoplasm of cells after gamma radiation, and changes in the nucleolus. J. C. MOTTRAM (J. Roy. Micros. Soc., 1933, **53**, 28—34).—The chromatic, cytoplasmic inclusions observed in cells following irradiation are nucleolar extrusions, supporting the view that chromatin is formed in the nucleolus. H. G. R.

Detoxication of copper and zinc by complex-formation. F. EICHHOLTZ and A. BIRCH-HIRSCHFELD (Arch. exp. Path. Pharm., 1933, **170**, 271—284).—Of 71 org. and inorg. substances capable of forming complexes with heavy metals, 35 significantly decreased the toxicity of Cu towards the isolated frog's heart, whilst of 34 substances of this type, only 4 decreased the toxicity of Zn. F. O. H.

Milk-, mucilage-, and fat-prophylaxis in lead poisoning. F. WEYRAUCH and A. NECKE (Z. Hyg., 1933, **114**, 629—636).—In dogs receiving 100 mg. Pb (as white lead) per kg. live wt., simultaneous administration of milk or mucilage had no effect on the resorption of Pb. The latter was markedly increased by administration of fats. A. G. P.

Quinones as enzyme models. IX. CO_2/NH_3 quotient in anaerobic amino-acid deamination. B. KISCH and S. STUTZKE (Biochem. Z., 1933, **259**, 455—457).—Whereas in the oxidative deamination of glycine and serine in presence of pyrocatechol, hydroxyquinol, adrenaline, gallic acid, or resorcinol (this vol., 313), CO_2 and NH_3 are eliminated in the ratio of 1 : 1, no decarboxylation occurs when the reaction is carried out anaerobically with dinitrobenzene or nitroanthraquinone as H acceptor. P. W. C.

Molecular weight of new oxidation enzyme. T. SVEDBERG and I. B. ERIKSSON (Naturwiss., 1933, **21**, 330).—Observations made by means of the ultracentrifuge of the rate of sedimentation and of the sedimentation equilibrium of two specimens of Warburg's oxidation enzyme indicate that, although not homogeneous in size, the particles have a mean mol. wt. of about 60,000. The purer sample gave N=2·9%, whilst the sp. vol. in solution was 0·655, so that the colloidal material is probably not protein. W. O. K.

Peroxidase from fruit of *Tribulus terrestris*, Linn. N. GHATAK and K. V. GIRI (Bull. Acad. Sci. Allahabad, 1933, **2**, 171—178).—Details of the prep. of the enzyme are given. The optimum conditions for its action are: p_H 5·3—5·5, 1·5 vol.-% H_2O_2, temp. 15—20°. Above 60° the activity falls rapidly; the enzyme is more labile at an acid p_H. P. G. M.

Chain character of catalase action. G. M. SCHWAB, B. ROSENFELD, and L. RUDOLPH (Ber., 1933, **66**, [*B*], 661—664).—The restrictive effect of mannitol, *p*- and *m*- (I) $C_6H_4(OH)_2$, PhCHO (II), $Pr^{\beta}OH$, $CH_2Ph{\cdot}OH$ (III), and stilbene on the action of liver-catalase on H_2O_2 has been examined. The order of activity is the same as that observed in the photolysis of H_2O_2, in which, however, the effect of (III) is more pronounced. The behaviour of (I) and (II) differs greatly from that observed in the photo-polymerisation of vinyl acetate or autoxidation of SO_3''. It cannot be considered that the restricting agent affects an identical chain carrier in the different reactions. The course of the chain reaction, if existent, is regarded as sp. and due to the mechanism of its causation. H. W.

Toxic action of sodium nitrite on catalase of ox blood. O. T. ROTINI and F. SNASSEL (Fermentforsch., 1933, **13**, 499—504).—The temp. coeffs. of the catalase (I) action of 1% aq. blood in presence of added H_2O_2 for temp. of 5—25° give a heat of activity (II) of 7220 ± 520 g.-cal. $NaNO_2$ in concns. of $< 2\%$ has an inhibitory action, which, however, is not proportional to the concn.; concns. $> 2\%$ totally inhibit the action of (I). The vals. for (II) and for the velocity of reaction, especially for temp. $< 15°$, indicate that $NaNO_2$ has a dual action. F. O. H.

Inactivation of amylase by heat. A. OPARIN and S. MANSKAJA (Biochem. Z., 1933, **260**, 170—179; cf. this vol., 187).—The resistance (I) of malt amylase to inactivation by heat (100°) is increased by sucrose and, to a smaller extent, by glycerol, being directly proportional to the concn. of the protective substances (II) and inversely proportional to the duration of heating. (II) increase the resistance (III) of proteins to coagulation by heat and factors {change in [H], duration of heating, concn. of (II)} which increase or diminish (III) also increase or diminish (I) in parallel. Part of the activity of the amylase lost on heating in presence of high concn. of (II) is restored by treatment with peptone. W. McC.

Amylosynthease. III. T. MINAGAWA (Proc. Imp. Acad. Tokyo, 1933, **9**, 97—100).—Polished rice is powdered, macerated with 3—4 pts. H_2O, and filtered. Addition of 0·01*M*-$CdCl_2$ ppts. amylosynthease and leaves amylase in solution. The $CdCl_2$ ppt. is suspended in H_2O and $(NH_4)_2SO_4$ added to saturation; an active ppt. of the enzyme remains suspended. Starches, which resemble natural sol. starch, can be obtained by polymerisation of dextrin or glycogen which has been treated with HCl. Trypsin and amylosynthease are antagonistic, but can be separated by fractional pptn. with $(NH_4)_2SO_4$. The optimum temp. for amylosynthease is 20—25°; it is destroyed by heating at 50° for 10 min. P. G. M.

Amylosynthease. II, IV—VII. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1932, **8**, 508—510, 811—814, 914—916, 1068—1069, 1310—1312).—II. An aq. extract of the residue of brewer's yeast after removal of amylase with glycerol affords on saturation with $(NH_4)_2SO_4$ a ppt. which gives a strong amylosynthease reaction. The enzyme is destroyed by $COMe_2$ and EtOH.

IV. Amylosynthease was separated from pressed and dried yeast. Nishimura's amylopectinase may be a mixture of amylase and amylosynthease. Achroodextrin, erythrodextrin, sol. rice starch, and hexahexosan give a bluish-violet colour with I–KI after treatment for 1 day with amylosynthease free from amylase.

V. 2 mols. of trihexosan were polymerised by yeast-amylosynthease at p_H 6·2.

VI. Amylosynthease can be separated from amylase by pptn. with $Pb(OAc)_2$ and decomp. of the ppt. with CO_2.

VII. Yeast-amylosynthease is adsorbed by Ca or Al phosphate, $Al(OH)_3$, kaolin, or active C, and removed by elution. Yeast extract with 24—25% $(NH_4)_2SO_4$ ppts. amylase; saturation of the filtrate with $(NH_4)_2SO_4$ then ppts. amylosynthease.

CH. ABS.

Koji diastase. M. ITO (J. Fac. Agric. Hokkaido, 1932, **30**, No. 5, 243—386).—The (non-colloidal) enzyme appears to consist of an active group, a polypeptide, a complex carbohydrate, and 5—12% of ash. Removal of Mg and PO_4 inactivates it; it is not inactivated at 100° or when heated for a short time at 130°. Various synthetic mixtures had some hydrolysing action on starch. CH. ABS.

Emulsin. XI. B. HELFERICH and O. LANG (Z. physiol. Chem., 1933, **216**, 123—126; cf. this vol., 379).—3-*Methyl*(*phenyl*-β-d-*glucoside*), m.p. 148·5—150° (corr.) [2-*monoacetate*, m.p. 154—155° (corr.); *triacetate*, m.p. 144—145° (corr.)], was not hydrolysed by emulsin. J. H. B.

Glyoxalase. II. p_H-activity curve with phenylglyoxal and the effect of glutathione. J. O. GIRŠAVIČIUS (Biochem. J., 1933, **27**, 537—542).—The optimum reaction, with phenylglyoxal as substrate, is at p_H 6·4—6·5. About 0·1% of reduced glutathione is required for full activation of glyoxalase (I). Rapid inactivation of (I) after a lag period is caused by O_2. A similar lag, with subsequent rapid inactivation, independent of O_2, characterises antiglyoxalase action.

H. G. R.

Enzymic ester synthesis in emulsions. W. FABISCH (Biochem. Z., 1933, **259**, 420—431).—Cetyl alcohol, C_5H_{11}·OH, and glycerol can be esterified with oleic, palmitic, and stearic acids in aq. emulsions in presence of Na oleate or deoxycholate by ammoniacal extracts of pig's pancreas. In the early stages of synthesis, the time, amount of enzyme, and extent of reaction are proportional. The velocity of synthesis is always greater using deoxycholate than oleate as emulsifier. Increasing the amount of emulsifier increases the velocity within certain limits. The activity–p_s curves for the synthesis of amyl oleate are given. H_2O did not influence the esterification of cetyl and amyl alcohols, but with glycerol and oleic acid it accelerated up to 7% and then inhibited.

P. W. C.

Enzymic hydrolysis of phosphatides. II. Lysolecithin. E. J. KING and M. DOLAN (Biochem. J., 1933, **27**, 403—409).—Lysolecithin (I) was prepared by the direct action of the venom of *Bothrops atrox* on egg-yolk by the method of Levene, Rolf, and Sims (A., 1924, vi, 438). Separation from lysokephalin was attained by dissolution of the crude product in glacial AcOH and fractional pptn. with Et_2O and $COMe_2$. 22 g. of original material yielded 16·7 g. of (I). The hæmolytic action of (I) was studied. The inorg. PO_4''' liberated by an aq. extract of rabbit intestinal mucosa (II) is a max. at p_H 7·8. In 48 hr. (I) is hydrolysed to twice as great an extent as lecithin (III) by (II) at a slightly lower optimum p_H, whilst the enzyme from a bone extract, more than twice as active as (II) with regard to glycerophosphate hydrolysis, scarcely attacks (III), but attacks (I) to a considerable extent. H. D.

Phosphatase in bovine kidneys. I—III. M. MORI (Arb. III Abt. anat. Inst. Univ. Kyoto, 1932, **C**, No. 3, 52—58, 68—72, 73—78).—I. Extraction of phosphatase from the cortical tissue is described.

II. The hydrolytic power of phosphatase obtained by autolysis of kidney tissue generally diminishes in the order: Ca sucrose phosphate, Ca salts of fructose 6-mono-, diethylpyro-, α-glycero-phosphoric esters. The enzyme is inactivated by dialysis.

III. *X*-Rays do not affect phosphatase.

CH. ABS.

Ortho- and pyro-phosphatase of bone and cartilage. III. Effect of arsenic and fluorine salts on bone-phosphatase. T. YAMANE (Arb. III Abt. anat. Inst. Univ. Kyoto, 1932, **C**, No. 3, 35—45).—K_3AsO_4 increases the effect of bone-phosphatase on fructose 6-mono-, glucose 6-mono-, and diethylpyrophosphate, but inhibits that on sucrose phosphate. The action on Et_2HPO_4 is unaffected. NaF increases the action of phosphatase in all cases. CH. ABS.

Phosphatase of body organs. I. Effect of manganese salts on the phosphatase of the kidney, digestive organs, and digestive juices. I. HORI, M. MORI, M. MORIMURA, and S. TOMIKAWA (Arb. III Abt. anat. Inst. Univ. Kyoto, 1932, **C**, No. 3, 7—29).—Fission of Ca fructose 6-monophosphate by phosphatase is retarded by Mn acetate, chloride, or nitrate; small quantities have, however, little effect on kidney-phosphatase. With sucrose phosphate

the action of the enzyme is inhibited by Mn salts. Rabbits' saliva contains no phosphatase; extracts of the salivary glands have strong enzymic activity towards ortho- and pyro-phosphoric esters. Dog's pancreas extract and pancreatin contain esterophosphatase; extract of rabbit's pancreas, dog's pancreatic juice, and rabbit's bile are inactive. Extracts and secretions of intestinal mucosa of the rabbit are strongly phospholytic. Organ extracts and secretions of the fœtus behave similarly to those of the human adult. The phosphatase is localised chiefly in the renal cortex. CH. ABS.

Protein-synthesising enzyme in spleen. S. G. HEDIN (Z. physiol. Chem., 1933, **216**, 203—204; cf. A., 1932, 777).—Previous results are amplified. J. H. B.

Specific production of protective enzymes by means of serum-globulin and -albumin and iodised and nitrated proteins. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1933, **13**, 505—543).—Parenteral administration of fibrin-, eu- and pseudo-globulin (I), and of serum-albumin (II) (from oxen and horses) into dogs and rabbits produces in each case the corresponding protective proteolytic enzyme (III), which is sp. not only for the type of protein, but also for its origin. This is true also for iodised or nitrated (I) and (II), the original protein not being degraded by the (III) arising from the corresponding I- or NO_2-derivative. Pepsin and trypsin-kinase hydrolyse (I) and (II) and, less readily, their I- and NO_2-derivatives. (II) is more readily hydrolysed by pepsin than (I), whilst the reverse is true for their I-derivatives. The application of the results to immunisation and to the characterisation of proteins of the same type but of different origin is discussed. F. O. H.

New syntheses and enzyme studies relating to proteins. M. BERGMANN (Klin. Woch., 1932, **11**, 1569—1572; Chem. Zentr., 1933, i, 239—240).—A lecture. A. A. E.

Activation of papain by cyanide. I. D. R. P. MURRAY (Biochem. J., 1933, **27**, 543—556).—The action of HCN (I) is not due to the removal of traces of toxic heavy metals (II) (cf. A., 1930, 957). The effect of (II) is a function of the substrate and p_H, whereas (I) is lost on storage and varies with the method of prep. The activation by citrate is additive to (I) and extends the zone of p_H activity in both directions. H. G. R.

Complex nature of "crystalline pepsin." E. WALDSCHMIDT-LEITZ and E. KOFRANYI (Naturwiss., 1933, **21**, 206—207).—The authors question the claim that Northrop's "cryst. pepsin" (A., 1932, 1166) is identical with the pure enzyme. The activity of the cryst. prep. may be adsorbed (94%) on cantaloupe-seed globulin, leaving a solution of the inactive protein component of the prep. The bearing of this result on the alleged protein nature of other enzymes is indicated. A. C.

Benzoic acid as preservative for foodstuffs. W. LIESE (Chem.-Ztg., 1933, **57**, 315).—BzOH has no sp. effect on the arrest of digestion of albumin by pepsin; 0·05% had no action, and 0·2% had only slightly greater inhibiting action than 0·4% NaCl solution (cf. A., 1932, 91). E. H. S.

Liver-proteinases and -polypeptidases. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1933, **13**, 544—562).—Preps. containing proteinases (I) and polypeptidases were obtained from liver press-juice and from autolysed liver. (I) have optima at p_H 3 and 7, that at 7 being probably due to peptones which are attacked only at that reaction. Autolysis of liver suspensions buffered at p_H 3·8 or 8·4 is accompanied by degradation of the tissue proteins by (I), whilst the presence of a carboxypolypeptidase (II) is shown by the hydrolysis of added sarcosyltyrosine and leucylglycyltyrosine; hydrolysis by aminopolypeptidases (III) or acylases (IV) does not occur. With autolysis in non-buffered media, (II) and (III) are active, whilst in buffered media at p_H 7 the activity of (III) and (IV) after 46 hr. is > that of (II). The (II) of liver autolysates, unlike that of trypsin preps., hydrolyses glycyl-*l*-tyrosine. With autolysis at p_H 8·4 the action of (IV) is evident before that of (III). Prolonged autolysis produces an increased activity of (I) and (IV). (I) are sp. in their action on the cell proteins. Chloroacetyl-*l*-alanine and -*o*-nitroaniline require different enzymes for their hydrolysis. Autolysis in acid media, especially at p_H 3·8, is more prolonged than that in neutral or alkaline media. F. O. H.

Nature of proteases. XII. Changes in viscosity of muscle-protein and collagen solutions during peptic digestion. I. A. SMORODINCEV and A. N. ADOVA (Fermentforsch., 1933, **13**, 563—572).—The viscosity (I) of muscle fibrils is unchanged by peptic digestion (II) for 24 hr., whilst that of collagen is increased 65—80%. This difference can be applied to the characterisation of tissues. The optimum conditions for (II) and for max. changes in (I) are determined. F. O. H.

Catheptic proteinase. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, **216**, 141—150).—In "zookinase-free" preps. from animal liver, spleen, and kidney, a part of the catheptic proteinase (up to 15%) is in the fully activated condition. The rest requires activation; part of this inactive material is activated in the minced organ by the thiol compounds present in the fresh pulp but absent from the extracted dried prep. Fresh extract is somewhat more active than dried tissue extract. These results are not in agreement with those of Waldschmidt-Leitz and others (A., 1930, 1217). J. H. B.

Action of iodoacetic acid on the proteases of tissue, on malignant tumour cells, and on cell-free extracts. D. MICHLIN and W. RUBEL (Biochem. Z., 1933, **260**, 121—128).—At p_H 4 (but not at p_H 7·4) the action of proteases (from kidney, liver, tumours, and in extracts of healthy and diseased tissue) on the digestion of gelatin is reduced or inhibited by 0·001*N*-$CH_2I{\cdot}CO_2H$. Probably the acid acts on the natural activator. W. McC.

Development of uricase in tadpoles of *Rana temporaria*. R. TRUSZKOWSKI and H. CZUPERSKI (Biochem. J., 1933, **27**, 66—68).—Uricase (A., 1930, 1476) is absent from the eggs, first appears on the fifteenth day of development, and remains practically const. from the nineteenth to the forty-sixth day, when it again abruptly rises. The first period of

activity is probably due to the formation of hepatic uricase, and the second to development of the mesonephros. F. O. H.

Urease. V. Oligodynamic action of some non-alkali metals of the first group on urease. A. RUCHELMANN (Biochem. Z., 1933, **259**, 358—364).—Tables show the effect of additions of powdered Cu, Cu_2O, CuO, and colloidal Au and Ag_2O on the kinetics of the urea–urease system under varying conditions. The activity of these compounds decreases in the order Cu_2O, Cu, CuO. Colloidal Au inhibits in the absence, but activates in the presence, of buffer. P. W. C.

Formation of thiocyanate in the animal body. K. LANG (Biochem. Z., 1933, **259**, 243—256).—Formation of thiocyanate from HCN and S or readily hydrolysable S compounds in the animal body is catalysed by an enzyme for which the name rhodanese is suggested. Rhodanese is present in almost all organs, but is absent from blood and muscle. It is sp., its p_H optimum is 8·3, and it is destroyed by heating above 56°. The reaction velocity is large, but is decreased by bivalent cations. Experiments for the isolation and purification of the enzyme are described. P. W. C.

Effect of body-fluids on fermentation. L. KARCZAG and M. HANAK (Biochem. Z., 1933, **260**, 39—43).—The fermentation of glucose (I) by yeast and that of $AcCO_2H$ by *B. coli* (II) is not affected by blood-serum (III), which, however, diminishes the fermentation of (I) by (II) sometimes very greatly. The inhibiting agent in (III) is probably in the albumin fraction, and hence ultra-filtrates of (III) and also of cerebrospinal fluid have no effect on these fermentations. W. McC.

Effect of amines on yeast poisoned with iodoacetic acid. E. F. SCHROEDER, G. E. WOODWARD, and M. E. PLATT (J. Biol. Chem., 1933, **100**, 525—535).—Evidence is given to show that the reactivating action of certain amines such as p-$C_6H_4(NH_2)_2$ and tyrosine on fermentation by yeast poisoned with iodoacetate (cf. Zuckerkandl and Messiner-Klebermass, this vol., 188) is due to the alkalinity of the reaction mixtures preventing the inhibitory action of the iodoacetate. Other factors influencing the fermentation are the destruction of iodoacetate by the amines and the stimulating or toxic effect of the latter on the fermentation. A. L.

Wildiers' bios. Fractionation of bios from yeast. W. L. MILLER, E. V. EASTCOTT, and J. E. MACONACHIE (J. Amer. Chem. Soc., 1933, **55**, 1502—1517).—Addition of *i*-inositol (I) to media containing aq. or aq.-EtOH extracts of yeast may or may not increase the yeast crop, according to the condition of the cells used for prep. of the extract. The liquid in which the cells of brewer's yeast (II) are suspended should be removed prior to the prep. of the extract, since it may contain sufficient (I) to render any further addition unnecessary; this may account for the results obtained by Williams *et al.* (A., 1929, 1339) and Narayanan (A., 1930, 375). The bios in extracts of (II) or Fleischmann's yeast (III) is fractionated by Lucas' method (A., 1924, i, 1338) or by $Pb(OAc)_2$ and aq. NH_3. Crude bios II from (III) is separated further by treatment of its solution with C into bios IIA (not adsorbed) and bios II*B* (adsorbed) (recovery is by extraction with aq. NH_3–$COMe_2$). Bios II from malt combings and tomatoes is similarly separable. The same behaviour of Wildiers' and Toronto yeasts in media containing one, two, or all of the three constituents renders unnecessary the assumption of the existence of a class of nutrilites differing from Wildiers' bios. The effects of bios II*A* and II*B* are not due to Tl (cf. Richards, A., 1932, 778). Solutions of crude bios I contain some II*A* [which remains dissolved when the solutions are treated with $Pb(OAc)_2$ and aq. NH_3 (cf. Lucas, *loc. cit.*)]. Various factors (agitation, aeration, p_H of culture medium) affecting the yeast crops have been investigated. H. B.

Conversion of glycerophosphoric acid into pyruvic acid by yeast and lactic acid bacteria. C. NEUBERG and M. KOBEL (Biochem. Z., 1933, **260**, 241—246; cf. A., 1929, 1337).—At p_H 6·6 in the presence of PhMe both yeast (I) and lactic acid bacteria (II) (*B. Delbrücki*) convert glycerophosphoric acid into $AcCO_2H$ (III), ordinary hydrolytic dephosphorylation occurring at the same time and MeCHO being produced in small amount when (I) is used. The accumulation of (III) is less with (II) than with (I). W. McC.

Production of acids and alcohol by *Aspergillus*. IV. Production of *d*-gluconic acid by *A. oryzæ*. V. Conditions of culturing for acid production by *A. oryzæ*. VII. Classification of koji moulds by selective fermentation of sugars. K. SAKAGUCHI (J. Agric. Chem. Soc. Japan, 1932, **8**, 264—265; 1931, **7**, 748—762; 1932, **8**, 531—546).—IV. *A. oryzæ* SH No. 12 produced *d*-gluconic acid (88·31% of glucose used) and $H_2C_2O_4$ from 5% glucose solution containing 2% $Ca(OH)_2$ in 5 days at 32°.

V. *A. oryzæ* SH No. 28 was grown in a solution containing glucose 100, KH_2PO_4 0·15, K_2HPO_4 0·15, $MgSO_4$ 0·1, $CaCl_2$ 0·1 g., NaCl and $FeCl_3$ trace, in 1 litre of H_2O. $H_2C_2O_4$ may be the secondary decomp. product of sugar. The quantity of kojic acid produced increased with the acidity of the solution, and citric acid was markedly produced at p_H 6·10. Production of gluconic acid was max. at neutrality. $H_2S_2O_4$ was produced only at $p_H > 7·84$. Production of citric acid occurred at 28—37° and was absent at < 20°. Kojic acid was markedly produced at 15—18°. Gluconic acid and Et_2O-sol. org. acids were generally produced at the lower temp. Peptone was preferable as source of N for the production of kojic acid, peptone, glycine, and $NaNO_3$ for that of citric acid, and NH_4 salts for that of gluconic acid.

VII. 116 species of koji-*Aspergillus* were classified in 16 groups according to their ability to ferment inulin, trehalose, raffinose, lactose, and galactose. CH. ABS.

Production of citric acid by moulds. III. Japanese black moulds. K. SAKAGUCHI and J. YAMAYA (J. Agric. Chem. Soc. Japan., 1932, **8**, 489—497).—Using *Aspergillus awamori*, Nakazawa, and *A. aureus*, Nak., peptone (0·4%) was the most suitable source of N. With $NaNO_3$, $H_2C_2O_4$ is also formed. The optimum conc. of molasses for formation of citric acid was respectively 15° and 18° Balling, and p_H 3·33

and 6·10. At p_H >7·84 $H_2C_2O_4$ is produced. 13 species of black moulds were compared. CH. ABS.

Formation of kojic acid by *Aspergillus oryzæ*. H. KATAGIRI and K. KITAHARA (Mem. Coll. Agric. Kyoto, 1933, No. 26, 1—29).—The optimum p_H for the production of kojic acid in any medium is 2·1; the max. yield is 63—66% using a 5—20% glucose solution. The mould grows slowly in 5% $CO(CH_2{\cdot}OH)_2$, but a yield of 55% of kojic acid is obtained when a 2% solution is used. No kojic acid is produced when the source of C is $COMe_2$, glycogen, or hexose mono- and di-phosphates. $(NH_4)_2SO_4$ is the best source of N. *A. tamarii* gives similar results. P. G. M.

Action of certain moulds on solutions of aldoses and other saccharine material. VII. Formation of *d*-gluconic acid from maltose. A. ANGELETTI (Annali Chim. Appl., 1933, **23**, 84—87; cf. A., 1932, 145).—Both *Penicillium luteum purpurogenum* and *P. crustaceum* (L.), Fries, form *d*-gluconic acid from maltose and hence presumably secrete maltase. T. H. P.

Formation of volatile arsenic compounds by moulds. F. CHALLENGER (Ind. Chem., 1933, **9**, 134).—Many moulds, such as *Penicillium brevicaule*, produce $AsMe_3$ from As_2O_3 or from org. As compounds. The gas gives two cryst. compounds with acid $HgCl_2$: $AsMe_3,2HgCl_2$, m.p. 264°, and $AsMe_3,HgCl_2$, m.p. 224—226°. The moulds can effect reduction of As^V to As^{III}. P. G. M.

Action of metals as co-catalysts of growth. N. NIELSEN and V. HARTELIUS (Biochem. Z., 1933, **259**, 340—350).—Filter paper does not catalyse the formation of the growth substance B (A., 1932, 661; this vol., 189), but acts as a co-catalyst of growth, substances (probably metallic) arising from the paper intensifying the feeble effect of the growth substance itself. Zn salts also act as co-catalysts of growth. P. W. C.

Action of aromatic sulphur compounds on pathogenic fungi. T. HACHIYA and J. NISHIMURA (J. Pharm. Soc. Japan, 1932, **52**, 756—765).—A no. of org. S compounds (including *K* β-*thiolnaphthoate*, *Na* p-*phenylthiocarbamidobenzenesulphonate* $+5H_2O$, and *Na* 1-*phenylthiocarbamidonaphthalene*-4-*sulphonate* $+0{\cdot}5H_2O$) have been prepared and their action on fungi such as *Tricophyton interdigitale* and *Achorion Schönleini* has been determined. NHPh·CS·OEt, which is fungicidal to *T. interdigitale* in a concn. of $1:10^4$ and to *A. Schönleini* in a concn. of 1 : 8000, is the only one to compare in potency with trypaflavine ($1:2\times10^4$ and $1:32\times10^4$, respectively). Alkali salts are less active than the free acids. P. G. M.

Effect of nitrogen source on oxygen consumption by *Rhizobium*. R. H. WALKER and D. A. ANDERSON (J. Bact., 1933, **25**, 53—54).—In four species examined, addition of yeast to a N-free medium considerably increased O_2 consumption. With *Rh. leguminosarum*, *Rh. trifolii*, and *Rh. phaseoli* NH_4Cl, $NaNO_3$, urea, and alanine had little effect, but with *Rh. meliloti* all four N sources increased the amount of O_2 consumed. A. G. P.

Physiology of certain nitrite-forming bacteria. D. W. CUTLER and L. M. CRUMP (Ann. Appl. Biol., 1933, **20**, 291—296).—Organisms from the waste H_2O of a sugar-beet factory were examined. Among NH_4 salts the nitrate was the most easily oxidised. In most cases the bacteria can utilise the NO_2 produced. A. G. P.

Aerial–earth circuit and biological activity. I. *Azotobacter chroococcum*. A. ITANO (Proc. Imp. Acad. Tokyo, 1933, **9**, 47—50).—Cultures of *Azotobacter chroococcum* containing two electrodes, one of which is earthed and the other connected to an antenna, grow more quickly and fix more N than those having no aerial and earth circuit. The effect of earthing alone is intermediate; that of connecting to the aerial only is not appreciable. A. L.

Catalysis of the biological fixation of nitrogen. H. BORTELS (Zentr. Bakt. Par., 1933, **87**, II, 476—477).—Stimulation of N-fixing organisms of legumes in sand culture by Mo and V is accompanied by an induced growth of green algæ in the upper layers of sand. A. G. P.

Influence of cations on bacterial sporogenesis in a liquid medium. F. W. FABIAN and C. S. BRYAN (J. Bact., 1933, **25**, 33—34).—Cations of uni-(but not of bi-, ter-, or quadri-)valent chlorides stimulate sporogenesis in aerobic bacteria. In the presence of univalent cations sporulation is greatest at points of max. growth. Sporogenesis is not the result of deficiency of nutrients or accumulation of metabolic products. Sporulation was not markedly affected by the reaction of the medium within p_H 5·0—7·5, although an acid reaction appeared slightly the more favourable. A. G. P.

Detection of microbial lipase by copper soap formation. J. A. BERRY (J. Bact., 1933, **25**, 433—434).—Fat is incorporated in an agar medium, and after solidification the surface is rinsed with $CuSO_4$ solution. Streak inoculations after incubation show lipase activity by the characteristic bluish-green lines of Cu soap. A. G. P.

Effect of medium on production of bacterial gelatinase. R. B. HAINES (Biochem. J., 1933, **27**, 466—474).—A linear relation exists between the change in viscosity of gelatin, (I) due to its incubation with centrifugates from various bacillary cultures, and the square root of the time of incubation, from which may be obtained a const., *k*, which gives a measure of the activity of the gelatinase (II) present. With broth cultures the most active (II) produced is that by *Pseudomonas* and *B. pyocyaneus*. The curve obtained by plotting *k* against the p_H of the incubated (I) has a max. at p_H 8. With cultures obtained from synthetic media using NH_4 salts as sources of N, the production of (II) ranges from nil to its optimum val., depending on the concn. of $Mg^{\cdot\cdot}$ and $Ca^{\cdot\cdot}$. The growth of cultures is best in a concn. of 0·002% $MgSO_4$ and absence of $CaCl_2$ when no (II) is formed, whereas optimum (II) formation occurs when the culture medium contains 0·002% $CaCl_2$ and $MgSO_4$. Mere addition of these salts to centrifugates from inactive cultures has no effect. H. D.

Effect of various substances on fat production by *B. megatherium*, *B. mycoides*, and *B. alboactis*. J. C. SPARROW (J. Bact., 1933, **25**, 36—37).—

Growth and fat production were not parallel processes. Fat formation probably results from catabolic processes, and does not represent the storage of synthesised material. A. G. P.

Metabolism of the sulphur-free purple bacteria. H. Gaffron (Biochem. Z., 1933, **260**, 1—17; cf. van Niel, A., 1932, 884).—*Rhodovibrio parvus* (rhodobacillus) (I), which grows anaerobically in light when alone and cannot assimilate CO_2 readily, does so in light if the salt (II) of a fatty acid is present. In the case of the lower fatty acids the absorption of CO_2 proceeds regularly in proportion to the amount of (II) present, about 0·5 mol. per CH_2 group being assimilated except at the transitions C_3–C_4 and C_6–C_7. Irregularities also occur amongst the higher acids. Dicarboxylic and unsaturated acids also serve in a similar way with the expected differences. During the process the metal is eliminated as hydroxide. (I) is not damaged by drying or by treatment with large amounts of sulphide (which is oxidised to SO_4''), but is very sensitive to acid reaction, to HCN [80% reduction of CO_2 assimilation (III)], and to octyl alcohol (inhibition). (III) is reduced by high concn. of substrate and by NO_3'. No metabolic products have been isolated, but dried (I) yields a *substance* $(C_4H_6O_2)_n$ (cryst. *osazone*). (III) in (I) resembles that in plants. W. McC.

Pyocyanine and growth potential changes of *Ps. pyocyaneus*. G. B. Reed and E. M. Boyd (Canad. J. Res., 1933, **8**, 173—179).—Measurements of growth potentials of *Ps. pyocyaneus* in broth and in a synthetic medium show that in the depths of the medium the potential becomes more negative than that of leucopyocyanine, whilst the surface layer remains more positive, as indicated by the formation of a blue layer. The synthetic medium used as a control maintained a high positive E_h under both aerobic and anaerobic conditions. Similar results were obtained with a strain of *Ps. pyocyaneus* producing no pyocyanine, the potential in the depths of the medium being slightly less negative. The potentials observed are therefore not primarily due to the presence of the pyocyanine, but diffusion of the pigment enables it to act as respiratory catalyst. A. A. L.

Respiratory catalysts in spores and vegetative cells of certain aerobic bacilli. H. L. A. Tarr (Biochem. J., 1933, **27**, 136—145).—Endospores (I) of *B. subtilis* (two strains), *B. mesentericus*, and *B. megatherium* dehydrogenated certain hexoses and disaccharides anaerobically with methylene-blue (II) as H acceptor. Vegetative cells (III) dehydrogenated glucose (IV) more rapidly than did the (I) which they produce. The dehydrogenation by (III) was accelerated by previous heating of suspensions of (III) at 80° for 30 min. or by aerobic incubation with (IV) for 30 min. at 40° before addition of (II). The latter treatment prevented the inhibition due to 5% of ethylurethane (V) which normally occurred with the dehydrogenase activity of (I) and (III). Saturated aq. phenylurethane (VI) had an inhibitory effect on (I) and (III), whilst KCN partly inhibited only (III). (I) exhibited a small endogenous O_2 uptake which was increased 10—40 times by addition of (IV). (III) oxidised (IV) more rapidly than their corresponding (I). In the oxidation of (IV), freshly prepared (I) had a time lag of 50—60 min., which was considerably decreased by previous heating at 60—90° for 30 min.; such treatment had little effect on the respiratory catalysts of (I). The aerobic oxidation of (IV) by (I) and (III) was inhibited by (V) and (VI). With one strain of *B. subtilis*, the aerobic oxidation by (III) was inhibited by KCN and H_2S, whilst with (I) of the same organism, H_2S accelerated and KCN inhibited the oxidation; with the three other species, H_2S had no effect, whilst KCN inhibited the oxidation. F. O. H.

Oxybiotic and anoxybiotic gas metabolism of pathogenic bacteria. IV. Semi-micro-method for measuring the respiration and fermentation of bacteria and other cells. T. Wohlfeil (Zentr. Bakt. Par., 1932, I, **125**, 200—216; Chem. Zentr., 1933, i, 442—443).—Air free from CO_2, N_2 free from O_2, or A is passed through the culture, and the effluent gas is analysed in a modified Haldane apparatus. A. A. E.

Utilisation of certain substituted sugars by bacteria. S. A. Koser and F. Saunders (J. Bact., 1933, **25**, 32).—Substitution of OMe for OH in the sugar mol. decreases the ease of bacterial attack. Glucosamino was utilised by most glucose-splitting organisms; gluconic acid was less generally attacked. No cultures examined fermented glucose ethylmercaptal. A. G. P.

Spore-forming bacteria concerned in butyric acid decomposition. W. Werner (Zentr. Bakt. Par., 1933, **87**, II, 446—475).—Activity of various species in various nutrient media is recorded. A. G. P.

Stimulating effect of potato extract on butyric acid bacteria. E. L. Tatum and W. H. Petersen (J. Bact., 1933, **25**, 26—27).—Increased activity of butyric acid bacteria on a maize mash medium, brought about by additions of aq. extract of potatoes, results in the complete destruction of starch and increased production of BuOH without change in the proportion of other fermentation products. The stimulatory factor was absent from cereals and synthetic media. Its isolation and chemical reactions are recorded. A. G. P.

Fermentation of acetoacetic acid and pyruvic acid by the acetone–butanol organism *Cl. acetobutylicum*. W. H. Peterson and M. J. Johnson (J. Bact., 1933, **25**, 69).—Addition of acetoacetic acid to actively fermenting cultures of *Cl. acetobutylicum* results in its transformation into $COMe_2$. The change is effected by actively reproducing cells or by cell suspensions, the latter being effective when buffered to p_H 5·2—6·4 with PO_4'''. Pyruvic acid under similar conditions yields AcOH, $COMe_2$, and acetylmethylcarbinol. A. G. P.

Gluconic acid fermentation. III. T. Takahashi and T. Asai (Zentr. Bakt. Par., 1933, **87**, II, 385—412).—Cultural characteristics of *B. Hoshigaki*, var. *glucuronicum I, II*, and *III*, are described and the effects of varying concns. of sugars, EtOH, AcOH, and NaCl on the activity of the organisms recorded. A. G. P.

Trimethylene glycol fermentation. C. H. WERKMAN, C. W. DAVIS, and C. A. TARNUTZER (J. Bact., 1933, **25**, 33).—Production of trimethylene glycol by organisms of the *Citrobacter* group is prevented by addition of fumaric acid (when succinic acid is formed), or of $NaHSO_3$. The latter fixes relatively large quantities of MeCHO and reduces AcOH production. Trimethylene glycol is probably not formed as a direct hydrogenation product of glycerol (Braak), but by way of an intermediate product, *e.g.*, hydracryl-, prop-, or glycer-aldehyde. Max. yield of the glycol is $\frac{1}{3}$ of the glycerol present. It is suggested that 1 mol. of glycerol acts as a H acceptor to provide for the dehydrogenation of 2 more mols. of glycerol. *E. coli* does not ferment glycerol under anaerobic conditions, but the addition of a H acceptor (peptone, asparagine, fumaric acid, or MeCHO) initiates the fermentation. A. G. P.

***Bacillus saprogenes sake*, Takahashi, and the lactic acid bacteria which putrefy sake.** T. TAKAHASHI and A. SUZUKI (J. Agric. Chem. Soc. Japan, 1932, **8**, 1064—1068).—*B. saprogenes* cannot usually be cultivated on koji extract, except from a few species of koji (*Aspergillus oryzæ*) which produce mainly EtOH. Fruit or vegetable juice promotes the growth of *B. saprogenes*. CH. ABS.

Aerobic cellulose-decomposing bacteria in soil. A. KALNINS (Latvij. univ. raksti, 1930, **11**, I, 221—312; Bied. Zentr., 1932, **3**, **A**, 130—131).—Data of numerous species are recorded. In general NO_3' and NH_4 salts form the best sources of N, although certain org. compounds (*e.g.*, peptone, NH_2-acids) may be utilised. Cellulose, the common sugars, and inulin serve as C sources. Sugar media, but not cellulose media, show an increased p_H with the growth of the organism. Cellulose decomp. produces a substance which reduces Fehling's solution, yields glucose-phenylosazone, is formed in greater quantity when the O_2 supply is restricted, and serves as an energy source for *Azotobacter chroococcum*. A. G. P.

Synthesis of cellulose by *Acetobacter xylinum* from mannitol and sorbitol. Y. KHOUVINE (Compt. rend., 1933, **196**, 1144—1146).—C balances are recorded for 11-, 15-, and 21-day cultures of *Acetobacter xylinum* containing (*a*) mannitol, and (*b*) sorbitol. In the longest cultures the yields of cellulose, sugar, and CO_2, in terms of the original alcohol, are 19·11, 54·95, and 17·6%, respectively, for (*a*), and 1·66, 88·96, and 5·96%, respectively, for (*b*). The products are formed by oxidative processes affording sufficient energy for the synthesis of cellulose. A. C.

Calcium-precipitating bacteria from mud of a fresh-water lake. F. T. WILLIAMS and E. MCCOY (J. Bact., 1933, **25**, 57—58).—Aerobic and facultative organisms which ppt. $CaCO_3$ in media containing org. or inorg. Ca salts (*e.g.*, $CaSO_4$, $CaCl_2$, Ca lactate) are described. No relationship exists between the extent of pptn. and the final p_H of the culture within the range 7·2—9·4. In media containing PO_4''' no PO_4''' occurs in the ppt. Pptn. also occurs in solid media containing mud extracts without additional Ca''. A. G. P.

Aggressin of *Gonococcus*. W. CASPER (Klin. Woch., 1932, **11**, 1996—1997; Chem. Zentr., 1933, i, 442).—The filtrate from *Gonococcus* grown on serum-bouillon (p_H 7·5) and the culture itself, when separately injected into a mouse, caused little toxic effect, but when administered together usually killed the animal. The filtrate causes toxic skin reactions in man. A. A. E.

Typhoid toxin purified by adsorption with aluminium hydroxide. I. M. YATO (Japan. Z. Mikrobiol. Path., 1932, **26**, 1015—1032).—The purified toxin of typhoid bacilli can produce immune bodies. CH. ABS.

Filterable fractions of tubercle toxin. C. NINNI (Ann. Inst. Pasteur, 1933, **50**, 504—538).—The ultra-virus of the tubercle bacillus, which can be obtained by filtration of a culture, will give rise to the normal acid-resisting bacillus following injection into the cervical ganglia of the guinea-pig. A granular state of the bacilli favours the formation of a biologically active filtrate. P. G. M.

Chromogenesis of acid-resistant bacilli. Effect of [H·]. G. SANDOR and G. ROUGEBIEF (Bull. Soc. Chim. biol., 1933, **15**, 415—417).—Grassberger's bacillus was grown in media containing glycerol, asparagine, and K_2HPO_4 at different p_H. In neutral or alkaline media the culture grows rapidly, but remains colourless until sufficient org. acid has been made to lower the p_H. In acid media the culture is poor, but coloured red from the beginning. H. D.

Biological effects of high pressures; action of very high pressures on bacteriophages and vaccinia virus. J. BASSET, E. WOLLMAN, M. A. MACHEBŒUF, and M. BARDACH (Compt. rend., 1933, **196**, 1138—1139; cf. this vol., 313).—Staphylococcal bacteriophage is destroyed by exposure to a pressure of 2000—3000 atm. for 45 min. Phages of *B. typhosus* and *B. subtilis* are more resistant, and not completely destroyed below 7000 atm. Their resistance is increased in the presence of the corresponding bacteria. Vaccinia virus (I) is inactivated in 45 min. at 4500 atm. The phages and (I) are much less resistant to pressure than enzymes and toxins. A. C.

Rationalisation, from the view-point of physical chemistry, of the behaviour of bacteria towards dyes with special reference to staining. A. E. STEARN (J. Bact., 1933, **25**, 21—23).—The discussion is based on the view that the bacterial cell is an equilibrated system of two components, one being more acidic than the other, the whole system possessing amphoteric properties. A. G. P.

Relation between the bacteriostatic action of gentian-violet and the oxidation-reduction potential of the medium. M. A. INGRAHAM and E. B. FRED (J. Bact., 1933, **25**, 23—24).—Lethal action of dyes on bacteria is examined. Presence of dyes in media tends to restrict changes in oxidation-reduction potential resulting from the addition of oxidising or reducing substances. A. G. P.

Antibacterial power of trypaflavine, isravin, panseptin, and mercurochrome. J. DOHI (Japan. J. Dermat. Urol., 1932, **32**, 952—956).—Fluorescein derivatives possessed greater bactericidal power than

acridine derivatives for *Staphylococcus albus, S. citreus, Streptococcus pyogenes,* and *Es. coli.* CH. ABS.

Determination of bactericidal properties of chemical sterilisers. R. P. MYERS and A. H. JOHNSON (Proc. Int. Assoc. Milk Dealers, Lab. Sect., 1932, **25**, 21—55).—The germicidal potency of OCl′ preps. is indicated by the ratio Cl : alkalinity (as Na_2O). Low corrosiveness and low bactericidal potency are associated with high alkalinity. CH. ABS.

Oligodynamic action of metals on bacteria. G. LA CAVA (Ann. Igiene, 1931, **41**, 612—619; Chem. Zentr., 1933, i, 442).—The action is due to colloidal dissolution of the metals and their penetration into the bacterial protoplasm. Ag probably dissolves as colloidal Ag_2O. A. A. E.

Toxicity of formaldehyde and mercuric chloride solutions to various sizes of sclerotia of *Rizoctonia solani*. G. B. SANFORD and J. W. MARRITT (Phytopath., 1933, **23**, 271—280).—The standard CH_2O treatment is not effective where medium and large sclerotia are present. Solutions of $HgCl_2$ (1 in 500) containing 1 vol.-% of HCl were more satisfactory. A. G. P.

Enhanced lethal effects of *X*-rays on *Escherichia coli* in presence of inorganic salts. W. D. CLAUS (J. Exp. Med., 1933, **57**, 335—347).—For 0·1*M* solutions, the synergistic effect is appreciable only with salts of heavy metals. For $Pb(NO_3)_2$ or KBr the synergistic effect is appreciable only at high concn. or absorption coeff. The no. of effective hits per bacterium per min. (α) depends on the nature of the salt, or possibly on its penetration into the cell; α increases as λ decreases. CH. ABS.

Physiology of the tonsils. I. L. KOSTYAL. **IV.** L. KOSTYAL and M. PENKERT (Arch. exp. Path. Pharm., 1933, **170**, 131—142, 143—150).—Subcutaneous injection of extracts of tonsils (I) into rabbits and children produces a hypoglycæmia (II) characterised by two phases. With intravenous injection a preliminary hyperglycæmia (III) is followed by a prolonged (II) also characterised by two phases. These reactions of (I) are probably due to an indirect action on the pancreas and liver. Atropine increases (III) but does not influence (II). (I) not only resemble insulin (IV) in their action, but also synergise (IV). With normal or diseased children, the higher is the initial blood-sugar level the greater is the (III) produced by injection of (I).

IV. Injection of (I) into rabbits and children produces changes in n of the blood, indicating a dilution similar to that occurring with (IV). Neither (I) nor (IV) inhibits the blood-diluting action of the other. Atropine does not influence the action of (I). No relationship exists between the blood-dilution and the (II) due to (I). F. O. H.

Mechanism of inhibition of gastric motility by fat. Inhibitory agent from intestinal mucosa. T. KOSAKA and R. K. S. LIM (Chinese J. Physiol., 1933, *7*, 5—11).—The gastric motility of dogs with fistulæ is inhibited by the following in order of decreasing activity: a prep. (using picric acid) of the intestinal mucosa, blood after oil feeding, colonic mucosa, intestinal plain muscle, and gastric mucosa. Leg-muscle, liver, and fasting blood do not inhibit. The secreto-inhibitory activities of these preps. are approx. parallel to their motor-inhibitory activities and hence these effects are probably due to a single substance. F. O. H.

Fractionation of liver extracts in respect of the anti-anæmic substance. K. FELIX and H. FRÜHWEIN (Z. physiol. Chem., 1933, **216**, 173—180).—Liver extracts freed from protein by means of tannic acid were fractionated by pptn. with heavy metals in order to concentrate the anti-anæmic substance. It is quantitatively pptd. from H_2SO_4 solution by $HgSO_4$ in presence of EtOH and Et_2O. It probably contains N but is not a peptide. J. H. B.

Hæmopoietin, the anti-anæmic substance in hog's stomach. I. L. KLEIN and J. F. WILKINSON (Biochem. J., 1933, **27**, 600—610).—An active extract can be obtained from fresh stomach tissue, ground with sand, by high pressure. Active fractions can then be obtained by pptn. with EtOH, the filtrate being inactive. Hæmopoietin is more unstable than, and has different properties from, the active substance in liver; it has a complex org. structure, is probably a protein, and enzyme-like in its nature. H. G. R.

Purification of secretin. G. ÅGREN and O. WILANDER (Biochem. Z., 1933, **259**, 365—373).—A prep. is obtained of which 0·005 mg. per kg. is active in cats. Spectrographic examination shows that this prep. contains no cyclic NH_2-acids and the Millon, xanthoproteic, ninhydrin, histidine, tryptophan, cystine, and cysteine reactions are negative, whilst the diacetyl reaction is more strongly positive than for protein. Its mol. wt. is below 1800 and it behaves as a base. P. W. C.

Effect of parathyroid hormone on the condition of [serum-]calcium. R. SPIEGLER and STERN (Klin. Woch., 1932, **11**, 1580—1586; Chem. Zentr., 1933, i, 448—449).—It is necessary to determine ultrafilterable Ca, electro-ultrafilterable Ca, and colloidal protein-Ca. Diminution of galvanic excitability after hormone treatment is accompanied by diminution in colloidal Ca and increase in free Ca, and *vice versa*. The increase in serum-total Ca after hormone treatment is much less in man than in animals. Other hormones also increase the total Ca. A. A. E.

Thymus extract and blood-calcium level. H. G. SCHOLTZ (Biochem. Z., 1933, **259**, 384—386).—No definite effect of thymocrescin on the blood-Ca in rabbits could be demonstrated, the detection being rendered difficult by the large normal variation in these animals. In dogs (small normal variation) decreases were obtained, but these were small, and normal vals. were reattained in about 24 hr. P. W. C.

Influence of thymus preparations in experimental hyperparathyroidism. H. G. SCHOLTZ (Z. ges. exp. Med., 1932, **85**, 547—558; Chem. Zentr., 1933, i, 447).—Rise in blood-Ca in rabbits caused by parathormone is prevented or diminished if thymus extract is also injected; decalcification of the bones is also prevented. Thymus extracts alone reduce the serum-Ca, but have no effect on the bone-Ca. A. A. E.

Influence of thyroxine on tissue oxidation. G. MYHRMAN (Klin. Woch., 1932, **11**, 2139—2140; cf. this vol., 430).—Treatment of animals with thyroxine during life caused no definite acceleration of methylene-blue reduction by the liver after death, normal livers showing a large variation. NUTR. ABS.

Mechanism of action of thyroxine. T. VON VEREBÉLY (Klin. Woch., 1932, **11**, 1705—1706; Chem. Zentr., 1933, i, 447).—Addition of thyroxine to suspensions of rat's muscle, or rat's or rabbit's liver, was not accompanied by increased oxidation, the O_2 demand being frequently diminished; with cat's or rabbit's brain a marked increase in O_2 demand was observed. A. A. E.

Factors which determine renal weight. XIII. Heat production of the rat as varied by thyroid administration. E. M. MACKAY, F. M. SMITH, and K. CLOSS. **XIV. Relative influence of amino-, urea-, and protein-nitrogen in the diet.** E. M. MACKAY (J. Nutrition, 1933, **6**, 151—156, 157—161). —XIII. In rats receiving thyroid preps. there is a linear relationship between renal wt. and heat requirement as measured by O_2 consumption.

XIV. The effect on renal wt. of NH_2-N (glutamic acid and glycine) is the same as that of protein-N (caseinogen) Urea-N is less effective. A. G. P.

Adrenal. III. Active extract of hormone of the adrenal cortex. A. GROLLMAN and W. M. FIROR (J. Biol. Chem., 1933, **100**, 429—439).—A cortical hormone is prepared by extraction of the frozen tissue with $COMe_2$ (I), removal of (I) in vac., and repeated extraction of the aq. residue with C_6H_6 (II). The (II) solution is shaken with saturated aq. $NaHCO_3$ to remove adrenaline and then with *N*-HCl. (II) is removed in vac. at 35—40° after adding 0·8% saline. The resulting solution is cooled and filtered. The first (I) extraction removes only 50% of the hormone; two subsequent extractions of the glandular residue give a further 50%. A cryst. specimen was obtained by evaporating the (II) solution to dryness. A method of assaying the hormone is described. H. D.

Internal secretion of adrenal cortex. E. SCHMITZ and J. KUHNAU (Biochem. Z., 1933, **259**, 301—319).—The chemical separation from an adrenal cortex of two substances: *A*, which causes an increase of the plasma-phospholipin content in the normal rabbit, and *B*, which causes a decrease of the plasma-cholesterol, is described. The formulæ $C_{25}H_{40}O_3$ and $C_{23}H_{36}O_3$ are assigned to *A* and *B*, respectively. Both are insol. in H_2O, not pptd. by digitonin, give brownish-green colours with $FeCl_3$ and brown Liebermann–Burchardt reactions with green fluorescence. Both, on acetylation by the method of Peterson and West, give vals. equiv. to one OH group. P. W. C.

Adrenal cortex. I. Cortical adrenal insufficiency and the action of the cortical hormone on the normal and adrenalectomised dog. G. A. HARROP and A. WEINSTEIN (J. Exp. Med., 1933, **57**, 305—333).—In Addison's disease and in adrenal insufficiency in dogs the blood-non-protein- and -urea-N, and the serum-K and -inorg. PO_4 increase, whilst the serum-total base decreases, owing to lack of the cortical hormone. When normal nutrition is restored by administration of the hormone, the blood-sugar is not decreased, there is no increased pigmentation, and no change in the basal respiratory metabolism; there is increased sensitivity to insulin and thyroid extract. CH. ABS.

Cortin and traumatic shock. N. E. FREEMAN (Science, 1933, **77**, 211—212).—A discussion (cf. this vol., 320). L. S. T.

Theories of cortico-adrenal function. S. W. BRITTON and H. SILVETTE (Science, 1933, **77**, 368).—A discussion. L. S. T.

Metabolism of animals on a carbohydrate-free diet. V. Effect of adrenaline on glycogen distribution in the rat. A. HYND and D. L. ROTTER (Biochem. J., 1933, **27**, 165—172).—Large doses of adrenaline (I) given to rats fed on either a carbohydrate-rich (II) or a carbohydrate-free diet (III) produce marked changes in the blood-sugar (IV) and the liver-glycogen (V), but have no definite effect on the liver-fat. During the first phase of 6 hr., (IV) increases, whilst (V) and muscle-glycogen (VI) decrease. The next phase of 20 hr. is attended by a normal or slightly low (IV) and by (V) increasing to a max. (in approx. 16 hr.) and then falling to normal levels; with (II), (VI) follows a course parallel to that of (V), whilst with (III), the changes in (VI) are retarded. The changes occurring during the first phase are probably true effects of (I), whilst those of the second, being of an opposite character, are secondary effects arising from a disturbed endocrine balance following administration of (I). F. O. H.

Effect of adrenaline on blood-lactic acid. J. A. COLLAZO and J. PUYAL (Klin. Woch., 1932, **11**, 1947—1949; Chem. Zentr., 1933, i, 446).—In rabbits, injection of 0·5 mg. of adrenaline per kg. causes a rise in blood-lactic acid. Hyperlactacidæmia and hyperglycæmia are accompanied by hyperlactaciduria. In man, injection of 1 mg. of adrenaline causes hyperlactaeidæmia (2 hr.). A. A. E.

Relation between sleep and the adrenaline content of the adrenals. A. G. HOLMQUIST (Skand. Arch. Physiol., 1932, **65**, 18—23; Chem. Zentr., 1933, i, 75).—With hedgehogs caught in June the adrenals contain twice as much adrenaline during waking periods as during sleep. A. A. E.

Spectrophotometric determination of adrenaline in extracts of adrenal glands. U. S. VON EULER (Biochem. Z., 1933, **260**, 18—25).—The method which is based on the reaction of Vulpian (Compt. rend., 1856, **43**, 663) yields results in good agreement with those of the biological (blood-pressure) method. No standard is required, but a blank determination must be made. The hexuronic acid in the extracts, which renders Chikano's method (A., 1929, 474) inapplicable, does not interfere. The errors are ±2%, ±5%, and ±10% when the amounts determined are 0·05, 0·02, and 0·01 mg., respectively. W. McC.

Accuracy of insulin assay on white mice. A. M. HEMMINGSEN (Quart. J. Pharm., 1933, **6**, 39—80).—A statistical rationalisation of results (min. convulsive dose) is made in order to overcome the inaccuracy

arising from the biological variation in response of individual mice. W. S.

Influence of temperature in assay of insulin by means of convulsions in mice. A. M. Hemmingsen and H. P. Marks (Quart. J. Pharm., 1933, 6, 81—89; cf. preceding abstract).—The authors consider 29° preferable to 37° (Trevan, A., 1927, 792) since (*a*) the latter temp. is more arduous for the mice and entails a higher rate of mortality, (*b*) the two methods yield similar distributions of the convulsive doses, and (*c*) the increased accuracy obtained at the higher temp. is not as great as claimed by Trevan. W. S.

Antagonism of insulin and atropine. S. Lang (Arch. exp. Path. Pharm., 1933, 170, 292—295).—Atropine does not influence the hypoglycæmic action of insulin (I) in the depancreatised dog (II), whilst in the normal dog (III) a marked antagonism occurs. With both (II) and (III), (I) temporarily decreases the NH_2-acid and lipin levels of the blood. The action of (I) does not involve the parasympathetic nervous system. F. O. H.

Anti-insulin and other hormones of anterior pituitary gland. H. Lucke (Arch. exp. Path. Pharm., 1933, 170, 166—175).—The anterior pituitary gland produces a hormone which is not ultra-filterable and which antagonises insulin in its action on carbohydrate metabolism. It is not identical with the thyreotropic, sexual, or gonadotropic hormone, but is possibly identical with the growth hormone. F. O. H.

Relation of the pituitary to experimental diabetes. J. F. Regan and B. O. Barnes (Science, 1933, 77, 214).—The finding that extirpation of the pituitary prevents severe diabetes in dogs appears to be confirmed. L. S. T.

Excretion of ketonic substances on a fat diet as affected by injection of pituitary (anterior lobe) extract and by pregnancy. J. H. Burn and H. W. Ling (Quart. J. Pharm., 1933, 6, 31—38).—Whereas normal adult female rats tolerate a fat diet, ketonic substances, in these circumstances, appear in the urine of (*a*) young rats, (*b*) adult female rats injected with pituitary extract, and (*c*) female rats during the last stages of pregnancy. W. S.

Influence of ovarian and pituitary hormones on calcium metabolism. T. F. Dixon (Biochem. J., 1933, 27, 410—418).—The serum-Ca (I) of dogs is less variable than that of rabbits. The (I) of rats in œstrus or diœstrus (II) or 7 days after injection of extracts of ox anterior pituitary, of parathyroidectomised rats in (II) or injected with trihydroxyœstrin, of pregnant or pseudo-pregnant rabbits, or of dogs injected with ovary or corpus luteum extracts, is not significantly abnormal. H. D.

Crystalline œstrogenic hormones. J. S. L. Browne (Canad. J. Res., 1933, 8, 180—197).—A *substance*, $C_{18}H_{24}O_3$ (I), m.p. 274°, believed to be a trihydroxyœstrin related to theelol has been isolated from "emmenin" (A., 1931, 398). A physiological comparison with theelol and theelin is described. (I) has the same effect as theelol on the immature intact rat, but is 5—10 times less effective on the adult ovariectomised rat. It is suggested that the presence of the immature ovary increases the activity of (I) and of theelol by increasing the rate of conversion into more active œstrogenic substances. A. A. L.

Female sexual hormone. IX. Comparison of theelol, emmenin, and follicular hormone hydrate. A. Butenandt and J. S. L. Browne (Z. physiol. Chem., 1933, 216, 49—56; cf. A., 1932, 781).—Theelol and follicular hormone hydrate are undoubtedly the same substance; emmenin (obtained from placenta) is probably identical, its somewhat higher physiological activity being due to impurity. J. H. B.

Post-mortem uterine findings after temporary hormonal sterilisation. M. Maino (Arch. Ist. Biochim. Ital., 1933, 5, 3—10).—Remains of fœtal bones were found in uterine cysts in rabbits in which fœtal resorption had been caused by administration of œstrin in late pregnancy (this vol., 194). R. K. C.

[Sex] hormone in urine and mammary secretion. E. W. Winter (Arch. Gyn., 1932, 151, 201—219; Chem. Zentr., 1933, i, 246).—Ovarian hormone (I) was found (Zondek) in the urine of newly-born infants up to the third, and anterior pituitary hormone (II) up to the ninth, day *post partum*. No hormone was found in the mammary gland. In pregnancy, colostrum contains (II) from the seventh month until the sixth day after delivery; (I) is not present. In the first stage of the climacteric the urine contains (I), and in the last stage follicular-ripening hormone. In sterility none of the hormones was found in the urine. A. A. E.

Physico-chemical properties of prolan. A. Mogilski (Farm. Zhur., 1932, 11—12, 337—338).—The brownish albuminous powder gives biuret and glyoxylic acid reactions, ppts. tannin, colloidal $Fe(OH)_3$, and $Pb(OAc)_2$, is salted out by conc. $(NH_4)_2SO_4$, does not coagulate when heated, and forms no ppt. with $CCl_3{\cdot}CO_2H$, $C_6H_3(OH)(SO_3H){\cdot}CO_2H$, or $C_6H_2(NO_2)_3{\cdot}OH$. Ch. Abs.

Source of the testicular hormone. A. Lipschütz (Med. Welt, 1932, 6, 1231—1234; Chem. Zentr., 1933, i, 445).

Changes produced by the testicular hormone in normal and castrated rats. V. Korenchevsky, M. Dennison, and A. Kohn-Speyer (Biochem. J., 1933, 27, 557—579).—In young, normal animals the physiological variations were small. Small doses give a slight decrease in wt. of the prostate and penis, whilst large doses give an increase together with an acceleration in the involution of the thymus. Castrated rats tend to a return of the organs to normal; an increase in wt. of the prostate, in direct proportion to the dose, and in the penis and thyroid, and an increased involution of the thymus were observed. H. G. R.

Detection of the male sexual hormone by means of the fish test. D. Glaser and O. Haempel (Deut. med. Woch., 1932, 58, 1247—1248; Chem. Zentr., 1933, i, 445).—The test is sp. A. A. E.

Katechins. F. Blum (Deut. med. Woch., 1932, 58, 1874—1876; Chem. Zentr., 1933, i, 444—445).—

" Katechins " are substances which diminish or arrest the action of hormones; thus " tyronorman " injected with thyroxine suppresses the rise in basal metabolism. Insulin is not a hormone, but a katechin "; the corresponding hyperglycæmic hormone is also present in the pancreas and in the blood. A. A. E.

Chemical nature of the antixerophthalmic vitamin-*A*. H. SEEL (Z. Vitaminforsch., 1933, 2, 82—93).—North Sea and N. Atlantic fish liver-oils (chiefly *Selachii* and *Batoidei*) show considerable variation in composition, vitamin-*A* potency, and blue val.; the two last are not parallel. Algæ possess marked growth-promoting power, but little antixerophthalmic action in rats, and the existence of two factors is suggested. A cryst. Bz derivative of vitamin-*A* has been obtained which is biologically active but gives no $SbCl_3$ reaction until saponified. Oxidised cholesterol promotes growth, but the $SbCl_3$ reaction shows certain differences from that of vitamin-*A* from other sources. R. K. C.

Vitamin-*A* in the pimento pepper. L. ASCHAM (Science, 1933, 77, 351).—Four mg. of pepper produced a growth response in rats > that of the Sherman unit. The dried material contains 200—300 mg. of carotene per kg. L. S. T.

Vitamin-*A* content of lucerne as affected by exposure to sunshine in the curing process. M. C. SMITH and I. A. BRIGGS (J. Agric. Res., 1933, 46, 229—234).—In comparison with samples dried in a dark chamber, lucerne leaves cured in the field lost a large proportion of their vitamin-*A* content (20—33% after 2¾ hr. and 96% after 7 days). No loss of green colour occurred in samples exposed for a few hr. A. G. P.

Absorption spectrum of vitamin-*A* at low temperatures. F. P. BOWDEN, S. D. D. MORRIS, and C. P. SNOW (Nature, 1933, 131, 582—583).—When vitamin-*A* concentrates are cooled to liquid air temp. the max. at 3280 Å. is displaced to 3350 Å. and new bands occur at 2900, 2770, 2580, 2510, and 2430 Å. When the product obtained by irradiating carotene is cooled, the band near 3280 Å. breaks up into a series at 3780, 3570, 3410, and 3210 Å. Hence the mol. produced by irradiating carotene differs from that associated with the 3280 Å. band in vitamin-*A* concentrates. L. S. T.

Vitamin-*A*. I. Absorption spectra of carotenoids. II. Properties of hydrocarotene. III. Relation between hydrocarotene and biosterol. K. KAWAKAMI (J. Agric. Chem. Soc. Japan, 1932, 8, 48—54, 55—63, 64—71).—I. Carotene has absorption bands between 3300 and 3400 Å. and between 2630 and 2950 Å.; biosterol has a band between 3300 and 3400 Å. The absorption bands of xanthophyll and lutein are indistinguishable from those of carotene; the bands of α-crocetin and capsanthin are different.

II. Hydrocarotene, obtained by reduction of carotene with Al–Hg and EtOH in C_6H_{14}, has reactions and absorption bands resembling those of biosterol, but it has not the physiological action of vitamin-*A*.

III. Biosterol and Grignard reagent afford CH_4; hence an OH group is present. Carotene and hydrocarotene do not react; hence hydrocarotene is not contained in biosterol. Xanthophyll is reduced by Al–Hg at 60—70° to hydroxanthophyll, which reacts with Grignard reagent and resembles biosterol in chemical properties and absorption spectrum, but has not the physiological action of vitamin-*A*. CH. ABS.

Value and limits of the chemical vitamin reaction of cod-liver oil. III. Chemical and biological determination of vitamin-*A* in cod-liver oil. W. BRANDRUP (Pharm. Ztg., 1933, 78, 433; cf. A., 1932, 973).—Vogan, a vitamin-*A* concentrate in vegetable oil solution, gives a blue colour comparable with a $CuSO_4$ solution in the $SbCl_3$–$CHCl_3$ test, whereas cod-liver oil gives a colour similar to that of alcoholic Victoria-blue solution. The difference in tone is ascribed to a constituent of cod-liver oil other than vitamin-*A*, and the reaction is suggested for the detection of cod-liver oil. E. H. S.

Influence of basal diet in the determination of vitamin-*A*. K. CULHANE (Biochem. J., 1933, 27, 69—82).—Dried yeast (I) and " light white casein " (II) contain vitamin-*A* (in insufficient quantity to maintain growth in rats) and -*D*. With rats on a diet containing fat, 5% of marmite is a sufficient source of *B*, whilst with fat-free diets, 5% of marmite or 8% of (I) does not prevent skin lesions. Complete deficiency of *A* invariably produces xerophthalmia (III), which, however, can be prevented or its onset retarded by a diet containing (I) or (II), and which does not readily occur when there is a deprivation of both *A* and *D*. The rate of incidence of (III) forms a satisfactory basis for the assay of *A*. The basal diet of Drummond and Watson (A., 1922, ii, 596) is deficient in no other vitamin necessary for the rat than *A*. F. O. H.

Vitamin-*A*-free basal diets. I. A. L. BACHARACH. **II.** A. L. BACHARACH and E. L. SMITH (Biochem. J., 1933, 27, 5—16, 17—21).—I. Rats fed on a vitamin-*A*-free basal diet (I) exhibit anomalous rates of growth. Thus, whilst some cease growing in 8—10 weeks, others continue to grow for several months; in a few cases a growth curve (II) similar to that obtained with the commencement of vitamin-*A* administration is given. With either a fat-free or fat-rich (I), the (II) and the degree of recovery under curative treatment appear to be independent of the type of caseinogen used as a source of protein. Curative treatment in no instance produces growth equal to that of normal animals on a stock diet. Hence (I) is deficient in some factor other than vitamin-*A*. The bearing of the results on the assay of vitamin-*A* is discussed.

II. The increased rate of growth due to the addition of vitamin-*A* to (I) is still less than that due to the stock diet. With such diets, the liver reserves of vitamin-*A* are parallel with the growth performance for each group. The passage of the vitamin from the mother to the embryo or suckling offspring is discussed. F. O. H.

Length of test period and accuracy obtainable in a vitamin-*A* test. K. H. COWARD (Biochem. J., 1933, 27, 445—450).—The mean variances (I) of the increase in wt. (II) of rats due to a dose of vitamin-*A* are plotted against the durations of the tests (III). In general (I) and the standard deviation of (II) increase with (III). Equations of curves of response (IV), obtained by

plotting the mean (II) of groups of rats against the dose of cod-liver oil given daily, are calc. From the standard deviations of the mean (II) and the slope of (IV) the degree of accuracy of the test obtained in any given (III) is calc., and is only slightly increased by prolonging (III) beyond 3 weeks. H. D.

Determination of vitamin-*A* in a concentrate, "Vogan." T. Moll, O. Dalmer, P. von Dobeneck, G. Domagk, and F. Laquer (Arch. exp. Path. Pharm., 1933, **170**, 176—207).—The vitamin-*A* content of a commercial fish-liver oil prep. (I) was determined colorimetrically and biologically. A "rat unit" is defined as the min. dose necessary to maintain growth of 3 g. per week in 60% of the test animals (young rats) which must also show freedom from xerophthalmia. (I) contained 40,000 "rat units" per c.c. Alleviation in spayed rats of colpokeratosis affords a more rapid but less accurate test than the rate of growth. Oral administration of excessive doses of vitamin-*A* to normal animals produces toxic symptoms. F. O. H.

Growth and cell-reserves in vitamin investigations. VII. Failure of vitamin-*A* as a growth-factor. W. Kollath (Arch. exp. Path. Pharm., 1933, **170**, 285—291; cf. A., 1932, 1173).—The failure of rats to grow on certain basal diets containing added vitamin-*A* (I) is due to the lack of another factor (II) ("*HG*-factor") which occurs in fresh and autoclaved yeast, germinated and ungerminated barley, crushed cereals, and bran. Histological investigation indicates that both (I) and (II) play a sp. part in tissue building. F. O. H.

Vitamin-*A* and -*D* studies with growing chicks. Comparison of cod-liver oil and pilchard oil as sources of vitamin-*A*. H. S. Gutteridge (Sci. Agric., 1933, **13**, 374—381; cf. A., 1932, 433).—Pilchard oil is as good as, and may be slightly superior to, cod-liver oil as a vitamin-*A* source for chicks. A. G. P.

Effects of moderate overdosage of vitamin-*D* and of -*A*+-*D* on the growth rate and longevity of the white mouse. II. T. B. Robertson, H. R. Marston, M. C. Dawbarn, J. W. Walters, and J. D. O. Wilson (Austral. J. Exp. Biol., 1933, **11**, 49—52).—Mice given a slight overdose of vitamin-*D* benefit in respect of growth rates, but when a large excess of vitamin-*A* was also administered the result was deleterious in respect of growth rate and of expectation of life in young animals, although the expectation of life of those animals which lived to 750 days was not altered significantly. W. O. K.

Production of vitamin-*D* by irradiation of ergosterol through rat's epidermis. N. S. Lucas (Biochem. J., 1933, **27**, 132—135).—A 0·003% solution of ergosterol (I) in EtOH was anaerobically exposed to ultra-violet light which had passed through the epidermis (II) of a day-old rat. The resulting solution showed changes in the ultra-violet absorption spectrum characteristic of vitamin-*D* formation, whilst biological assay indicated a potency of 500 international units per mg. of original (I). Support is thus given to the theory of intracapillary formation of vitamin-*D* due to penetration of (II) by ultra-violet rays. F. O. H.

Antirachitic properties of some vitamin-*D* preparations. A. van Harreveld (Arch. neerland. Physiol., 1933, **18**, 139—144).—Prep. "*L*" of Reerink and Van Wijk (A., 1930, 175) has approx. the same antirachitic activity as calciferol. H. G. R.

Antirachitic value of lucerne as affected by exposure to sunshine in the curing process. M. C. Smith and I. A. Briggs (J. Agric. Res., 1933, **46**, 235—240).—Lucerne cured in darkness is deficient in vitamin-*D*. A synthesis of this vitamin during curing in sunshine is indicated. Material exposed for approx. 24 hr. had a mild calcifying action and after 7 days was highly antirachitic. A. G. P.

Effect of vitamins on blood-catalase. H. J. Jusatz (Klin. Woch., 1932, **11**, 1501—1504; Chem. Zentr., 1933, i, 453).—Administration of vitamin-*D* to rabbits increases the blood-catalase owing to its effect on oxidative metabolism. The increase is more marked when dried yeast is also given. In hypervitaminosis-*D* the blood-catalase falls. A. A. E.

Overdosage of irradiated ergosterol in rabbits. Changes in distribution of phosphorus in blood-cells and plasma. G. M. Guest and J. Warkany (J. Biol. Chem., 1933, **100**, 445—454).—Large doses of irradiated ergosterol produce a rise of plasma-inorg. P and erythrocyte-org.-acid-sol. P. The same effect is produced more slowly by repeated smaller doses. H. D.

Accuracy obtainable by line test in vitamin-*D* determinations. K. H. Coward and K. M. Key (Biochem. J., 1933, **27**, 451—465). H. D.

Commercial assay of vitamin-*D*. W. A. Broom (J.S.C.I., 1933, **52**, 105—108T).—Existing methods for the biological assay of vitamin-*D* are reviewed and a method combining the *X*-ray and line test techniques is advanced. A simple photographic procedure for the prep. of permanent records of line test bones is described.

The *B*-vitamins. II. H. Simonnet (Z. Vitaminforsch., 1933, **2**, 94—109; cf. this vol., 432).—A review.

Formula of vitamin-B_1. B. C. P. Jansen, J. P. Wibaut, P. J. Hubers, and P. W. Wiardi (Rec. trav. chim., 1933, **52**, 366—370).—The prep., by slight modifications of standard methods, of samples of probably pure vitamin-B_1 from rice-polishings (A., 1929, 1344) and from yeast (Chick and Roscoe, *ibid.*, 852) is described. Analytical data for these samples together with those already published agree best with the formula $C_{12}H_{18}O_2N_4S,2HCl$ for the air-dried vitamin hydrochloride which, contrary to Windaus, probably does not contain 1 mol. of H_2O. J. W. B.

Ultra-violet absorption of crystalline preparations of vitamin-B_1. R. A. Peters and J. St. L. Philpot (Proc. Roy. Soc., 1933, **B**, **113**, 48—56).—A highly active cryst. prep. (this vol., 99) has max. absorption at 245—249 mμ. When its acid solution is brought to p_H 13 a broad band appears at 330—340 mμ (I), with max. absorption at 233 mμ. (I) disappears on heating, and subsequent acidification restores absorption at 245 mμ. The cycle of changes may be repeated and is accompanied by considerable loss of activity. A. C.

Relative extractability of vitamins-*B* [B_1] and -*G* [B_2] by plain and acidified alcohol. H. K. STIEBELING and I. L. ALLEMAN (J. Amer. Chem. Soc., 1933, **55**, 1477—1480).—About 50% of the vitamin-B_1 (I) in skim-milk powder is recovered from the extracts obtained using 80% (wt.) EtOH alone or containing (0·1*M*) gallic acid, BzOH, or HCl; 35—40% of (I) remains in the residue. Approx. 30% of the vitamin-B_2 (II) is extracted by the EtOH–gallic acid and practically none with EtOH–HCl; about 33% of (II) is left in the residue. Large losses of (II) are encountered in all the fractionations. Acidification does not increase the extractability of either (I) or (II). H. B.

Nutrition. XII. Comparative vitamin-B_1 values of animal foodstuffs. R. H. A. PLIMMER, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1933, **27**, 58—65; cf. A., 1931, 988, 1464).—The following vals. (calc. for wet and dry material, respectively, in comparison with yeast as 100) were obtained: egg yolk, 7, 13; liver, 7, 23; kidney, 8, 33; heart, 8, 36; dried skimmed milk, 10, 11; hard roe, 13, 62. Brain, lung, tripe, pancreas, beefsteak, soft roe, fish muscle, and mussels contained only traces. Thus in the fresh state animal foodstuffs are inferior to cereals and pulses but superior to fruits and vegetables, whilst when dried they are superior to cereals and pulses. F. O. H.

Variability of the need of the vitamin-*B* complex. A. DE VRIES and G. J. PUISTER (Arch. néerland. Physiol., 1933, **18**, 71—78).—15% of cod-liver oil in diet delays growth and causes loss of hair. This is prevented by 12% of yeast, vitamin-B_2 being the effective agent. H. G. R.

Studies on growth. I. Growth factors in liver. II. Effect of vitamins-B_1 and -B_2 on the consumption and utilisation of food. C. E. GRAHAM and W. H. GRIFFITH (J. Nutrition, 1933, **6**, 169—194, 195—204).—I. Liver was superior to yeast as a source of vitamin-B_2 for rats.

II. Vitamins-B_1 and -B_2 stimulate the consumption and utilisation of food. A. G. P.

Vitamin-B_4 and adenine. R. D. HEARD, H. W. KINNERSLEY, J. R. O'BRIEN, R. A. PETERS, and V. READER (Nature, 1933, **131**, 617—618).—Vitamin-B_4 and adenine are not identical. Active crystals previously prepared (this vol., 325) consist largely of adenine, and the active residue has yet to be separated. Irradiated adenine so far has not shown vitamin-B_4 activity. L. S. T.

Antiscorbutic action of ascorbic acid. J. BRÜGGEMANN (Z. physiol. Chem., 1933, **216**, 139—140).—The antiscorbutic activity is confirmed. J. H. B.

Hexuronic (ascorbic) acid as the antiscorbutic factor. L. J. HARRIS and S. N. RAY (Biochem. J., 1933, **27**, 580—589).—Hexuronic acid (I) from different sources and after repurification did not vary in antiscorbutic activity (II). The content of (I) in some cases, measured by the intensity of adsorption at 265 mμ, of 30 natural sources accounts quantitatively for (II). The rate of destruction of (I) under varying conditions and its loss with the development of scurvy resembled those of (II). (I) is synthesised concurrently with (II) by the plant on germination. H. G. R.

Occurrence of vitamin-*C* in the Eriwan grape. A. JOHANNISSIAN and H. BUNIATIAN (Bull. inst. sci. R.S.S. Arménie, 1931, 213—218).—All the samples gave a positive Bezssonov colour reaction, which may be employed quantitatively. Orthuzi-Djilari, Muscat, Chardji, and Chatschabasch grapes were richest in vitamin-*C*. CH. ABS.

Determination of vitamin-*C* in diploid and tetraploid tomatoes. K. M. KEY (Biochem. J., 1933, **27**, 153—156).—The juice from normal tomatoes contained 22 international units of vitamin-*C* per c.c. No difference existed between the contents of diploid and tetraploid tomatoes of the same genetic constitution. Hence the no. of chromosomes is not the sole factor controlling the vitamin-*C* content. F. O. H.

Reduction experiments with vitamin-*C* and carbohydrate derivatives. H. VON EULER (Naturwiss., 1933, **21**, 236).—The adrenal glands have the largest vitamin-*C* content of any organ; injection of adrenaline lowers this content. On warming with dil. alkali hexose solutions show an absorption band in the ultra-violet spectrum at 260—300 mμ, similar to that given by pure vitamin-*C* preps., and have similar reducing properties. P. G. M.

Microchemical method for determining the hexuronic content (vitamin-*C*) of foodstuffs. J. W. BIRCH, L. J. HARRIS, and S. N. RAY (Biochem. J., 1933, **27**, 590—594).—The material is extracted with $CCl_3{\cdot}CO_2H$ and titrated with 2:6-dichlorophenol-indophenol. In acid solution, other reducing substances, *e.g.*, glutathione, do not interfere; in the presence of cysteine a special control is necessary. H. G. R.

Titration curve and dissociation constants of vitamin-*C*. J. W. BIRCH and L. J. HARRIS (Biochem. J., 1933, **27**, 595—599).—Determined by a micro-method, using 0·1 c.c. of solution $p_{K_{a_1}}=4{\cdot}17$, $P_K=11{\cdot}57$, (if anv) $=>14$. The combining wt. agreed with $C_6H_8O_6$. H. G. R.

Narcotine and vitamin-*C*. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 259—273).—Pure methylnornarcotine (I) could not be prepared by Rygh's method from narcotine. The % purity of specimens was calc. from the OMe content. Doses of impure specimens of (I) equiv. to 10—30$\times 10^{-6}$ g., with or without addition of inactivated lemon juice, failed to delay the onset of scurvy in guinea-pigs on a *C*-deficient diet. P. G. M.

Vegetable assimilation and respiration. XXI. Induction phases in photosynthesis and their bearing on the mechanism of the process. G. E. BRIGGS (Proc. Roy. Soc., 1933, **B**, **113**, 1—41).—The influence of intensity of illumination and temp. on the ratio between the initial and final rates of CO_2 assimilation has been studied on a moss, *Mnium undulatum*. Schemes for the mechanism of the photosynthetic process, which permit mathematical treatment, are formulated. A. C.

Products of photosynthesis in leaves in artificial and in natural light. R. H. DASTUR and

K. M. SAMANT (Ann. Bot., 1933, **47**, 295—304).—Starch formation in certain leaves in artificial light was approx. one third of that in daylight, but sucrose formation was practically the same under both conditions. In diffused sunlight the total carbohydrate formed was > twice that produced in artificial light. In non-starch-forming leaves (*Allium cepa*) sugar formation in diffused light was > three times that in artificial light. Differences in carbohydrate formation are ascribed to differences in quality rather than intensity of the light source. A. G. P.

Influence of gaseous impurities of the atmosphere on plant transpiration and a method of measuring transpiration rates. A. HEILING (Phytopath. Z., 1933, **5**, 435—492).—Small proportions of SO_2 in the air accelerated and larger amounts restricted the transpiration of plants. The intake of H_2O by leaves of low H_2O content from moist air is increased by the presence of low concns. of SO_2. Relationships between SO_2 concn., transpiration rates, and sensitiveness to injury are examined. Apparatus for determining transpiration rates is described. A. G. P.

Dependence of plant catalase activity on nourishment and growth. M. BILETZKY (Fermentforsch., 1933, **13**, 467—498).—A high N content [as $Ca(NO_3)_2$] in the soil produces a high catalase activity (I) in germinating or developed barley and peas, whilst with a high P [as $CaH_4(PO_4)_2$] and low N and K content (I) is absent. Fertilisation with KCl leads to a val. of (I) intermediate between those due to N and P. Other constituents of the soil, *e.g.*, Na, Mg, and Ca, appear to influence the (I) of germinating plants. Sunlight and, to a smaller extent, lack of H_2O reduce (I), which shows a max. val. with plants kept in the dark at low temp. F. O. H.

Effect of pCO$_2$ on the nitrogen-fixation process of certain leguminous plants. P. W. WILSON and E. B. FRED (J. Bact., 1933, **25**, 54).—An increase in pCO_2 from 0·03 to 0·1% considerably increases the growth of clover plants, nodulation, and fixation of N. Further increases in pCO_2 do not produce correspondingly greater development. Nodules of CO_2-treated plants are greater in size and no. and more evenly distributed throughout the root system than in untreated controls. A. G. P.

Influence of various nitrogenous compounds and mannitol on nodule formation by clover. E. W. HOPKINS and E. B. FRED (Plant Physiol., 1933, **8**, 141—155).—The effect on agar cultures of red clover of KNO_3, $(NH_4)_2SO_4$, urea, asparagine, yeast, and a clover-seed extract varied considerably, but in all cases the size of the nodules decreased with increasing concns. of N. Nodules were distributed mainly on the secondary roots. When mannitol was supplied in addition to N, nodules occurred principally on the tap roots (as in untreated controls), but the actual size of the nodules was inversely related to the N dosage. A. G. P.

Nutrition of *Euglena*. I. *Euglena gracilis*. H. DUSI (Ann. Inst. Pasteur, 1933, **50**, 550—597).—Cultures can be grown in a synthetic medium in which the source of N is a nitrate or an NH_4 salt, the initial p_H being 6·5—7·5. With $(NH_4)_2SO_4$ and an initial p_H of 7·0, acid is produced, and the final p_H after 17 weeks is 4·2. $Ca(NO_3)_2$ cannot be utilised, and Ca ions appear to be unnecessary for development. Of a large no. of NH_2-acids utilised as a source of N, only the simple aliphatic acids, asparagine, histidine, and phenylalanine yielded good cultures. Peptone produces the best results. In the dark, media containing peptones or polypeptides as the source of N are rendered more effective by the addition of NaOAc. Only those fatty acids having < 7 C atoms were able to replace AcOH. Strains grown in the light do not require the addition of a fatty acid to the medium. P. G. M.

Nitrogen metabolism of sugar-beet seedlings: dependence on the ammonia- and nitrate nutrition. L. S. LUBARSKAJA (Z. Pflanz. Düng., 1933, **28**, A, 340—368).—The intake of NO_3-N by sugar-beet seedlings in daylight is less rapid than that of NH_3-N. The intake and utilisation of N from NH_4NO_3 resemble more closely those of $(NH_4)_2SO_4$ than of KNO_3. The utilisation of absorbed $NH_4^{\cdot}$ is dependent on the C : N ratio of the plants and therefore on their age and growth conditions. A large proportion of the $NH_4^{\cdot}$ intake is transformed into more complex N compounds within 3 hr., the surplus being stored as NH_3. The toxic limit of accumulation of NH_3 varies considerably with different plants and is influenced by a no. of factors. The elaboration of NO_3-N resembles that of $NH_4^{\cdot}$-N except that the surplus accumulates as NO_3'. Assimilation rates of N are reduced in darkness, $NH_4^{\cdot}$ being more affected than NO_3'. Etiolated seedlings cannot utilise the N taken up, and there follows some protein decomp. with a narrowing of the C : N ratio. The latter affects not only the rate of utilisation of N, but also the actual intake of $NH_4^{\cdot}$. A. G. P.

Distribution of nitrogen in tobacco when the supplies of nitrogen and of light are varied during the growing period. W. S. EISENMENGER (J. Agric. Res., 1933, **46**, 255—265).—Stems of tobacco plants had higher contents of total N and NH_3-N than any other plant organs, whereas leaves showed high vals. for % dry matter and protein. Max. NO_3' occurred in all instances in the mid-vein of the leaf. Plants grown in darkness for 11 days contained more NH_3-N than those grown in light. In the tissues of plants deprived of N for 11 days there remained an ample supply of NO_3-N. Differences in lighting affect principally the NO_3' and α-NH_2-acid contents. Large excess of N as compared with other nutrients produced plants of low dry matter content but high proportions of NO_3'. A. G. P.

Cytology, microchemistry, and micrographics of the tobacco plant. M. J. CHAZE (Mem. Manuf. Etat. Tabacs, 1930, **6**, 298; Bied. Zentr., 1932, **3**, A, 62).—Nicotine could not be detected in plant tissues by customary alkaloid reagents. Solution of I in KI yielded the characteristic ppt. only after washing the tissue in EtOH containing tartaric acid. Nicotine contents of tissues increased with vacuole formation and in general nicotine accumulated in surface tissues, *e.g.*, near stomata, root hairs, and epidermal cells.

Nicotine is not a growth activator, but an excretion product of the synthesis of N compounds. A. G. P.

Development of structural constituents in the barley plant. A. G. NORMAN (J. Agric. Sci., 1933, **23**, 216—227).—With advancing growth of barley plants the ash and protein constituents increase at first, but fall steadily to maturity. The cellulose fraction shows an initial peak followed by a stationary period. The cellulosan (or associated polysaccharide) portion of the cellulose increases with age more especially after the period when growth increments begin to decline. Lignin increases steadily with growth until maturity is approached, and decreases during the final 7—15 days. The pentose content of the hemicelluloses varies considerably, but is lower in mature than in young plants, although the total pentose material in the plant increased with age. In the young plants, pentoses occur mainly as polyuronides and in mature plant in the cellulosans. A. G. P.

Choline metabolism in plants. II. G. KLEIN and H. LINSER (Biochem. Z., 1933, **260**, 215—225; cf. A., 1932, 1179).—The variations in the free and combined (lecithin) choline contents which occur during growth in the various parts of plants (not young), and the transport of lecithin from one part of the plant to another which takes place, resemble the corresponding changes occurring in seedlings. It is probable that some of the free choline is derived from the lecithin and that a converse process does not occur. W. McC.

Role of allantoic acid in higher plants. R. FOSSE, P. DE GRAEVE, and P. E. THOMAS (Compt. rend., 1933, **196**, 1264—1267).—A number of plant seeds contain uric acid, allantoin, and allantoic acid (I), formed by successive enzyme actions. The amount of (I) increases greatly during germination of *Trifolium sativum* seeds in the dark at 31°. It is stable at p_H 7·3, but at p_H 6·8 rapidly gives carbamide and $CHO{\cdot}CO_2H$. R. S. C.

Formation of sterols in germination. H. BEUMER (Biochem. Z., 1933, **259**, 469—470).—During germination and growth of peas and beans sterol formation in etiolated is > in normal plants. P. W. C.

Changes during ripening in the fat, phosphatide, and protein contents of seeds. B. REWALD and W. RIEDE (Biochem. Z., 1933, **260**, 147—152).—In the growing soya plant great preferential development of the beans (I) at the expense of other parts (II) occurs, and whereas in (II) ripening is accompanied by large decreases in the protein (66—75%), fat (50%), and phosphatide (III) contents all these remain unchanged in (I). In the pods the decrease in (III) is especially pronounced. The decreases are sometimes followed, in the last stages of growth, by slight increases. The I val. of the oil of (I) is > that of the oil of (II), and in (I) the degree of unsaturation of the oil also increases as ripening proceeds. W. McC.

Phosphorus metabolism in higher plants. I. Determination of pyro- and meta-phosphate, phosphite, and hypophosphate in plant material. H. MENGDEHL. **II. Sterile cultures of higher plants.** J. WEISSFLOG. **III. Intake and utilisation of organic phosphorus compounds by plants. IV. Intake and utilisation of inorganic phosphorus compounds by plants.** J. WEISSFLOG and H. MENGDEHL (Planta [Z. wiss. Biol.], 1933, **19**, 154—169, 170—181, 182—241, 242—271).—I. Meta- and pyro-phosphates are determined by hydrolysis to orthophosphate with *N*-HCl at 100° (cf. Lohmann, A., 1929, 208). Phosphites are oxidised by 0·01*N*-I in presence of NaOAc and hypophosphites by 0·02*N*-Br and determined as phosphate.

II. Methods and apparatus are described. Powdered SiO_2 gel is used as protection against infection by atm. organisms.

III. Various org. P compounds served as P sources for maize in sterile cultures and in acid nutrients frequently produced plant yields > from orthophosphates. According to their effects on plants three groups of P compounds are differentiated: (*a*) Phytin group (*e.g.*, phytic and nucleic acids), (*b*) ortho-group (H_3PO_4, hexose diphosphate), and (*c*) esters (hexose monophosphate, glyceryl and sucrose phosphates). The % of total P in plants varied with the P source in the order of groups $(a)<(c)<(b)$, but the total dry matter yield from (*a*) was ≮ that from (*c*). Plants receiving (*a*) tended to accumulate in the roots sol. org. P and insol. P. Highest proportions of orthophosphate occurred in plants receiving (*b*). The stability of the P compounds with respect to the phosphatase of maize was in the order, phytic acid >nucleic acid>glyceryl phosphate>hexose diphosphate.

IV. Pyro- and meta-phosphates, phosphites, and hypophosphites were all taken up by plants. The phosphates were transformed into ortho-salts before passing out of the root system. Phosphites and hypophosphites were translocated throughout the stems and leaves, but were not utilised by the plant. Highest P contents occurred in plants receiving orthophosphates or KPO_3. Most of the total P of plants is present as orthophosphate. A. G. P.

Intake of ions by the plant and its relation to the respiration of the root. A. H. K. PETRIE (Austral. J. Exp. Biol., 1933, **11**, 25—34).—When the rate of respiration of the roots of Algerian oats grown in an artificial mineral salt medium is decreased by reducing the O_2 supply, the intake of ions by the roots is diminished and the growth of the roots, and to a smaller extent of the shoots, is retarded. These results are discussed on the basis of a general hypothesis of the mechanism of the intake of ions by plant roots from the environment. W. O. K.

Seasonal absorption of nutrient salts by the French prune grown in solution cultures. H. L. COLBY (Plant Physiol., 1933, **8**, 1—34).—NO_3' absorption was affected by SO_4'' starvation < by the absence of any other essential nutrient. K, Mg, and P starvation heavily depressed the NO_3' intake and in some cases a portion of the absorbed NO_3' was eliminated from the roots late in the season. Absence of Ca entirely prevented root growth and the absorption of other nutrients in any appreciable degree. Transference of trees from Ca nutrients to Ca-free nutrients resulted in death of the root tips, the survival period depending on the amount of Ca previously supplied. Absence of Mg restricted the PO_4''' intake

to a much greater extent than did absence of $K^{\cdot}$ or SO_4''. The K absorption curve closely resembled that of N, but with a slight lag in the early part of the season. Close correlation is recorded between temp. and rates of K and P intake. A. G. P.

Utilisation of adsorbed ions by plants. H. JENNY and E. W. COWAN (Science, 1933, **77**, 394—396).—Experiments with soya-bean plants grown in systems containing only one nutrient ion, Ca, show that total analysis of a soil is an inadequate indication of soil fertility, since there is no differentiation between adsorbed and non-exchangeable lattice ions. Since the plant can feed on the former, the significance of the soil solution appears to have been exaggerated. The solubility concept is not adequate to account for plant growth in humid regions; ionic exchange must be taken into account. The study of adsorbed ions in soils should lead to a better understanding of many soil–plant relationships and fertility problems. L. S. T.

Role of calcium in the assimilation of iron by plants. A. G. SCHESTAKOV (Ergeb. Veg. Lab.-arb. Prianischnikov, 1930, **15**, 49—81; Bied. Zentr., 1933, **A**, **3**, 229).—Small concns. of Fe salts may injure plant roots, unless $Ca^{\cdot\cdot}$ is present in sufficient amounts to exert a protective action. Roots of young maize plants injured by Fe develop new root hairs after addition of $CaSO_4$ to the nutrient. Injury by Fe is intensified if the supply of PO_4''' is deficient. A. G. P.

Potash [and plant life]. K. SCHMALFUSS (Z. Pflanz. Düng., 1933, **28**, **A**, 330—335).—The role of K in physiological and metabolic changes in plants is discussed. The influence of K on the state of dispersion of cell colloids and its consequent regulatory effect on the H_2O status and electrolyte concn. in the tissues is emphasised. A. G. P.

Physiological importance of the mineral elements in plants. IV. Distribution of potassium in the potato plant. W. O. JAMES and N. L. PENSTON (Ann. Bot., 1933, **47**, 279—293).—All organs of the plant contained K, which was particularly abundant in actively growing tissues. The average amount of K per unit wt. of dry matter is closely related to the rate of dry matter production. No evidence was obtained that K accumulation precedes or induces active growth. Similarity in the distribution of K and of protein suggests that translocation of K occurs in the form of K salts of NH_2-acids. Storage of K occurs in the upper-middle portion of the haulm, but does not contribute to any great extent to tuber formation. Distribution of H_2O in stems resembles that of K. A continuous circulation of K in plants is suggested, viz., movement toward leaves in the transpiration stream and from leaves by way of the phloem. A. G. P.

Influence of variety on the mineral content of grain. P. SCHRUMPF-PIERRON (Compt. rend. Soc. Biol., 1932, **111**, 846—848; Proc. Internat. Soc. Soil Sci., 1933, **8**, 33).—Varietal differences in ash, Mg, Ca, K, and P_2O_5 contents are considerable, the widest range of differences occurring in the Mg vals. A. G. P.

Manganese and the growth of *Lemnaceæ*. A. SAEGER (Amer. J. Bot., 1933, **20**, 234—245).—Mn is essential for the growth of *Lemnaceæ*. In nutrients containing 0·001 mg. Mn per litre normal growth occurs, but with 1 mg. per litre there is some retardation. Al, B, Cu, F, I, or Zn (0·001 mg. per litre) could not replace Mn for this purpose. *Lemnaceæ* can accumulate reserve supplies of Mn if supplied in appropriate amounts. A. G. P.

Manganese and the growth of *Lemna*. N. A. CLARK (Plant Physiol., 1933, **8**, 157—161).—Manganese is an essential nutrient for *Lemna major*. Normal growth occurred in nutrients containing Mn (1 in 3×10^6). Fe supplied as $FeCl_3$ in similar concn. produced large plants of lighter colour. Fe citrate produced dense chlorophyll but smaller plants. The rate of reproduction increased with the proportion of Mn in the nutrient up to a max. beyond which more Mn had no effect. A. G. P.

Vacuum infiltration in [plant] nutrition experiments. Assimilation of ammonium. K. MOTHES (Planta [Z. wiss. Biol.], 1933, **19**, 117—138).—A method whereby nutrient solutions may be introduced directly into the leaf tissues is described. Infiltration of NH_4 salts of org. acids into C-deficient leaves (*e.g.*, after exclusion of light for 3—4 days) results in the formation of amides, which is relatively rapid in the case of malic, fumaric, and succinic acids, less rapid for tartaric, pyruvic, and lactic acids, and very slight for AcOH. Asparagine is produced from NH_4 malate. From pyruvic acid more NH_2- than amide-N is formed. The reverse holds for lactic acid. A. G. P.

Antagonism. II. Effect of previous immersion of potato tuber tissue in solutions of univalent, bivalent, and tervalent cations on subsequent absorption of ammonium ion. G. F. ASPREY (Proc. Roy. Soc., 1933, **B**, **113**, 71—82).—Immersion of potato tissue in aq. KCl, NaCl, or LiCl increases the subsequent absorption of NH_4 from aq. NH_4Cl, Li having a much greater effect than Na or K. $CaCl_2$, $MgCl_2$, and $AlCl_3$ decrease absorption. For each salt a factor, approx. const. for periods of immersion up to 24 hr., is obtained relating absorption by treated and untreated tissue. The effects described represent the sp. effect on tissue previously postulated (this vol., 436) as one factor in antagonism. A. C.

Relation between the composition of exuded plant sap and the soil solution. W. H. PIERRE and G. G. POHLMAN (J. Amer. Soc. Agron., 1933, **25**, 144—160).—Maize sap contained approx. 3700 p.p.m. of total solids, of which approx. one third was in the inorg. form. The total electrolyte content of the sap was in nearly all cases $>$ that of the displaced soil solution. Of the total P in saps of maize, sorghum, and Sudan grass (150—450 p.p.m.) $>$ two thirds was in the inorg. form. The concn. of P and Si in saps averaged, respectively, 500—5000 and 15—35 times that in soil solutions, whereas the $[Ca^{\cdot\cdot}]$ and $[Cl']$ were lower and the $[NO_3']$ was very variable. A correlation between the proportion of P in saps and in the corresponding soil solutions is indicated. Variations in soil acidity of p_H 4·6—6·6 affected neither

the p_H of the sap, which maintained a fairly const. level (4·4—4·8), nor its Ca", P, and Cl′ contents. With higher ranges of p_H there was an increased Si content. Poor growth of sorghum and Sudan grass on acid soils cannot be attributed to inability of the plants to accumulate Ca and P in their saps. Successive daily samples of sap contained const. amounts of total P but increasing proportions of inorg. P and Cl′. No consistent variations in Ca" and Si contents were observed. A. G. P.

Nature of potassium compounds in plants. S. L. INOSEMZEV (Ergeb. Veg. Lab.-arb. Prianischnikov, 1930, **15**, 85—101; Biod. Zentr., 1933, **3**, A, 225—226).—The greater part of the K of plants exists in a complex non-dialysable form. During electrodialysis 35% of the total K of young pea plants and 14% of that in mature plants appears at the cathode and 16·2 and 18%, respectively, at the anode. Dialysable K is probably in an org. form. Rates of deposition of anodic and cathodic K (in respect to the total deposited in each case) are similar and unaffected by the nature of the membrane used. A. G. P.

Distinctive effects of the deficiency of certain essential elements on the growth of tobacco plants in culture solutions. J. E. MCMURTREY (U.S. Dept. Agric., Tech. Bull., 1933, No. 340, 42 pp.).—Leaves of plants growing in N-deficient solutions are light green, the lower ones tending to yellow, and roots are long, little branched, and white. P starvation produces dark green leaves, and long roots which are little branched and brown as a result of accumulation of Fe on the surface. Deficiency of K and Mg produces more localised effects, notably typical forms of chlorosis on older leaves. Absence of Mn, Fe, S, B, and Ca affects principally the young growing tips. Chlorosis caused by lack of Fe is characterised by retention of green colour by the leaf veins and in the case of Mn by general necrotic spotting. Chlorosis induced by S starvation is shown by leaf veins remaining paler than the tissue. Roots are more abundant and whiter than in Mn or Fe chlorosis. Deficiency of Ca or B results in the death of terminal buds, the breakdown process being of a characteristic kind in each case. A. G. P.

Phosphorus concentration of the exuded sap of maize as a measure of the available phosphorus of the soil. G. G. POHLMANN and W. H. PIERRE (J. Amer. Soc. Agron., 1933, **25**, 160—171).—Under greenhouse conditions the inorg. P content of maize sap was closely correlated with the H_2O-sol. PO_4''', the available PO_4''' (Truog), and with the response of the plant to P fertilisers. Some increase in $[PO_4''']$ of the sap with the age of the plant was general. A. G. P.

Intracellular hydrogen-ion concentration studies. VIII. Cytoplasm and vacuole of *Limnobium* root-hair cells. R. CHAMBERS and T. KERR (J. Cell. Comp. Physiol., 1932, **2**, 105—119).—Penetration of various dyes and their behaviour on ingestion is examined. The normal cytoplasmic p_H was 6·9, changing, on injury, to 5·2; that of the vacuole was 5·2, irrespective of the reaction of the medium or of seasonal or growth changes, but changing on death to 6·4. The wall of the root hair in living and dead cells was more permeable to NH_3 at the tip than elsewhere (cf. this vol., 627). A. G. P.

Rate of penetration of dyes into *Valonia* with special reference to solubility theories of permeability. S. C. BROOKS and M. M. BROOKS (J. Cell. Comp. Physiol., 1932, **2**, 53—73).—Basic dyes penetrate irrespective of their degree of dissociation. Acid dyes penetrate only if their pK vals. are > a certain val. lying between 3·0 and 5·3. Sulphonic acid dyes examined did not penetrate. A. G. P.

Chemical *versus* morphological species differences. S. C. BROOKS (Science, 1933, **77**, 221—222).—Chemical characteristics (sap analysis) and environmental data for different reputed species of *Valonia* are discussed. L. S. T.

Distribution of copper in the Karaka tree (*Corynocarpus lævigata*). N. P. PITCAITHLY and F. P. WORLEY (J. Agric. Sci., 1933, **23**, 204—207).—Cu occurred in all organs of the tree and especially in leaves and the flesh of the fruit. A considerable proportion is sol. in EtOH. A. G. P.

Mineral constituents of *Artemisia afra*. G. W. B. VAN DER LINGEN (Analyst, 1933, **58**, 280).—The dried leaves contained K_2O 3·32, Na_2O 1·19, MgO 0·68, CaO 1·95, P_2O_5 0·79, Fe_2O_3 0·03, Cl 0·57, protein 17·63, total ash 8·94, and SiO_2 1·05%. J. G.

Comparative composition of homologous vine leaves taken from fruitful stems and stems deprived of grapes. H. LAGATU and L. MAUME (Compt. rend., 1933, **196**, 1168—1170).—The N, K_2O, CaO, and the sum of N, K_2O, and P_2O_5 contents of vine leaves are less on fruit-bearing than on sterile stems, whilst the individual val. for P_2O_5 is greater in the same sense. K vals. indicate K debt. A. C.

***Amphiachyris dracunculoides* (DC.), Nutt.: flowering branches.** L. E. HARRIS and I. GRIFFITH (J. Amer. Pharm. Assoc., 1933, **22**, 306—309).—The dried flowering tops (5·22% ash) gave 5% of material, sol. in light petroleum, having sap. val. 158·36 and I val. 38·31. The EtOH extract (13·75%) contained a glucoside. E. H. S.

Products of *Cocos nucifera*. II. J. P. C. CHANDRASENA (Biochem. J., 1933, **27**, 3—4).—The following data were obtained for the "milk" of the coconut before and during germination, respectively: d 1·014—1·025, 1·008—1·020; p_H, 4·8—5·4, 4·8—5·9; % total solids, 4·01—7·31, 2·90—5·02; % ash of total solids, 9·94—18·99, 11·37—14·30. The p_H, which remains const. even during germination, approximates to the optimum for *Ricinus* lipase. F. O. H.

Occurrence of rotenone and related compounds in the roots of *Cracca virginiana*. E. P. CLARK (Science, 1933, **77**, 311—312).—Rotenone, dehydrorotenone, tephrosin, and a colourless cryst. substance, $C_{22}H_{24}O_4$, m.p. 131°, have been obtained from the roots of *C. virginiana*. L. S. T.

Rotenone in a species of *Spatholobus*. H. A. JONES (J. Amer. Chem. Soc., 1933, **55**, 1737—1738).—Rotenone is isolated in about 1% yield from the $COMe_2$ extract of the root of *S. roxburghii*, Benth. H. B.

Constituent of santonin-free worm seed. H. NAKAMURA, T. OHTA, and G. HUKUTI (Proc. Imp. Acad. Tokyo, 1933, **9**, 91—93).—A cryst. compound, *temisin* ($C_{15}H_{20}O_3$), has been obtained in 0·3—0·5% yield from a variety of *Artemisia maritima* by the following procedure: the drug is boiled for 5—6 hr. with milk of lime, the filtrate is acidified and extracted with $CHCl_3$, and the residue from the extract is taken up in warm 20% EtOH; the temisin which separates is recryst. from EtOH, m.p. 228°, $[\alpha]_D^{32}$ +65·69° (*Ac* derivative, m.p. 86°; *Bz* derivative, m.p. 133°). Oxidation with $Na_2Cr_2O_7$ yields *temisone*, m.p. 130—131° (*oxime*, m.p. 232—233°; *tetrahydro*-compound, m.p. 111—112°); hydrogenation yields *tetrahydrotemisin*, m.p. 231° (sublimes), $[\alpha]_D^{16}$ +79·64° (*Ac* derivative, m.p. 83°); heating with Se at 320—340° yields a colourless oil, b.p. 133—138° at 16 mm. [*picrate*, m.p. 96° ($C_{13}H_{14}{\cdot}C_6H_3O_7N_3$)]. P. G. M.

Isolation of pyrocatechol from pigmented onion scales and its relation to disease-resistance in onions. K. P. LINK (J. Biol. Chem., 1933, **100**, 379—383).—Pyrocatechol (I) was isolated from pigmented onion skins by taking up the residue from the $COMe_2$ extract (A., 1929, 613; 1930, 122), with H_2O, pptn. with neutral $Pb(OAc)_2$, filtering, and decomp. of the Pb compound with H_2SO_4. The filtrate is made alkaline with $NaHCO_3$, extracted with Et_2O, conc., and extracted with C_6H_6; the latter is removed and the residue recryst. from H_2O. (I) is not obtained from non-pigmented skins and is more toxic to *Colletotrichum circinans* than protocatechuic acid. H. D.

Effect of geographical factors and the type of forests on the turpentines from *Pinus sylvestris*. V. KRESTINSKI, S. MALEVSKAYA, and F. SOLODKI (J. Appl. Chem., Russia, 1932, **5**, 950—957).—The variety of the tree, and not the local conditions, governs the type of the product. CH. ABS.

***Nigella damascena*, L.** G. OTTOLINO (Officina, 1932, **5**, 273—276).—Oil (32—40%) extracted from the seeds by Et_2O has sap. val. 230, acids (as oleic) 41·73, ester val. 146·68, volatile fatty acids 4·4, non-volatile [acids] 83·62%, m.p. 10—12°, f.p. −16° to −20°. CH. ABS.

Seeds of *Psoralea corylifolia*, Linn. I. H. S. JOIS, B. L. MANJUNATH, and S. V. RAO (J. Indian Chem. Soc., 1933, **10**, 41—46).—The light petroleum extract of the crushed seeds contained a cryst. solid, *psoralen*, $C_{11}H_6O_3$, m.p. 162°, and an oil which on saponification gave resinous materials with the colour reactions of sterols, and palmitic, oleic, linoleic, stearic, lignoceric, linolenic, and resin acids. H. A. P.

Composition of seeds of *Thevetia neriifolia*, Juss. I. N. GHATAK (Bull. Acad. Sci. Allahabad, 1932, **2**, 79—84).—Extraction of the air-dried kernels with light petroleum yields 68·7% of a non-drying oil. The oil-free kernels are extracted with 95% EtOH and the extract is evaporated in vac. to a syrup, which solidifies and is extracted again with $CHCl_3$. The residue, after evaporation of $CHCl_3$, is recryst. from dil. EtOH in needles (*thevetin*, m.p. 192°, $C_{20}H_{30}O_6$, $[\alpha]_D^{31}$ −66·85°). Thevetin is tasteless and non-toxic, whilst *thevetoxin* ($C_{16}H_{24}O_8$, m.p. 178°, $[\alpha]^{30}$ −76·1°), which is isolated from the residue after $CHCl_3$ extraction, is bitter and very toxic. Thevetin is a glucoside which, on hydrolysis, yields glucose and *thevetigenin*, m.p. 83° (pink in conc. H_2SO_4 with green fluorescence); thevetoxin similarly yields glucose and *thevetoxigenin*, m.p. 81°. P. G. M.

Composition of the fruit of *Tribulus terrestris*, Linn. N. GHATAK (Bull. Acad. Sci. Allahabad, 1933, **2**, 163—170).—5% of oil is extracted from the powdered fruit with light petroleum; on keeping, behenic acid, m.p. 83°, separates. Saponification gives mixed fatty acids which contain oleic acid 27, linoleic acid 57, and saturated acids (palmitic and stearic), 16%. From the residue after petroleum extraction there was obtained an impure glucoside, a phlobaphen, and an acidic substance, m.p. 189—191°. P. G. M.

Composition of the non-phenolic portion of bay oil. S. PALKIN and P. A. WELLS (J. Amer. Chem. Soc., 1933, **55**, 1549—1556).—The constituents are myrcene, cineol, dipentene, and limonene, and small amounts of citral, α-phellandrene, α-pinene, and an unidentified geraniol-like alcohol. Little or no methylchavicol and methyleugenol are present. H. B.

Chavicol and eugenol from oil of bay. S. PALKIN and P. A. WELLS (J. Amer. Chem. Soc., 1933, **55**, 1556—1558).—Details are given for the separation of chavicol, m.p. 16°, and eugenol, m.p. −7·5°, from the phenolic portion of the oil. H. B.

Absorption spectrum of the unsaponifiable matter from wheat-germ oil. R. A. MORTON and J. R. EDISBURY (Nature, 1933, **131**, 618).—Data for four different samples of wheat-germ oil extracts are recorded. L. S. T.

Sterols of the bark of *Lophopetalum toxicum*. I. H. DIETERLE, H. LEONHARDT, and K. DORNER (Arch. Pharm., 1933, **271**, 264—268).—The bark (100 g.) contains lupeol (2 g.), betulin (0·7—0·8 g.) (*dipropionate*, m.p. 164—165°), and a *sterol*, probably $C_{29}H_{48}O_3$, m.p. 279—281° (0·3 g.). R. S. C.

Carotenoids of the apricot (*Prunus armeniaca*). H. BROCKMANN (Z. physiol. Chem., 1933, **216**, 45—48).—Apricots contain considerable amounts of β-carotene and traces of γ-carotene and lycopene. J. H. B.

Colouring matter of Japanese egg-plant (Nasu). C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1933, **9**, 51—52).—The aglucone obtained by hydrolysis of the colouring matter of egg-plant is identified as delphinidin chloride (I). The glucoside, in addition to the decomp. products of (I), gives *p*-coumaric acid on hydrolysis and when fused with NaOH. A. L.

Calibration of flower-colour indicators. E. P. SMITH (Protoplasma, 1933, **18**, 112—125).—The colour-p_H ranges of anthocyanin colours are determined and their relationships to the reaction of cell saps discussed. Colour charts are given. A. G. P.

Conversion of pigments of red algæ into mesobilirubin and mesodehydrobilirubin. R. LEMBERG and G. BADER (Naturwiss., 1933, **21**, 206).—

Further evidence is given for the close relation between these and the bile pigments. Scission of the chromoproteins is effected by hot MeOH–KOH, and the phycobilins formed are converted into mesodehydrobilirubin (I). Phycoerythrin gives, in addition, mesobilirubin (II). These are identified as Me_2 esters. The bluish-green dehydrobilirubins form the most stable stage of hydrogenation in the bile pigments. (I) is identical with mesobiliverdin, and is the first (green) phase of the Gmelin reaction for (II). Phycoerythrobilin appears to be identical with urobilin of urine, and phycocyanobilin a dehydrogenation product or isomeride of (I). The formulation of phycobilins as bile pigments with saturated side-chains indicates their origin from chlorophyll or one of its precursors. A. C.

Soluble sugars of *Lemanea nodosa*, Kütz. H. Colin and J. Augier (Compt. rend., 1933, **196**, 1042—1043).—The principal sugar in the EtOH extract of fresh-water *Lemanea* is floridoside, identical with that obtained from *Rhodymenia palmata* (A., 1930, 825). Trehalose is found in the EtOH mother-liquors. A. C.

Occurrence of polylævans in nature and their possible relationship to primarily formed sugar. W. Flörsheim (Diss., Hamburg, 1930; Bied. Zentr., 1932, **3**, A, 50—51).—Polylævans were present in *Scilla maritima*. The glucose content of hydrolysed polylævans decreased with increasing mol. wts. The reducing substances produced by acid hydrolysis increased in the order mono-, di-, tetra-lævans. Sucrose is probably the first sugar formed. All plants containing polylævans in leaves or stems accumulate this material in rhizomes. All polylævans in admixture with sugars are fermented by yeast. A. G. P.

Occurrence and microchemistry of the amyloids in plant-cell membranes. O. Hopmann (Diss., Münster, 1930; Bied. Zentr., 1932, **3**, A, 50).—With various plant materials examined removal of amyloids by suitable solvents from cell walls leaves a framework of cellulose, and conversely the dissolution of cellulose leaves a membrane showing amyloid reactions. In certain cases lamellæ prior to lignification exhibited amyloid properties. A. G. P.

Tanret's "synanthrin." H. Colin and A. Chaudun (Bull. Soc. Chim. biol., 1933, **15**, 402—406).—β-Methylglucoside is obtained from "synanthrin" (A., 1893. i, 618) after acid hydrolysis by treatment with 70% MeOH. H. D.

***Persica vulgaris*. I. Presence of amygdonitrile-glucoside.** J. Rabaté (Bull. Soc. Chim. biol., 1933, **15**, 385—394).—The EtOH extracts of *P. vulgaris* are treated successively with invertase and emulsin, and the changes in optical rotation and reducing power observed. The formation of HCN was noticed. Amygdonitrile-glucoside (I) is obtained by extraction with boiling 85% EtOH, cooling to remove wax, distillation of EtOH, and filtration of the aq. residue to remove chlorophyll, addition of $Pb(OAc)_2$, removal of the Pb, and concn. of the solution in vac. The residue is extracted with EtOAc and the latter removed. (I) is recrystallised from the residue. It is rapidly hydrolysed by emulsin. *l*-Phenylglycollic acid is produced from (I) by boiling with conc. HCl, dilution with H_2O, and extraction with Et_2O. H. D.

Presence of sucrose in vine leaves. G. Barbera (Annali Chim. Appl., 1933, **23**, 99—104).—This is confirmed by the change in rotation accompanying the action of invertase on the saccharine extracts of the leaves, and by determinations of the sugars. T. H. P.

Nectar secretion of the tulip tree or yellow poplar. G. E. Marvin (J. Econ. Entom., 1933, **26**, 170—176).—The average sugar content of nectar from freshly-opened flowers was 16·7%, rising to 35·9% on the second day. The total nectar per flower was from 0·5 to 3·2 g. A. G. P.

Rate at which honey bees ripen honey. O. W. Park (J. Econ. Entom., 1933, **26**, 188—193).—Nectar containing 45% sugar contained approx. 60% of sugar when deposited in the comb. Green honey in the comb screened from bees increased in sugar concn. from 65 to 80% in 3 days. A. G. P.

Alcohol as a sugar extractant in plant-tissue analysis. A. C. Hulme (Biochem. J., 1933, **27**, 116—120).—No appreciable error (by the formation of aldehydes etc.) results from the use of hot EtOH in the determination of sugar in plant leaves, the results so obtained being comparable with those given by aq. extraction. F. O. H.

Nitrogenous constituents of a variety of *Rhaphanus sativus*, "Sakurajima-daikon." K. Yoshimura, T. Efuji, and T. Iwata (J. Agric. Chem. Soc. Japan, 1932, **8**, 1060—1063).—From 66·09 kg., adenine (HCl) 0·6, arginine (HNO_3) 1·2, choline (Au) 0·6, and trigonelline (HCl) 0·1 g. were isolated. Ch. Abs.

***l*-Tyrosine from *Vicia faba*, L.** H. Schmalfuss, A. Heider, and K. Winkelmann (Biochem. Z., 1933, **259**, 465—468).—A $Pb(OAc)_2$ method is given for separation of tyrosine from dihydroxyphenylalanine. The green pods of *Vicia faba* contain *l*-tyrosine and this with 3 : 4-dihydroxyphenylalanine correspond in the bean with tyramine and hydroxytyramine of broom-pods. In both cases the amount of monohydroxy-compound is small and of the dihydroxy-compound relatively large. P. W. C.

Alkaloids from *Leontice ewersmani*. A. P. Orekhov and R. A. Konovalova (Khim. Farm. Prom., 1932, **10**, 371—375).—Dried bulbs of *L. ewersmani* (alkaloids 0·4%) contain *leontamine*, $C_{14}H_{26}N_2$ (*hydrochloride*; *di-iodomethylate*; *chloroplatinate*; *picrate*), and leontidine, m.p. 116—118°. Ch. Abs.

Alkaloids of Chinese *Corydalis ambigua*, Cham. et Sch. (Yen-hu-so). IV. Corydalis-*J* and -*K*. T. Q. Chou and G. H. Wang (Chinese J. Physiol., 1933, **7**, 35—38).—In addition to the nine alkaloids previously obtained (A., 1929, 1085), *corydalis*-J, $C_{30}H_{36}O_5N_2$, m.p. 118°, $[\alpha]_D^{25}$ +125° in EtOH (*hydrochloride*, m.p. 235°), and *corydalis*-K, m.p. 225°, $[\alpha]_D^{25}$ −250° in $CHCl_3$, have been isolated. The physiological properties of the two alkaloids are briefly described. F. O. H.

Alkaloids of Chinese drug Pei-mu, *Fritillaria roylei*. II. Fritimine. T. Q. Chou and K. K.

CHEN (Chinese J. Physiol., 1933, **7**, 41—43).—Pei-mu of the Szechuan variety (I) appears to contain active principles different from those of the variety previously investigated (A., 1932, 1178). From the corms of (I) was isolated *fritimine*, $C_{38}H_{62}O_3N_2$, m.p. 167°, $[\alpha]^{22}$ −50° in EtOH (*hydrochloride*, m.p. 230°). The alkaloid has a min. lethal dose of 40 mg. per kg. body-wt. in mice and raises the blood-sugar of rabbits. F. O. H.

Diminution in the amount of alkaloids in *Polygonum amphibium* owing to the protective action of water. A. SANNA (Annali Chim. Appl., 1933, **23**, 51—56).—Plants growing in soil which was flooded during the first and fourth years and dry during the second and third were examined. During the dry years the plants were covered with hairs, emitted a viscous liquid over the epidermis of stem and leaves, and contained appreciable proportions of alkaloids. During the wet years they showed no hairs or liquid excretion, and only traces of alkaloids. T. H. P.

Penetration of chlorides into the root of the turnip (*Brassica campestris*). M. V. HOMES (Protoplasma, 1933, **18**, 161—193).—Relationships between the rate of penetration of Cl′, the concn. of the cell sap and of the external solution, and the survival period (I) of the cells are examined. The proportion of Cl′ entering the cell and (I) are influenced by the cation associated with the Cl′. Among chlorides examined the penetration of Cl was least and the toxicity greatest in the case of NH_4Cl. A. G. P.

Behaviour of plant cells towards heavy-metal salts. H. KAHO (Planta [Z. wiss. Biol.], 1933, **18**, 664—682).—The toxic action towards the plasma of red cabbage cells of Zn salts was in the order $Br' > Cl' > NO_3' > OAc' > SO_4''$; of Cd salts, $I > NO_3' > Cl'$, $OAc' > Br' > SO_4''$, and of Co salts, $CNS' > Br'$, $NO_3' > Cl'$, $OAc' > SO_4''$. Relationships are demonstrated between the toxic effects of these salts and their action on the swelling of hydrophilic gels and their diffusion rates in gelatin and agar. Heavy-metal salts on contact with the plasma surface produce a protective layer (by irreversible coagulation) which reduces the rate of further penetration of the salt. The permeability of this layer to salts of the same metal decreases in the order of the lyotropic series $CNS' > I' \ldots SO_4''$. A. G. P.

Toxic action. VI. Toxicity of aliphatic ketones towards potato tuber. W. J. REES (Protoplasma, 1933, **17**, 499—508).—The toxic action of ketones, as measured by the exosmosis of electrolytes from cut potato tubers, resembles that of the alcohols rather than aldehydes. The relative increase in toxicity associated with each increment of CH_2 to the C chain is less consistent for ketones than for alcohols. $COMeBu^{\beta}$ is more toxic than $COMeBu^{\alpha}$. A. G. P.

Effect of eighteen normal aliphatic alcohols on growth of *Lupinus albus*. D. I. MACHT and J. D. MEYER (Amer. J. Bot., 1933, **20**, 145—149).—Toxicity of the simple aliphatic alcohols increased directly with mol. wt. for the first five of the series, but not thereafter. *sec.*-Alcohols are in general less toxic than the corresponding primary alcohols. Mixtures of alcohols produce in some cases antagonistic, and in others synergistic, pharmacological effects. A. G. P.

Nutritional disorders [of plants] in alkaline soils as caused by deficiency of carbon dioxide. J. F. BREZEALE and W. T. MCGEORGE (Arizona Agric. Exp. Sta. Tech. Bull., 1932, No. 41, 113—153).—Black alkali soils do not, in most cases, contain sufficient alkali to be directly toxic. Extreme deficiency of CO_2 is an important factor in their low fertility. Plants are unable to absorb PO_4''' or NO_3' from solutions having $p_H > 7{\cdot}6$ approx. Optimum absorption occurs at p_H 6·8—7·0. The reaction of acid or alkaline nutrient solutions is gradually changed by growing plants towards neutrality, the change from alkalinity being more rapid than that from acidity. Plants absorb PO_4''' from phosphates at approx. equal rates irrespective of the base present, and do so more rapidly in daylight than in darkness. The effect of variations of p_H on nutrient absorption is the same for a no. of different species of plants. PO_4''' absorption is slightly depressed by a high concn. of neutral salts in the nutrient. Transpiration rates of plants are not materially affected by alkalinity up to p_H 9. Transpiration and ion absorption occur independently. In alkaline media plant roots elongate, although PO_4''' and NO_3' are not absorbed. The ameliorative action of farmyard manure on black alkali soils is largely due to the CO_2 evolved during its decomp. A. G. P.

Buffer capacity [of plant saps] and the incidence of plant disease. F. WILLE (Zentr. Bakt. Par., 1933, II, **87**, 301—331).—The period of infection of conifers with a no. of diseases is associated with low p_H and low buffer capacity in the saps, low H_2O content, and rapid CO_2 assimilation. Buffer capacities of saps with respect to HCl, H_2SO_4, HNO_3, H_2SiF_6, and HF are recorded. The significance of the results in the protection of plants against disease is noted. A. G. P.

Chemical composition of spores of vegetable parasites of cereals. S. CAMPANILE (Ann. R. Staz. chim.-agrar. sperim. Roma, 1932, **14**, No. 286, 3—11).—The ashes of oat-, rye-, wheat-, and maize-smut spores (*Ustilago* spp.) are similar in composition to those of the affected parts of the hosts, and the sp. variations in the hosts are reproduced in the parasites. Notably high amounts of K and N are found in the spores. R. K. C.

Variations in the total nitrogen content of normal and leaf-roll potatoes. G. COCKERHAM (Proc. Leeds Phil. Soc., 1933, **2**, 375—382).—Pronounced differences in the diurnal variations of the total N content of laminæ and petioles of normal and leaf-roll potatoes indicate an interference with the normal metabolism of nitrogenous substances by the presence of the sp. virus. N. M. B.

Walnut yellows in relation to ash composition, manganese, iron, and other ash constituents. A. R. C. HAAS (Bot. Gaz., 1933, **94**, 495—511).—In diseased trees the bark had higher Ca, Mg, Mn, inorg. PO_4''', and total ash contents, and the leaves higher Mg, Mn, Fe, and inorg. PO_4''' contents than did healthy trees. A. G. P.

Influence of infection on the temperature of and carbon dioxide evolution from potatoes. M. EGLITS (Phytopath. Z., 1933, 5, 341—379).—Infection of tubers with *B. phytophthorus* results in a rise in temp. accompanied by increased CO_2 production. A. G. P.

Influence on infection by rust of the immersion of inoculated leaves in solutions of mineral salts and other substances. G. GASSNER and K. HASSEBRAUK (Phytopath. Z., 1933, 5, 323—342).—Immersion during 3—4 nights in K^+ and PO_4''' solutions retarded, and in those of N compounds (NO_3', NH_4 salts, asparagine, glycine, etc.) increased, the infection. The effect of N compounds is closely related to the C supply of the plants. A. G. P.

Preparation of palæobotanical sections by the peel method. R. GRAHAM (Stain Tech., 1933, 8, 65—68).—A plane surface of the petrifaction is etched with acid. This removes a thin layer of matrix, leaving the carbonaceous material (I) standing in relief. A solution of cellulose nitrate is poured over the surface. After evaporation of the solvent, the film, containing the embedded (I), is peeled off and used as a thin section. Various grades of cellulose nitrate were tried, and the effect of various solvents and plasticisers was studied. H. W. D.

Metal extraction apparatus for phytochemical work A. F. SIEVERS (J. Amer. Pharm. Assoc., 1933, 22, 182—184).—A modification of Bryant's apparatus (A., 1929, 1161) consists of a tubular condenser and a jacketed receiver, and the whole apparatus is made of Sn-lined Cu. E. H. S.

Method and apparatus for the study of permeability of gases through the bird's egg-shell. A. L. ROMANOFF (Science, 1933, 77, 393—394). L. S. T.

Determination of fluorine [in plant materials]. O. B. WINTER and L. BUTLER (J. Assoc. Off. Agric. Chem., 1933, 16, 105—107; cf. this vol., 242).—5—20 g. of material are moistened with saturated aq. $Ca(OH)_2$, dried, and ignited at dull redness. If not thoroughly ashed it is broken up, moistened with H_2O, dried, and re-ignited. The residue is mixed with a few pieces of glass or porous pot, aq. $HClO_4$ is added, and the F determined by distilling off the H_2SiF_6 as described previously. J. W. S.

Determination of iodine in biological material. J. SCHWAIBOLD (Biochem. Z., 1933, 259, 453—454).—A reply to Pfeiffer (this vol., 330). P. W. C.

Determination of total base [in biological material]. S. L. WRIGHT and C. L. ALLISON (J. Biol. Chem., 1933, 100, 1—11).—Removal of the PO_4 allows the use of the benzidine method for material rich in Ca and P. Preliminary titration for excess H_2SO_4 has been eliminated and the ignition standardised. H. G. R.

Colorimetric micro-titration of bases in non-aqueous solvents. I. O. M. HENRIQUES (Biochem. Z., 1933, 260, 72—104).—"Non-aq." solvents (*e.g.*, a mixture of C_6H_6 61·6, EtOH 37·1, and H_2O 1·3%) have many advantages (*e.g.*, longer p_H scale, reduced dissociation of weak electrolytes, low solubility products, no CO_2 error) over aq. solvents. Forty suitable indicators are listed and complete details of procedure are given (example, titration and determination of dissociation const. of $AlCl_3,6H_2O$), whilst modifications and applications to biochemical and clinical work are indicated. W. McC.

Absorption apparatus for micro-determination of volatile substances. I. Micro-determination of ammonia. E. J. CONWAY and A. BYRNE. **II. Determination of urea and ammonia in body fluids.** E. J. CONWAY (Biochem. J., 1933, 27, 419—429, 430—434).—I. The test solution is placed in the outer of two chambers (I) formed by the outer wall of a circular dish and a concentric glass ring within; the NH_3 liberated by addition of saturated aq. K_2CO_3 is absorbed by standard acid in the inner chamber (II), and the excess titrated. The influence of variation of temp., p_H, the vol. of (I) and (II), and of salt addition to (I) is studied; 99·5% absorption occurring in 60 min. at 40° or in 100 min. at room temp. For the titration, a modification of Tashiro's indicator is described. Amounts of NH_4 salts containing $\ll$ 0·014 mg. N can be determined with a coeff. of variation of 0·5%.

II. Blood-urea is determined by placing 1 c.c. of 0·00667*N*-H_2SO_4 in (II) and 0·2 c.c. of blood together with a glycerol extract of urease diluted with aq. NaH_2PO_4 in (I). The apparatus is incubated for 10 min. at 38°. 1 c.c. of saturated aq. K_2CO_3 is added to (I) and the incubation repeated for 1 hr., when the excess acid is titrated. Protein-free filtrates and urine may be analysed in the same way. The error (standard deviation) is 0·6 mg. per 100 c.c. H. D.

Micro-iodometric determination of gold in animal organs. S. TUKATS (Biochem. Z., 1933, 260, 143—146).—Org. matter is destroyed by heating with H_2SO_4 and HNO_3 successively and pptn. of the Au is completed by addition of $H_2C_2O_4$. The ppt. is dissolved in aqua regia and aq. Cl_2. HNO_3 and Cl_2 are removed, KI and starch are added, and the solution is titrated with 0·005*N*-$Na_2S_2O_3$. 0·5—1·5 mg. of Au can be determined with an error of 3—1·3%. W. McC.

Folin–Denis colorimetric method. H. FUJIWARA and E. KATAOKA (Z. physiol. Chem., 1933, 216, 133—137).—Aromatic amines, phenols, hydroxyphenyl derivatives, aromatic aldehydes, naphthol, hydroxyquinoline, aliphatic hydroxy- and keto-acids, NH_2OH, dimethylaminoantipyrine (but not antipyrine), indole derivatives, and most morphine alkaloids reduce phosphotungstic and phosphomolybdic acids and $K_3Fe(CN)_6+FeCl_3$, giving a blue colour. Of the sugars, only fructose, hydroxymethylfurfuraldehyde, and inulin give the reaction. J. H. B.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1933.

General, Physical, and Inorganic Chemistry.

Effect of helium on the continuous and secondary spectra of hydrogen. A. S. Roy (Proc. Nat. Acad. Sci., 1933, 19, 441—444).—The lines of the triplet system were, in general, increased in intensity relative to the lines of the singlet system, and the continuous spectrum was very much stronger. This is attributed to the limitation of electron velocities by the He, which would increase the probability of exciting the triplet states of H. N. M. B.

Characteristic structure of the hydrogen resonance line λ 1216 Å. M. Kulp and H. E. Binkele (Physikal. Z., 1933, 34, 420—423). A. J. M.

Spectra emitted by high-frequency and direct-current discharges in helium. J. E. Keyston (Phil. Mag., 1933, [vii], 15, 1162—1173).—The light emitted by He discharges in the visible and ultra-violet regions has been investigated spectroscopically. The results are discussed with reference to the theory of Townsend (A., 1932, 440). J. W. S.

Laboratory excitation of nebular lines N_1 and N_2. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1933, 9, 146—148; cf. A., 1932, 552).—Using a modification of the disruptive discharge method described previously the nebular lines 5006·8 and 4958·97 Å. have been reproduced in the laboratory. J. W. S.

Opposite asymmetry of the widening of different lines of a series. C. Fuchtbauer and F. Gossler (Naturwiss., 1933, 21, 315).—The widening of the three principal series lines of Cs in different gases was studied. There is a marked change in the widening in the transition between second and third series members. In Ne and N_2, the first and second lines (8521·1 and 4555·3 Å.) were widened a little towards the red, whilst the third (3876·7 Å.) was widened considerably towards the violet. A. J. M.

Infra-red spectra of neon, argon, and krypton. W. F. Meggers and C. J. Humphreys (Bur. Stand. J. Res., 1933, 10, 427—448).—About 200 infra-red lines between 7600 and 12,200 Å. were photographed for each of the gases Ne, A, and Kr. New H-like terms from *f*-type electrons were found, and missing 3*d* terms in the A I and Kr I spectra identified. New infra-red wave-length standards are suggested. H. J. E.

Continuous spectrum of sodium. H. Hamada (Sci. Rep. Tohoku, 1933, 22, 31—54).—The spectrum is described and discussed. It can be explained in the same way as those of Hg, Cd, Zn, and Mg. A. J. M.

Excitation of resonance series in sodium vapour by illumination with the *D*-line. W. G. Brown and P. Pringsheim (Z. Physik, 1933, 82, 584—588). A. B. D. C.

Excitation potential of the argon atom. R. G. Loyarte (Physikal. Z., 1933, 34, 416—420).—A no. of new potentials are recorded, especially in the range $1s_2$—$2p_{10}$. A. J. M.

Electrodeless ring discharge through potassium vapour. B. Arakatsu and Y. Uemura (Mem. Fac. Sci. Agric. Taihoku, 1932, 5, 159—161).—With the electrodeless ring discharge in K vapour at low pressure a dark bluish-violet after-glow is observed. The spectrum of the glow shows no arc lines, but intense spark lines. The glow is attributed to the positive ions of atoms expelled from the discharge region by the electrostatic field set up at the instant of the excitations of the ring discharge. J. W. S.

Absorption of the 1*s*—3*d* lines by potassium. T. Okuda (Sci. Rep. Tohoku, 1933, 22, 9—12).—Forbidden lines of the 1*s*—3*d* series were observed in the absorption spectrum of K. The effect of admixture of H_2 and N_2 with the Na vapour was investigated. A. J. M.

Absolute value of the terms of As. W. M. Hicks (Phil. Mag., 1933, [vii], 15, 1080—1085).—Theoretical. The ounmultiple law is applied to recent data. J. W. S.

Spectrum of selenium. II. Se III. J. S. Badami and K. R. Rao (Proc. Roy. Soc., 1933, A, 140, 387—398).—The spectrum of doubly-ionised Se has been studied with the aid of data obtained from the analysis of the spectra of Se IV and Se V (A., 1931, 664). The largest term, $4p^3P_0 = 274{,}924$ cm.$^{-1}$, leads to a val. of 33·9 volts for the third ionisation potential of Se. A special feature of the analysis is the discovery of multiplets involving a transition of one of the inner electrons. L. L. B.

Multiplets in the spectra of Nb III and Mo IV. A. Y. Eliason (Physical Rev., 1933, [ii], 43, 745—748).—Term vals. for the multiplets in Nb III and Mo IV are obtained by an application of the Moseley law and the irregular doublet law to the corresponding multiplets in Y I and Zr II. N. M. B.

Extension of the Pd I-like isoelectronic sequence to antimony VI and tellurium VII. G. K. Schoepfle (Physical Rev., 1933, [ii], 43, 742—744).—Wave-lengths, frequencies, and term vals. for the region 784—1331 Å. are tabulated. N. M. B.

Fine structure of the resonance Ag I lines. W. E. WILLIAMS and A. MIDDLETON (Nature, 1933, **131**, 692).—The structure previously observed (A., 1931, 993) is due to self-reversal. L. S. T.

Structure of the lines of the arc spectrum of silver. D. A. JACKSON (Nature, 1933, **131**, 691—692).—All the more important lines are simple (cf. preceding abstract). L. S. T.

Change of optical absorption of iodine on being bound. J. H. DE BOER and J. F. H. CUSTERS (Z. physikal. Chem., 1933, B, **21**, 208—224; cf. A., 1931, 1226).—The absorption curve of I_2 mols. adsorbed on a vac.-sublimed CaF_2 film is displaced considerably towards the violet, compared with that of gaseous I_2. The curve is the more sharply defined the smaller is the amount of I_2 adsorbed, m. When m is small, the absorption curve has max. at 342 and 283 $m\mu$, but as m increases, there are superimposed on this curve the curves for the less active centres, which lie nearer the red. The absorptive power of the I_2 first adsorbed is more than 100 times $>$ than that of I_2 taken up when the surface is already partly occupied, and 10,000 times that of I_2 dissolved in H_2O. The possible interpretations of the absorption curves are examined with the aid of potential curves and surfaces. R. C.

Temperature dependence of the absorption of excited mercury vapour. O. MASAKI (J. Sci. Hiroshima Univ., 1933, **3**, 187—192; cf. A., 1931, 276).—The absorption of light by excited Hg vapour in presence of excess Ne corresponding with the transitions $2^3P_{0\,1\,2}-3^3D_{1,2,3}$ shows great variation with temp. Other transitions and intercombination lines show little variation. J. S. A.

Spectra of Pb II, Hg I, Sb I, Cl II, and I II. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 285—297).—Terms are classified with the aid of hyperfine structure. Lines of Cl II and I II are classified. Nuclear moments are Sb^{121} 5/2, Sb^{123} 7/2, I 5/2. N. M. B.

Effect of moisture on the spark potential in air. C. DEI (Nuovo Cim., 1932, **9**, 150—155; Chem. Zentr., 1933, i, 23—24).—A method for studying the effect of moderate humidities, where vals. decrease with decreasing H_2O tension, is described. A. A. E.

Contour of spectral lines excited by electron collision. W. HEITLER (Z. Physik, 1933, **82**, 146—150).—A spectral line excited by monochromatic electrons has a contour which falls off towards the red more slowly than the natural line. A. B. D. C.

Solar ultra-violet radiometry. W. D. FLEMING (Philippine J. Sci., 1933, **50**, 279—299).—The application of thermopiles to the determination of the intensities of the spectral bands 290—310, 310—370, 370—400, and 400—460 mμ in sunlight is described. C. W. G.

High-frequency discharge in argon in presence of mercury. R. ZOUCKERMANN (Compt. rend., 1933, **196**, 1478—1480; cf. A., 1928, 214; 1931, 403). C. A. S.

Activation of air by the electrodeless ring discharge. B. ARAKATSU and K. KIMURA (Mem. Fac. Sci. Agric. Taihoku, 1932, **5**, 143—157).—Three distinct types of after-glow have been observed with air after passage at low pressure through the electrodeless discharge, viz., green at 1—0·07 mm. pressure, sky-blue at 0·07—0·05, and orange below 0·05 mm. The possible chemical reactions causing these different phenomena are discussed. J. W. S.

Conditions for striking low-voltage arcs and grid-directed low-voltage arcs. F. KLAIBER (Physikal. Z., 1933, **34**, 441—447). A. J. M.

Experimental investigation of grating ghosts. W. RUDOLPH (Z. Physik, 1933, **82**, 372—396).—Ghosts due to several Rowland gratings were determined. A. B. D. C.

Determination of reflexion capacity of metals in the visible and ultra-violet. K. VON FRAGSTEIN (Ann. Physik, 1933, [v], **17**, 1—21).—The reflexion capacity of steels of various composition was determined by a spectrophotometric method in the visible, whilst in the ultra-violet several other substances were examined as well. A. J. M.

Structure of *K*-rays of light elements. A. HAUTOT (J. Phys. Radium, 1933, [vii], **4**, 236—245).—An amplified account of work already published (this vol., 108, 201, 440).

Dependence of *K* lines of elements from Cu to Ti on chemical combination. S. YOSHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 298—310).—Using the method of cold excitation with X-rays, no effects of chemical combination on $K\alpha_1\alpha_2$ and $K\alpha_{3,4}$ were detected. $K\beta'$ and $K\beta_1$ are distinctly separated in strongly paramagnetic compounds; slight displacements of $K\beta_5$ were observed for Mn, Cr, and Ti. A new line $K'\beta_5$ was always observed for substances which show a sharp absorption line on the long wave-length side of the absorption edge. N. M. B.

***K* series spectrum of tungsten.** J. C. HUDSON and H. G. VOGT (Proc. Nat. Acad. Sci., 1933, **19**, 444—448).—The β and γ doublets were resolved and photographed together with the δ line. Using the vals. 0·21341 and 0·20860 for the α_2 and α_1 line, respectively, the wave-lengths were calc. as β_2 0·18477, β_1 0·18397, γ_2 0·17917, γ_1 0·17899, δ 0·17803 Å. The averaged vals. for the β and γ doublets on the basis that the shorter wave-length line has twice the intensity of the longer component are 0·18423 and 0·17905 Å., respectively. N. M. B.

Analysis of secondary radiation from aluminium, nickel, silver, and gold at the entrance and exit of *X*-rays. H. SCHENCK (Ann. Physik, 1933, [v], **17**, 146—168).—The dependence of the electron emission from Al, Ni, Ag, and Au on the hardness of the X-rays employed and on the thickness of the irradiated element was investigated for both entrance and exit of the rays. The total emission was analysed into (*a*) characteristic secondary radiation, (*b*) electron emission due to primary radiation, and (*c*) electrons of the third kind, which are set free by the re-absorption by the metal of the characteristic radiation. The emission of secondary scattered radiation is negligible. The asymmetry of the electrons set free by primary radiation is const. with

respect to hardness of rays for Au. It increases as at. no. decreases. A. J. M.

X-Ray emission spectra of gaseous elements: *K* spectrum of krypton. (MLLE.) Y. CAUCHOIS and H. HULUBEI (Compt. rend., 1933, **196**, 1590—1592; cf. this vol., 248, 450).—The authors' method, with Se, Br, and Rb as reference elements, gives for Kr $K\alpha_2$ 982·1, 978·1, , 876·7, and $K\beta_2$ 864·3 X (cf. A., 1931, 4). C. A. S.

Relation between line and continuous X-ray spectra. W. W. HANSEN and K. B. STODDARD (Physical Rev., 1933, [ii], **43**, 701—706).—For Pd up to 180 kv. there is a const. ratio between the probability of ejection of a *K* electron and the probability of emission of a quantum of continuous radiation when an electron collides with a Pd atom. The val. 2 is found for the ratio, for a thick target, of the amount of $K\alpha$ radiation resulting from ionisation by collision and that from fluorescence. N. M. B.

Excitation potentials of light metals. II. Beryllium. H. W. B. SKINNER (Proc. Roy. Soc., 1933, **A**, **140**, 277—301; cf. A., 1932, 316).—Measurements have been made of the "excitation curve" ($\Delta i/\Delta V$ plotted against V) for Be, using both W and dull-emitter filaments, and it is found that the "break potentials" (vals. of V for which abrupt changes in $\Delta i/\Delta V$ occur) are displaced correspondingly with the change of filament. When a correction for the work function of the filament is applied, the break potentials are consistent. Excitation starts at 8·5 volts, rises continuously up to 92 volts, when large and abrupt changes in $\Delta i/\Delta V$ occur and persist up to 125 volts. There is an appreciable difference between the min. *K*-excitation potentials of Be in the form of metal and of a polar compound. An approx. model for the excited state of the metal, based on the state of the corresponding at. system, is proposed. L. L. B.

Ionisation of argon, neon, and helium by A, Ne, and He atoms. C. J. BRASEFIELD (Physical Rev., 1933, [ii], **43**, 785—787; cf. A., 1932, 1185).—Using a method eliminating errors due to secondary electrons, ionisation of each gas, bombarded by its own atoms, set in at approx. 100 equiv. volts. Bombardment of any of the gases by atoms of either of the other two caused no detectable ionisation. N. M. B.

Energy distribution of photo-electrons. L. A. DU BRIDGE (Physical Rev., 1933, [ii], **43**, 727—741).—Expressions are derived for the form of the normal and total energy distribution and current–voltage curves in the vicinity of the apparent max. energy, which cannot be sharply defined, owing to the thermal energies of the electrons. Results are in agreement with experimental data for Mo. N. M. B.

Relations between the combination coefficients of atmospheric ions. F. J. W. WHIPPLE (Proc. Physical Soc., 1933, **45**, 367—380).—Experimental evidence and possible applications of a formula dealing with the combination coeffs. for large and small ions are discussed. W. R. A.

Scattering of rapid protons by light elements on close approximation to the nucleus. G. SCHNEIDER (Naturwiss., 1933, **21**, 349).—The scattering at C and B of protons of 75—300 kv. is considered. The scattering curve, drawn between the proton velocity and the no. of particles possessing a given velocity shows a max. for B, but not for C. A. J. M.

Action of mercury metastable atoms on a tungsten surface. S. SONKIN (Physical Rev., 1933, [ii], **43**, 788—803).—Factors and conditions effecting the sensitivity of a metal surface to electron emission were investigated. Heating and outgassing produced a const. normal sensitivity. For a W surface the deposition of Hg atoms was essential for the formation of a surface sensitive to Hg metastable atoms. Residual O_2 resulted in the establishment of a stable complex arrangement of Hg and O atoms on the W. Transient sensitivities 50—100 times the normal val. were found at a certain stage at which the formation of a monat. film was possible. For the normal surface not more than 1 or 2% of metastable atoms cause electron emission. N. M. B.

Influence of condensation nuclei and dust particles on atmospheric ionisation. P. J. NOLAN (Proc. Roy. Irish Acad., 1933, **A**, **41**, 61—69).—Available data on the relation between the rate of disappearance of small ions in a closed vessel and the concn. of nuclei and dust agree with the deduction that small ions combine with dust particles as well as with condensation nuclei. Respective combination coeffs. are deduced. The square-root law of recombination is explained in the experimental indications that at high concns. the disappearance rate is proportional to the square of the concn., and is a coagulation process, and at low concns. is proportional to the concn., and is a diffusion process. N. M. B.

Secondary emission of electrons from molybdenum. P. L. COPELAND (J. Franklin Inst., 1933, **215**, 593—598).—The ratio of the no. of secondary to primary electrons of various energies incident on a Mo plate, previously heat-treated, gives results agreeing more closely with those of Hyatt (cf. A., 1929, 229) than of Petry (cf. A., 1925, ii, 1017). N. M. B.

Diffraction of electrons in amorphous and in crystalline antimony. J. A. PRINS (Nature, 1933, **131**, 760—761).—Electron diffraction patterns of Sb obtained by evaporation in a vac. show that the structure is amorphous and remains so indefinitely when the films are very thin. Films of medium thickness soon develop cryst. spots and become wholly cryst. in 2 hr.; thick deposits are always cryst. L. S. T.

Diffraction of electrons by metal surfaces. L. H. GERMER (Physical Rev., 1933, [ii], **43**, 724—726).—Fast electrons scattered from polished metal surfaces do not form diffraction patterns. A strong Debye–Scherrer pattern is produced by electrons scattered by a roughened surface through the irregularities of which electrons can pass. Results indicate that there is no considerable amorphous layer on a polished metal surface, and that Debye–Scherrer patterns are formed only by transmitted electrons. Fast electrons scattered at a small glancing angle from an etched polycryst. surface form a diffraction pattern only if the surface is rough. N. M. B.

Electron diffraction and photo-electric effect for alkali metal surfaces. W. KLUGE and E. RUPP (Z. Physik, 1933, **82**, 568—583).—Previous results are confirmed (A., 1932, 893). At −170° max. appear as the energy of the electrons is increased, but not when decreased; similarly, several edges in the reflexion curves appear at higher energies with increasing energy and at lower energies with decreasing energy of the beam. The first phenomenon may be due to adsorbed electrons. A. B. D. C.

Dependence of electron-ray concentration on the type of gas. E. F. RICHTER (Physikal. Z., 1933, **34**, 457—458).—Beams of electrons in various gases were investigated. The pressure range in which a "thread" ray (*i.e.*, a beam which, after passing through a relatively strong, non-homogeneous magnetic field, does not become diffuse) exists varies in different gases, changing from 10^{-1} to 10^{-3} mm. from He to Xe. The results were compared with the efficiencies of ionisation derived by Tate and Smith (A., 1932, 321) for the gases and electron velocities used in the experiment. A. J. M.

Electron diffraction by vapours. H. DE LASZLO (Nature, 1933, **131**, 803).—Preliminary photographs of the electron diffraction of the vapour of org. compounds have been taken. L. S. T.

Elastic electron scattering in gases. S. WERNER (Nature, 1933, **131**, 726—727).—Anomalies discovered in the velocity scattering curves for Ne and A are discussed. L. S. T.

Diffraction of electrons in mercury vapour. II. F. L. ARNOT (Proc. Roy. Soc., 1933, **A**, **140**, 334—344).—An extension of previous work (A., 1931, 542, 1347) to larger angles and to lower electron energies. L. L. B.

Diffraction of electrons at some gaseous halides (OsF_8, HgI_2, $HgBr_2$, $HgCl_2$). H. BRAUNE and S. KNOKE (Naturwiss., 1933, **21**, 349—350).—Owing to the ease of decomp. of OsF_8, it is not possible to decide the arrangement of the F atoms. The distance Os–F is almost the same for the two models put forward for this substance—dice model and Archimedean antiprism. The distance Hg–I in HgI_2 is 2·55; Hg–Br in $HgBr_2$ 2·40; and Hg–Cl in $HgCl_2$ 2·17 Å. A. J. M.

Electron diffraction by gaseous sulphur, selenium, and tellurium hexafluorides. H. BRAUNE and S. KNOKE (Z. physikal. Chem., 1933, **B**, **21**, 297—309).—The results agree with an octahedral structure in which the distances between F and the central atom are SF_6, 1·56; SeF_6, 1·67; TeF_6, 1·82 Å. R. C.

Determination of crystal lattice constants by electron diffraction. G. I. FINCH and A. G. QUARRELL (Nature, 1933, **131**, 842).—An accurate comparison method for the determination of crystal lattice consts. by electron diffraction is described. L. S. T.

Interference pattern obtained by irradiation of single brucite crystals with rapid electrons. G. AMINOFF (Arkiv Kemi, Min. Geol., 1933, **11 B**, No. 10, 4 pp.).—The pattern is described. A. J. M.

Transition of electrons to the region of negative energy values. S. SZCZENIOWSKI (Bull. Acad. Polonaise, 1933, **A**, 21—39).—The tunnel effect is investigated for one dimension using Dirac's wave equation. A. B. D. C.

Free positive electrons resulting from the impact on atomic nuclei of the photons from thorium-*C*″. C. D. ANDERSON (Science, 1933, **77**, 432).—Free positive electrons are ejected from Pb by the γ-radiation of Th-*C*″, showing that when absorbed by nuclei, photons eject both positive and negative electrons, as is the case with cosmic rays (cf. A., 1932, 76, 238; this vol., 441). L. S. T.

Origin of positive electrons. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1933, **196**, 1581—1583; cf. this vol., 549).—The emission of both positive and negative electrons when radiation from Po+Be falls on Pb is reduced by 40% by the interposition of 2 cm. Pb; with a radiator of UO_2 the emission is slightly increased, with one of Cu greatly diminished. The max. energy of negative and positive electrons is respectively 4·7 and $2·2\times10^6$ ev. Trajectories of both kinds of electron sometimes appear to start from the same point, and the proportion of positive electrons increases with the at. wt. of the radiator. It is concluded that both positive and negative electrons are due to nuclear absorption of γ-radiation. This view is supported by examination of the electrons produced by the action on Pb of γ-rays from Th-*C*″ and the deductions therefrom as to the energies of the electrons and γ-rays concerned. C. A. S.

Possible property of the positive electron. W. ELSASSER (Nature, 1933, **131**, 764).—Theoretical. If the proton consists of a neutron and a positive electron, the latter should obey Bose statistics and have an integral spin momentum (0 or 1). L. S. T.

Electrolytic isolation of the heavier hydrogen isotope by the method of G. N. Lewis. M. POLANYI (Naturwiss., 1933, **21**, 316—317).—The causes of the large difference in overvoltage of the two H isotopes, which has been suggested by Lewis (this vol., 442) as providing a suitable method for effecting their separation, and the nature of the phenomenon, are discussed on the basis of quantum mechanics. The overvoltage seems to be due to an energy barrier over which the proton has to rise in order to reach the surface of the electrode. A. J. M.

Isotope separation by the method of Hertz. H. HARMSEN (Z. Physik, 1933, **82**, 589—609).—The method is developed to give almost complete separation of Ne^{20} and Ne^{22}. A. B. D. C.

Calcium isotope with mass 41 and the radioactive half-period of potassium. J. KENDALL, W. W. SMITH, and T. TAIT (Nature, 1933, **131**, 688—689).—Ca extracted from a felspar (10^9 years old) from Rhiconich, Sutherlandshire, gave an at. wt. of 40·092±0·0006, whilst that from a pegmatite (6×10^8 years old) from Portsoy, Banffshire, gave 40·089± 0·0004. Ca derived from recent marine sources, seashells, and Bermuda limestone, gave 40·076 and 40·077, respectively. The calc. radioactive half-period of K^{41} is of the order 1×10^{12} years in both cases (cf. A., 1930, 1496). L. S. T.

Revision of at. wt. of selenium. Synthesis of silver selenide. O. HONIGSCHMID and W. KAPFENBERGER (Z. anorg. Chem., 1933, **212**, 198—208).—By direct combination of Ag with Se vapour at 400°, the val. $2Ag : Ag_2Se = 0{\cdot}732081$ has been obtained, whence Se = 78·962 ± 0·002, in agreement with Aston's figure. J. S. A.

At. wt. of lead from Katanga pitchblende. G. P. BAXTER and C. M. ALTER (Science, 1933, **77**, 431—432).—The at. wt. of Pb obtained by extraction with HCl of the yellow portion of Katanga pitchblende (I) is 205·97, whilst that obtained from the remaining black portion is 206·00; average 205·99 for the whole (I). Vals. for common Pb from Cœur d'Alene and for Pb from Bedford cyrtolite simultaneously determined are 207·22 and 205·94, respectively. Assuming Aston's isotopic composition for Katanga Pb, the results give the low val. of 205·90—205·93 for Pb^{206}. The difference in at. wts. of Pb from the yellow and black portions of (I) is discussed. L. S. T.

Revision of the at. wt. of arsenic. Comparison of arsenic trichloride with iodine pentoxide. G. P. BAXTER and W. E. SHAEFER (J. Amer. Chem. Soc., 1933, **55**, 1957—1963; cf. this vol., 442).—The at. wt. of As is 74·91 from determinations of the ratio $6AsCl_3 : I_2O_5$, and the data show that I_2O_5 has the normal composition (cf. A., 1931, 543). J. G. A. G.

Revision of the at. wt. of indium. G. P. BAXTER and C. M. ALTER (J. Amer. Chem. Soc., 1933, **55**, 1943—1946).—The at. wt. of In is 114·76 from determinations of the ratios $InCl_3 : 3Ag$ and $InBr_3 : 3Ag$. J. G. A. G.

Interpretation of Aston's data. W. SWIENTOSLAWSKI (Compt. rend., 1933, **196**, 1600—1602).—From the differences in the masses of the nuclei of various pairs of isotopes the average mass of a neutron is deduced as 0·9997, and that of a demihelion, $D_h = (A_n - 0{\cdot}9997x)/n$, where A_n is the mass of the at. nucleus of element no n, and x the no. of neutrons. D_h diminishes from 2·00053 for He to 1·9974 for Kr, and then rises to 1·9998 for Pb and (by extrapolation) to 2·00032 for U. Deducing from this the mass of the at. nucleus of U, the loss of mass consequent on the radioactive transformation of U into Pb is 0·033, which agrees fairly with that (0·041) calc. from the heat emitted. C. A. S.

α-Ionisation in pressure chambers. J. C. JACOBSEN and C. B. MADSEN (Naturwiss., 1933, **21**, 350).—α-Particle ionisation falls rapidly with increasing pressure. A. J. M.

Direct measurement of intensities of fine structure of α-particles. S. ROSENBLUM and P. CHEVALLIER (Compt. rend., 1933, **196**, 1484—1486).—An arrangement in which a Geiger counter replaces the photographic plate is described whereby individual α-particles can be recorded. Applied to determining the fine structure of α-particles from Th-*C*, it gives results in close agreement with those obtained photographically. C. A. S.

Radiation excited by α-particles in fluorine. P. SAVEL (Compt. rend., 1933, **196**, 1482—1484).—Using an ionisation chamber containing A or H_2 under 30 atm. pressure, the radiation emitted by F (as CaF_2) under the action of α-particles from Po is composed of homogeneous γ-rays of mass absorption coeff. $\mu/\rho = 0{\cdot}058$ and energy $1{\cdot}3 \times 10^6$ ev. and consisting mainly of photons, and of very penetrating neutrons half absorbed by 5·5 cm. of Pb. The min. energies of the α-particles which excite γ-rays and neutrons are respectively 0·9—1·2 and 2·5—2·7 ev. These results, with those of Chadwick and Constable (cf. A., 1932, 318), imply that there are at least two sources of γ-rays, possibly excited with and without capture of the α-particle as suggested for Li (cf. this vol., 334). C. A. S.

Fine structure of the magnetic spectrum of α-particles from radioactinium and its derivatives. (MME.) P. CURIE and S. ROSENBLUM (Compt. rend., 1933, **196**, 1598—1600; cf. A., 1932, 555).—Revised and additional data are given for intensities and energies of 11 lines of Rd-Ac, 3 of Ac-*X*, and 3 of An (cf. A., 1932, 671). Close agreement between twelve energy differences of Rd-Ac and two of An with the energies of corresponding γ-rays is demonstrated. C. A. S.

Absolute velocities of principal groups of α-particles. S. ROSENBLUM and G. DUPOUY (J. Phys. Radium, 1933, [vii], **4**, 262—268).—A detailed account of work already noted (A., 1932, 671).

Anomalous absorption of γ-rays. Possibility of the quantum jump of the rest-mass of an electron. B. ARAKATSU (Mem. Fac. Sci. Agric. Taihoku, 1932, **5**, 163—168).—Theoretical. J. W. S.

Emission of slightly penetrating radiation by some metals. J. REBOUL (Compt. rend., 1933, **196**, 1596—1598; cf. A., 1896, ii, 601).—The impression produced by Zn on a photographic plate thought to be due to emission of vapour of Zn is stated to be due to a radiation emitted by the Zn capable of exciting the air or other substance intervening between the Zn and the plate. C. A. S.

Atomic disintegration with neutron emission. G. KIRSCH (Naturwiss., 1933, **21**, 332).—At. disintegration of C, N, Mg, Al, S, Fe, Ni, Cu, Zn, Mo, Pd, As, Sn, W, Pt, Au, and Pb can be brought about with Po α-rays, neutrons being emitted. The elements already examined, Li, Be, and B, give greater effects than the above. A. J. M.

Chemical proof of artificial transmutation of elements. F. PANETH and P. L. GUNTHER (Naturwiss., 1933, **21**, 367—368).—The sensitivity of chemical methods of proving that transmutation has taken place is discussed. A. J. M.

Interaction of neutrons and protons. J. SOLOMON (J. Phys. Radium, 1933, [viii], **4**, 210—220).—Mathematical. Models for taking account of proton–neutron interaction are reviewed. Assuming a similar nature for the neutron–proton binding in the H^2 isotope and the forces involved in neutron–proton collisions, a relation between the effective section for collisions and the mass defect of H_2 is established. N. M. B.

Proof of the wave nature of molecular radiation by scattering in mercury vapour. F. KNAUER

(Naturwiss., 1933, **21**, 366—367).—Results on the scattering of mol. radiation from He and H_2 by Hg vapour cannot be reconciled with the classical theory, but are in agreement with wave mechanics. A. J. M.

Significance of recent measurements of cosmic rays. A. H. COMPTON (Science, 1933, **77**, 480—482).—Recent experiments favour the view that cosmic rays are electrified particles and the data are in accord with Lemaitre's theory of their origin. L. S. T.

Mass of the neutron. J. J. PLACINTEANU (Compt. rend., 1933, **196**, 1474—1476).—To explain the fact that the mass of the neutron, m_n, is < the sum of the masses of the proton, m_p, and electron m_e, of which it is regarded as constituted, it is suggested that it consists of a proton and Dirac's electron of negative energy (cf. A., 1930, 271). This gives results for mass (m_p—m_e) and energy radiated in agreement with experiment. C. A. S.

Electron spin and theory of the neutron. W. WESSEL (Z. Physik, 1933, **82**, 415—444).—Completion of Dirac's equation by addition of a spin potential leaves H fine structure unchanged, but gives proper functions of very high energy vals., and these may be identified with neutrons. A. B. D. C.

Masses of atoms and the structure of atomic nuclei. K. T. BAINBRIDGE (J. Franklin Inst., 1933, **215**, 509—534).—A general survey. N. M. B.

Theory of atomic nuclei. III. E. N. GAPON (Z. Physik, 1933, **82**, 404—407; cf. this vol., 443).—Anomalous absorption of γ-rays is explained, and the no. of free neutrons in at. nuclei determined. A. B. D. C.

Relativistic treatment of the Fermi atom. H. JENSEN (Z. Physik, 1933, **82**, 794—802).

Theory of the nucleus. E. MAJORANA (Z. Physik, 1933, **82**, 137—145).—A statistical method is developed for the nucleus from Heisenberg's theory (this vol., 335). A. B. D. C.

Application of the phase integral method to the hydrogen molecule ion. E. M. VAN ENGERS and H. A. KRAMERS (Z. Physik, 1933, **82**, 328—336).—The phase integral method gives results in agreement with earlier calculations. A. B. D. C.

Constitution of metallic sodium. E. WIGNER and F. SEITZ (Physical Rev., 1933, [ii], **43**, 804—810).—Mathematical. The chemical properties are investigated using the free electron concept. The lattice const., binding energy, and compressibility are calc. by wave mechanics. N. M. B.

Thermodynamic functions of radiation. F. G. DONNAN (J. Indian Chem. Soc., 1933, Ray No., 61—64).—Theoretical. H. J. E.

Degrees of freedom and the constant M/m. V. V. NARLIKER (J. Indian Chem. Soc., 1933, Ray No., 141—142).—Theoretical. H. J. E.

General chemical equation. W. HARRISON (Chem. and Ind., 1933, 370).—If the elements are represented by formulæ of the type A_xN_y, where x is the at. wt. and y the at. no., radioactive changes and the transmutations of light elements may be represented by equations which resemble ordinary chemical equations, *e.g.*, Li+H=2He becomes $A_7N_3+A_1N_1-2A_4N_2$. D. R. D.

Band spectrum of potassium hydride. T. HORI (Mem. Ryojun Coll. Eng., 1933, **6**, 1—33).—KH shows an extensive band spectrum in the region 4090—6610 Å., corresponding with a $^1\Sigma \longrightarrow {}^1\Sigma$ combination. The spectrum is classified into 62 bands and 5 v'-band systems. The intensity distribution is in agreement with the unusually large change in the moment of inertia ($I_e''=8{\cdot}12\times10^{-40}$; $I_e'=21{\cdot}20\times10^{-40}$) and with the wide Franck–Condon parabola. Decomp. of the mols. yields K and H atoms in the ground state. J. W. S.

Ultra-violet absorption bands of ammonia. J. K. DIXON (Physical Rev., 1933, [ii], **43**, 711—715).—Frequencies and classifications for a no. of intense double-headed bands in the region 2400—1900 Å. are tabulated. The doublet separation is 70 cm.$^{-1}$ Fundamental frequencies in the upper state are at 890 and 2720 cm.$^{-1}$ The double-headed bands at 46,140 and 47,030 cm.$^{-1}$, on heating to 150° or 300°, shift to the red and become triple-headed. Predissociation in the excited state is discussed and explained. N. M. B.

Fine structure of absorption bands of sulphur dioxide in the ultra-violet. A. IONESCU (Compt. rend., 1933, **196**, 1476—1478).—The absorption band spectrum of SO_2 has been analysed with reference to the three possible moments of inertia of the mol. by application of the asymmetric top theory. C. A. S.

Atmospheric transmission in the water vapour bands ρ and ϕ according to spectrographic measurements made in Tunisia in 1926—1927. W. GORCZYŃSKI and E. STENZ (Bull. Acad. Polonaise, 1933, **A**, 53—64). A. B. D. C.

Ultra-violet bands of oxide of phosphorus. P. N. GHOSH and A. K. SEN-GUPTA (Nature, 1933, **131**, 841).—Mol. consts. have been obtained for the spectrum attributed to PO. L. S. T.

Extension of the visible absorption system of NO_2 to longer wave-lengths. J. CURRY and G. HERZBERG (Nature, 1933, **131**, 842).—A series of bands starting at approx. 8900 Å. and extending to shorter wave-lengths has been observed. L. S. T.

Interpretation of ultra-violet absorption bands of alkali halides. W. KLEMM (Z. Physik, 1933, **82**, 529—537).—Absorption may occur within the crystal if asymmetrical polarisation of the ions is taken into account (cf. Born, this vol., 5). A. B. D. C.

Optical investigation of uranium compounds. F. EPHRAIM (J. Indian Chem. Soc., 1933, Ray No., 243—250).—Absorption spectra of UF_4, UCl_4, and UBr_4 at 18° and −180° were measured. They resemble those of the rare earths, and are attributed to similar abnormalities of electron arrangement (cf. A., 1927, 121). H. J. E.

Relation of emission and absorption spectra of salts of rare earths in the solid state. I. Phosphorescence due to impurities. R. TOMASCHEK and O. DEUTSCHBEIN (Z. Physik, 1933, **82**, 309—327).—Emission and absorption spectra due to ions of the rare earths were investigated between 4000

and 9000 Å. Emission may coincide with absorption in the long-wave but not in the short-wave region. A. B. D. C.

Displacement of absorption bands of rare-earth salts. Y. UZUMASA (J. Fac. Sci. Hokkaido, 1933, **1**, 383—393; cf. A., 1932, 557).—The influence of the solvent and of the anion on the position of the absorption max. has been studied for salts of Pr, Nd, Sm, and Er. For Er the influence of added salts with a common anion has also been studied. F. L. U.

Absorption of ultra-violet light by some organic substances. XXVIII. W. GABRYELSKI and L. MARCHLEWSKI. **XXIX.** L. MARCHLEWSKI and T. SURZYCKI (Bull. Acad. Polonaise, 1933, **A**, 87—94, 95—98).—XXVIII. Absorption due to cellobiose, raffinose, cellobiose acetate, lactobiose β-acetate, sucrose acetate, and maltose acetate was investigated between 2200 and 3600 Å.

XXIX. Pyridine-2-, -3-, and -4-carboxyldiethylamide were investigated between 2200 and 3000 Å. A. B. D. C.

Purification and ultra-violet transmission of ethyl alcohol. L. HARRIS (J. Amer. Chem. Soc., 1933, **55**, 1940—1942; cf. A., 1931, 1110).—Commercial abs. EtOH is purified by means of Zn. Physical consts. and absorption coeffs. between 2450 and 2120 Å. are recorded. J. G. A. G.

Continuous absorption spectrum of polyatomic molecules. II. Y. HUKUMOTO (Sci. Rep. Tohoku, 1933, **22**, 13—30; cf. this vol., 336).—The effect of foreign gases (air, H_2, N_2, O_2) on the absorption spectra of the vapours of alkyl halides was found to be negligible. The absorption spectrum of $(CHCl)_2$ is affected by temp., which may be due to the existence of two stereoisomeric forms. The mechanism of the photo-dissociation is discussed. A. J. M.

Spectroscopic investigation of the explosion zones of methane and other hydrocarbons. F. J. LAUER (Z. Physik, 1933, **82**, 179—191).—Flames of CH_4, C_2H_2, and C_6H_6 in O_2 were investigated spectroscopically between 6200 and 2200 Å. The active explosion zone of CH_4 gave the CH band at 3142 Å., and in addition to the known bands due to OH, CH, and C_2, a band due to CH_r was observed at 3672 Å. Reaction mechanisms are discussed. A. B. D. C.

Band spectra and molecular structure. I. W. WEIZEL (Physikal. Z., 1933, **34**, 425—440).—A review.

Spectroscopy in the service of chemistry. M. N. SAHA (J. Indian Chem. Soc., 1933, Ray No., 293—307).—A review. H. J. E.

Water vapour absorption in the infra-red part of the solar spectrum according to spectrographic measurements made at the Mediterranean coast during 1931—1932. E. STENZ (Bull. Acad. Polonaise, 1933, **A**, 65—76).—Infra-red absorption gives a more accurate estimate of H_2O vapour content than ordinary methods, and shows that before rainfall and cloudy periods atm. absorption increases. A. B. D. C.

Infra-red spectrum of carbon dioxide. I. A. ADEL and D. M. DENNISON (Physical Rev., 1933, [ii], **43**, 716—723; cf. A., 1932, 982).—Mathematical. Previous work is extended by introducing a second-order perturbation. N. M. B.

Infra-red absorption measurements of organic substances. I. Apparatus and absorption of some solvents and organic dyes. G. BUSS. **II. Absorption of some organic liquids below 2·7 μ.** O. EICHMANN (Z. Physik, 1933, **82**, 445—460, 461—472).—I. Absorption between 0·8 and 2·4 μ was determined for C_6H_6, H_2O, EtOH, glycerol, and azo-, phthalein, $CHPh_3$, and acridine dyes.

II. CH_2PhCl, Me salicylate, EtOBz, anethole, paraldehyde, *l*- and *d*-pinene, $C_5H_{11}\cdot OH$, $C_5H_{11}\cdot O\cdot NO$, $EtCO_2H$, and $Et_2C_2O_4$ were investigated. A. B. D. C.

Fine structure of residual rays. M. BORN and M. BLACKMAN (Z. Physik, 1933, **82**, 551—558).—Anharmonic coupling of normal vibrations of a lattice gives various overtones in the infra-red spectrum, and from this are deduced the positions of subsidiary max. A. B. D. C.

Raman spectrum of rock-salt. M. BLACKMAN (Naturwiss., 1933, **21**, 367).—The Raman spectrum of rock-salt shows more intensity max. than indicated by the simple theory. An explanation is discussed. A. J. M.

Raman effect. XXV. Raman spectrum of monobasic organic acids. K. W. F. KOHLRAUSCH, F. KOPPL, and A. PONGRATZ (Z. physikal. Chem., 1933, **B**, **21**, 242—255).—The Raman spectra of sixteen fatty acids, the chloroacetic acids, and BzOH have been determined. From the variation in intensity of the lines with the length of the chain, it is concluded that the characteristic frequencies of the normal acids $\Delta\nu$=1650, 1410, and 1110 cm.$^{-1}$ correspond with the vibrations of groups which occur only once in the mol., whilst the frequencies 1300 and 1450 cm.$^{-1}$ belong to groups the no. of which in the mol. is proportional to the length of the chain. With increasing branching of the chain in the α position there is a slight depression of the CO frequency 1650 cm.$^{-1}$ R. C.

Raman effect and depolarisation factor. O. SPECCHIA (Nuovo Cim., 1932, **9**, 133—137; Chem. Zentr., 1933, i, 17).—Two methods for determining the depolarisation factor of Raman bands are described, and used for H_2O bands. Results are compared with those of Ramaswamy. A. A. E.

Halochromism of ketones in acids. L. C. ANDERSON (J. Amer. Chem. Soc., 1933, **55**, 2094—2098).—The absorption curves of benzoquinone in Et_2O and $HClO_4$ and of anthraquinone, $COPh_2$, and xanthone in Et_2O and conc. H_2SO_4 indicate that the colours produced in acid are concerned with the reactivity of the CO group. In some cases, quinonoid-ation may be also responsible. H. B.

Thermo-luminescence spectrum of calcite. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, 274—284).—The spectrum of calcite containing traces of the rare earths and of Th showed a continuous single band in the range 670—535 mμ, coinciding with the spectra of cathodo- and photo-luminescence. A close agreement with the combustion spectrum of Ca in O_2 indicates the explanation as the chemo-luminescence due to the combustion of free O_2

and colloidal Ca which causes the coloration of the crystal. The theory of the mechanism of luminescence in fluorite is developed to apply to the present case. N. M. B.

Fluorescence of pure salts of the rare earths. R. TOMASCHEK and O. DEUTSCHBEIN (Physikal. Z., 1933, **34**, 374—376; cf. this vol., 446).—The spectra, especially at low temp., are very sharp. Some emission lines coincide with absorption lines. The fluorescence spectra of solutions of salts of the rare earths are also examined. A. J. M.

Fluorescence of "special salt." S. OKA and S. YAGI (J. Soc. Chem. Ind. Japan, 1933, **36**, 143—144B).—NaCl and KCl crystals from solutions containing Mn, Sn, or Pb are fluorescent. Luminescence and transparency run parallel. J. S. A.

Blue rock-salt. E. REXER (Naturwiss., 1933, **21**, 332).—When a specimen of blue rock-salt is placed in a beam of *X*-rays which ordinarily produce a yellow colour in the salt, the yellow colouring of the previously colourless regions is considerably more intense than that where the blue colour was, and shows the normal absorption bands. By photo-electric colouring there is a complete reversal of the form of the coloured part. A. J. M.

Efficiency of anti-Stokes fluorescence in dyes. A. JABLOŃSKI (Nature, 1933, **131**, 839—840).—Theoretical. L. S. T.

Transparent crystals of potassium halides. S. OKA (J. Soc. Chem. Ind. Japan, 1933, **36**, 141—143B).—The presence of Sb, Bi, Pb, and Sn ions markedly alters the crystal habit of KCl and KBr. With Pb and Sn present, perfectly transparent octahedral crystals which fluoresce in ultra-violet light are formed. J. S. A.

Internal photo-electric effect in liquid dielectrics. G. LIANDRAT (Compt. rend., 1933, **196**, 1385—1386; cf. A., 1930, 398).—The initial conductivity, 10^{-15} ohm^{-1} per cm., of the CCl_4 used, which after exposure for 1 hr. to a Hg arc rose to 10^{-14}, and regained its initial val. in 2 hr. after removal of the arc, was so high and irregular as to indicate that the CCl_4 was insufficiently pure to permit a decision as to its photoconductivity. C. A. S.

New type of photo-electric effect in cuprous oxide in a magnetic field. I. KIKOIN and M. NOSKOV (Nature, 1933, **131**, 725—726).—When a plate immersed in liquid air and placed in a magnetic field parallel to its plane is illuminated by a beam of white light perpendicular to this plane, an e.m.f. is developed between the ends of the plate at right angles to the light and the magnetic field. The direction of supposed flow of negative electrons appears to coincide with that of the light. The effect disappears when red light is used, and is not observed at room temp. A peculiar Hall effect of the moving photo-electrons produced at the entrance of the light into the plate appears to be involved. L. S. T.

Thermo-electric force and voltaic potential of cuprous oxide. G. MONCH (Naturwiss., 1933, **21**, 367).—A thermo-element made up of metal–Cu_2O–metal has a comparatively large thermo-electric force due to the different electron concn. in the semi-conducting Cu_2O. The same potential should be obtained at the ends of a polycryst. rod of Cu_2O maintained at a temp. difference. Such an arrangement gave 0·4—0·5 volt, for 100° temp. difference. Part of this is due to the voltaic potential of the free Cu_2O surface which varies with temp., amounting to about 0·15 volt for 100° temp. difference. A. J. M.

Photo-electric effect in specially active layers of a carborundum crystal. O. V. LOSSEV (Physikal. Z., 1933, **34**, 397—403).—Rectification by a carborundum crystal may be due to the presence of an active layer at the surface, the thickness of which can be measured with a microscope. The electrical conductivity of the layer at various depths was found for small c.d., and the potential distribution inside the layer was determined. The photo-electric effect can take place in the active layer, but the source of the photo-electrons is the boundary between the active layer and the crystal itself. In many respects the SiC crystal behaves similarly to the Cu_2O "sperrschicht" cell. The presence of active layers on galena crystals, and on single crystals of Si containing Al, Cu, and Fe, is reported. A. J. M.

Mechanism of action of light on electrodes photosensitised with copper salts. R. AUDUBERT (Compt. rend., 1933, **196**, 1588—1590).—Measurements of the photopotential of electrodes of Cu coated with Cu_2O, CuO, CuI, or CuCl in aq. $CuSO_4$ of varying concn. agree with the results calc. on the theory that a positive photopotential is connected with oxidation, negative with reduction, *i.e.*, that the photovoltaic behaviour in such electrodes is due to the photolysis of H_2O (cf. A., 1931, 999). C. A. S.

Photo-electric properties of magnesium. G. DEJARDIN and (MLLE.) R. SCHWEGLER (Compt. rend., 1933, **196**, 1585—1587; cf. A., 1932, 789).—Photo-electric cells with Mg were prepared (*a*) by condensing Mg vapour on the glass wall, (*b*) by cathodic sputtering, and (*c*) by partial volatilisation of a Mg–Ba (70—75 : 30—25) alloy. (*a*) showed a threshold at 3400—3500 Å., and emission (in 10^{-5} amp. watt) of 0·4—1·0 for 3130 Å., and 4·0—7·9 for 2537 Å.; with (*b*) and (*c*) if volatilisation occurred at $\gtrsim$ 900°, results were similar, but with volatilisation at a higher temp. (*c*) gave results indicating presence of Ba, the threshold being at 5000—5500 Å. C. A. S.

Photo-electric sensitivity of magnesium. R. J. CASHMAN and W. S. HUXFORD (Physical Rev., 1933, [ii], **43**, 811—818).—The photo-electric sensitivity of gas-free surfaces of Mg deposited on glass was determined in the visible region of the spectrum; the long-wave limit for all such surfaces deposited in vac. is approx. 5100 Å. Traces of air, or O_2, or N_2 activated by glow discharge sensitise the surface to light of longer wave-lengths. Further oxidation of the surface shifts the threshold into the ultra-violet. N. M. B.

Determination of photo-electric wave-length limit for rhenium. A. ENGELMANN (Ann. Physik, 1933, [v], **17**, 185—208).—The photo-electric wave-length limit for Re at various stages of outgassing was determined; for complete outgassing it was about 250 mμ. The presence of vapours of hydrocarbons causes a considerable displacement of the red limit

towards the longer waves. The results agree with the theory of Fowler on the analysis of spectral distribution curves at various temp. A. J. M.

[Electrical] conductivity of mixtures of gases. S. P. McCallum and L. Klatzow (Nature, 1933, **131**, 841).—Curves for He, A, and He +0·025% A are given and discussed. A large no. of new ions, attributed to direct collisions of electrons with A atoms, are formed in the He–A mixture when the potential between the parallel plates increases from 9 to 18 volts. L. S. T.

Piezoelectric and dielectric properties of Rochelle salt. E. Schwartz (Elek. Nach. Tech., 1932, **9**, 481—495). Ch. Abs.

Ionic polarisation in crystals. J. Errera and H. Brasseur (Physikal. Z., 1933, **34**, 368—373).—The dielectric const. of crystals along their principal axes is measured, and from this the ionic polarisation is derived. A. J. M.

Dielectric polarisation in solids. S. O. Morgan, W. A. Yager, and A. H. White (J. Amer. Chem. Soc., 1933, **55**, 2171—2172).—A transition in the solid state accompanied by changes of heat capacity and dielectric const. occurs in *d*-camphor between −37° and −32°, in *dl*-camphor between −70° and −80°, and in borneol and *iso*borneol at 70—80° and 25—45°, respectively. The data are discussed with reference to at. polarisation or group rotation which depends on temp. J. G. A. G.

Dipole rotation and the transitions in the crystalline hydrogen halides. C. P. Smyth and C. S. Hitchcock (J. Amer. Chem. Soc., 1933, **55**, 1830—1840).—Dielectric consts. and sp. conductances have been determined between −37° and −189° at frequencies between 300 and 60,000, and the data confirm the transition points revealed by sp. heat determinations. For some distance below the m.p. the mols. in the cryst. solids orient in the externally applied electric field to almost the same extent as in the liquid, and in general, the polarisations vary inversely as the abs. temp. between the transitions. Below −174·6°, the dielectric const., ε, of HCl falls to very low vals., indicating negligible rotatory oscillation of the mols. Vals. of ε for HI increase rapidly with fall of temp. below −147·5° owing to an increasing no. of mols. passing from states of complete rotation to rotatory oscillation as the temp. falls. For HBr, ε has a strong sharp max. between −183° and −185°. The results are discussed with reference to Pauling's theory. J. G. A. G.

Electric moments of nitrogen dioxide and nitrogen tetroxide. C. T. Zahn (Physikal. Z., 1933, **34**, 461—462).—The dielectric consts. of the equilibrium mixture $2NO_2 \rightleftharpoons N_2O_4$ were determined between 296° and 397° abs., and at pressures between 0 and 1 atm. It is very probable that both NO_2 and N_2O_4 have definite dipole moments, that of N_2O_4 being the greater. The vals. given as upper limits are $0{\cdot}5_5\times10^{-18}$ and $0{\cdot}3_9\times10^{-18}$, respectively. A. J. M.

Refractivities of liquid compounds of phosphorus. W. J. Jones, W. C. Davies, and W. J. C. Dyke (J. Physical Chem., 1933, **37**, 583—596).—Vals. of the density, *n*, and mol. refractivities of 84 liquid P compounds are tabulated. At. and group refractivities are tabulated, and their relation to mol. structure is discussed. H. J. E.

Molecular refraction of alums. K. Wendekamm (Z. Krist., 1933, **85**, 169—198).—Density, mol. vol., and mol. refraction of the alums $XY(SO_4)_2,12H_2O$, where X=K, Rb, Cs, Tl^I, NH_4, NH_3Me, and NH_3OH, Y=Al, Cr, and also the corresponding double Al selenates, have been determined and compared *inter se* and with V and Fe alums by plotting the vals. of these properties for the other series against those of the Al alum series. In almost every case the relation is linear, as also in the case of the double sulphates $M^I_2M^{II}(SO_4)_2,6H_2O$. Tl^I derivatives show the greatest deviation. C. A. S.

Refractive dispersion of eugenol and *iso*-eugenol. G. Thompson (J.C.S., 1933, 557; cf. *ibid.*, 1923, 1594).—Vals. of *n* for the two isomerides at 20° are tabulated (cf. Eykman, A., 1890, 748). H. J. E.

Dispersion of electric birefringence in ethyl ether. M. Schwob (Compt. rend., 1933, **196**, 1383—1384; cf. A., 1925, ii, 755).—The electric birefringence of Et_2O at 17° for λ 5780, 5460, and 4360 is 20·1, 20·9, and 27·6, respectively (that of CS_2 being 100), giving dispersions $\rho_{4360}/\beta_{5780}=1{\cdot}37$, and $\beta_{4360}/\beta_{5460}=1{\cdot}31$, as compared with 1·33 and 1·25 by Havelock's formula. C. A. S.

Variation with temperature of magnetic birefringence of liquid oxygen. P. Laine (Compt. rend., 1933, **196**, 1594—1596; cf. this vol., 556).—Langevin's theory as regards the temp. variation of magnetic birefringence (I) of paramagnetic substances gives the correct ratio between (I) of liquid O_2 at 77·9° and 90·1° abs., whereas his theory, based on the same fundamental ideas, for the variation of the magnetic susceptibility gives a result double experimental (cf. A., 1910, ii, 578). Weiss attributes this to the mol. field, which, however, should affect (I) similarly. For (I) the result is explicable if the effect of the mol. field is exactly counterbalanced by change with temp. of the optical anisotropy as in the case of HCO_2H and AcOH. C. A. S.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. VI. Magneto-optical dispersion of acetic acid and *n*-propyl acetate. W. J. Lewis and G. E. Jones (Phil. Mag., 1933, [vii], **13**, 1065—1079; cf. A., 1931, 24).—Data are tabulated for the magneto-optical dispersion of these compounds in the region 0·46—0·27 μ, and for the natural dispersion in the region 0·6678—0·2766 μ. Expressions are deduced which accord with these data. The absorption bands in the Schumann–Lyman region are at 0·1042 μ and 0·1077 μ, and the calc. vals. of e/m are $0{\cdot}91_6\times10^7$ and $1{\cdot}01\times10^7$ e.m.u., respectively. J. W. S.

Theory of the Kerr effect of diatomic molecules. G. Neugebauer (Z. Physik, 1933, **82**, 660—673).—Quantum theory leads to classical results. A. B. D. C.

Kerr's law at high field strengths. J. A. Hootman (Physical Rev., 1933, [ii], **43**, 749—755).—In pure non-polar CS_2 Kerr's law held for all fields; in polar

liquids, Et_2O and $CHCl_3$, deviations were found. Curves for the variation of the Kerr const. with electric field strength are given for Et_2O at $-78{\cdot}5°$ and $CHCl_3$ at $-22{\cdot}5°$. N. M. B.

Stereomagnetism. I. Significance of atomic interaction for magnetism. II. Problem of perminvar. O. VON AUWERS and H. KUHLEWEIN (Ann. Physik, 1933, [v], **17**, 107—120, 121—145).—I. The effect of at. coupling and cryst. superstructure on the magnetic properties of substances in general is discussed.

II. The properties of Fe–Co–Ni alloys which after heating and subsequent slow cooling possess const. permeability are discussed in connexion with the theory previously put forward. A special model is used to investigate the action of the coupling field in a mixed crystal lattice with ferromagnetic components with superstructure, from which an explanation of the behaviour of perminvar is obtained. A. J. M.

Susceptibilities of paramagnetic solutions. C. J. GORTER (Physikal. Z., 1933, **34**, 462—464; cf. A., 1932, 900).—Polemical against Fahlenbrach (this vol., 340). A. J. M.

Diamagnetism of carbon tetrachloride, benzene, and toluene at different temperatures. G. F. BOEKER (Physical Rev., 1933, [ii], **43**, 756—760; cf. this vol., 212).—Experimental data are tabulated and plotted. The mass susceptibilities show a decrease $< 1\%$ with rise of temp. N. M. B.

Temperature and diamagnetism. S. S. BHATNAGAR (J. Indian Chem. Soc., 1933, Spec. No., 171—176).—Change of temp. generally changes the diamagnetism more in aromatic than in aliphatic compounds. H. J. E.

Magne-crystallic action. II. Paramagnetics. K. S. KRISHNAN, N. C. CHAKRAVORTY, and S. BANERJEE (Phil. Trans., 1933, **A, 232**, 99—115).—The principal magnetic susceptibilities of the hydrated sulphates of $Fe^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, and $Cu^{\cdot\cdot}$, their double sulphates with K and NH_4, $MnSO_4,(NH_4)_2SO_4,6H_2O$, $CoSO_4,CuSO_4,7H_2O$, and $FeCO_3$ have been measured by methods already described (A., 1927, 192; this vol., 340). Errors in Jackson's method of calculation (cf. A., 1928, 1081) are corrected. D. R. D.

Magnetic structure of an iron alum in strong fields. J. FORREST (Phil. Mag., 1933, [vii], **15**, 1153—1162; cf. A., 1927, 299; 1931, 154).—The magnetic anisotropic character of crystals of $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$ has been confirmed. J. W. S.

Influence of light on paramagnetic susceptibility. P. W. SELWOOD (Nature, 1933, **131**, 762).—Solutions of $FeCl_3$, $CrCl_3$, and $Nd(NO_3)_3$ show a slow decrease in paramagnetic susceptibility on exposure to light (cf. A., 1932, 900). L. S. T.

Structure of basic salts of bivalent metals. W. FEITKNECHT (Helv. Chim. Acta, 1933, **16**, 427—454; cf. A., 1930, 436).—*X*-Ray examination of basic Zn salts $ZnX_2,4Zn(OH)_2$ and $ZnY,3Zn(OH)_2$ (X=Cl, Br, I, NO_3; Y=SO_4, CO_3) shows that normal salt and hydroxide occur in alternate layers in the lattice. Corresponding salts (excluding bromides and iodides) of Co, Ni, Mn^{II}, Cd, Fe^{II}, and Mg show similar structure. H_2O of crystallisation is held between the layers. On dehydration the distance between the latter decreases, the lattice remaining intact. Basic Zn salts readily take part in topochemical changes, in which the action takes place along the plane of the layers. Two kinds of mixed basic salts have been prepared, in one of which only the cation of the normal salt component is replaceable, whilst in the other the cation of the hydroxide component is also replaceable. Werner's conception of basic salts as " hexol salts " is incorrect. F. L. U.

Electronic structure of ethylenic carbon. G. ALLARD (Compt. rend., 1933, **196**, 1500—1502).—One of the linkings in C:C is represented by $1/\sqrt{3}s+\sqrt{\frac{2}{3}}p_x, 1/\sqrt{3}s-1/\sqrt{6}p_x+1/\sqrt{2}p_y$, or $1/\sqrt{3}s-1/\sqrt{6}p_x-1/\sqrt{2}p_y$, whilst the other (which has a small energy and restricts free rotation) is represented by p_z. The first three functions represent three valencies situated in the same plane at angles of 120°; the fourth is normal to the plane of the other three. H. B.

Structure of hypophosphoric acid. P. NYLEN and O. STELLING (Z. anorg. Chem., 1933, **212**, 169—181).—Cryoscopic measurements on aq. solutions of the acid and its Na salt support the double formula $H_4P_2O_6$. *X*-Ray examination of the Na and Ba salt shows only one *K* absorption edge, corresponding with that expected for the structure $R_4(O_3P{\cdot}PO_3)$. J. S. A.

Structure of pyrophosphoric acid. P. NYLEN (Z. anorg. Chem., 1933, **212**, 182—186).—Treatment of $NaPO(OEt)_2$ with I or with $POCl(OEt)_2$, air oxidation of $Et_4P_2O_6$, and action of EtI on $Ag_4P_2O_7$ lead to formation of $Et_4P_2O_7$. This, when shaken with $BaCO_3$ and H_2O, forms $Ba(Et_2PO_4)_2$. The symmetrical formula $R_4(O_3P{\cdot}O{\cdot}PO_3)$ is therefore indicated for $R_4P_2O_7$. J. S. A.

Formulæ of antimonic acid and the antimonates. L. PAULING (J. Amer. Chem. Soc., 1933, **55**, 1895—1900).—From the ratios of ionic radii and geometrical considerations, formulæ are assigned to the oxy-acids of many elements in their highest valency states. Evidence is adduced in favour of the formula $HSb(OH)_6$ for antimonic acid. The change from an ortho- to a meta-acid (or salt), *e.g.*, H_3BO_3 to $(HBO_2)_x$, $HSb(OH)_6$ to $(HSbO_3)_y$, generally involves polymerisation rather than a change in co-ordination no. J. G. A. G.

Constitution of molecular compounds. P. R. RAY (J. Indian Chem. Soc., 1933, Ray No., 161—169).—A review. H. J. E.

Quantum mechanics and the benzene problem. I, II. G. ELSEN (Chem. Weekblad, 1933, **30**, 310—317, 322—328).—A review of recent work. H. F. G.

Quantum mechanics of chemical valency. H. HELLMANN (Z. Physik, 1933, **82**, 192—223).—The method of Heitler, Rumer, and Weyl is generalised semi-empirically. Coulomb are separated from exchange forces, and evaluations of each from known data for simple mols. are used to predict structures of more complex mols. Thus, exchange and Coulomb (including polarisation) terms are evaluated for the at. pairs H–H, H–N, N–N, C–H, C–C, and C– –H, and

are used to discuss the mols. N_2H_4, N_nH (linear), CH_4, C_2H_2, C_2H_4, and C_2H_6. A. B. D. C.

Calculation of intramolecular atomic distances from dissociation constants of dibasic acids. II. Acidity of dicarboxylic acids and polymethylenediammonium ions in aqueous alcohol. III. Acidity of substituted malonic acids in aqueous alcohol. G. SCHWARZENBACH (Helv. Chim. Acta, 1933, **16**, 522—528, 529—533; cf. this vol., 25).—II. The empirical relation $\phi=k/D^a$ (ϕ—work done in removing the second H$^\cdot$ from the univalent ion of a dicarboxylic acid, D=dielectric const. of medium) is valid for the acids $CO_2H\cdot[CH_2]_n\cdot CO_2H$ (n=1, 2, 3, and 6), which have been examined in 0, 20, 40, 60, and 80% aq. EtOH. The same relation (with changed sign) applies to the removal of the first H$^\cdot$ from the ion $^\cdot NH_3\cdot[CH_2]_n\cdot NH_3^\cdot$ (n=2, 3, 4, 5, and 8). The val. of a increases with the length of the C chain, but is always < 1.

III. Similar experiments with alkyl-substituted malonic acids show that a is smaller than for malonic acid, the effect increasing with the size of the substituent group. F. L. U.

Quantitative crystal analysis by *X*-rays. M. E. NAHMIAS (Z. Krist., 1933, **85**, 319—321; cf. this vol., 44).—Further details of the method are given. C. A. S.

Production of single crystals with prescribed axial orientation. P. A. PALIBIN and A. I. FROIMAN (Z. Krist., 1933, **85**, 322—325).—A method for obtaining crystals of, *e.g.*, Zn or Cd with the hexagonal axis parallel to their length is described. C. A. S.

Laue reflexion photographs with oscillating quartz rod. E. BLECHSCHMIDT and W. BOAS (Z. Krist., 1933, **85**, 329; cf. A., 1932, 363; this vol., 213).—A quartz rod with sides parallel and perpendicular to a digonal and parallel to the hexagonal axis, respectively, oscillating in the direction of its length, had no effect on reflexion Laue photographs. C. A. S.

Reflexion and refraction of *X*-rays by perfect crystals. G. W. BRINDLEY (Proc. Roy. Soc., 1933, **A, 140**, 301—313; cf. A., 1932, 903). L. L. B.

Effects of mechanical strain in the intensity of *X*-rays reflected by a crystal. E. FUKUSIMA (J. Sci. Hiroshima Univ., 1933, **3**, 177—186).—Local mechanical strain increases the reflecting power by eliminating internal extinctions. The effect is greater with perfect crystals (*e.g.*, quartz) than with imperfect (*e.g.*, rock-salt). J. S. A.

New representation of geometrical crystallography. B. DELAUNAY (Z. Krist., 1933, **85**, 332; cf. this vol., 213).—A correction. C. A. S.

Total reflexion of *X*-rays by thin layers. A. I. ALICHANOV and L. A. ARZIMOVIC (Z. Physik, 1933, **82**, 489—506).—Total reflexion was observed with Ag and W layers on glass, Ag layers on Al, Al on Ag, and Ag on Pt and W. A. B. D. C.

Formation of crystal nuclei in piperonal and *allo*cinnamic acid. E. BIILMANN and A. KLIT (Kgl. Danske Vidensk. Selskab, 1933, **12**, No. 4, 3—51).—The no. of nuclei formed in melts of piperonal on cooling decreases as the temp. of the melt is raised and with duration of the heating. In under-cooled melts the no. of nuclei decreases with time, indicating that there is no essential difference in the liquid phase above and below the m.p. Reproducible results can be obtained under const. conditions when the glass tubes used have been used previously. Fresh glass surfaces may provide crystallisation centres. When the melting conditions are const. the no of nuclei formed increases with the degree of cooling, if the lowest temp. reached is not too far below the m.p. Formation and disappearance of the nuclei are not reversible. The observations are explained by supposing that crystallisation centres are formed by dust particles of colloidal dimensions, which acquire a sheath of oriented mols. of the melt. This view is supported by the fact that the nuclei can be centrifuged. Similar phenomena are observed in melts of the three modifications of *allo*cinnamic acid. The results suggest that these modifications are polymorphic. E. S. H.

Needle-shaped crystals of sodium chloride. W. S. HINEGARDNER (J. Amer. Chem. Soc., 1933, **55**, 1461—1462; cf. A., 1932, 797).—Fine needles of NaCl appeared after unwashed SiO_2 gel from Na silicate and HCl had dried sufficiently to fracture. J. G. A. G.

Crystalline state of thin sputtered films of platinum. G. P. THOMSON, N. STUART, and C. A. MURISON (Proc. Physical Soc., 1933, **45**, 381—388).—Films of Pt sputtered in various gases have been examined by electron diffraction. They show patterns indicating that the small crystals are oriented with one face parallel to the surface of the specimen, the crystals being otherwise at random. The width of the rings formed by diffraction shows that in many cases the crystals are very small, of the order of 5×10^{-7} cm. Some films of PtO_2 showed crystals of the order of 2×10^{-7} cm. W. R. A.

Crystal structure of α-(β-)tungsten. M. C. NEUBURGER (Z. Krist., **85**, 232—238; cf. A., 1931, 805, 1377).—As the new modification is stable only below 650°, the designations β and α have been interchanged. The unit cell has a 5·038 and contains 8 W, space-group T_h^3-O_h^3, the lattice being of a new type. The at. vol. is 9·70, that of ordinary (β-)W being 9·547. C. A. S.

Lattice constant of beryllium. M. C. NEUBURGER (Z. Krist., 1933, **85**, 325—328; cf. A., 1923, ii, 766).—Specially pure Be has a 2·2679, c 3·5942 Å., with 2 mols. in the unit cell; d^{20} 1·85, at. radius 1·112 Å. C. A. S.

Anomalous scattering of *X*-rays by copper. A. A. RUSTERHOLZ (Z. Physik, 1933, **82**, 538—550).—The atom factor for the (220) face of Cu was determined for different wave-lengths. A. B. D. C.

Transformation of cobalt single crystals. U. DEHLINGER, E. OSSWALD, and H. BUMM (Z. Metallk., 1933, **25**, 62—63).—Single crystals of Co have been obtained by very slow cooling of the metal from 1480° in an induction furnace. The hexagonal crystals during transformation to the cubic form behave similarly to the Tl crystals previously examined (A., 1932, 1193); they can be converted into the

cubic form and back into the hexagonal many times without breaking down into several crystals. A theoretical explanation is given. A. R. P.

Crystal structure of indium. F. P. DWYER and D. P. MELLOR (J. Proc. Roy. Soc. New South Wales. 1933, **66**, 234—239).—There are four atoms per unit cell; a_0, 4·588±0·002, b_0, 4·946±0·002 Å., $a : c$= 1·078±0·002. C. W. G.

Crystal structure and lattice constants of mercury. M. C. NEUBURGER (Z. anorg. Chem., 1933, **212**, 40—44).—*X*-Ray diffraction lines attributed by Alsén and Aminoff to Hg (A., 1924, ii, 554) are shown to be due to solid CO_2. The lattice of solid Hg is rhombohedral, and not hexagonal. H. J. E.

Diffuse scattering of *X*-rays from sylvine. III. Scattering at the temperature of liquid air. G. G. HARVEY (Physical Rev., 1933, [ii], **43**, 707—710).—An extension of previous work (cf. this vol., 549). A general expression for the intensity of scattering over the full temp. range is found. N. M. B.

Crystal structure of potassium thiocyanate. H. P. KLUG (Z. Krist., 1933, **85**, 214—222).—KCNS is orthorhombic with a 6·66, b 7·58, c 6·635 Å., and 2 mols. in the unit cell, space-group probably V^{11}. C, N, and S in CNS′ are in a straight line; the structure is similar to that of KCNO (cf. A., 1926, 113). C. A. S.

Crystal form of dinitrocobaltammines. W. M. MCNABB and H. A. ALSENTZER, jun. (Z. Krist., 1933, **85**, 297—304).—1 : 6-Dinitrotetramminocobaltic iodide and chromate, and 1 : 2-dinitrotetramminocobaltic chromate and dichromate are respectively: hexagonal, $a : c$=1 : 0·6757; hemihedral tetragonal, $a : c$= 1 : 1·4901; tetragonal, $a : c$— (from H_2O) 1 : 1·5034, from aq. $(NH_4)_2CO_3$ 1 : 1·2957; and monoclinic, $a : b : c$=1·2023 : 1 : 1·7388, β 115° 1′. C. A. S.

Cobaltinitrites of ammonium, potassium, rubidium, cæsium, and thallium. A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1933, [vi], **17**, 390—398; cf. A., 1932, 483).—The following vals. of a (Å.) and d, respectively, were obtained for the compounds of the general formula $M_3[Co(NO_2)_6]$, where M=metal atom or NH_4: NH_4, 10·81±0·02, 2·00; K, 10·44± 0·02, 2·64; Rb, 10·73±0·01, 3·18; Cs, 11·15±0·01, 3·51; Tl, 10·72±0·02, 5·10. The unit cell contains 4 mols. in every case. The NH_4 compound may contain $1·5H_2O$ and the Rb and Cs compounds $1H_2O$. $Pb_3[Co(NO_2)_6]_2$ is anhyd. and isomorphous with $K_6[Co(NO_2)_6]_2$. O. J. W.

***X*-Ray and thermal characterisation of lattice formation of zinc oxide.** R. FRICKE and P. ACKERMANN (Naturwiss., 1933, **21**, 366).—By varying the temp. of heating $Zn(OH)_2$ to produce ZnO the latter can be made in varying degrees of energy content as indicated by the mol. heat of dissolution. *X*-Ray photographs of the oxides showed a diminution of the abs. line intensity and a stronger decrease in the intensities of higher-order spectra with increase in energy content. The larger energy of the oxides prepared at lower temp. is due to incomplete lattice formation. A. J. M.

Crystalline structure of calcium–nitrogen compounds. H. H. FRANCK, M. A. BREDIG, and G. HOFFMANN (Naturwiss., 1933, **21**, 330—331).—There are three Ca nitrides differing in structure: black (a) formed between 650° and 750°, brown (b) between 750° and 1150°, and yellow (c) at 1150—1200°. b is space-centred cubic, resembling Mg_3N_2. a is either hexagonal or simple tetragonal. When H_2 is passed over Ca_3N_2 a yellowish-green compound, containing H, probably CaNH, and having a cryst. structure similar to CaO, is formed. A. J. M.

Crystal orientation in spherulites. W. JANSEN (Z. Krist., 1933, **85**, 239—270).—*X*-Ray examination of ten spherulitic minerals shows that the axis of the constituent fibres always coincides with a crystallographic axis, with but very slight distortion. The precise axis depends on the direction of most rapid growth and is in accordance with the Gross–Moller selection principles. Wavellite, $4AlPO_4,2Al(OH)_3,9H_2O$, rhombic, has a 7·27, b 14·41, c 10·80 Å., with 2 mols. in the unit cell. Salol, rhombic, has a 11·24, b 11·62, c 8·08 Å. C. A. S.

***X*-Ray study of opals, silica glass, and silica gel.** I. LEVIN and E. OTT (Z. Krist., 1933, **85**, 305—318; cf. A., 1925, ii, 638; 1932, 451). C. A. S.

Macromolecular lattice of polyethylene oxide. E. SAUTER (Z. physikal. Chem., 1933, **B**, **21**, 161—185).—*X*-Ray examination of polyethylene oxide fractions of mol. wt. 2400—100,000 has shown them all to have the same macromol. lattice. The eucolloidal oxide of mol. wt. 100,000 gives a fibre diagram when stretched. The macromol. lattice has b 19·5, a 9·5, c 12·0 Å., β 101°, the unit cell is simple primitive, and the probable space-group C_{2h}^5. There are 36 primary mols. in the basal cell. The polyethylene oxide principal valency chain in the cryst. state has the "meander" form deduced from viscosity data; a model is suggested. R. C.

Model of principal valency chain in macromolecular lattice of polyoxymethylenes. E. SAUTER (Z. physikal. Chem., 1933, **B**, **21**, 186—197).—The model has been deduced from a consideration of the arrangement of the primary mols. in the principal valency chains of polyethylene oxides (cf. preceding abstract). It accounts qualitatively for the intensity relations of the *X*-ray diagram and for the conversion of trioxy- into polyoxy-methylene. R. C.

Crystal structure of phenyldiphenylyl. E. HERTEL and G. H. ROMER (Z. physikal. Chem., 1933, **B**, 21, 292—296).—The space-group is C_{2h}^5, and the unit cell, which contains 2 mols., has I_a 8·14, I_b 5·64, I_c 14·1 A., β 105°. In the mol. the three C_6 nuclei are coplanar and lie in a straight line in the direction of the c axis. R. C.

***X*-Ray fibre diagram as a quantitative measure of change in structural units of cellulose fibre caused by chemical processes.** K. HESS and C. TROGUS (Z. physikal. Chem., 1933, **B**, **21**, 349—352; cf. A., 1932, 234).—Polemical against Schramek (this vol., 452). *X*-Ray fibre diagrams cannot be used for the above purpose. R. C.

Law of discontinuous distribution of Curie points. II. R. FORRER (J. Phys. Radium, 1933, [vii], 4, 186—209; cf. A., 1932, 449, 452; this vol., 556).—Application of the law to a large no. of ferromagnetics of known crystal lattice enables their electronic orientation lattice to be determined, and in certain cases, the direction for optimum magnetisation. Vals. of the function Θ for the limiting range of alloys as solid solutions, and the relation to efficacious contacts of the grouping of Curie points, are considered; their relation to the significance of solid solution is discussed. N. M. B.

Magnetism and crystal distortions. X-Ray investigations of α-iron. F. REGLER (Z. Physik, 1933, 82, 337—354).—Changes in the crystal lattice due to magnetisation were observed; they vary with the intensity of the magnetic field and the state of strain of the crystal. A. B. D. C.

Magnetic properties of metals at low temperatures. W. J. DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 263—270; cf. this vol., 14).—In general, the susceptibility of diamagnetic metals increases as temp. is lowered, but, excepting Cd, shows little change between 20·4° and 14·2° abs., whereas with paramagnetic metals a marked change occurs in this region. F. L. U.

Change of resistance of metals in a magnetic field at low temperatures. W. J. DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 253—262; cf. this vol., 14).—The resistance of pure metals and alloys in a magnetic field has been measured at 14—77° abs. The effect of impurities on change of resistance is greater at low temp. than at high. F. L. U.

Selective lattice distortion in wires under torsion. W. A. WOOD (Nature, 1933, 131, 842).—Lattice distortion has been detected in Cu and Ni wires under torsion, by *X*-ray diffraction. L. S. T.

Plasticity in single crystals. H. SCHLECHTWEG (Physikal. Z., 1933, 34, 404—407).—The classical method of calculating plasticity fails when considering single crystals. The phenomenon of plastic slipping in a single crystal can be explained without assuming a mosaic structure by means of a combination of the Polanyi theory and the Prandtl model of a solid body based on the kinetic theory. A. J. M.

Stretching of tin crystals. J. OBINATA and E. SCHMID (Z. Physik, 1933, 82, 224—234).—A redetermination of the translation system of white Sn confirmed earlier results (Polanyi and Schmid, A., 1925, ii, 752). No simple relation was observed between rigidity and translation, and at higher temp. behaviour of the crystal indicated no transition point. A. B. D. C.

Tensile strength of mica and the problem of technical strength. E. OROWAN (Z. Physik, 1933, 82, 235—266).—The discrepancy between the technical and theoretical tensile strengths of mica is shown to be due not to internal flaws, but to fissures on the boundaries of the crystals; eliminating these gave a tensile strength of 32,000 kg. per sq. cm. A. B. D. C.

Breakdown strength of the thinnest Ta_2O_5 and Al_2O_3 layers in relation to layer thickness. H. BETZ (Z. Physik, 1933, 82, 644—649).—An extension of Just's work (cf. this vol., 555) using Cu, Al, Zn, Mg, W, and Ta as electrodes. A. B. D. C.

Diffraction of light by ultra-sound waves. R. BAR and E. MEYER (Physikal. Z., 1933, 34, 393—396).—Demonstration experiments are described. A method for determining the wave-length of ultrasonic waves in liquids, making use of a wire grating in a way similar to an ordinary diffraction grating, is given. The results are in good agreement with those obtained by an optical method. A. J. M.

Mechanism of superconductivity. C. BENEDICKS (Ann. Physik, 1933, [v], 17, 169—184).—The "phoretic" theory of electrical conductivity in metals is developed to provide an explanation of the facts of superconductivity. Previous objections to the theory are removed. A model illustrating the mechanism of superconductivity and the effect on it of crit. current strength and a magnetic field is constructed. A. J. M.

Specific heat, m.p., and latent heat of fusion of hydrogen fluoride. J. DAHMLOS and G. JUNG (Z. physikal. Chem., 1933, B, 21, 317—322).—Sp. heats of solid and liquid HF have been measured at 98—273° abs. The latent heat of fusion of 20 g. of HF is 1094 g.-cal. R. C.

Exact measurement of specific heats at higher temperatures. XI. Variability of specific heats of fused and solidified silver. F. M. JAEGER, E. ROSENBOHM, and W. A. VEENSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 291—298; cf. this vol., 343).—Anomalies in the sp. heat of Ag have been traced to the presence of O. The measurements show that O_2 absorbed by the liquid metal is not completely given off on solidification. True vals. of C_p and C_v from 0° to 800° are given. F. L. U.

Determination of the specific heat, specific heat ratio, or the equation of state of a gas from the velocity of sound. Velocity of sound in gaseous helium at the temperature of liquid hydrogen. A. VAN ITTERBEEK and W. H. KEESOM (Comm. phys. Lab. Leiden, 1932, No. 209, 19—31; Chem. Zentr., 1933, i, 29).

Estimation of latent heats of vaporisation. J. H. ARNOLD (Ind. Eng. Chem., 1933, 25, 659—661).—A review of available calorimetric data shows that the Dieterici equation $M\lambda=P(V_2-V_1)+CRT\times\log_e(V_2/V_1)$ is trustworthy to within 5% from room temp. to the crit. point; M is the mol. wt., λ the total latent heat, and V_2 and V_1 are the molal vols. of the vapour and liquid, respectively. C is always near to 1·70 at low temp., but varies from 1·66 to 1·86 at higher temp. A. G.

Purification and physical properties of organic compounds. I. Interpretation of time-temperature curves in f.-p. determinations and as a criterion of purity. E. L. SKAU (Proc. Amer. Acad. Arts Sci., 1933, 67, 551—576).—An apparatus which permits manipulation of the sample in vac. is described. The interpretation of the curves is dis-

cussed and the relative merits of comparative and non-comparative criteria are examined. CH. ABS.

Purification and physical properties of organic compounds. II. F.p. of thermometer calibration standards for low temperatures. E. L. SKAU (J. Physical Chem., 1933, **37**, 609—614; cf. preceding abstract).—The vals. were: CCl_4 $-22{\cdot}8_5°$, PhCl $-45{\cdot}2_0°$, $CHCl_3$ $-63{\cdot}4_5°$, EtOAc $-83{\cdot}6_0°$, CS_2 $-111{\cdot}8_5°$, Et_2O (stable) $-116{\cdot}3°$, Et_2O (unstable) $-123{\cdot}3°$, methyl*cyclo*hexane $-126{\cdot}3_5°$. H. J. E.

Joule–Thomson effect and heat capacity at constant pressure for ammonia. K. C. SU and T. C. HUANG (J. Chinese Chem. Soc., 1933, **1**, 1—9).—A modification of the Scatchard equation (A., 1931, 295) is developed, expressing μC_p and C_p as functions of p and T (μ, Joule–Thomson coeff.; C_p, heat capacity at const. p). Vals. for μ and C_p calc. for NH_3 between 0 and 20 atm. and 0° and 150° agree with experimental vals. for μ above 30° and for C_p above 100°. H. J. E.

Equation of state of unimolecular films. J. GUASTALLA (Compt. rend., 1933, **196**, 1376—1378).—Superficial pressure, P, is regarded as the resultant of the kinetic pressure of the mols. of the film, RT/Nl^2 (N is Avogadro's no., and l the distance between adjacent mols.); of pressure caused by interaction of the mols. of the film due to their dipolarity, $=6{\cdot}3m^2/l^5$, where m is the electric moment; and of that due to change in capillary tension of the H_2O below the film caused by its electric field, which may be represented by $-B/l^3$. The equation of state takes the form $P=Al^{-5}-Bl^{-3}+Cl^{-2}$. C. A. S.

Influence of intensive desiccation on certain physical properties of benzene. A. W. C. MENZIES and D. A. LACOSS (Proc. Nat. Acad. Sci., 1933, **19**, 393—396).—Using an improved isoteniscope the v.p. near 80° of superdried C_6H_6 in absence of dust was markedly lower after drying at room temp., and slightly raised after drying above 80°. The max. const. rise after 20 months' drying was 2·2°. The v.p. reverted to normal on admission of air. In the sealed apparatus no reversion was shown on keeping at room temp. Samples the b.p. of which had been raised 0·4° by drying at room temp. reverted after heating at 78° out of contact with P_2O_5; a sample similarly raised 2·2° showed no reversion after heating at 150° for 9 days. N. M. B.

Vapour pressure of cæsium. J. H. DE BOER and C. J. DIPPEL (Z. physikal. Chem., 1933, **B**, **21**, 273—277).—The various published equations for the v.p. of Cs are critically reviewed. R. C.

Vapour pressure of cadmium oxide. W. B. HINCKE (J. Amer. Chem. Soc., 1933, **55**, 1751—1753).—The v.p. of CdO in the range 1140—1311° abs. is given by $\log_{10} p_{mm.}=9{\cdot}59-12{,}150/T$, from which the mol. heat of vaporisation is 55,600 g.-cal. The normal sublimation point is 1813°. J. G. A. G.

Vapour pressure of corrosive substances. K. ARII (Sci. Rep. Tohoku, 1933, **22**, 182—199).—The v.p. of $POCl_3$, $TiCl_4$, and $SOCl_2$ have been determined by means of a glass spring manometer at temp. from 20° to their respective b.p. Results show that these are normal liquids. A. J. M.

Physical constants of organic liquids at low temperatures. T. TONOMURA (Sci. Rep. Tohoku, 1933, **22**, 104—130).—The densities of $Pr^{\beta}OH$, $Bu^{\alpha}OH$, $C_3H_5{\cdot}OH$, PhMe, and COMeEt, and the viscosities of Et_2O, $COMe_2$, EtOH, $Pr^{\alpha}OH$, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, and $Bu^{\beta}OH$, were determined over the temp. range 0° to −100°. The surface tensions of Et_2O, $COMe_2$, MeOH, and PhMe, determined by the method of capillary rise at temp. between 0° and −100°, obeyed the Eotvos law satisfactorily with the exception of MeOH, for which an empirical relationship is put forward. A. J. M.

Application of the law of mathematical probability to the behaviour of gases in their pressure–volume–temperature relations. G. A. LINHART (J. Physical Chem., 1933, **37**, 645—653). H. J. E.

Viscosity of gases and other problems on the kinetic theory. N. GERASIMOV (Physikal. Z., 1933, **34**, 387—388).—Mathematical. A. J. M.

Viscosity anomalies of self-separating systems. II. Structure viscosity of mesomorphic fusions. Wo. OSTWALD and H. MALSS (Kolloid-Z., 1933, **63**, 192—203; cf. this vol., 456).—Cholesteryl acetate, propionate, and butyrate exhibit at temp. above their respective clearing points a normal viscosity coeff. independent of rate of shear. When cooled to the temp. at which the liquids become anisotropic there is a sudden rise in the val. of the coeff., and at 1—2° lower a sudden fall. The viscosity–temp. curve then resumes a normal course. At temp. between the clearing and m.p. the viscosity varies with the rate of shear. Et *p*-azoxybenzoate may become rigid in the region in which the others show variable viscosity, but its behaviour is complicated by hysteresis effects. The phenomena closely resemble those observed with binary liquid mixtures near their crit. unmixing temp. F. L. U.

Viscosity of gases at high temperatures. P. BREMOND (Compt. rend., 1933, **196**, 1472—1474).—The coeffs. of viscosity of air and CO_2 determined experimentally for temp. 0—1134° by application of Poiseuille's law agree with those deduced from Breitenbach's vals. for Sutherland's const. (cf. A., 1899, ii, 403), the average differences being 1·16 and 1·39% respectively. C. A. S.

Viscous damping of vibrating metal bars. K. SEZAWA (Nature, 1933, **131**, 803).—The coeff. of solid viscosity in c.g.s. units is $7{\cdot}5\sim8{\cdot}0\times10^6$ for duralumin, $5{\cdot}9\sim6{\cdot}8\times10^6$ for Al, $9{\cdot}3\sim11{\cdot}6\times10^6$ for Cu, and $12{\cdot}7\sim15{\cdot}0\times10^6$ for brass. The coeff. varies with amplitude of vibration. L. S. T.

Effect of water vapour on the diffusion coefficients of ions in nitrogen and oxygen. J. J. NOLAN and A. C. GALVIN (Proc. Roy. Soc., 1933, **A**, **140**, 452—456; cf. A., 1930, 658).—The vals. for the diffusion coeffs. of ions in N_2 containing various amounts of H_2O vapour do not show the type of oscillation previously found with air (*loc. cit.*). When observations are made in O_2 the oscillations reappear. The effects in air and O_2 are attributed to the formation of O_3 and oxides of N by the action of the α-particles. L. L. B.

Liquid–vapour composition curves of acetic acid and water at sub-atmospheric pressures. D. B. KEYES (Ind. Eng. Chem., 1933, **25**, 569).—For mixtures which contain > 50 mol.-% H_2O the composition of the vapour phase at reduced pressures is nearer that of the liquid phase than at atm. pressure. A. G.

Application of Henglein's equation to solutions and mixtures. V. KIREJEV (Z. Elektrochem., 1933, **39**, 268—269; cf. A., 1920, ii, 732).—The equation $\log T_1 = a \log T_2 + b$ is shown to apply to the b.p. of solutions and mixtures. The b.p. of H_2O–$COMe_2$ mixtures are recorded. H. J. E.

Specific heats of aqueous solutions of potassium *n*-octoate at 15°. D. G. DAVIES (J.C.S., 1933, 551—552; cf. A., 1932, 1091).—Sp. heats have been measured at 13·5—16·5° at concns. up to 20%. There is a break in the sp. heat–concn. graph between 6 and 8%, which is the crit. concn. for micelle formation according to *d*, f.p., and dew-point data. H. J. E.

Influence of small amounts of acids on the refractive index of liquid mixtures. T. TOMONARI (Angew. Chem., 1933, **46**, 269—271).—The *n* of MeOH–$COMe_2$ and MeOH–*cyclo*hexanone mixtures increases with the addition of small amounts of HNO_3, HCl, H_2SO_4, or AcOH. The increase is linear up to about 0·3% HNO_3, after which little further change occurs. The position of the break in the curve is independent of the composition of the mixture, except with AcOH, in which it is not so well defined. No break is observed when these acids are replaced by NaCl, Na_2SO_4, $NaNO_3$, KNO_3, or $Ca(NO_3)_2$, but the behaviour of $AgNO_3$, when kept for some days under the influence of light, is similar to that of HNO_3. A similar effect is obtained with a by-product of the nitration of cellulose. E. S. H.

Validity of Raoult's law in molten solutions of lead chloride and lead bromide. J. SHRAWDER, jun. (J. Amer. Chem. Soc., 1933, **55**, 1975—1976; cf. A., 1931, 309).—Polemical against Jellinek and Golubovski (A., 1930, 849). J. G. A. G.

Determination of the vapour pressures of amalgams by a dynamic method. J. S. PEDDER and S. BARRATT (J.C.S., 1933, 537—546; cf. A., 1930, 4).—The partial pressure of Hg over Cd amalgams (16·88—84·93 mol.-% Hg) at 283·5°, over Zn amalgams (43·5—83·7 mol.-% Hg) at 284°, over K amalgams (4·3—42·8 mol.-% K) at 300°, and that of K and Hg over K amalgams (41·1—72 mol.-% K) at 387·5° were measured by a flow method. From the abnormal slope of the K partial pressure–composition graph at 387·5°, the formation of a compound, probably KHg, in the vapour phase is inferred. H. J. E.

Diffusion in crystals. G. VON HEVESY (Naturwiss., 1933, **21**, 357—362).—A summary. A. J. M.

Self-diffusion in solid lead. W. SEITH and A. KEIL (Z. Metallk., 1933, **25**, 104—106).—By two different methods using Th-*B* as radioactive indicator the rate of self-diffusion in Pb at 106° and 324° has been calc. to be $1{\cdot}45 \times 10^{-11}$ and $4{\cdot}58 \times 10^{-5}$ sq. cm. per day. The temp. coeff. is given by $D = 5{\cdot}76 \times 10^5 . e^{-14{,}025/T}$; from this it follows that the heat of loosening of the Pb lattice is 27,870 g.-cal. The self-diffusion appears to be independent of the crystal structure of the specimen. A. R. P.

Grain boundary effects as a factor in heterogeneous equilibrium of alloy systems. A. PHILLIPS and R. M. BRICK (J. Franklin Inst., 1933, **215**, 557—577).—*X*-Ray observations on Cu–Al alloys show that for fine- and coarse-grained wires and powder the lattice const. of a single crystal is larger than that of a polycryst. aggregate. The time for complete pptn. in the single crystal is much longer than in polycryst. alloys of the same composition (cf. Wiest, A., 1932, 330). N. M. B.

Relation between mean atomic volume and composition in silver–zinc alloys. E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1933, **A**, **140**, 344—358).—Ag–Zn alloys in the α-phase region were prepared by the process of interdiffusion, and the mean at. vols. of the different phases at 380° studied by means of the *X*-ray precision camera. As in the Cu–Zn system, the mean at. vol. at a const. temp. changes almost linearly with composition, decreasing with increasing Zn content in the α-, γ-, and δ-regions. That of both phases in the mixed regions, however, remains const. The results form the basis of the determination of the positions of phase boundaries. L. L. B.

Thermoelectric properties of platinum–rhodium alloys. F. R. CALDWELL (Bur. Stand. J. Res., 1933, **10**, 373—380).—The thermal e.m.f. and thermoelectric powers of Rh and Pt–Rh alloys against pure Pt have been determined between 0° and 1200°. The results are compared with published data. J. W. S.

Röntgen analysis of the systems iron–boron, cobalt–boron, and nickel–boron. T. BJURSTRÖM (Arkiv Kemi, Min., Geol., 1933, **11 A**, No. 5, 1—12).—*X*-Ray analysis of the systems containing 0—20% B indicates the existence of Fe_2B, FeB, Co_2B, CoB, and Ni_2B. Fe_2B, Co_2B, and Ni_2B form space-centred tetragonal crystals with space-group D_{4h}^{19} and 4 mols. in the unit cell; *a* and *c* (in Å.) are: 5·099, 4·240 for Fe_2B; 5·006, 4·212 for Co_2B; 4·980, 4·236 for Ni_2B. FeB and CoB are rhombic, with space-group V_h^{16} and 4 mols. per unit cell; *a*, *b*, and *c* are 4·053, 5·495, and 2·946 Å. for FeB, and 3·948, 5·243, and 3·037 Å. for CoB. Detailed structures are deduced. D. R. D.

Influence of nickel and silicon on the miscibility gap of the system Fe–Cu in the solid state (20°). F. ROLL (Z. anorg. Chem., 1933, **212**, 61—64).—The solubility of Cu in Fe is increased more by Ni than by Si. The alloys contained 0·8—2% of C. Sections of the ternary diagrams are given. H. J. E.

Influence of a third metal on the constitution of brasses. V. Manganese. O. BAUER and M. HANSEN (Z. Metallk., 1933, **25**, 17—22).—The system Mn–Zn–Cu in the range 70—50% Cu and 0—6% Mn has been investigated by thermal methods and micrographic examination. The solidus is similar to that of binary Zn–Cu alloys. The peritectic reaction $\alpha + \text{liq.} \rightleftharpoons \beta$, which occurs at 905° in the

Zn–Cu system, takes place at slightly lower temp. on addition of Mn, the max. lowering being 45° with 5·5—7% Mn according to the Cu content. Mn displaces the (α+β)-boundary further from the Cu side, and in alloys containing β causes the separation of a Mn-rich phase below 375° when the Mn is > 4—4·7%, since Mn is much less sol. in β-brass than in α and its solubility in β decreases rapidly with fall in temp. A. R. P.

Fluidity of ternary alloys. A. PORTEVIN and P. BASTIEN (Compt. rend., 1933, **196**, 1396—1398; cf. B., 1933, 24).—For a difference of 100° between the temp. of pouring and that of the commencement of primary crystallisation, the flowability of Sn–Bi, Bi–Pb, and Pb–Sn alloys follows the laws previously enunciated. The data for the ternary alloys Sn–Bi–Pb show that the flowability is a max. for the ternary eutectic. The limits of solid solution have been revised (cf. A., 1903, ii, 77). C. A. S.

Ternary system aluminium–antimony–magnesium. W. GUERTLER and A. BERGMANN (Z. Metallk., 1933, **25**, 81—84, 111—116).—In the binary Al–Sb system the solidus rises slowly to a max. at 82% Sb corresponding with the formation of AlSb, which, however, appears to dissociate at the m.p., since free Al occurs as minute particles in air-cooled alloys containing > 82% Sb. AlSb is rapidly decomposed by moisture, becoming first brown and then falling to a grey powder; it forms an ill-defined eutectic with Al at 657° and < 2% Sb and a well-defined eutectic with Sb at 623° and < 1% Al. In the ternary system Al–Mg–Sb no ternary compound is formed and the following quasi-binary systems exist: (*A*) Al_3Mg_4–Mg_3Sb_2, (*B*) Al_3Mg_2–Mg_3Sb_2, (*C*) Mg_3Sb_2–AlSb, (*D*) Al–Mg_3Sb_2. In *D* there is a miscibility gap extending from 9 to 98% Mg_3Sb_2 and in the ternary system this extends to 41% Mg in the Mg corner and to 73% Sb in the Sb corner. Binary eutectics occur in all the quasi-binary systems and ternary eutectics in the quasi-ternary systems: Al_3Mg_4–Mg_3Sb_2–Mg, Al_3Mg_4–Al_3Mg_2–Mg_3Sb_2, Al–AlSb–Mg_3Sb_2, and AlSb–Sb–Mg_3Sb_2, but not in Al_3Mg_2–Al–Mg_3Sb_2. A. R. P.

Ternary system cobalt–chromium–tungsten. W. KOSTER (Z. Metallk., 1933, **25**, 22—27).—The system contains a ternary eutectic between the α, γ, and δ phases at 1380° (Cr, 25, W 25·5, Co 49·5%); in the eutectic the α phase is a solid solution containing Cr 32, W 33, Co 35%, and the γ phase a solid solution containing Cr 24, W 18, Co 58%. The temp. at which α separates in the Co–Cr system is raised by addition of W from 1271° to 1330°. At 1330° the ternary peritectic reaction α+γ+δ=η occurs, the η phase containing Cr 27, W 36, Co 37%. The reactions in the solid state are very complex; equilibrium diagrams for const. W contents of 0, 5, 15, 20, 30, and 40% W and a space model of the ternary system are shown. Alloys in the γ+δ field can be age-hardened by quenching from 1300° and ageing at 800—900°; a max. Brinell hardness of 600 is obtained in this way with alloys containing 5% W and 45% Cr or 30% W and 10% Cr. A. R. P.

Equilibrium in liquid systems of three components. W. T. REDBURN and W. N. SHEARER (J. Amer. Chem. Soc., 1933, **55**, 1774—1779).—Miscibility data, chiefly at 25°, are recorded for the ternary systems H_2O–halogen acid–org. liquid. The mutual solubility of H_2O with *iso*amyl alcohol, $Bu^{\beta}OH$, and *cyclo*hexanone is increased by HCl < HBr < HI and the results agree qualitatively with Harkins' theory of miscibility. J. G. A. G.

Rate of dissolution of oxygen in alcoholic solutions of anhydrous stannous chloride. S. MIYAMOTO and E. UTUNOMIYA (J. Sci. Hiroshima Univ., 1933, **3**, 193—208; cf. this vol., 233).—The rate of absorption is better explained on the author's theory than on the diffusion layer theory. At low concns. the rate of dissolution is independent of the $SnCl_2$ concn. At high concns., the rate of absorption decreases with increase of the concn. J. S. A.

Solubility of barium nitrate in water. J. N. FRIEND and W. N. WHEAT (J.C.S., 1933, 501—502).—Data are recorded between 0° and 95°. No evidence for a dihydrate has been obtained (cf. Hirzel, Z. Pharm., 1854, 49). H. J. E.

Effect of glycine and alanine on the insoluble salts of silver and lead. H. M. MAPARA and A. M. PATEL (Kolloid-Z., 1933, **63**, 291—295).—In the pptn. of the chlorides, bromides, iodides, and chromates of Ag and Pb by addition of a sol. K salt, the amount of glycine or alanine required to prevent pptn. increases with the concn. of the Ag or Pb salt solution, when the amount of the pptg. solution is const. Alanine is the more effective inhibitor. The amount of non-electrolyte required is independent of the vol. of the system. The non-electrolyte does not exert a peptising influence and forms no simple compound with any of the cations present, but a complex compound is probably formed. E. S. H.

Medium effect of various solvents on silver bromate at 25°. B. B. OWEN (J. Amer. Chem. Soc., 1933, **55**, 1922—1928).—The solubility of $AgBrO_3$ in binary mixtures of H_2O with MeOH, EtOH, $Pr^{\alpha}OH$, $COMe_2$, glycol, glycerol, mannitol, and glycine is a linear function of the dielectric const., with a characteristic slope for each alcohol (cf. this vol., 19). The medium effects are characteristic of the non-electrolyte as well as of the dielectric const. and thus Born's simple theory is inadequate. J. G. A. G.

Solvation of molecules of glucose penta-acetate and cellobiose octa-acetate in organic liquids. I. SAKURADA and M. TANIGUCHI (Kolloid-Z., 1933, **63**, 169—175; cf. B., 1929, 713).—The solubility of the acetates in a series of liquids has been determined, and is seen in most cases to increase with the val. of μ/V or μ^2/ε (μ=dipole moment, ε=dielectric const.). H_2O and alcohols are exceptions. The viscosity of the solutions at concns. ⩾ 2% follows Einstein's law. Solvation, calc. from viscosity data, varies from 0 to 0·3 c.c. of solvent per c.c. of acetate. No solvation is observed in non-polar solvents. F. L. U.

Kinetic proof of the law of Berthelot and Jungfleisch concerning the partition of a substance between two immiscible solvents. A. SCONZO (Gazzetta, 1933, **63**, 186—189).—The simple partition law is derived from the kinetic theory. O. J. W.

A phenomenon of surface chemistry. R. DUBRISAY and (MLLE.) P. DROUOT (Compt. rend., 1933, **196**, 1392—1394; cf. A., 1932, 460).—When solutions containing NaOH, KOH, or $N(C_2H_4{\cdot}OH)_3$ and lauric acid are shaken, the ratio of base to acid in the foam is reduced in comparison with the ratio in the solutions. If a mixture of the acid with two bases is similarly treated, the stronger base accumulates in the foam. C. A. S.

Determination of dynamic activity of adsorbents. S. URAZOVSKI and N. SENJUTA (Ukrain. Chem. J., 1932, **7**, [Sci.], 228—240).—When air containing C_6H_6 or Cl_2 is passed through a tube filled with adsorbent, the time necessary for attainment of const. wt. is proportional to the dynamic activity of the adsorbent and to the length of the tube. R. T.

Significance of Freundlich's adsorption isotherm. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1933, **8**, 120—125).—Theoretical. The isotherm is derived from Gibbs' equation and a two-dimensional equation of state, and the physical meaning of the const. is discussed. F. L. U.

Adsorption of cæsium on calcium fluoride films. J. H. DE BOER and C. J. DIPPEL [with J. A. OTTEN] (Z. physikal. Chem., 1933, B, **21**, 278—291).—The isotherms for the adsorption of Cs vapour on vac.-sublimed CaF_2 at 20° consist of two parts intersecting at an angle. It appears that the formation of a monat. film, in which the most active points of the surface are occupied first, is accompanied by the formation of a polyat. film, varying in thickness from point to point. Ultimately the interlamellar spaces in the CaF_2 fill up, and the second part of the adsorption isotherm corresponds with adsorption on the remaining surface. Reaction between Cs and glass, with formation of H_2 and Cs_2O, is perceptible at 100° and rapid above 200° R. C.

Factors affecting the ratio of adsorption of radium-*B* and -*C* on metal. J. A. CRANSTON and C. BENSON (J. Roy. Tech. Coll., 1933, **3**, 52—56).—The ratio of Ra-*C* to Ra-*B* adsorbed on Ni from a solution containing these elements increases progressively with decreasing p_H and is little affected by the electrode potential between the Ni and the solution. The potential of Ni in 0·001*N*-HCl falls with the time of contact, rapidly at first and then more slowly, reaching an approx. const. val. after 1 hr. A. R. P.

Adsorption in solutions and physical properties of the solvent. II. Complete adsorption isotherms of binary liquid mixtures. E. HEYMANN and E. BOYE (Kolloid-Z., 1933, **63**, 154—165; cf. A., 1930, 408, 1364; 1932, 689).—Changes in the composition of pairs of miscible liquids caused by adsorption on C have been measured interferometrically. When the apparent adsorption of one component is plotted against the mole fraction, a curve passing through a max. and then descending asymptotically to the composition axis is obtained for mixtures in which one component is much more adsorbable than the other, and in which the heats of wetting of the components differ markedly. When these properties are nearly the same for the two components, a curve is obtained which passes through a max., cuts the composition axis, and then passes through a min. In mixtures of CCl_4 with $C_nH_{2n+1}{\cdot}OH$ Traube's rule is reversed. F. L. U.

Interface equilibria and inner equilibria in heterogeneous systems. I. Exchange and charging processes on surfaces of heteropolar crystals. II. Theory of fractional crystallisation. L. IMRE (Z. physikal. Chem., 1933, **164**, 343—363, 364—376).—I. Measurements of the adsorption of Th-*B* ($Pb^{\cdot\cdot}$) on $PbSO_4$ and PbI_2 at various temp. have been used to calculate the heat of adsorption, Q; on $PbSO_4$ this is approx. half and on PbI_2 one third of the negative heat of dissolution, S. Theory indicates that for the adsorption of the ions of a heteropolar salt with n ions $Q=S/n$. Extension of this interpretation of Q to cases where larger amounts of ions are adsorbed, and the surface consequently acquires a charge, permits the calculation of the consts. of the adsorption isotherm in simple systems; the results for AgI–$Ag^{\cdot}$ and AgI–I' agree with experiment. In these systems the incorporation of the adsorbed ion into the inner layers of the adsorbent may be characterised by the same heat effect as the surface adsorption.

II. The separation of an ion present in small amount with a heteropolar salt with which it forms mixed crystals has been investigated under conditions favourable to rapid crystallisation. If the adsorbabilities of the constituents of the mixed crystal are regarded as characterised by their heats of adsorption, the experimental data for partition coeffs. for fractional crystallisation in the systems $Ra^{\cdot\cdot}$–$BaSO_4$ and $Pb^{\cdot\cdot}$–$BaSO_4$ are accounted for. If the lattice structures of the salts composing the mixed crystals are very similar, the energy effects for the addition of the various components to the mixed crystals seem to be the same as for addition to the lattices of the pure components. R. C.

Exchange adsorption and its influence on the solubility of precipitates with ionic lattices in electrolyte solutions. I. M. KOLTHOFF and E. B. SANDELL (J. Amer. Chem. Soc., 1933, **55**, 2170—2171; cf. this vol., 346).—Pptd. CaC_2O_4,H_2O adsorbs the anions from aq. solutions of alkali iodates, sulphates, and NaOH, and the cations from solutions of $BaCl_2$ and $MnCl_2$. The solubility of the oxalate in the electrolyte solutions is a function of the total surface exposed by the solid. J. G. A. G.

Adsorption and solution volume. II. Dependence of ionic exchange on dilution. E. IVANOVA and A. RABINERSON (Kolloid-Z., 1933, **63**, 165—169; cf. A., 1929, 999).—Using 10 g. of chernozem soil and solutions containing respectively 100 milliequiv. of NaCl and 10 and 1 of Na_2CO_3, the exchange adsorption ($Na^{\cdot}$ in, $Ca^{\cdot\cdot}$ out) varies with the dilution (v) according to $X=Kv^{-1/n}$. A dilution effect is absent in the system 1·17 g. Na-kaolin + 2 milliequiv. $BaCl_2$. In general, factors which increase adsorption diminish the dilution effect. F. L. U.

Surface tension of oils. E. CANALS and RAMAHENINA-RANAIVO (J. Pharm. Chim., 1933, [viii], **17**, 505—508).—The surface tensions of sweet almond

oil, olive oil, and cod-liver oil vary linearly with temp., and at the same rate. J. S. A.

Measurements of the surface tension of solutions of the sodium and potassium salts of higher fatty acids by the ring method. I. A. LOTTERMOSER and E. SCHLADITZ (Kolloid-Z., 1933, **63**, 295—304).—The surface tension–concn. curves for several Na soaps have been determined at temp. between 5° and 90°. The results at temp. below the m.p. of the corresponding fatty acid are not readily reproducible. Comparison of data obtained at the m.p. of the respective fatty acids shows that the surface tension is at a min. when the concn. is about 10^{-3} to 10^{-4} g. per c.c., but the breadth of the min. increases throughout the series palmitate—laurate. As the no. of C atoms increases the min. is reached at a lower concn. of soap. With solutions of K soaps, the results are reproducible at temp. 10—20° < the m.p. of the corresponding fatty acids. E. S. H.

Spreading of water on asphalt bitumen and tar. F. J. NELLENSTEYN and N. M. ROODENBURG (Kolloid-Z., 1933, **63**, 339—347).—Measurements of surface tension in the system bitumen–H_2O at different temp. confirm the validity of Antonow's rule. From these data the contact angle of H_2O against different bitumens is calc. for temp. between 0° and 100°. E. S. H.

Wetting of hydrophilic and hydrophobic powders in a system of two non-miscible liquids. II. Adsorption and wetting phenomena with lead glance and zinc blende powders. E. BERL, B. SCHMITT, and H. SCHULZ (Kolloid-Z., 1933, **63**, 327—338; cf. A., 1932, 1200).—Powdered PbS and ZnS become converted partly into sulphates when kept in the air. Cations are adsorbed at the sulphidic portions of the particle, and anions at the parts covered by SO_4''. Thus, the S : SO_4 ratio determines the adsorption of flotation agents and the wetting by C_6H_6. Adsorption of anions leads to the formation of readily sol. adsorption compounds and improvement of the conditions for adsorption of the flotation agent. The conditions are also improved by adsorption of the CO_3'' of ordinary H_2O and the sol. components of ZnS powder at the parts covered by SO_4''. NaCN, Na_2S, and Na_2CO_3 reduce the wettability of partly oxidised ZnS and improve that of PbS. E. S. H.

Theory of unimolecular adsorbed film. N. FUCHS (Z. physikal. Chem., 1933, **B**, **21**, 235—241).—From Langmuir's adsorption theory and consideration of the intermol. forces in a unimol. adsorbed film, Langmuir's isotherm has been statistically deduced for linear adsorption. The theory excludes the possibility of a two-dimensional condensation in the adsorbed film. R. C.

Structure of unimolecular films. II. Surface films of proteins. R. J. FOSBINDER and (MISS) A. E. LESSIG (J. Franklin Inst., 1933, **215**, 579—591).—For isodisperse proteins having a particle mass > 34,500, spontaneous spreading to form a homogeneous film does not occur if the [H·] of the substrate is within the [H·] stability range of the protein. The tryptic digestion of casein and albumin films has been investigated. The α-keratin type of structure is the probable form of the protein micelles in a close-packed film. N. M. B.

Interaction between soot films and oil. J. H. COSTE (Nature, 1933, **131**, 691).—The patterns formed when certain oils or substances such as $CHCl_3$, $PhNO_2$, NH_2Ph, etc. are allowed to fall on a smoked glass surface are described. L. S. T.

Sintering phenomena in vacuum-sublimed films of salts. J. H. DE BOER and C. J. DIPPEL (Z. physikal. Chem., 1933, **B**, **21**, 198—207).—On heating vac.-sublimed films of CaF_2, BaF_2, and $BaCl_2$ the lamellar structure sinters together and the total surface area decreases (cf. A., 1931, 1226). The I adsorption isotherms show that the active centres suffer most in this change, which is most marked with $BaCl_2$ and least with CaF_2. The sintering increases with rise in temp., but at a given temp. soon ceases. If adsorbed I is already present, it is included. At higher temp. recrystallisation may occur, probably under the influence of H_2O released from the glass; with sol. films moist air at room temp. causes recrystallisation. R. C.

Two-dimensional reactions. I. S. E. BRESLER, W. W. DRUSCHININ, and D. L. TALMUD (Z. physikal. Chem., 1933, **164**, 389—392).—A preliminary qual. investigation of the formation of the ester from cetyl alcohol and myristic acid and of the acetal from cetyl alcohol and palmitaldehyde in the unimol. film at an air–H_2O interface at room temp. is described. The reactions are followed by change in the two-dimensional surface pressure. R. C.

Determination of distribution of pores according to their size in filters and ultra-filters. F. ERBE (Kolloid-Z., 1933, **63**, 277—285).—A discussion of the calculation of results obtained by the existing methods. E. S. H.

Capillary systems. XIV (2). Dynamics of plasmolysis. I. Mathematical treatment of semipermeable protoplasts. E. MANEGOLD and C. STUBER (Kolloid-Z., 1933, **63**, 316—323). E. S. H.

Capillary systems. XII (2). Calculation of material content of homogeneous filter structures. I. Sphere planes and sphere layers as structural elements of homogeneous sphere lattices. W. NOWACKI (Kolloid-Z., 1933, **63**, 352—353). E. MANEGOLD and W. VON ENGELHARDT (*ibid.*, 353—354).—A criticism on crystallographic grounds (cf. this vol., 458) and a reply. E. S. H.

Capillary systems. XII (4). Calculation of material content of heterogeneous structures. I. Material content of regular binary sphere-aggregates of type AB. E. MANEGOLD and W. VON ENGELHARDT (Kolloid-Z., 1933, **63**, 149—154; cf. A., 1931, 1123). F. L. U.

Pore statistics and sieve action in ultra-filters and animal membranes. M. PISA (Kolloid-Z., 1933, **63**, 139—148).—The distribution of pore size in natural and artificial membranes has been studied by measuring the rate of flow of liquids at a series of

pressures, in conjunction with determinations of the size of pore groups by the max. bubble pressure method. In "cellafilters" the sieve action cannot be deduced merely from the flow characteristics of the membrane, since the size distribution varies from place to place. The permeability of collodion filters for hæmoglobin increases with the age of the solution used in their prep. Pores of 58 diam., and probably those of 40 mμ, are completely permeable to hæmoglobin. The pore characteristics of amnion and chorion membranes from sheep are little changed by ageing, although in the former they may vary considerably in different pieces of the same membrane. F. L. U.

Permeability. Passage of substances through lipin membranes. J. SIVADJIAN (J. Pharm. Chim., 1933, [viii], 17, 457—461).—Aq. acetates of Zn (I), Pb, Mn, and U (II), at concns. corresponding with max. stability (A., 1887, 767), have been dialysed in collodion–castor oil sacs against H_2O. Whilst control solutions remain perfectly clear, ppts. form in the sac [greatest with (II), least with (I)] and AcOH is present in the external fluid. In addition to hydrolysis, double decomp. of mixtures such as $ZnCl_2$+NaOAc or the hydrochloride of a local anæsthetic+NaOAc is also accelerated by the membrane. NH_3 diffuses from a saturated solution of AgCl in aq. NH_3 and AgCl separates as crystals > 2 mm. in length. F. O. H.

Multiphase equilibria in systems subdivided by membranes. R. EISENSCHITZ (Z. physikal. Chem., 1933, 164, 393).—The theoretical methods used in a previous paper (*ibid.*, 1932, 162, 216) are compared with those of other authors. R. C.

Osmotic systems in which non-diffusing substances may occur. IV. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 285—291; cf. this vol., 122).—Mathematical. F. L. U.

Relative impermeability of plastic sediments for rain-water, spring water, and alkaline solutions. P. URBAIN (Compt. rend., 1933, 196, 1036—1038).—The observed rates of filtration of (1) rain-water, p_H 5·5; (2) spring water, p_H 7·2, containing 2·1 g. solids (mainly $CaSO_4$) per litre; (3) aq. NaOH, p_H 7·2; and (4) aq. NaOH, p_H 9·3, through a layer of marl are in the ratio 1 : 28 : 1·6 : 330. The slowness with (1) and (3) is due to adsorption of H_2O by, and consequent swelling of, the particles of halloysite, which is counteracted more or less by the ions in (2) and (4). C. A. S.

Cryoscopic determination of hydration of ions of sodium chloride. F. BOURION and (MLLE.) O. HUN (Compt. rend., 1933, 196, 1489—1491; cf. this vol., 566).—The hydration of the ions in *M*- and 0·5*M*-NaCl is represented by $NaCl,13{\cdot}2H_2O$ and $NaCl,15{\cdot}6H_2O$, respectively. C. A. S.

Distribution of particle diameters in disperse liquid phases. C. ROSSI (Gazzetta, 1933, 63, 190—199).—The dispersion of one liquid phase in another is discussed, and is shown to be influenced to a greater extent by the mechanical dispersion process employed than by the physico-chemical factors which characterise the emulsion already formed. Assuming that the interfacial tension affects the dispersion process and not the stability of the emulsion, then the distribution of the size of the particles should not be uniform, but should follow some statistical law. Using the Boltzmann expression, a formula for the distribution of particle size is derived, which is used to define the degree of dispersion. O. J. W.

Indefinite concepts in colloid science. V. COFMAN (Protoplasma, 1933, 18, 141—152).—Reports of a series of lectures. A. G. P.

Preparation of colloidal solutions of the alkali metals. M. I. GEN, I. L. ZELMANOV, and A. I. SCHALNIKOV (Kolloid-Z., 1933, 63, 263—268).—When the vapours of Na and an org. liquid impinge together on a surface cooled by liquid air a Na organosol is formed. A technical process is also described, in which the vapour of the metal condenses directly in the liquid dispersion medium. By this means sols of Na in xylene and butadiene can be prepared; these may reach a concn. of 0·3% and are stable for several weeks. E. S. H.

Colloidal silicic acid. II. W. D. TREADWELL and W. KÖNIG (Helv. Chim. Acta, 1933, 16, 468—478; cf. this vol., 348).—In the prep. of colloidal silicic acid by electrolysis of Na silicate with a Hg cathode, the p_H falls continuously, with a step at 11·3 corresponding with the formation of $Na_2Si_2O_5$, and finally reaching 3·2 in 0·5*M* solution. At this stage the product contains no detectable Cl or Na. The time of gelatinisation of a 0·5*M* solution is a min. (1 hr.) at p_H 5·8. The acidity of all solutions decreases with time, the total decrease (after 260 days) being proportional to the initial acidity. Pptn. of albumin is a min. with solutions containing mainly $Na_2Si_2O_5$, and increases rapidly with decreasing p_H. A curve showing the potentiometric titration of completely desalted silicic acid with NaOH is given. F. L. U.

Relations between the different viscosity formulæ for lyophilic colloids. I. SAKURADA (Kolloid-Z., 1933, 63, 311—315).—Mathematical. E. S. H.

Highly-polymerised compounds. LXXXII. Viscosities of solutions of derivatives of higher paraffins with branched chains. H. STAUDINGER and R. C. BAUER (Helv. Chim. Acta, 1933, 16, 418—426; cf. this vol., 370).—Measurements have been made with C_6H_6 and CCl_4 solutions of alcohols, acids, esters, and ketones derived from *iso*paraffins. The sp. viscosity of a 1·4% solution is in all cases proportional to the no. of C atoms in the chain, counting O atoms as C if in the main chain, and is not affected by the presence of a double linking. Temp. coeffs. are also given. F. L. U.

Viscosimetric behaviour of heavy-metal ferrocyanides precipitated in dilute solution. W. D. TREADWELL, W. KÖNIG, and B. ADAM (Helv. Chim. Acta, 1933, 16, 375—382).—Viscosities of 0·01*M* solutions of various heavy-metal salts, when increasing quantities of 0·01*M*-alkali ferrocyanide are added, exhibit max. corresponding approx. with stoicheiometric proportions of the reacting ions. A time effect may be present owing to the permutite-like character of the ppts. The results are interpreted

on the assumption of growing chains of primary particles giving rise to a network in which liquid is enmeshed. F. L. U.

Viscosity anomalies of self-separating systems. III. Structure viscosity and flow elasticity of sulphur melts and other disperse systems. Wo. Ostwald and H. Malss (Kolloid-Z., 1933, **63**, 305—310; cf. this vol., 668).—Molten S at 120—150° (below the viscosity max.) exhibits structure viscosity and elastic properties. These effects continue to increase up to 160°, although the abs. viscosity decreases at that temp. Structure viscosity has also been observed in foams of K stearate. These results confirm the colloid nature of such systems. E. S. H.

Effect of slipping on the viscosity of suspensions. R. Eisenschitz (Physikal. Z., 1933, **34**, 411—415).—The supposition that a viscous liquid is completely arrested when it comes into contact with a small particle in the liquid is probably not true. If there is complete slip at the liquid–particle interface, the viscosity will be independent of the thickness of the particle, assumed, for purposes of calculation, to be rod-like. A. J. M.

Surface tension of colloidal solutions, and the action of light on soap solutions. P. L. du Nouy (Nature, 1933, **131**, 689; cf. A., 1932, 333).—The fall in surface tension of colloidal solutions is due to adsorption; in the case of soaps light increases the magnitude of the effect. L. S. T.

Coagulation of colloids from the viewpoint of Smoluchowski's theory. IV. Variation of surface tension during coagulation of manganese dioxide sol. S. S. Joshi and A. N. Lal (J. Indian Chem. Soc., 1933, **10**, 61—70).—Coagulation of MnO_2 sol (A., 1921, ii, 642) by KCl and $BaCl_2$ results in a continuous diminution of γ (except when Na oleate is added). Sucrose has no appreciable effect on the progress of coagulation. The reasons for the discrepancies between calc. vals. and the results of Mukherjee and Mazumdar (A., 1924, ii, 395) are discussed. J. L. D.

Range of orienting forces and the stability of foams and emulsions. S. E. Bresler and D. T. Talmud (Kolloid-Z., 1933, **63**, 323—327).—The orientation by surface forces of the quasi-cryst. complexes in liquids, leading to the formation of a quasi-monocryst. film, is considered as a factor determining the stability of foams and emulsions. Data for the stability (as a function of time) of (*a*) H_2O in C_6H_6, (*b*) C_6H_6 in H_2O emulsions in presence of electrolytes and non-electrolytes are given. E. S. H.

Radial precipitation of strontium carbonate. (Mlle.) S. Veil (Compt. rend., 1933, **196**, 1491—1492; cf. A., 1931, 301).—The Liesegang rings formed by a drop of aq. $SrCl_2$ on gelatin impregnated with K_2CO_3 are described. They are made up of a series of separate spots, the inner ones connected by radial lines. C. A. S.

Viscosimetric effect in the pasting of starches. I. W. Seck, F. Dittmar, and H. Blume (Kolloid-Z., 1933, **63**, 347—352).—Sufficiently conc. pastes undergo a decrease in viscosity on heating. The effect is more pronounced in potato- than in maize-starch, and is accelerated by stirring. The crit. concn., above which the effect is observed, depends on the kind of starch and on its grain size. The change is not due to mechanical rupture, but to partial conversion into a sol. E. S. H.

Relation of concentration to action of gelatinising agents on starch. C. E. Mangels and C. H. Bailey (J. Amer. Chem. Soc., 1933, **55**, 1981—1988).—The effect of aq. solutions of various reagents has been studied by changes in the viscosity at 30° (cf. Ostwald and Frenkel, A., 1928, 122). In general, increased concn. causes an increase in their swelling power. The lyotropic effect of Na salts leads to the series $Cl<Br<I<CNS<$salicylate$<OH$; Cl' has no measurable effect at any concn. NaOH is more effective than KOH at concns. $<0{\cdot}3M$; there is little difference at $0{\cdot}3$—$0{\cdot}5M$, whilst at $0{\cdot}75M$, KOH is the more effective. For the thiocyanates: $NH_4<Na<K$ at $1{\cdot}4$—$2M$, $NH_4<K<Na$ at $2{\cdot}2$—$4M$, and $K<NH_4<Na$ at higher concns. Iodides show $Na<K$ at concns. up to $2{\cdot}4M$ and $K<Na$ above this. Microscopical examination indicates that increase in viscosity at the lower concns. is due to the friction between swollen granules; with increased concn., the granules burst and the amylopectin is dispersed (forming a true colloidal system). H. B.

Diffusion coefficient of crystalline trypsin. H. W. Scherp (J. Gen. Physiol., 1933, **16**, 795—800).—The diffusion coeff. in half-saturated $MgSO_4$ at 5° is $0{\cdot}020\pm0{\cdot}001$ sq. cm. per day, corresponding with a mol. radius of $2{\cdot}6\times10^{-7}$ cm. The rate of diffusion of the proteolytic activity is the same as that of the protein-N. H. G. R.

Dielectric constants of aqueous solutions of amino-acids and polypeptides. M. Frankenthal (Z. physikal. Chem., 1933, **B**, **21**, 310—316).—The results previously reported (this vol., 125) are corr. and compared with those of Devoto (this vol., 447). R. C.

Isoelectric point of proteins. I. K. O. Pedersen (Kolloid-Z., 1933, **63**, 268—277).—Electrophoretic measurements with the respiratory proteins of the blood of lower animals show that, contrary to the conclusions of Svedberg and Eriksson (this vol., 171), these substances have different properties. The isoelectric points of 12 proteins are given. The solubility is a min. at the isoelectric point. E. S. H.

Formation of spiral rings in drying gels. S. Ghosh and S. Prakash (Kolloid-Z., 1933, **63**, 315).—Spiral structures have been observed at the surface of drying gels of Fe^{III} phosphate and arsenate. E. S. H.

Effect of pressure on equilibrium in the system $C_2H_4+H_2O\rightleftharpoons EtOH$. A. H. Loveless and W. Wright (J. Roy. Tech. Coll., 1933, **3**, 65—75).—High-pressure apparatus for studying the reaction between C_2H_4 and H_2O at high temp. in the presence of a catalyst is described in detail. With an active C catalyst an exothermic reaction occurs at 60 atm. and 200° with the formation of $COMe_2$, HCO_2H, and EtOH; with Al_2O_3 catalyst MeCHO,

EtOH, and AcOH are formed. The thermodynamics of the action are discussed. A. R. P.

Theory of the calculation of dissociation constants from the electrometric titration of acids. E. SODERBACK (Arkiv Kemi, Min., Geol., 1933, **11 A**, No. 8, 1—48).—The formulæ applicable to an n-basic acid are deduced on the lines suggested by Auerbach and Smolczyk (A., 1925, ii, 118), avoiding the approximations made by these authors. D. R. D.

Second dissociation constant of phosphoric acid from 20° to 50°. L. F. NIMS (J. Amer. Chem. Soc., 1933, **55**, 1946—1951).—From e.m.f. measurements of cells of the type

$H_2|NaH_2PO_4(m_1),Na_2HPO_4(m_2),NaCl(m_3)|AgCl|Ag$

K_2 is found to have a max. at 43°. J. G. A. G.

Amino-nitrogen of proteins. I. Dissociation constants of asparagine. M. GIORDANI (Annali Chim. Appl., 1933, **23**, 159—168).—For l-β-asparagine at 25° the vals. of K_A and K_B are found to be $0{\cdot}16\times10^{-1}$ and $0{\cdot}17\times10^{-8}$, respectively. T. H. P.

Acid strength and its dependence on the nature of the solvent. W. F. K. WYNNE-JONES (Proc. Roy. Soc., 1933, **A, 140**, 440—451).—Theoretical. The existing data for acids in H_2O, MeOH, and EtOH are in accord with the relation $\Delta \log K_r \propto \Delta(1/D)$, where K_r is the relative strength of an acid and D the dielectric const. of the solvent. It is suggested that the "intrinsic" strength of an acid is its relative strength in a solvent of infinite D. On this basis vals. for the intrinsic strengths of several acids are derived by extrapolation. L. L. B.

Indicator studies of acids and bases in benzene. V. K. LA MER and H. C. DOWNES (J. Amer. Chem. Soc., 1933, **55**, 1840—1864; cf. A., 1931, 584).—An improved technique for the electrometric titration of acids and bases in C_6H_6 is described. The vals. of e.m.f. are nearly double those predicted by the Nernst equation (cf. *ibid.*, 1015). Relative strengths of acids and bases in C_6H_6 have been determined quantitatively by a colorimetric method, and 16 acid–base systems, including 7 indicators, have been investigated. Whilst the uncharged acids retain the same numerical differences of p_K in C_6H_6 as in H_2O, the indicators exhibit marked changes and their colours show strong salt effects. The extent of salt formation has been determined and it is shown that the action of $NHEt_2$ and piperidine in dil. solution is not a sp. indication of the strength of an acid. The indicator properties of Me-red in C_6H_6 are anomalous. J. G. A. G.

Activity coefficients of nitric acid. F. HARTMANN and P. ROSENFELD (Z. physikal. Chem., 1933, **164**, 377—385).—Activity coeffs. have been calc. from f.-p. measurements with solutions containing 0·03—6·6 mols. per 1000 g. H_2O. R. C.

Properties of electrolytes in the solvent sulphuric acid. L. P. HAMMETT and A. J. DEYRUP (J. Amer. Chem. Soc., 1933, **55**, 1900—1909; cf. this vol., 26).—F.-p. data for H_2SO_4 containing H_2O, $KHSO_4$, $NaHSO_4$, and $BaH_2(SO_4)_2$ are consistent with the large degree of dissociation of the H_2SO_4. Ionic activity coeffs. are const. over a wide range of concn., and the solubility product principle is applicable to the effect of H_2O on the solubility of $BaSO_4$ in H_2SO_4. The van 't Hoff factor, i, for 15 org. bases in pure H_2SO_4 has been determined. J. G. A. G.

Equilibria, complex ions, and electrometric titrations. I. Iodine or bromine in hydrochloric acid. J. H. FAULL, jun., and G. S. FORBES. **II. Iodine, bromine, and hydrobromic acid. Iodine tribromide.** G. S. FORBES and J. H. FAULL, jun. (J. Amer. Chem. Soc., 1933, **55**, 1809—1820, 1820—1830).—I. From the e.m.f. of cells of the type $Hg,Hg_2Cl_2|4N\text{-}HCl|4N\text{-}HCl+Br_2$(or I)$|Pt$–Ir at 25°, vals. of $K=[I']^2[Cl_2]/[I_2][Cl']^2$ at high dilution were found to be $1{\cdot}67\times10^{-27}$ and $1{\cdot}05\times10^{-27}$ in $4N$- and $6N$-HCl, respectively, after correcting for the formation of complex halogen ions and interhalogen compounds. In the presence of O_2, the potential of I in HCl is much > the predicted val. owing to ICl formation. If O_2 is excluded and loss of halogen avoided, the electrometric titration of $<0{\cdot}1M$-I with Cl_2 is accurate to within 0·02% in 2—$6N$-HCl. The anomalous variation of e.m.f. with $[Br_2]$ in HCl (cf. A., 1927, 209) is in quant. agreement with calculations in which allowance is made for complex ion and interhalogen compound formation. Electrometric titration of Br_2 with Cl_2 is impracticable especially in the presence of ICl. ICl,I_2 and $BrCl_3$ do not exist under the conditions.

II. From e.m.f. data, the M-potential of Br_2 is 1·0548 and 0·8706 over a wide range of concn., and vals. of $K=[Br_2][I']^2/[I_2][Br']^2$ are 5×10^{-17} and 8×10^{-18}, in 0·974 and 4·72N-HBr, respectively, when corr. for complex formation. The corresponding dissociation consts. of IBr (uncorr. for complex formation) are 2×10^{-8} and 3×10^{-8}. Electrometric titrations through the I and IBr points are within 0·01% of stoicheiometric and the existence of IBr_3 (or IBr_4', dissociation const. 0·3+0·2) is demonstrated. J. G. A. G.

Complex ions formed by iodine cyanide with cyanide and iodide ions. Vapour pressure, free energy, and dissociation of iodine cyanide. D. M. YOST and W. E. STONE (J. Amer. Chem. Soc., 1933, **55**, 1889—1895).—From the distribution of ICN between CCl_4 and H_2O, aq. KI, and aq. KCN the following equilibrium consts. at 25° have been calc.: $[I_2CN']/[ICN][I']=1{\cdot}17$, $[I(CN)_2']/[ICN][CN']=2{\cdot}5$. The v.p. of solid ICN between 25° and 101° is given by $\log_{10} p_{mm}=10{\cdot}225-13{\cdot}940/2{\cdot}3026RT$, and the free energy of formation of gaseous ICN is $\Delta F°_{298}=45{,}940\pm1500$ g.-cal. Gaseous I_2 and $(CN)_2$ do not react appreciably to form ICN; this agrees with calculations based on the third law of thermodynamics. J. G. A. G.

Reduction potential of vanadic acid to vanadyl ion in hydrochloric acid solutions. C. D. CORYELL and D. M. YOST (J. Amer. Chem. Soc., 1933, **55**, 1909—1915).—From the e.m.f. of the cell $Pt|VOCl_2(c_1)+HVO_3(c_2)+HCl(c_3)|HCl(c_3)|HgCl(s),Hg(l)$, the reduction potential, E, of vanadic acid to vanadyl ion in M-HCl at 25° is −1·0216 volt with reference to the M-H_2 electrode. E varies greatly with concn. of HCl, since the activity coeff. of HVO_3 decreases with the increased solubility of V_2O_5 in conc. HCl.

From the temp. coeff. of the e.m.f. between 25° and 33·9°, the change in heat content, ΔH, accompanying the reaction $VO^{\cdot\cdot}+2H_2O(l)=HVO_3$ (in M-HCl)+ $3H^{\cdot}+0{\cdot}5H_2$ (1 atm.) is 29,350 g.-cal. J. G. A. G.

Binary systems : nitrates of metals of group II and water. II. $Be(NO_3)_2$–H_2O, $Zn(NO_3)_2$–H_2O, and $Cd(NO_3)_2$–H_2O. A. Sieverts and W. Petzold (Z. anorg. Chem., 1933, **212**, 49—60; cf. A., 1932, 573).—Solubility data are recorded. The respective eutectic temp. are $< -90°$, $-32{\cdot}0°$, and $-16°$. $Be(NO_3)_2,4H_2O$ has a congruent m.p. at 61·0°. $Zn(NO_3)_2,9H_2O$ is stable below $-17{\cdot}6°$; above $-17{\cdot}6°$ $Zn(NO_3)_2+6H_2O$, $4H_2O$, $2H_2O$, and $1H_2O$ are successively stable. The compounds with 6, 4, and 2 mols. H_2O have congruent m.p. at 36·4°, 45·5°, and 54·1—54·2°, respectively. The anhyd. salt has not been observed. $Cd(NO_3)_2,9H_2O$ is stable below 3·5°. $Cd(NO_3)_2,4H_2O$ has a congruent m.p. at 59·5°, and $Cd(NO_3)_2,2H_2O$ an incongruent m.p. at 56·8°. Above 56·8° the solution is in equilibrium with anhyd. salt. This has not been isolated. H. J. E.

Crystalline form in the formation of solid solutions. IX. Thermal analysis of the anhydrous systems $CoCl_2$–$SnCl_2$ and $FeCl_2$–$SnCl_2$. X. Thermal analysis of the anhydrous systems $CoCl_2$–$PbCl_2$ and $FeCl_2$–$PbCl_2$. A. Ferrari and C. Colla (Atti R. Accad. Lincei, 1933, [vi], **17**, 312—317, 473—475; cf. A., 1931, 901).—IX. In both systems eutectics occur at about 240° containing 4 mol.-% $CoCl_2$ and 2 mol.-% $FeCl_2$, respectively.

X. Eutectics occur at 424° (23·5 mol.-% $CoCl_2$) and 421° (28·5 mol.-% $FeCl_2$), respectively. O. J. W.

Thermal analysis of system BCl_3–Cl_2. W. Graff (Compt. rend., 1933, **196**, 1390—1392).—The thermal diagram shows a eutectic at $-135{\cdot}4°\pm 0{\cdot}3$, and 65·5% BCl_3; there is no evidence of any compound containing more Cl than BCl_3. M.p. of Cl_2 $-103°\pm0{\cdot}3°$; of BCl_3 $-108{\cdot}7°\pm0{\cdot}3°$. C. A. S.

Active oxides. LXIV. Alteration in magnetic and X-ray spectroscopic properties during the transformation of a mixture of magnesium oxide and iron oxide into spinel. H. Kittel, G. F. Huttig, and Z. Hermann (Z. anorg. Chem., 1933, **212**, 209—213; cf. this vol., 560).—Mixtures of MgO and Fe_2O_3 showed no change of magnetic susceptibility (I) when heated together below 500°. At 500—550°, (I) increased, but ferromagnetism did not appear below 600°, indicating no spinel formation below this temp. X-Ray examination of crystal structure affords similar results. J. S. A.

System $MgSO_4$–H_2SO_4–H_2O. R. Arditti (Compt. rend., 1933, **196**, 1388—1390).—Data for 0°, 19°, and 35·5° show the existence of $MgSO_4,7H_2O$; $MgSO_4,H_2SO_4,3H_2O$; $MgSO_4,H_2SO_4$; $3MgSO_4,2H_2SO_4$; and $3MgSO_4,H_2SO_4$, all of which were obtained in cryst. form. C. A. S.

Thermodynamic studies on potassium and sodium sulphates. F. L. E. Shibata, S. Oda, and S. Furukawa (J. Sci. Hiroshima Univ., 1933, **3**, 227—242; cf. A., 1932, 573).—For $2K+S$ (rhombic)$+2O_2$ $=K_2SO_4$, $\Delta F=-313{,}524$ g.-cal.; $\Delta H=-339{,}662$ g.-cal.; entropy of $K_2SO_4=51{\cdot}5$. For $Na_2SO_4+10H_2O=$ $Na_2SO_4,10H_2O$, $\Delta F=1612$ g.-cal.; $\Delta H=-22{,}290$ g.-cal. For $2Na+S$(rhombic)$+2O_2=Na_2SO_4$, $\Delta F=$ $-301{,}672$ g.-cal.; $\Delta H=-330{,}103$ g.-cal.; entropy of $Na_2SO_4=35{\cdot}0$. J. S. A.

Heat of combustion, entropy, and free energy of cyanogen gas. J. McMorris and R. M. Badger (J. Amer. Chem. Soc., 1933, **55**, 1952—1957).—The directly determined heat of combustion of $(CN)_2$ gas is $251{,}400\pm1200$ g.-cal. (15°), from which the heat of formation is $H_{298{\cdot}2}=62{,}900$ g.-cal. The entropy of the gas at 298·2° abs. and 1 atm. is $57{\cdot}8\pm2{\cdot}0$ e.u. and the free energy, $F_{298{\cdot}2}=60{,}000$ g.-cal. J. G. A. G.

Heat of combustion of cyanogen. H. von Wartenberg and H. Schutza (Z. physikal. Chem., 1933, **164**, 386—388).—The heat of combustion at const. pressure is $261{\cdot}3\pm0{\cdot}2$ kg.-cal. R. C.

Heat of formation of compounds between praseodymium and magnesium and between praseodymium and aluminium. G. Canneri and A. Rossi (Gazzetta, 1933, **63**, 182—185; cf. A., 1932, 575).—The heats of dissolution of Pr, PrMg, $PrMg_3$, and $PrAl_4$ in HCl (1 mol./8·808 mols. H_2O) are 166·7, 271·3, 494·1, and 616·17 kg.-cal. per mol., respectively. The calc. vals. of the heat of formation of the three compounds are 8·2, 11·0, and 52·1 kg.-cal. per mol., respectively. O. J. W.

Standard states for bomb calorimetry. E. W. Washburn (Bur. Stand. J. Res., 1933, **10**, 525—558).—Standard vals. for the temp. and pressure of the reactants and products are suggested. Methods for correcting observed vals. and for calculating the intrinsic energy change for the reaction defined by these standard states are described. H. J. E.

Conductance of electrolytes. V. Redetermination of the conductance of standard potassium chloride solutions in absolute units. G. Jones and B. C. Bradshaw (J. Amer. Chem. Soc., 1933, **55**, 1780—1800).—Full details are given for determining the abs. sp. conductance of solutions in cells for which the consts. are determined by resistance measurements when the cells are filled with Hg. The data refer to 0°, 18°, and 25° and KCl solutions containing 71·1352, 7·41913, and 0·745263 g. KCl per 1000 g. of solution (in vac.). Vals. of the conductivity are 0·02—0·12% > those recorded by Parker (A., 1924, ii, 304). J. G. A. G.

Electrical conductivity of mixtures of acetic acid with amines. N. A. Pushin and P. S. Tutundzió (Z. Elektrochem., 1933, **39**, 305—308; cf. A., 1932, 1197, 1204).—Conductivities of mixtures of AcOH with C_5H_5N, α-picoline, 2 : 4-dimethylpyridine, quinoline, and $NPhEt{\cdot}CH_2Ph$ have been measured. All show max. vals. between 80 and 95 mol.-% AcOH, decreasing in the above order. Compound formation does not seem to be indicated. H. J. E.

Simultaneous conduction by electrolytes during the measurement of the resistance of palladium wire containing hydrogen. C. A. Knorr and E. Schwartz (Z. Elektrochem., 1933, **39**, 281—283).—The resistance of a Pd wire charged with H_2 and immersed in aq. H_2SO_4 is at first too low, due to conduction by the electrolyte. The latter quickly

polarises, and the resistance of the wire rises to its true val. Pd uncharged with H_2 does not show the effect. H. J. E.

Weston standard cells with buffered electrolytes. R. J. Priepke and W. C. Vosburgh (J. Amer. Chem. Soc., 1933, **55**, 1801—1809; cf. A., 1931, 1129).—The e.m.f. of Weston standard cells with electrolytes at p_H 4·1—4·8 buffered with $Cd(OAc)_2$ and AcOH is const. over long periods, and hysteresis due to temp. change is small at p_H 4·1 and p_H 8·1. If Hg_2SO_4 is replaced by basic Hg_2SO_4, the e.m.f. decreases with decreasing $H^·$ activity, and an approx. val. of p_H can be calc. at which basic and normal Hg_2SO_4 exist in equilibrium with saturated $CdSO_4$. Cells with a mixture of the normal and basic salts at the Hg electrode have high e.m.f. if the p_H is above, but the e.m.f. is normal if the p_H is below, the transition point. When the layer of Hg_2SO_4 is thin (1—2 mm.) the e.m.f. is variable if the p_H is below the transition point. The interpretation of these phenomena is discussed. J. G. A. G.

Cadmium iodide and zinc iodide cells. A. E. Salzar (Anal. Univ. Chile, Santiago, 1933, 5—15).—A preliminary report of determinations of the e.m.f. of the cells M|aq. MI_2|I (where M is Cd or Zn) at 20—30°. E. S. H.

Potential [at metallic electrodes] in electrolytes with foreign ions. V. The halogen electrode. A. Schmid and P. Vögele. **VI. Development of potential.** A. Schmid, W. Winkelmann, and P. Vögele (Helv. Chim. Acta, 1933, **16**, 366—375, 398—403; cf. this vol., 354).—V. The efficiency of a "diffusion" electrode when used with Cl_2 or Br varies with the porosity of the material, and the concn. of halogen in the electrolyte is indefinite. Satisfactory measurements are possible when an externally prepared halogen–electrolyte solution is caused to flow at const. speed over a Pt anode. Experiments with a Zn–Br(Pt) cell are described, in which the concn. of Br and electrolyte was const. and other factors were varied. The observed variation of efficiency of the anode with the nature of the electrolyte supports the authors' views on the influence of the oppositely charged ions.

VI. Theoretical. The classical laws governing electrochemical potential are valid only in limiting cases. It is necessary also to recognise the occurrence of a process involving the electromotively active substance and ions of opposite charge, these latter being essential for the development of the max. e.m.f. F. L. U.

Conductivity and potential measurements with salts of higher alkylsulphuric acids. A. Lottermoser and F. Püschel (Kolloid-Z., 1933, **63**, 175—192).—Conductivities of aq. solutions of Na salts of alkylsulphuric acids containing 12, 14, 16, and 18 C atoms have been determined. The Λ–c curves pass through a max. at high and a min. at intermediate concns., the min. being displaced towards smaller concns. with increasing mol. wt. The free acids behave similarly. Activities of $Ag^·$ in solutions of the Ag salts (*Ag* salts with C_{16} and C_{18}) show a similar relation to concn. The general behaviour closely resembles that of Na or K soaps, but there is practically no hydrolysis. Salts with bivalent cations are more strongly aggregated than those with univalent. The min. in the surface tension curves (this vol., 458) occurs at concns. at which formation of neutral micelle begins to be marked. F. L. U.

Free energy of lactic acid oxidation. Scale for biological oxidation-reduction potentials. A. Szent-Gyorgyi.—See this vol., 748.

Oxidation–reduction potential of ascorbic acid. K. Laki.—See this vol., 756.

Thermoelectric investigations on solid electrolytes. H. Reinhold and A. Blachny (Z. Elektrochem., 1933, **39**, 290—305; cf. A., 1928, 846; 1931, 312).—The thermal e.m.f. of the following chains has been measured: Ag|Ag_2S|Ag, Ag|Ag_2Se|Ag, Ag|Ag_2Te|Ag, Cu|CuCl|Cu, Cu|CuBr|Cu, Cu|CuI|Cu, Cu|Cu_2S|Cu, Pb|$PbBr_2$|Pb, Pb|PbI_2|Pb, Br$_2$|$PbBr_2$|Br$_2$, Ag|AgCl|$PbCl_2$|AgCl|Ag, Pb|$PbCl_2$|AgCl|$PbCl_2$|Pb, Pb|$PbCl_2$|$PbBr_2$|Pb, Ag|AgBr|AgI|Ag. Except for chains with Ag_2S, Ag_2Se, Ag_2Te, and CuS, the observed e.m.f. is determined largely by a homogeneous effect, and not by the temp. coeff. of the phase boundary potentials. H. J. E.

Hydrogen effect. H. von Halban and G. Kortum (Z. Elektrochem., 1933, **39**, 288—289).—Wolf's experimental results (A., 1932, 1207) are not confirmed. H. J. E.

Electrolysis of water under pressure. H. Cassel and J. Voigt (Naturwiss., 1933, **21**, 331).—The H overvoltage at a Ni electrode in the electrolysis of *N* solutions of H_2SO_4, HCl, and KOH with c.d. of 1—10 ma. has been determined at pressures of 1—25 atm. Increase in pressure results in a parallel displacement of the current–potential curve in the direction of decreasing overvoltage. This is in agreement with the theory of Erdey-Gruz and Volmer (cf. A., 1932, 24). A. J. M.

Structure of electrodeposited alloys. II. Effect of current density and temperature of deposition on the structure of silver–cadmium deposits. C. W. Stillwell and H. I. Feinberg (J. Amer. Chem. Soc., 1933, **55**, 1864—1870; cf. A., 1932, 989).—The % of Cd in the deposit rises with increase of c.d. from 0·1 to 1000 amp. per sq. dm., but decreases with rise of temp. from 27° to 90°. An alloy deposited at low c.d. is more homogeneous than one of the same composition deposited at high c.d., and in the former, the crystals are oriented with respect to the cathode. High c.d. and high temp. favour the formation of (1) non-adherent deposits which contain $Cd(OH)_2$ and (2) traces of the metastable β′-phase. J. G. A. G.

Thermal decomposition of ozone. A. Glissmann and H. J. Schumacher (Z. physikal. Chem 1933, **B**, **21**, 323—348).—The decomp. has been investigated at 70—110° with O_3 at 20—400 mm. and in presence of O_2 at 3—600 mm. The effect of the wall is in general $< 10\%$ of the total reaction. A slight decomp. of O_3 starts on the wall, and some reaction chains are also broken there. In absence of O_2 the decomp. is essentially a homogeneous bimol. reaction. O_2 has an accelerating action, which

causes the velocity coeff. to rise as reaction proceeds, and also a retarding action. In explanation of the kinetics of the decomp. it is suggested that there are two independent reactions: (1) $O_3+O_3=3O_2$*, (2) $O_2+O_3=2O_2+O$. (2) is followed by $O+O_3=2O_2$*, $O+O_2+M=O_3+M$, O_2*$+O_3=2O_2+O$, O_2*$+O_3=O_2+O_3$, O_2*$+O_2=2O_2$. Insertion in the resulting velocity equation of vals. for consts. derived from data for the photochemical decomp. and for the thermal decomp. under limiting conditions indicates that the above scheme is fundamentally correct. The O_2* mols. formed by reaction (1) are capable of secondary activation of further O_3 mols., but this effect is of moment only at high pressures and O_3 concns. He, N_2, and CO_2 have an accelerating effect which increases in this order, and can be qualitatively interpreted. R. C.

Mechanism of flame movement. III. Speed of flame in currents of mixtures of methane and air. H. F. Coward and E. H. M. Georgeson (J.C.S., 1933, 546—551).—The effect of current speed on the speed of flame in CH_4–air mixtures is approx. additive, the increase being slightly > the mean speed of current but < the axial speed. J. S. A.

Ignition temperatures of ammonia–air mixtures. P. Laffitte and H. Picard (Compt. rend., 1933, **196**, 1486—1488; cf. A., 1930, 38).—The temp. decrease from 960° to a min. of 917° to rise to 1002° for mixtures containing respectively 8·9, 23·3, and 57·4% NH_3. Presence of H_2O has no effect, but addition of even 1% H_2 lowers the temp. substantially (cf. A., 1913, ii, 478). C. A. S.

Upper limit in explosive chain reactions. H. W. Melville and H. L. Roxburgh (Nature, 1933, **131**, 690—691).—Experiments with PH_3–O_2 mixtures show that in the region above the upper limit there is a gradual decrease in the length of the reaction chains as the O_2 pressure is increased (cf. this vol., 355). L. S. T.

Slow combustion of ethane at high pressures. D. M. Newitt and A. M. Bloch (Proc. Roy. Soc., 1933, **A**, **140**, 426—439).—In the slow combustion of 85—90% C_2H_6 : 15—10% O_2 mixtures at pressures up to 100 atm. each of the six possible "hydroxylation" steps may be represented by one or more of the intermediate products isolated. At 100 atm. > 60% of the C burnt survived as condensable and H_2O-sol. intermediate products, with EtOH and/or AcOH predominating. The influence of an increase in the reaction pressure is favourable to the survival of products (EtOH, MeCHO, and AcOH) of which the formation does not involve any rupture of the C_2H_6 mol.; a lowering of the pressure favours the formation of MeOH, CH_2O, and HCO_2H. L. L. B.

Decomposition of ozone in aqueous solution. K. Sennewald (Z. physikal. Chem., 1933, **164**, 305—317).—The decomp. at 0° in buffer solutions of p_H 5·3—8, in pure H_2O, and in 0·01—0·5M-K_2SO_4 follows the bimol. law. The velocity coeff., the logarithm of which in absence of salts increases linearly with the p_H, is increased by the presence of a salt by an amount approx. proportional to the salt activity, suggesting that the salt brings about a second bimol. reaction independent of [H·]. Ozonised O_2 on passage through buffer solutions undergoes appreciable decomp. only above p_H 10, but at p_H 14 decomp. is very rapid. Borate promotes the decomp., perhaps owing to the intermediate formation of perborate. R. C.

Kinetics of the carbon dioxide–carbonic acid reaction. R. Brinkman, R. Margaria, and F. J. W. Roughton (Phil. Trans., 1933, **A**, **232**, 65—97).—Manometric and photo-electric methods are described for the measurement of the velocity of the reaction $CO_2+H_2O \rightleftharpoons H_2CO_3$. The change in the nature of the reaction with p_H (A., 1925, ii, 295) is confirmed, but the velocity coeffs. are considerably > those observed by Faurholt (*e.g.*, k 1·70, k' 0·0026, $k_{CO_2\cdot OH}$ 840 at 0°; k 11·1, k' 0·24, $k_{CO_2\cdot OH}$ 2050 at 18°). It is calc. that $H^{\cdot}+CO_3''=HCO_3'+3750$ g.-cal. at room temp. D. R. D.

Reaction velocity and the "equi-valence-change principle." P. A. Shaffer (J. Amer. Chem. Soc., 1933, **55**, 2169—2170).—It is suggested, irrespective of activity or free energy decrease, that an oxidation–reduction reaction will not occur as a bimol. reaction if the no. of electrons which may be lost or shared by the reductant is not the same as required by the oxidant. The inactivity of Tl_2SO_4 towards $Ce(SO_4)_2$ is attributed to the fact that the oxidation of $Tl^{\cdot}$ requires the loss of two electrons whilst $Ce^{\cdot\cdot\cdot\cdot}$ can accept only one, to give known valency states. The catalysis of this reaction by $MnSO_4$ is consistent with the theory. J. G. A. G.

Supersaturation of liquids with gases. T. N. Richardson and K. C. Bailey (Nature, 1933, **131**, 762).—The velocity coeffs. obtained for the oxidation of N_2H_4 by $K_3Fe(CN)_6$ are much > those found by Gilbert (A., 1932, 348) owing to an increase in the rate of evolution of N_2 with rate of stirring up to approx. 1000 r.p.m. This is due to supersaturation of the solution by gas, and the amount of N_2 which may accumulate in the unstirred solution is 7—8 times the normal solubility. Supersaturation may thus invalidate quant. work on chemical kinetics. L. S. T.

Kinetics of the iodine–oxalate reaction. N. R. Dhar, A. K. Bhattacharya, and B. L. Mukerji (Nature, 1933, **131**, 840—841).—For N-$K_2C_2O_4$ and N/850-I the relation between velocity and light intensity varies approx. from 1/3 to 5/4 for wave-lengths between 3500 and 8750 Å. The addition of N/277-KI decreases the velocity and $k^{32°}/k^{22°}$ is 8·84 in the dark. L. S. T.

Kinetics of the action of iodine on potassium oxalate. A. Berthoud (Helv. Chim. Acta, 1933, **16**, 393—398; cf. A., 1931, 1135).—The velocity of the "dark" reaction $I_2+K_2C_2O_4 \longrightarrow 2KI+2CO_2$ is approx. given by $K[C_2O_4'']^{\frac{1}{2}}[\Sigma I_2]^{\frac{1}{2}}/[I']^{\frac{1}{2}}$, ΣI_2 denoting total titratable I. The velocity of the corresponding photochemical change differs only in being $\propto 1/[I']$. Possible mechanisms are discussed. F. L. U.

Velocity of splitting off of chlorine from monochloroacetate. S. Matuura (Bull. Chem. Soc. Japan, 1933, **8**, 113—120).—In the early stages the hydrolysis of the K or Na salt is unimol. Measurements at 20—35° are recorded. The velocity coeff. is

greatly increased by the addition of KOH or NaOH, and diminished by addition of a neutral salt with a common cation. F. L. U.

Velocities of hydrolysis of methoxydiphenylketimines. J. D. CULBERTSON and A. L. BRESSON (Proc. Iowa Acad. Sci., 1391, **38**, 169—170).—Velocities of hydrolysis to the corresponding ketones are in the order: 3->4->2-methoxydiphenylketimine HCl, all < diphenylketimine HCl. CH. ABS.

Velocities of hydrolysis of mono- and polyhydroxydiphenylketimines. J. B. CULBERTSON and J. L. NAUMAN (Proc. Iowa Acad. Sci., 1931, **38**, 170).—The phenolic group in 2- and 4-hydroxydiphenylketimine retards hydrolysis, and in the 3-isomeride facilitates it. CH. ABS.

Reaction velocity–temperature constant of yeast invertase in supercooled solutions. Z. I. KERTESZ (Z. physiol. Chem., 1933, **216**, 229—232).—The velocity of inversion of sucrose by yeast decreases only slowly below 0°. The Arrhenius const. A falls rapidly from 11,800 at 0° to 6300 at −3·75° and 1400 at −6·25°. J. H. B.

Rate of absorption of gases by liquids. R. C. BRIMLEY (Chem. and Ind., 1933, 472—473).—The rate of dissolution of CO_2 in H_2O or aq. NaOH is controlled by the low rate of diffusion of CO_2 through the surface layer of the liquid and varies with the age of the surface. The same conclusion can be reached from the data of Dirken and Mook (A., 1930, 799). D. R. D.

Kinetics of surface processes in crystal lattices. II. Elementary processes in formation of a boundary layer consisting of several components. L. IMRE (Z. physikal. Chem., 1933, **164**, 327—342; cf. A., 1931, 421).—Investigation of the rates of adsorption of Ac from aq. solution on $BaSO_4$, $PbSO_4$, and $BaIO_3$ has led to some modification of the theory previously advanced. The supposed "second stage" in the adsorption involves the embodiment of the adsorbate ion in the solid surface layer of the adsorbent. In this process the dehydration equilibrium of the adsorbate ion is established immeasurably rapidly even if the adsorption compound is readily sol. The gradual incorporation of the ion into the lattice is explicable by the theory of crystal growth. R. C.

Theory of metallic corrosion in the light of quantitative measurements. VI. Distribution of corrosion. G. D. BENGOUGH and F. WORMWELL (Proc. Roy. Soc., 1933, **A**, **140**, 399—425).—An attempt has been made to estimate the limits, if any, within which the differential aeration principle of corrosion holds. Three of the most important methods of producing differential aeration sufficient to affect corrosion distribution have been used, viz., partial immersion, deposits of corrosion products and neutral bodies, and crevices. Corrosion distribution, on Zn and mild steel in stagnant conditions, is not determined by the rate of O_2 supply but by the distribution of protective films which cause the metal to be locally cathodic to bare, or less completely protected, metal. When the films are widespread, corrosion may be sufficiently localised to be called "pitting"; when the films are restricted, corrosion may finally cover the whole metallic surface. Factors influencing the character, distribution, and continued adherence of films in the solutions and conditions studied are: alkali distribution (affected by sites of depolarisation by O_2, creep tendency, and neutralisation by metallic salts or atm. gases), surface tension factors, presence of specially reactive areas at the metal surface, gravity, movement of liquid, alternate wet and dry conditions, presence of certain foreign bodies, and nature of the solution. The average rate of corrosion is often determined by the total rate of O_2 supply to the total surface of both protected and attacked areas, but the intensity of corrosion at any given part is determined by the film distribution. L. L. B.

Rate of oxidation of monolayers of unsaturated fatty acids. A. H. HUGHES and E. K. RIDEAL (Proc. Roy. Soc., 1933, **A**, **140**, 253—269).—The rate of oxidation of unimol. films of oleic, Δ^{α}-*iso*oleic, *cis*-petroselic, and chaulmoogric acids by dil. $KMnO_4$ in 0·01N-H_2SO_4 has been studied by measurements of the change of surface potentials with time. The reaction velocity decreases with the compression of the film, and depends on the accessibility of the double linking to the oxidising agent. It is also affected by the position of the double linking in relation to the polar CO_2H head group. α- and β-Elæostearic acids exhibit autoxidation, and the effect of quinol as an antioxygen to this reaction has been examined. L. L. B.

Rate of dissolution of marble in dilute acids. C. V. KING and CHENG LING LIU (J. Amer. Chem. Soc., 1933, **55**, 1928—1940).—The rate of dissolution, R, of cylinders of marble in 0·002—0·04M-HCl and AcOH between 15° and 35° tends to a max. with increasing speed of rotation. The temp. coeff. per 10° varies from 1·32 to 1·94. In general, the initial R is parallel to the ionisation consts. of the 10 acids used. Added NaCl increases R in HCl, and whilst it has no effect at low [AcOH], at higher [AcOH], R has a max. at a particular [NaCl]. Depression of p_H by adding salts of weak acids to the corresponding acids decreases R markedly, but in a manner which indicates some attack of the marble by mols. of undissociated acid. With increasing concn. of HCl, the effect of adding AcOH becomes smaller owing to suppression of ionisation. The results are compared with those obtained with metals (cf. A., 1931, 1373). The data are consistent with the diffusion theory when allowance is made for the fact that H_2CO_3 is not negligibly weak, that freshly liberated H_2CO_3 is a stronger acid than the usual equilibrium mixture of H_2CO_3 and CO_2, and that the dehydration of H_2CO_3 is sufficiently slow to influence R considerably. J. G. A. G.

Relation between dehydration and hydrolysis of magnesium chloride on heating the crystalline salt. J. G. SCHTSCHERBAKOV and A. K. RASPOPINA (Kali, Russia, 1932, No. 10, 16—19).—On gradual heating of $MgCl_2,6H_2O$ to 300—350° and then to the m.p., the % H_2O (y) and MgO (x) are related by $-dy/dx=ky^2$. CH. ABS.

Initial act in auto-oxidation. H. N. STEPHENS (J. Physical Chem., 1933, 37, 655).—Polemical. H. J. E.

Collision activation and homogeneous catalysis of decomposition of nitrous oxide in foreign gases. M. VOLMER and M. BOGDAN (Z. physikal. Chem., 1933, **B**, 21, 257—272; cf. this vol., 30).—The heat of activation, variation of reaction velocity with pressure of foreign gas, and comparison of the velocity coeff. with show that Hg, Br, and I catalyse the decomp.; with I and Br the catalyst is the halogen atom. H_2 reduces N_2O directly. In presence of H_2, Ne, A, Kr, and Xe the reaction is unimol. and the relative probability of activation by collision of N_2O with the foreign gas mol. has been calc. It decreases with increasing mol. wt. of the foreign gas. R. C.

Catalytic oxidation of organic compounds in the vapour state. G. CHARLOT (Compt. rend., 1933, 196, 1224—1226; cf. A., 1932, 235).—The extent of complete oxidation as measured by CO_2 production has been determined for several hydrocarbons in the presence of MgO, NiO, MoO_3, and WO_3 as catalysts at different temp. Each catalyst has a sp. action causing, at a given temp., an approx. const. rate of CO_2 production, independent, within limits, of the nature, concn., or rate of flow of the vapour oxidised. A. C.

Ozone as an oxidising catalyst. V. Ozonation of sodium sulphite; influence of dilution of ozone and concentration of hydrogen ions. E. BRINER and H. BIEDERMANN (Helv. Chim. Acta, 1933, 16, 548—555; cf. this vol., 234).—Oxidation of aq. Na_2SO_3 induced by O_3 increases markedly on dilution of the latter with O_2, or on acidifying the liquid. The results are discussed. F. L. U.

Influence of sodium borate on the reaction between alkali cyanides and reducing sugars. J. BOUGAULT, Z. HARDY, and A. PINGUET (J. Pharm. Chim., 1933, [viii], 17, 462—469).—The presence of $Na_2B_4O_7$ accelerates the reaction between CN′ and reducing sugars (cf. A., 1920, ii, 452). The reaction, however, is not rendered more applicable to sugar determinations owing to increased instability of CN′. F. O. H.

Reduction of methylene-blue by products of the alkaline fission of sugars. H. VON EULER and E. KLUSSMANN (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 13, 6 pp.).—Decolorisation of methylene-blue (I) by a mixture of 2% glucose (II) (and other sugars) (1 c.c.) and 0·01*N*-NaOH (1 c.c.) under anaerobic conditions is accelerated by KCN (1 mg.). The times of decolorisation by (II) and fructose (III) increase with diminished concn. of NaOH, but the ratio time (II) : time (III) remains almost const. Reduction is accelerated by NH_2-acids. The results with dil. NaOH+PO_4''' differ from those of Blix (A., 1928, 250). (I) is reduced more readily by an extract of the cortex than of the medulla of the suprarenal gland; heating the extracts at 80° in N_2 causes a loss in reducing power. H. B.

Catalysis of air oxidations by iron salts, phosphates, and pyrophosphates. E. J. THERIAULT, C. T. BUTTERFIELD, and P. D. MCNAMEE (J. Amer. Chem. Soc., 1933, 55, 2012—2024).—Fe pyrophosphates (I) do not catalyse the oxidation of glucose by air at 20—50° at p_H vals. within the physiological range provided bacteria are excluded from the solutions. Doubt is cast on the validity of the claims made by Spoehr (A., 1924, i, 836; cf. A., 1926, 385) and by Degering and Upson (A., 1932, 147) regarding the activity of their pyrophosphate complexes at 38° and 48°. Numerous varieties of bacteria exist which are indifferent to (I) and it appears that (I) does not catalyse the oxidations accomplished by bacteria alone or by symbiotic growths of bacteria and plankton (*Colpidium*). The assumption of the presence of a highly specialised intracellular catalyst in biological oxidations appears to be unnecessary. H. B.

Heterogeneous catalysis of para-hydrogen transformation. K. F. BONHOEFFER, A. FARKAS, and K. W. RUMMEL (Z. physikal. Chem., 1933, **B**, 21, 225—234).—The reaction has been investigated on various catalysts, the order being between 0 and 1. At low temp. transformation occurs principally by the unimol. conversion of an isolated adsorbed H_2 mol. from one form into the other, whilst at high temp. it depends on at. adsorption. The low-temp. mechanism is responsible for the negative temp. coeff. of the catalysis; the high-temp. mechanism has a positive temp. coeff. Mol. adsorbed O_2 greatly accelerates the reaction on C at low temp., probably by virtue of its paramagnetism, but poisons other catalysts. R. C.

Preparation of oxide catalysts for the carbon monoxide oxidation. C. M. LOANE (J. Physical Chem., 1933, 37, 615—622).—Active oxides of Ni, Co, Fe, Mn, and Cu were made by the regulated oxidation of pyrophoric metals made (1) by preparing the Hg amalgam and distilling off the Hg in vac., (2) by reduction of a metal salt by Na in NH_3 solution. The activity of these oxides in the CO–O_2 reaction is comparable with that of pptd. oxides. H. J. E.

Energetics of catalysis. I. Energetic homogeneity of a platinum surface. E. B. MAXTED and G. J. LEWIS (J.C.S., 1933, 502—504).—The catalytic activity of Pt-black towards the decomp. of H_2O_2 in presence of small concns. of poison ($HgCl_2$) varies linearly with the concn. of poison. The energy of activation is const. and independent of the concn. of poison, implying energetic homogeneity of the surface. J. S. A.

Various classes of hydrogenation catalysts. O. SCHMIDT (Naturwiss., 1933, 21, 351).—The metals are classified according to their capacity for bringing about the hydrogenation of C_2H_4 between 0° and 200°, at atm. pressure. The first class contains Cs, Ca, Sr, and Ba, which possess large at. vol., small electron expulsion work, and form stable hydrides in which H functions as a negative ion. The second contains Cu, Cr, Mn, Re, Fe, Co, Ni, Pd, Pt, which have small at. vol., large electron expulsion work, are transition elements, and form unstable hydrides, or take up H_2 in solid solution, in which the H acts as a positive ion. Usually the mechanism of H activation is quite different in the two classes. Whilst in the first class the formation of negative H ions at the surface, through

the ease of formation of free electrons and the electronic affinity of H atoms, is favoured, a similar process is not possible in the second class owing to the high electron affinity of the surfaces of these metals. In this case there is formation of positive H ions in the lattice spaces in the interior of the metal. A. J. M.

Benzine synthesis from carbon monoxide and hydrogen at atmospheric pressure. XIII, XIV. Nickel catalysts. K. FUJIMURA and S. TSUNEOKA. —See B., 1933, 452.

Suppression of aminolysis at a carbon contact. K. WUNDERLY (Helv. Chim. Acta, 1933, **16**, 515—521; cf. A., 1932, 836).—Aminolysis of aq. *dl*-aspartic acid at a surface of animal C is unaffected by treatment of the latter with HCN or H_2S, either of which abolishes its O-carrying capacity, or with capillary-active compounds. Between p_H 4 and 9 aminolysis increases with acidity. F. L. U.

Active oxides. LXI. Catalytic activity of zinc oxide, treated at different high pressures. O. KOSTELITZ and G. F. HUTTIG (Z. Elektrochem., 1933, **39**, 362—368; cf. this vol., 348).—ZnO pellets, prepared by crushing basic Zn carbonate (I) or ZnC_2O_4 at 50—10,000 atm. and heating at 300—400°, catalyse the decomp. of MeOH at 300° and of EtOH at 320°. About 70—80% of the MeOH is decomposed into H_2 and CO, the remaining products being CO_2, CH_4, CH_2O, and HCO_2Me. The main products produced from EtOH are H_2 and MeCHO. The course of the catalysis varies somewhat with the conditions of prep. of the ZnO. The catalytic activity per unit wt. of catalyst decreases with increase of the pressure originally applied, but at the same time the activity per unit vol. increases. The magnetic susceptibility of the compressed undecomposed (I) decreases with increasing pressure. E. S. H.

Active oxides. LXII. Chromic oxide as catalyst for the decomposition of methyl alcohol. G. F. HUTTIG and K. STRIAL [with H. KITTEL] (Z. Elektrochem., 1933, **39**, 368—373; cf. preceding abstract).—Cr_2O_3 has been prepared in 22 different ways, and the efficiency of the products in catalysing the reaction $MeOH \longrightarrow CO+2H_2$ determined. The results vary considerably among the individual preps. and no generalisation is clear. The catalytic activity of the preps. is compared with the magnetic susceptibility and the adsorbent power for dyes. E. S. H.

Thermal dissociation of gypsum in presence of catalysts. I. E. ADADUROV, L. GALAMECVA, and D. V. GERNET (J. Appl. Chem., Russia, 1932, **5**, 736—743).—Up to 430° dissociation is due to increase in mobility of the lattice. The change of α-silicic acid to tridymite at 900—1200° is a secondary reaction. Anomalies observed in presence of Fe_2O_3 are attributed to formation of silicates of the type FeO,SiO_2+CaO,SiO_2, or $3FeO,SiO_2+CaO,SiO_2$. CH. ABS.

Theory of ammonia catalysis. W. FRANKENBURGER (Z. Elektrochem., 1933, **39**, 269—281).—A comprehensive review. H. J. E.

Electrolysis of metal salts in liquid ammonia (Faraday's law). M. C. DEL BOCA (Helv. Chim. Acta, 1933, **16**, 565—571).—Anodic dissolution of Zn, Cd, Sb, or Al in solutions of their respective hexammino-nitrates or -iodides in liquid NH_3 is 44—100% in excess of that required by Faraday's law. Mg does not dissolve under these conditions. If the Pt cathode is enclosed in a canvas bag a part of the metal is deposited on the latter. F. L. U.

Influence of anions on the electrolytic deposition and dissolution of cadmium and zinc. E. MULLER and H. BARCHMANN (Z. Elektrochem., 1933, **39**, 341—352).—The c.d.–p.d. curves for the deposition and dissolution of Cd and Zn are influenced strongly by the nature of the anion present. The steepness of the curves increases in the order ClO_4', SO_4'', Br′, Cl′, suggesting a relation with the radius of the anion. At higher temp. the variations are less pronounced, but in the same order. In the deposition of Cd from several electrolyte solutions the current efficiency at medium c.d. is 94—99% and increases with rising temp. Increase in the concn. of the anion, the Cd" ion remaining const., has a depolarising effect. Thick coatings of Cd can be deposited from $Cd(ClO_4)_2$ solution, especially in presence of excess of $NaClO_4$. Addition of gelatin raises the p.d., especially in solutions containing large anions. Thick layers of Cd can be deposited from $CdSO_4$ solutions when gelatin is added. The anion also has an influence on the structure of the deposited metal. In general, the grain is refined by rising temp., increased concn., stirring, and the presence of gelatin, and is rendered coarser by increase of c.d. E. S. H.

Electrolytic deposition of metallic niobium and its separation from tantalum. N. ISGARISCHEV and A. F. PREDE (Z. Elektrochem., 1933, **39**, 283—288).—The separation of Ta_2O_5–Nb_2O_5 mixtures from minerals is described. The oxide mixture was then fused with $K_2S_2O_7$, and the melt (I) extracted with H_2O, then with 40% aq. KOH. Electrolysis of the KOH extract +1—1·5% dextrin with a Pt anode and a Cu cathode yielded pure Nb. Alternatively (I) was extracted with aq. $(NH_4)_2C_2O_4+H_2C_2O_4$ or with aq. citric acid and electrolysed at > 80°. Nb was deposited quantitatively. Ta was recovered as Ta_2O_5 on acidifying the residual electrolyte with H_2SO_4. Nb deposits were resistant to corrosion by mineral acids. Electrolysis in acid solution may be used for electro-analysis of Nb–Ta mixtures. H. J. E.

Amino-acids and related compounds. I. Electrolytic oxidation of glutamic acid. Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, **8**, 125—133).—Oxidation of *d*-glutamic acid dissolved in *N*-H_2SO_4 at a PbO_2 anode yielded NH_3, AcOH, succinic and succinamic acids. A mechanism is suggested. F. L. U.

Polarographic studies with the dropping mercury cathode. XXXII. Activation of hydrogen in the thiol group of some thio-acids in cobalt salt solutions. R. BRDIČKA (Coll. Czech. Chem. Comm., 1933, **5**, 148—164).—The catalysed electrolytic deposition of H_2 at the Hg dropping cathode in the presence of thioglycollic acid (I), cysteine (II), cysteylglycine (III), and glutathione (IV) (in both

S_2 and SH forms) in ammoniacal solutions of $CoCl_2$ in NH_4Cl was studied by polarographic methods. Since the reduction of cystine (2e per mol.) occurs at a more positive cathode than that at which the catalytic wave appears, the catalytic effect is due to (II). Since similar catalytic effects are observed with (I), (III), and (IV) it is due to the SH group, and its absence in solutions containing hexamminocobaltic chloride shows the necessity of Co$^{\cdot\cdot}$ ions. The effect of $[NH_3]$ and $[NH_4^{\cdot}]$ was also studied and on the basis of the results it is suggested that the co-ordinate linking between the ·SH group in the Co$^{\cdot\cdot}$ complexes increases the distance between the H^+ and the positive S nucleus in the dipole $-(S-H)^+$, which is transported with Co$^{\cdot\cdot}$ ions to the negatively-charged interface between Hg and H_2O where the increasing potential gradient deforms the dipole so that S′ and H^+ become separated, the H atom removed by discharge being replaced by the reaction $-S' + H_2O \rightarrow \cdot SH + OH'$. Hence OH′ ions must be removed from the cathode interface by NH_4 ions or by buffering. The catalytic effect is very sensitive and can be employed for the determination of thio-acids. J. W. B.

Heterogeneous reactions in the silent electric discharge. V. S. Miyamoto (J. Sci. Hiroshima Univ., 1933, **3**, 209—226; cf. this vol., 33).—The following solid substances were reduced by gaseous H_2 in the silent discharge: Li_2SO_4, Na_2SO_4, $Ti(SO_4)_2$, K Fe alum, $(NH_4)_2SO_4,CoSO_4,6H_2O$, $CdCl_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $NaNO_3$, $NaNO_2$, and $AgNO_3$. Details of reaction products are given. J. S. A.

Electrochemical properties of photosensitive electrodes in copper salts. R. Audubert (Compt. rend., 1933, **196**, 1386—1387).—From the fact that a Cu plate covered with a photosensitive substance, when functioning as an electrode in aq. $CuSO_4$, behaves as one of pure Cu, it is inferred that within p_H limits for which the photovoltaic e.m.f. is reproducible and the photosensitive substance is unaltered the electrode potential depends solely on an oxido–reduction process. C. A. S.

Photolysis of solutions of alkali metals in liquid ammonia. R. A. Ogg, jun., P. A. Leighton, and F. W. Bergstrom (J. Amer. Chem. Soc., 1933, **55**, 1754—1766).—Pure liquid NH_3 is not decomposed, but 0·002—0·1*N* solutions of Na, K, and Cs in liquid NH_3 afford H_2 and the metallic amide in light of wave-lengths 2144—2550 Å. The quantum efficiency increases, with increasing concn. of metal, to 0·25, has a max. at about 2300 Å. and a long wave-length threshold. Liquid NH_3 absorbs light of wave-length < 2500 Å., whilst the solutions of metals and their amides exhibit continuous absorption throughout the ultra-violet. The mechanism of the reaction is discussed in relation to the photo-decomp. of gaseous NH_3. The Na–NH_2 linking is probably ionic. J. G. A. G

Photo-reduction of alcoholic solutions of ferric chloride in light. M. Prasad and P. S. Limaye (J. Indian Chem. Soc., 1933, **10**, 91—99; cf. A., 1931, 1378).—Photo-reduction proceeds in two stages, both zero-mol., although the first is faster than the second. A striking change occurs in the solution at a certain stage (as shown by measurements of extinction coeffs.), probably owing to the formation of a complex containing Fe^{III}. Colloidal $Fe(OH)_3$ inhibits the reaction, the extent of inhibition increasing with the progress of the reduction, although the course of the reaction from the first to the second stage is unchanged. J. L. D.

Quantum efficiency of the photo-reduction of alcoholic solutions of ferric chloride. M. Prasad and P. S. Limaye (J. Indian Chem. Soc., 1933, **10**, 101—105; cf. preceding abstract).—The quantum efficiency (0·6—4) in dil. is $<$ that in more conc. solutions; in any solution the quantum efficiency is greater in light of lower λ, and increases with rise in temp. The primary effect of light absorption is the breaking up of the $FeCl_3$ into $FeCl_2$ and Cl′. No other side reaction is detected. J. L. D.

Photolysis of aliphatic aldehydes. II. Acetaldehyde. P. A. Leighton and F. E. Blacet (J. Amer. Chem. Soc., 1933, **55**, 1766—1774; cf. A., 1932, 1006).—The quantum efficiency, γ, of the polymerisation and decomp. of MeCHO in homogeneous light of wave-lengths between 2537 and 3342 Å. has been determined. In general, γ is independent of light intensity, but the polymerisation (γ_p 0·08—0·64) decreases and the decomp. (γ_d 0·2—0·95) increases as wave-length is decreased. The vapour fluoresces in light absorbed in the regions of distinct and diffuse bands but not in the region of continuous absorption. The data are explained in terms of the absorption spectrum, which is interpreted as consisting of bands with a background of continuous absorption. J. G. A. G.

Germ and pro-germ formation in relation to the developable centres of the exposed homogeneous silver bromide grain. L. Hamburger (Phot. J., 1933, **73**, 95—105; cf. this vol., 350, 359).—Theoretical. Available data are shown to be quantitatively compatible with the author's theory that the crit. developable size of a Ag (or Ag_2S etc.) germ (nucleus) is 3 atoms; smaller centres are named pro-germs. The distribution of germs and pro-germs on Ag grains and its relation to exposure are considered mathematically. Larger or smaller crit. germ sizes are shown to be erroneous. J. L.

Relationship between reciprocity law failure and the intermittency effect in photographic exposure. J. H. Webb (J. Opt. Soc. Amer., 1933, **23**, 157—169).—Identical photographic effects are obtained with an intermittent exposure of average intensity I and with a continuous exposure of abs. intensity I, provided that the frequency of the former is that at which only one quantum per flash is incident on the receptive area of a photographic grain. C. W. G.

Photographic reversal by desensitising dyes. B. H. Carroll and C. M. Kretchmian (Bur. Stand. J. Res., 1933, **10**, 449—464).—The latent image on an exposed plate, which has been bathed in a solution of a desensitising dye, may be destroyed by a second exposure to light of the proper wave-length. The dyes used were pinakryptol-green and -yellow, para-rosaniline, safranine (I), and tolusafranine. The reversal corresponds with the energy absorption by the dyed AgBr between 3500 and 8000 Å. The

effects of bromide and dye concn. were examined. (I) may produce either reversal or normal sensitisation, depending on [Br']. The reversal process is an oxidation, and is chemically and photographically the reverse of ordinary sensitisation. H. J. E.

Concentration of the heavy hydrogen isotope. I. L. NEWELL and J. B. FICKLEN (J. Amer. Chem. Soc., 1933, **55**, 2167).—Determinations of d of H_2O from Cr-plating baths which have been operated for three years indicate the presence of about 0·6% of H_2O containing the heavier H isotope. J. G. A. G.

Increase of concentration of H^1H^2 by fractional evaporation and rectification. W. H. KEESOM, H. VAN DIJK, and J. HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 248—252).—By the fractional evaporation of 40 litres of liquid H_2 and rectification of the resulting 500 c.c. at a temp. near the triple point, 2 litres of gas were obtained, the d of which showed it to contain 3 vol.-% of H^1H^2. F. L. U.

Thermal decomposition of magnesium silicides. G. GIRE (Compt. rend., 1933, **196**, 1404—1406; cf. A., 1908, ii, 184; 1926, 368).—Finely powdered Mg (20 parts) and Si (6 parts) react in vac. at 450°. On removing excess of Mg by $EtI+Et_2O$, $SiMg_2$ remains. At 550° this loses 25% of its Mg, leaving Si_2Mg_3 as a dark grey powder which does not evolve spontaneously inflammable H silicide on treatment with HCl, and begins to decompose at 650°. C. A. S.

Soluble anhydrite as a desiccating agent. I. Preparation and general characteristics. W. A. HAMMOND and J. R. WITHROW (Ind. Eng. Chem., 1933, **25**, 653—659).—Sol. anhydrite, prepared by heating $CaSO_4,2H_2O$ or $CaSO_4,0{\cdot}5H_2O$ (I) at 170—300°, is an efficient desiccating agent. The v.p. of (I) is 0·005 mm. and thus < that obtained over $CaCl_2$ or H_2SO_4. The anhyd. material can be repeatedly regenerated by heating and its physical properties are good. It may be used for HCl, SO_2, Cl_2, or most org. liquids. A. G.

Alkaline-earth metal hydrides. P. REMY-GENNETE (Ann. Chim., 1933, [x], **19**, 353—426; cf. this vol., 569).—Partly a more detailed account of work previously reviewed (A., 1930, 1262; 1932, 1217). The following is new. Ca which has been kept in CO_2 or obtained (in a finely divided state) by decomp. of CaN_6 does not adsorb H_2 at 20° during about 3·5 months or 40 days, respectively; adsorption occurs readily with redistilled Ca (I) (kept out of contact with air). Slow but definite adsorption of H_2 by (I) occurs at −80°. Similar results are found for Sr (finely divided Sr, obtained by decomp. of SrN_6, is, however, active) and Li; the rates of adsorption vary. Adsorption of N_2 by (I) occurs slowly during 9 days at 20° and then ceases; the resultant product adsorbs H_2. Freshly distilled Sr is attacked superficially when kept in dry CO_2: $5Sr+2CO_2 \longrightarrow SrC_2+4SrO$. Ba adsorbs H_2 at 20° irrespective of its method of prep. (cf. *loc. cit.*). H. B.

Action of white phosphorus on copper salts, and of copper on white phosphorus, in presence of water. H. PELABON (Bull. Soc. chim., 1933, [iv], 53, 260—264).—P immersed in aq. $CuSO_4$ causes the formation of a black deposit of Cu_5P, leaving H_2SO_4, H_3PO_4, and H_3PO_3 in solution. From dil. solutions, or by immersing Cu+P in acidified H_2O, large Cu crystals may be obtained. The presence of O_2 is necessary. Ag salts behave similarly. J. S. A.

Carbon with metallic lustre; new form of carbon? U. HOFMANN (Z. Krist., 1933, **85**, 330; cf. this vol., 12).—The previous deduction of similar results is pointed out (cf. B., 1927, 802; A., 1928, 464; 1932, 217, 903, 1078). C. A. S.

Formation of phosgene in thermal decomposition of carbon tetrachloride. A. HAMILTON (Ind. Eng. Chem., 1933, **25**, 539—541).—Evidence is summarised to show that when fires in enclosed spaces are extinguished with CCl_4 there is some risk of poisoning by $COCl_2$ formed from it. A. G.

[Formation of phosgene in thermal decomposition of carbon tetrachloride.] J. C. OLSEN (Ind. Eng. Chem., 1933, **25**, 541—542).—It is claimed that the danger of $COCl_2$ poisoning (see preceding abstract) is negligible. A. G.

Mechanism of the formation of acid oxides at carbon surfaces. B. BRUNS, M. MAXIMOVA, and E. POS (Kolloid-Z., 1933, **63**, 286—291).—The surface oxides produced by direct oxidation of C with O_2 are not reduced at room temp. by H_2 in presence of Pt and are not removed by shaking with H_2O. The formation of acid oxides, especially at lower temp., depends on the treatment of the C; activated C gives smaller amounts than non-activated C, possibly because of the smaller content of org. impurities. The presence of Pt reduces the amount of acid oxides formed. Weakly oxidised C adsorbs both cations and anions from solutions of neutral salts. E. S. H.

Nitrogen compounds of germanium. IV. Action of ammonia and amines on germanium tetraiodide. W. C. JOHNSON and A. E. SIDWELL (J. Amer. Chem. Soc., 1933, **55**, 1884—1889; cf. this vol., 38).—The reaction of GeI_4 with NH_3 and NH_2Et at −33·5° and in CCl_4 at room temp. is represented by $GeI_4+6RNH_2=Ge(NR)_2+4RNH_3I$. Aminolysis is also effected by $NHEt_2$, whilst NEt_3 forms the additive compound $GeI_4,5NEt_3$ (cf. A., 1932, 132). J. G. A. G.

Peroxidation of cerium. A. FOUCHET (Bull. Soc. chim., 1933, [iv], **53**, 218—221).—A criticism (cf. Lortie, A., 1931, 182). J. S. A.

Anhydrous hydrazine. VI. Hydrazine trinitride monohydrazinate, $N_2H_5N_3,N_2H_4$. A. L. DRESSER and A. W. BROWNE [with C. W. MASON] (J. Amer. Chem. Soc., 1933, **55**, 1963—1967).—F.-p. data for the system N_2H_4–$N_2H_5N_3$ (m.p. 75·4°) have been determined. *Hydrazine azide monohydrazinate*, m.p. 66·4°, has been isolated. Crystallographic data are recorded. J. G. A. G.

Behaviour of hydronitrogens and their derivatives in liquid ammonia. VII. Formation of hydrazine by thermal action of incandescent filaments immersed in liquid ammonia. D. H. HOWARD, jun., and A. W. BROWNE (J. Amer. Chem.

Soc., 1933, 55, 1968—1974).—W filaments gave the highest yields of N_2H_4 (max. 0·25% of NH_3 decomposed) and these are (1) independent of the temp. of the liquid NH_3, (2) doubled by increasing the filament temp. from 2000—2400° to 2500—3400°, (3) increased by decreasing the diameter of the filament. The mechanism of the reaction is discussed and it is inferred that thermionic emission from the filament is not an important factor. J. G. A. G.

Complex acids. X. Precipitation of metallic vanadates, with a note on Moser and Brandl's method of determining vanadium. H. T. S. Britton and R. A. Robinson (J.C.S., 1933, 512—517; cf. this vol., 580).—Solutions of Na ortho-, meta-, and pyro-vanadate give with $AgNO_3$ the corresponding Ag vanadate; from "unboiled" solutions pptn. was delayed. Pptn. of vanadate from solutions of Mg, Be, Zn, Zr, and Hg begins at the same p_H as for the hydroxide, basic salt separating. With Pb and Ag pptn. occurs at a lower p_H than for the hydroxide. Pptn. of Ag_3VO_4 in presence of NaOAc and NH_3 by Moser and Brandl's method gives low and variable results. J. S. A.

Precipitation of antimonious iodide and its hydrolysis. F. François (Compt. rend., 1933, **196**, 1398—1400; cf. A., 1920, ii, 197).—If KI is added to a M/30-$SbCl_3$+3M-H_2SO_4 solution pure bright red SbI_3 is pptd.; the H_2SO_4 acts as a dehydrator and can be replaced only by conc. H_3PO_4. With less conc. H_2SO_4 an orange oxyiodide is pptd. Examination of the interaction of variable amounts of SbI_3 with a fixed vol. of H_2O or 0·1—0·6N-HI demonstrates the existence of only $2Sb_2O_3$,SbI_3, but with indications also of a solid tending towards SbOI, and a liquid in which SbI_3 and HI are present in the ratio 3 : 8. C. A. S.

Preparation of oxygen by means of ammoniacal cobalt salt solutions. W. Gluud, K. Keller, and H. Nordt (Ber. Ges. Kohlentech., 1933, 4, 210—254).—Compounds of the type $[Co(NH_3)_6]X_2$ readily absorb O_2 with loss of NH_3 producing peroxides $[(NH_3)_5Co]_2O_2X_2$ and these give up their O when heated. A small part of the O is used each time in oxidising Co$^{\cdot\cdot}$ to Co$^{\cdot\cdot\cdot}$, and this must be reduced again. The process is not economic owing to the cost of Co and NH_3 and the necessary electrolytic reduction of Co$^{\cdot\cdot\cdot}$. A detailed study of the reaction under varying conditions is given, and many other Co complexes were studied. The oxidation loss was greatly minimised by addition of $AlCl_3$ or to a smaller degree by $MgCl_2$, although these additions reduce the absorption capacity of the solution.

Higher homologues of sulphur hexafluoride. K. G. Denbigh and R. Whytlaw-Gray (Nature, 1933, **131**, 763).—Fractional sublimation of SF_6 at low temp. yields probably S_2F_{10}, b.p. near 0°, which is not readily hydrolysed. A volatile oil has been obtained which is immiscible with and not attacked by H_2O, and may be a still higher homologue. L. S. T.

Action of nitric acid on hydrogen sulphide and on certain sulphides in presence of hydrazine. A. Kesans [Keschan] (Latvij. Univ. Raksti, 1933, **2**, 311—320; cf. A., 1931, 1134).—PbS, CdS, SnS_2, SnS, Sb_2S_3, and As_2S_3 react with HNO_3 (6—10N) with production of H_2S, the solubility of the sulphides diminishing in the order given; N_2H_4 inhibits the reaction to an extent proportional to its concn., and inversely proportional to the solubility of the sulphide, to the temp., and to the concn. of HNO_3. CuS, Bi_2S_3, and Ag_2S do not react with H$^{\cdot}$ but with NO_3', and N_2H_4 very strongly inhibits this reaction. Inhibition is ascribed to oxidation of S$''$ by HNO_3, as a result of which the cation concn. rises, but [S$''$] falls; in view of the constancy of the solubility product dissolution of sulphide and oxidation by NO_3' cease. At the same time HNO_3, which acts on undissolved sulphide, is removed by N_2H_4, with formation of HN_3, N_2O, N_2, etc. R. T.

Lead chamber process. IV. Spectrographic measurements. E. Berl and K. Winnacker (Z. anorg. Chem., 1933, **212**, 113—133; cf. A., 1932, 1219).—Spectrophotometric study of the "violet acid" SO_5NH_2 and of blue H_2SO_4 solutions of HSO_5N shows their nature to be entirely different, and the colour of the latter to be due to its hydrolysis products (HNO_2). In agreement with this, the transparency max. coincides with that of N_2O_3 at low temp. and in H_2O under pressure. J. S. A.

Theory of the lead chamber reaction. W. J. Müller (Z. Elektrochem., 1933, **39**, 309; cf. this vol., 241).—The unstable intermediate HNO, formed in the reaction $H_2SO_3+HNO_2=H_2SO_4+HNO$, decomposes to form NO and not N_2O or N_2 (cf. Abel, this vol., 233). H. J. E.

Action of sulphuryl chloride on metal oxides. H. Danneel and W. Hesse (Z. anorg. Chem., 1933, **212**, 214—224).—The action of SO_2Cl_2 on oxides of Cd, Zn, Ag, Cu, Fe, Cr, Mg, Pb, and Hg gives mixtures of the chloride and sulphate in varying proportions, depending on the metal, the conditions of experiment, and the presence of impurities. Dissociation need not precede reaction, since Fe_2O_3 reacts with SO_2Cl_2 at room temp., but with Cl_2 only at 500°. J. S. A.

Decomposition of thiosulphates with sulphuric acid. W. Gluud, W. Klempt, and H. Hill (Ber. Ges. Kohlentech., 1933, 4, 203—209).—The stages are (1) $(NH_4)_2S_2O_3+H_2SO_4=(NH_4)_2SO_4+H_2S_2O_3$, (2) $H_2S_2O_3=SO_2+H_2O+S$. These proceed to the extent of ⅓ conversion followed by (3) $2(NH_4)_2S_2O_3+SO_2=2(NH_4)_2SO_4+3S$. For the complete disappearance of $(NH_4)_2S_2O_3$ and SO_2 a 3—5% excess of H_2SO_4 is necessary. The above reactions proceed only if SO_2 is destroyed or removed as formed. With rising acid concn. side reactions leading to polythionates occur and the decomp. of these gives an increased free acid concn. which was actually observed. The decomp. of $H_2S_2O_3$ is not completely represented by (2). C. I.

Ammines. VIII. Dihydroxotetrammino-chromic hydroxide and its derivatives. H. J. S. King (J.C.S., 1933, 520—523).—Trituration of $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ with Ag_2O yields $[Cr(NH_3)_4(OH)_2]OH$, as is shown by conductivity measurements. Salts of this series are not isolable but exist in solution. By the action of 2 equivs. of acid, hydroxoaquotetramminochromic salts, and with 3 equivs. of acid acidoaquotetramminochromic salts,

are obtained. The following mobilities at 0° are calc.: $[Cr(NH_3)_4(OH)_2]^{\cdot}$ 30·4; $[Cr(NH_3)_4(C_2O_4)]^{\cdot}$ 30·6; $[Cr(NH_3)_4(H_2O)(OH)]^{\cdot\cdot}$ 60·5 mhos. The following *compounds* are described:

$[Cr(NH_3)_4(H_2O)(OH)](NO_3)_2$;
$[Cr(NH_3)_4(H_2O)(OH)]I_2$;
$[Cr(NH_3)_4(H_2O)(OH)]C_2O_4$;
$[Cr(NH_3)_4(H_2O)(OH)](C_6H_2O_7N_3)_2$;
$[Cr(NH_3)_4(C_2O_4)](C_6H_2O_7N_3)$;
$[Cr(NH_3)_4(H_2O)(NO_3)](NO_3)_2$;
$[Cr(NH_3)_4(H_2O)(C_6H_2O_7N_3)](C_6H_2O_7N_3)_2,3H_2O$.

J. S. A.

Luminous reduction of selenium dioxide. H. J. Emeleus and H. L. Riley (Proc. Roy. Soc., 1933, A, **140**, 378—387).—SeO_2 vapour reacts with MeOH, EtOH, PrOH, $COMe_2$, MeCHO, Et_2O, C_3H_4, C_2H_2, C_6H_6, PhMe, NH_3, H_2S, and CS_2 at about 400°, giving bright blue flames. All the flames have the same spectrum, the bands being attributed to the Se_2 mol. and possibly also to SeO_2. The same bands occur in the flame of Se burning in O_2. A phosphorescent flame is obtained by heating SeO_2 in an NH_3 stream at 100—300°. L. L. B.

Metallic tungstates. A. Karl (Compt. rend., 1933, **196**, 1403—1404).—Molten NaCl dissolves up to 0·5WO_3, thus: $4NaCl+2WO_3+O_2=2Na_2WO_4+2Cl_2$. NaBr, KCl, KBr, and LiCl behave similarly. If the calc. amount of a metallic oxide or carbonate be added to the mixture $NaCl+WO_3$, the corresponding tungstate is formed. Well-cryst. Cd, Zn, Mn, Fe, Ca, Ba, and Sr tungstates and artificial wolframite and hubnerite have been thus prepared. C. A. S.

Action of hydrogen peroxide on permanganate. P. Dubois (Compt. rend., 1933, **196**, 1401—1403; cf. A., 1890, 1062; 1932, 823).—The variation in the composition of the oxide MnO_n, formed by this action when the concn. of $KMnO_4$ and H_2O_2 and p_H are varied, is shown by plotting n against concn. or p_H. In no case has n a definite val., although it appears to have the vals. 1·58 and 1·88 fairly const. over certain intervals. C. A. S.

Rhenium. I. Potassium rhenichloride and organic derivatives of quadrivalent rhenium. H. Schmid (Z. anorg. Chem., 1933, **212**, 187—197).—Solutions of K_2ReCl_6, which may be conveniently prepared by electrolytic reduction of $KReO_4$, using a Hg cathode, undergo hydrolysis to $ReO_2,2H_2O$, and consequently do not obey Beer's law. The following *compounds*, obtainable also from $ReCl_4$, are described: $ReCl_4,X_2,2HCl$, where $X=C_6H_4Me\cdot NH_2$, C_9H_7N, or C_5H_5N. J. S. A.

Induced reactions and the higher oxides of iron. W. Manchot (J. Physical Chem., 1933, **37**, 655—656).—A criticism (cf. Hale, A., 1930, 41). H. J. E.

Thermal degradation of complex cyanides of iron. A. Perret and A. Gislon (Bull. Soc. chim., 1933, [iv], **53**, 283—293).—The progressive thermal decomp. of various ferri- and ferro-cyanides in vac. at temp. up to 650° was studied quantitatively and, on the basis of the observations, the following schemes are adduced: $Na[K]_4Fe(CN)_6 \xrightarrow{>450^\circ} 4Na[K]CN+Fe+2C+N_2$, a similar scheme applying to the Li salt but here interaction of LiCN with Fe above 600° gives $LiCN_2$: $Ag_4Fe(CN)_6 \longrightarrow 4Ag+Fe(CN)_2+2(CN)_2$, 10% of N_2 $\xrightarrow{315-410^\circ}$ also being obtained at 440°: $2K_3Fe(CN)_6 \longrightarrow K_2Fe[Fe(CN)_6]+K_4Fe(CN)_6+(CN)_2$(57%) + $(CN)_x$, and at > 450° further decomp. of the complex cyanides into KCN, Fe, C, and N_2 occurs. Decomp. of $Na_2[Fe(CN)_5NO]$ begins at 200° and at < 450° $\longrightarrow Na_2Fe[Fe(CN)_6]+Na_4Fe(CN)_6+3NO+1{\cdot}5(CN)_2$, the solid residue being a mixture and not $Na_2Fe(CN)_4$ as stated by Etard and Bemont (A., 1885, 233); at > 450° further decomp. of the ferrocyanides gives N_2. *$Be_2Fe(CN)_6,6{\cdot}8H_2O$* [prep. from $Be(OH)_2$ and $H_4Fe(CN)_6$ described] decomposes above 200° to give Be_3N_2, Fe, C, and N_2, hydrolysis of the intermediate $Be(CN)_2$ by remaining H_2O giving some HCN and $(NH_4)_2CO_3$. Similarly $Mg_2Fe(CN)_6 \longrightarrow Mg(CN)_2$ (I) + $Fe(CN)_2$ (II), followed by $6(I) \longrightarrow 6MgCN_2+6C \longrightarrow 2Mg_3N_2+6C+4N_2$, and $(II) \longrightarrow Fe+2C+N_2$, a little HCN and H_2O also being evolved; above 450° pure N_2 is obtained. The decomp. $Ca_2Fe(CN)_6 \xrightarrow{650^\circ} 2CaCN_2$(75% yield) $+Fe+N_2+(CN)_2$ (with some HCN and its products of hydrolysis > 500°) confirms the earlier work of Pincass (A., 1922, i, 532), the Sr and Ba salts decomposing similarly although only 20% $\xrightarrow{>300^\circ}$ of $BaCN_2$ is obtained. Decomp. of $Zn_2Fe(CN)_6 \longrightarrow 2Zn(CN)_2$ (III) $+N[Fe(CN)_2]$ (IV) followed by (III) $\longrightarrow 2ZnCN_2+2C \longrightarrow 2Zn+4C+2N_2$ and (IV) $\longrightarrow Fe+2C+N_2$, a similar scheme applying to $Cd_2Fe(CN)_6$. J. W. B.

Metal carbonyls. XIX. Iron carbonyl hydride. W. Hieber and H. Vetter (Z. anorg. Chem., 1933, **212**, 145—168; cf. this vol., 476).—Pure $Fe(CO)_4H_2$ has been isolated by fractionation of the product of the action of H_2SO_4 on Fe(CO)- treated with NaOH. It has m.p. −70°; v.p. from −10° to −50° is given by $6{\cdot}122-1337/T$, mol. heat of evaporation 6·11 kg.-cal. $Fe(CO)_4H_2$ does not react with dry HCl or HI; with I, $Fe(CO)_4I_2$ is formed. Methylene-blue is quantitatively reduced, and the active H may be so determined. C_5H_5N and *o*-phenanthroline yield the stable *compounds* $Fe(CO)_4H_2,(C_5H_5N)_x$, $Fe(CO)_4H_2,2C_{12}H_8N_2$; the H in the latter compound no longer reduces methylene-blue. J. S. A.

Decomposition products of potassium thionitroprusside. G. Scagliarini and F. Gentile (Atti R. Accad. Lincei, 1933, [vi], **17**, 398—401; cf. A., 1928, 160).—An aq. solution of $K_4[Fe(CN)_5NOS]$ when kept for 10 days decomposes giving KNO_2, $K_4Fe(CN)_6$, S, $Fe(OH)_2$, and $Fe(OH)_3$, whilst considerable quantities of N_2 and NO are evolved. The NOS group is probably loosened from the complex and reacts thus: $4(NOS)'=N_2+2NO_2'+4S$, whilst the resulting aquopentacyanide is transformed into ferrocyanide and $Fe(OH)_2$. These reactions and the behaviour with finely divided Ag ($\longrightarrow Ag_2S$, $[Fe(CN)_5(H_2O)]''''$, and NO_2') agree with the proposed structure, $K_4\left|Fe^{II}(CN)_5N\begin{matrix}O\\ \diagdown\\ \diagup\\ S\end{matrix}\right|$. O. J. W.

Ammines. VII. Action of acids on dihydroxotetramminocobaltic hydroxide. H. J. S. KING (J.C.S., 1933, 517—520; cf. A., 1932, 585).—The action of 3 equivs. of acid on $[Co(NH_3)_4(OH)_2]OH$ introduces an acid group into the complex. With *o*-$C_6H_4(OH)\cdot CO_2H$ and HI, however, $[Co\{Co(NH_3)_4(OH)_2\}_3]X_6$ (X=NO_3, I) were obtained. $[Co(NH_3)_4(H_2O)(SO_4)]NO_3$ was shown by conductivity measurement to be hydrolysed in aq. solution, but not $[Co(NH_3)_4X^{II}]NO_3$, where $X^{II}=C_2O_4$, $CH_2(CO_2)_2$. Mobilities of the last two cations at 0° are, respectively, 19·1 and 26·0 mhos. The following *compounds* were prepared: $[Co(NH_3)_4(C_2O_4)]NO_3,H_2O$; $[Co(NH_3)_4(H_2O)Cl](C_6H_2O_7N_3)_2,2H_2O$; $[Co(NH_3)_4(H_2O)(C_6H_2O_7N_3)](C_6H_2O_7N_3)_2,4H_2O$; $[Co\{Co(NH_3)_4(OH)_2\}_3]I_6,3H_2O$. J. S. A.

Nickel carbonyl. Mechanism of its formation from nickel sulphide and carbon monoxide. M. M. WINDSOR and A. A. BLANCHARD (J. Amer. Chem. Soc., 1933, **55**, 1877—1883).—At room temp., the optimal yield of $Ni(CO)_4$ is obtained by shaking CO with a liquid originally containing *M*-NaOH, 0·1*M*-Na_2S, and 0·5*M*-$NiSO_4$ (cf. A., 1929, 526). It is suggested that the tendency of NiS to dissociate into its atoms is such as to permit the formation of $Ni(CO)_4$ in the presence of S-removing reagents. NiSe under similar conditions yields $Ni(CO)_4$. The reaction $CO+H_2O\longrightarrow H_2+CO_2$ occurs to a small extent in the presence of OH′ ions under the catalytic influence of $Ni(CO)_4$. J. G. A. G.

From the ponderable to the imponderable. O. HAHN (Science, 1933, **77**, 397—403).—A review of the limits of qual. and quant. detection of substances. L. S. T.

Consideration of the "rare" elements in mineral analysis. V. M. GOLDSCHMIDT, H. HAUPTMANN, and C. PETERS (Naturwiss., 1933, **21**, 362—365).—It is considered that insufficient attention is paid to the occurrence of rare metals in silicate minerals, and methods are suggested for their determination. A. J. M.

Indirect volumetric determinations. J. EISENBRAND (Arch. Pharm., 1933, **271**, 315—316).—The theoretical reasoning of Bordeianu (this vol., 582) is incorrect. R. S. C.

Use of salicylic acid as an acidimetric standard. S. ŠKRAMOVSKY (Coll. Czech. Chem. Comm., 1933, **5**, 143—147).—Salicylic acid purified by sublimation can be used in aq. EtOH instead of $H_2C_2O_4$ or BzOH as a standard in acidimetry. With *N*-KOH the factors are identical, and with 0·1*N*-KOH only 0·10% < those obtained using these two acids. J. W. B.

Colorimetric p_H determination with the simplified original Tödt drop apparatus. G. GOLLNOW (Chem.-Ztg., 1933, **57**, 374—375). E. C. S.

Determination of the alkalinity of boiler water. J. LEICK.—See B., 1933, 495.

Photometric micro-analysis of drinking and service water. IV. Determination of phosphorus. C. URBACH.—See B., 1933, 494.

Determination of water of crystallisation. V. CERCHEZ and C. PANAITESCU (Bull. Soc. chim., 1933, [iv], **53**, 243—248).—H_2O of crystallisation evolved at < 135° is removed by refluxing with xylene, and its vol. is measured. Pure anhyd. $H_2C_2O_4$ may be made by refluxing $H_2C_2O_4,2H_2O$ with C_6H_6. J. S. A.

Nephelometric determination of chloride. I. M. KOLTHOFF and H. YUTZY (J. Amer. Chem. Soc., 1933, **55**, 1915—1922; cf. A., 1922, ii, 383).—The effect of various factors on the stability and turbidity of AgCl suspensions has been investigated. 0·0008—0·42 mg. Cl′ in 10 c.c. is determined to within 2% by adding the solution rapidly, with shaking, to 25 c.c. of EtOH containing 1 c.c. of 0·5*N*-$AgNO_3$ and 5 c.c. of 0·5*N*-HNO_3 and comparing nephelometrically after 1 hr. with simultaneously prepared standards. SO_4'' interferes. J. G. A. G.

Determination of chloride in presence of bromide and iodide. M. STSCHIGOL (Z. anal. Chem., 1933, **92**, 420—425).—To 10 c.c. of the solution are added 35—40 c.c. of 2% aq. NH_3 and sufficient $AgNO_3$ solution to react with all the halide present; 50 c.c. of the filtrate, which contains all the Cl′ as $Ag(NH_3)_2Cl$, are treated with 3—4 g. of Na_2CO_3 and 15—20 c.c. of Na_3AsO_3 solution (8 g. of As_2O_3 and 21 g. of Na_2CO_3 per 100 g.), and the whole is boiled until the pptd. Ag_3AsO_3 is reduced. The Ag is collected, dissolved in HNO_3, and titrated with NH_4CNS. Reduction of the AgCl in presence of AgBr and AgCl yields high results. H. F. G.

Micro-determination of bromine in presence of chlorine and iodine. S. H. BERTRAM (Biochem. Z., 1933, **261**, 202—206).—By oxidising with $KMnO_4$ in a solution maintained suitably acid with $KHSO_4$ and K_2SO_4 ionised halogens can be separated (Cl′ is not oxidised; I′ is converted into HIO_3) and 0·01—0·005 mg. of Br′ can be determined in material containing ≯ 0·3 g. of Cl′ and 0·0025 g. of I′. N compounds and metals (other than alkali metals) must be absent. The Br is twice distilled into a solution of KI and $KHSO_4$ and the liberated I titrated with 0·001*N*-$Na_2S_2O_3$. W. McC.

Determination of bromide in mixtures of silver chloride and bromide. D. H. P. VOLLER (Chem. Weekblad, 1933, **30**, 331—332).—The mixture is distilled with a solution of NaCl and $KMnO_4$, H_2SO_4 being added gradually through a side tube, and the Cl_2 and Br evolved are passed into cold *N*-NaOH. The NaBr and NaOBr formed are oxidised (by the NaOCl present) by adding Na_2SO_4 and H_3BO_3 and heating to 85—90°; after cooling, H_2O_2 is added, and the excess is removed by boiling the slightly alkaline solution. $NaBrO_3$ is then determined by adding KI and HCl, with a trace of molybdic acid, and titrating with $Na_2S_2O_3$. The reagents must be free from NO_3'. H. F. G.

Determination of fluorine by Carnot's method. H. HERLEMONT and J. DELABRE (Compt. rend., 1933, **196**, 1502—1504; cf. A., 1892, 911).—The low result obtained by this method is due to loss of F as HF; it is completely avoided (even if the substance analysed contains SiO_2) by adding about 2 g. of Fe–Si (75% Si)

for each (approx.) 0·1 g. F, drying thoroughly, and then adding H_2SO_4 and heating at 140° etc. as usual. An accurate result is equally obtained if the gases evolved in the ordinary method are passed over Fe–Si before absorption. C. A. S.

Determination of sulphates. V. Njegovan and V. Marjanovic (Arh. Hemiju, 1933, 7, 36—41).—Berlin porcelain filter-crucibles are unsuitable for the determination of SO_4'' as $BaSO_4$, owing to adsorption of sol. salts from the reaction mixture; these may, in the absence of SO_4'', amount to > 50 mg. after 40 determinations. Ordinary Gooch crucibles should be used. R. T.

Colour reaction for sulphur dioxide. Z. Rudnitski (Ukrain. Chem. J., 1932, 7, [Sci.], 226—227).—SO_3'' gives characteristic colorations with various tanning extracts in the presence of $Fe(CN)_6'''$, Cr_2O_7'', or CrO_4''. Oak-bark extract is the most suitable for the purpose, giving an intense reddish-violet colour. Should NH_3 be present, the reaction should be performed in slightly acid solution. R. T.

Reactions for detection of sulphites and thiosulphates, and the sensitivity of reactions for sulphides and sulphates. N. S. Schub (Ukrain. Chem. J., 1932, 7, [Sci.], 189—202).—SO_3'' (< 0·04 mg.) instantly decolorises 2 c.c. of 0·035% fuchsin; the optimal p_H is 8·2. S'', if present, should first be pptd. as PbS by adding an alkaline solution of $PbCO_3$. S_2O_3'' (< 11 mg. per c.c.) is detected by boiling with aq. HCl, when turbidity due to separation of S appears; $Fe(CN)_6''''$, AsO_3''', S'', and SO_3'' should first be pptd. as Zn salts. SO_4'' (< 1 mg. per c.c.) gives a ppt. or turbidity with 10% $BaCl_2$ in 2*N*-HCl; $Fe(CN)_6''''$, AsO_3''', S'', and SO_3'' should be removed. S'' (< 0·0017 mg. per c.c.) gives a brown coloration with aq. Na_2PbO_2. F', Cl', Br', I', CN', CNS', NO_3', AcO', PO_4''', CO_3'', and C_2O_4'' do not interfere with the above reactions. R. T.

Colorimetric determination of hydrogen sulphide in water by means of phosphotungstic acid. L. N. Lapin and W. O. Hein.—See B., 1933, 526.

Separation of sulphur bases from sulphur acids, and detection of the elements in group II. C. Candea and L. I. SaucIuc (Bul. Soc. Chim. Romania, 1933, **14**, 179—181).—The separation of group II elements by the solubility of As, Sb, and Sn sulphides in aq. NaOH is described. F. R. S.

Assay of nitrogen monoxide. J. C. Krantz, jun., W. F. Reindollar, and C. J. Carr.—See B., 1933, 505.

Detection of nitrites and their determination by means of the step-photometer. L. Jendrassik and E. Falcsik-Szabó (Biochem. Z., 1933, **261**, 110—115).—For the determination of NO_2' in concn. equiv. to 0·2—35·0 mg. per litre by means of the step-photometer a mixture of α-$C_{10}H_7{\cdot}NH_2$ (I) and a derivative (II) of p-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (*e.g.*, novocaine) is used. (II) is diazotised and coupled with (I) producing a stable sol. dye. The error, when the concn. is 1—15 mg. per litre, is ±0·6% and outside these limits ±2·5%. The procedure may also be applied colorimetrically using hæmatoxylin as standard colour. W. McC.

Detection of nitrites in water by peroxide reagents. G. Carpentier.—See B., 1933, 494.

Volumetric determination of phosphoric acid and of potassium by the use of a new method of washing. T. Khoi (Ann. Falsif., 1933, **26**, 217—222).—A circular piece of filter-paper is cut to fit the bottom of a Gooch crucible, and replaces the usual asbestos. The filtration of the NH_4 phosphomolybdate ppt. and of the $K_3Co(NO_2)_6$ ppt. is satisfactory, and the method facilitates washing. The results obtained are trustworthy. E. B. H.

Gravimetric determination of phosphate ion, and the solubility product of magnesium ammonium phosphate. N. A. Tananaev and P. S. Savtschenko (Ukrain. Chem. J., 1932, 7, [Sci.], 203—225).—The solubility S of $MgNH_4PO_4{,}6H_2O$ (I) in H_2O at 25° is 0·0987 g. per litre, and the solubility product is $7{\cdot}88\times10^{-14}$. S is slightly lowered by < 0·02*N*-NH_4Cl, but is greatly augmented at higher concn., whilst aq. NH_3 lowers S at all concns. These results are ascribed to the acid reaction of aq. NH_4Cl and to reversal of ionisation due to excess of $NH_4^{\cdot}$. It is concluded that the concn. of NH_4Cl in solutions from which (I) is to be pptd. should not exceed 0·02*N*. R. T.

Modification of Bettendorff's arsenic test, with adaptation for mercury determination. W. B. King and F. E. Brown (Ind. Eng. Chem. [Anal.], 1933, **5**, 168—171).—The sensitivity of Bettendorff's test for As is increased 10—100 times by the presence of 0·00001*M*-$HgCl_2$; the coloration also appears more rapidly and the test can be made in a lower concn. of HCl. At this dilution $HgCl_2$ does not form a turbidity with $SnCl_2$. The rate of formation of the coloration is a function of the concn. of $HgCl_2$. By comparing the rate with that in presence of known concns. of $HgCl_2$ the test may also be used to determine $HgCl_2$ at concns. < 0·00000002*M*. E. S. H.

Detection of traces of carbon monoxide in air. H. Hartridge.—See B., 1933, 525.

Accuracy of the rapid semi-micro-determination of carbon dioxide in air. L. W. Winkler.—See B., 1933, 493.

Colorimetric determination of oxalic acid. C. A. Mitchell (Analyst, 1933, **58**, 279).—The orange-red colour produced on adding 5 c.c. of 1% $NaVO_3$ solution and 3 c.c. of H_2O_2 to 5 c.c. of 0·1% $H_2C_2O_4$ is matched against that from a standard (sensitiveness 3 in 10^4). Tartaric acid gives a similar reaction (sensitiveness 12 in 10^4), citric acid a yellow colour, and succinic and malic acids transient red colours. Mineral acids produce a pervanadic acid of similar colour, and must be absent. J. G.

Determination of silica in silicates by the difference method. G. T. Galfajan and W. M. Tarajan (Z. anal. Chem., 1933, **92**, 417—420).—$H_2C_2O_4$ cannot be used for the quant. conversion of fluorides into carbonates, and the method of Tananaev and Pertschik (A., 1932, 922) is therefore not satis-

factory. Sulphates are, however, quantitatively converted into orthophosphates by $NaPO_3$. In the method recommended, the powdered sample (0·5—1 g.) is heated with 1 : 1 H_2SO_4 and 5—7 c.c. of HF, and after a second evaporation with H_2SO_4, 3—4 g. of $NaPO_3$ are added and the whole is ignited to const. wt. The method is rapid (5—6 hr.), and the results are accurate to within 0·1%, even in presence of 29% of Al_2O_3. H. F. G.

Determination of potassium by sodium cobaltinitrite. J. E. SCHUELER and R. P. THOMAS (Ind. Eng. Chem. [Anal.], 1933, **5**, 163—165).—Variations of standard procedure are described with respect to the temp. of pptn., the pptg. medium, the time of pptn., washing of the ppt., and the titration. The method is very accurate for 3—10 mg. K and may be used for <1 to >50 mg. NH_4 salts interfere and org. matter should not be present. E. S. H.

Gravimetric and polarographic determination of total alkali. V. MAJER (Z. anal. Chem., 1933, **92**, 401—405).—If total alkali (K+Na) is determined by weighing as sulphate and calculating as K_2O (Na_2O), the error does not exceed 0·20% if $\geq$ 1% of Na_2O (K_2O) is present. Weighing as chloride or as sulphate gives practically the same result if the mixture contains $\geq$ 5% of one alkali, whilst the gravimetric and polarographic methods agree closely if $\geq$ 10% of one alkali is present. H. F. G.

Preparation of sodium hydroxide solutions of low carbonate content by centrifugation. N. ALLEN and G. W. LOW, jun. (Ind. Eng. Chem. [Anal.], 1933, **5**, 192).—Conc. aq. solutions of NaOH (1 : 1) are freed from undissolved Na_2CO_3 by centrifuging. E. S. H.

Reagent for lithium in presence of other alkalis; separation of lithium and magnesium; determination of lithium; separation of arsenites and arsenates. T. GASPAR Y ARNAL (Ann. Chim. Analyt., 1933, [ii], **15**, 193—194).—Na_3AsO_4 in alkaline EtOH solution gives with $Li^{\cdot}$ a pale pink ppt. which may be used for the determination of Li. Mg, but not Li, is pptd. by Na_3AsO_3. Hence, AsO_4''' may be pptd. by $Li^{\cdot}$+aq. NH_3+EtOH; AsO_3''' in the filtrate may be pptd. by Mg. J. S. A.

Detection of silver in bismuth salts. J. F. REITH.—See B., 1933, 505.

Gravimetric determination of beryllium and thorium using selenous acid, and its application to their separation from certain elements. J. KOT'A (Chem. Listy, 1933, **27**, 79—84, 100—105, 150—154, 194—197).—Be^{II} ($\leq$ 0·5 mg.-% BeO) is quantitatively pptd. from alkaline solution as basic selenite by H_2SeO_3; $NH_4^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, and $Li^{\cdot}$ do not interfere with the reaction. The BeO obtained by ignition of the ppt. is readily sol. in HNO_3 or HCl. Zr^{IV} and Bi are quantitatively pptd. by H_2SeO_3 from acid solutions (0·2*N*-HCl and 0·4*N*-HNO_3, respectively); Be, if also present, can be pptd. from the filtrate by adding aq. NH_3 and H_2SeO_3. Al, Mn, U, Mg, Ca, Ce^{III}, La, and Y do not interfere with the determination of Zr by this method. Ti is pptd. from acid solution, and Th^{IV} from neutral solution in presence of NH_4OAc. Should considerable quantities of Be be present, the pptn. of Th should be repeated. R. T.

Quantitative separation of small amounts of zinc from material rich in iron. F. G. HILLS (Ind. Eng. Chem. [Anal.], 1933, **5**, 201).—The solution in HCl is almost neutralised with aq. NH_3, excess of Na citrate is added, the solution is diluted, and H_2S is passed until the ZnS ppt. coagulates. The ppt. is filtered, dissolved in dil. HNO_3, evaporated to dryness, redissolved in HCl with addition of NH_4Cl, and Zn is determined in the solution by the usual methods. E. S. H.

Colorimetric determination of thallium [in rodenticides]. P. A. SHAW.—See B., 1933, 494.

Quantitative separation of aluminium from iron. J. HASLAM (Analyst, 1933, **58**, 270—272).—Fe was pptd. at the b.p. with H_2S in the presence of tartaric acid followed by an excess of aq. NH_3, and the filtrate, after removal of the FeS, acidified with HCl, neutralised with aq. NH_3 to Me-orange, and 2·5 c.c. of NH_3 added in excess. Al was then pptd. by slow addition of hydroxyquinoline sulphate solution (5 c.c. in excess), coagulated at 90°, and filtered after 4 hr. (cf. A., 1927, 848). The max. recorded error on 0·0048—0·0289 g. of Al in the presence of 0·1 g. of Fe''' is 0·1 mg. J. G.

Detection and determination of iron in drinking water. J. PRESCHER.—See B., 1933, 526.

Conductivity titrations of basic chromium sulphate solutions. E. R. THEIS, A. W. GOETZ, and R. G. SNYDER.—See B., 1933, 505.

Potentiometric determination of molybdenum in steel. P. DICKENS and R. BRENNECKE.—See B., 1933, 510.

Molybdenum and tungsten content of minerals. G. VON HEVESY and R. HOBBIE (Z. anorg. Chem., 1933, **212**, 134—144).—The mineral is fused with NaOH, the melt acidified with HCl, and Mo and W oxidised with H_2O_2. Excess of $BaCl_2$ is added, and then NaOH. The ppt. is immediately filtered, dried by means of $COMe_2$, and heated in Cl_2 at 600°. The sublimate is dissolved in acid, and MoS_2 pptd. in presence of Cu. The MoS_2 is dissolved in acid, Cu removed electrolytically, and Mo determined colorimetrically by the method of Montignie (A., 1930, 313). W is determined *X*-ray spectrographically in the filtrate from the MoS_2 pptn. The mean Mo content of igneous rocks is $1·5\times10^{-5}$; that of W $6·9\times10^{-5}$. J. S. A.

Volumetric determination of uranium with potassium dichromate as reagent and the application of the method to the indirect titration of minute quantities of sodium. I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1933, **55**, 1871—1876).—$\leq$ 6 mg. of U^{IV} in 100 c.c. is determined to within 1% by titration with $K_2Cr_2O_7$ in the presence of H_3PO_4 with Ba diphenylaminesulphonate and $FeCl_3$ as indicator (cf. A., 1926, 40; 1931, 1026). 0·08—0·8 mg. of Na is determined to within 5% by pptn. as Na uranyl Zn acetate (A., 1928, 859) which is reduced in H_2SO_4 solution (*loc. cit.*) and the U^{IV} titrated with $K_2Cr_2O_7$ as above. J. G. A. G.

Determination of small amounts of antimony in copper. B. PARK and E. J. LEWIS (Ind. Eng. Chem. [Anal.], 1933, **5**, 182—183).—Addition of $KMnO_4$ and $MnSO_4$ to the acid solution of Cu ppts. MnO_2 and carries down the Sb. The ppt. is dissolved in HCl, repptd. as Sb_2S_3, again dissolved in HCl and evaporated, and a measured amount (0·1 c.c.) is transferred to a hollow bored in the top of a pure graphite electrode. Sb is then determined spectrographically. 1 part of Sb in 5×10^6 parts of Cu can be determined. E. S. H.

Electrical resistance thermometers as applied to human calorimetry. G. F. SODERSTROM (Rev. Sci. Instr., 1933, [ii], **4**, 285—288).—Constructional details are given. C. W. G.

Temporary depression of zero point of sensitive mercury thermometers. F. HOPPLER (Chem.-Ztg., 1933, **57**, 394).—By comparison of two specially prepared thermometers, it is shown that the depression of zero point by previous heating for 5 min. in boiling H_2O disappears only after about 1 week. F. R. S.

U-type mercury thermoregulator. J. B. RAMSEY (Ind. Eng. Chem. [Anal.], 1933, **5**, 218—219).—A method of maintaining a supply of H_2 at the Hg contact is described. E. S. H.

Cryostat for low and very low temperatures. P. WOOG, J. GIVAUDON, and F. DAYAN (Bull. Soc. chim., 1933, [iv], **53**, 240—243).—A thermostat for the range 0° to −60° is described. J. S. A.

Thermostat for lower temperatures. T. J. B. STIER and W. J. CROZIER (J. Gen. Physiol., 1933, **16**, 757—766).—The thermostats maintain precise temp. (±0·001°) down to 0°, and the temp. may be rapidly adjusted. H. G. R.

Determination of absolute thermal coefficients of expansion of liquids. J. ZAHRADNICEK (Physikal. Z., 1933, **34**, 386).—A modified Dulong and Petit apparatus is described in which two U-tubes, connected together, are used. A. J. M.

Absorption trough for use with the Bürker universal spectroscope. W. SIERADZKI (Z. physiol. Chem., 1933, **216**, 138). J. H. B.

New type of spectrographic slit. G. FASSIN (J. Opt. Soc. Amer., 1933, **23**, 186—188).—A satisfactory bilateral slit which can be made without specialised labour is described. C. W G.

Focus of a concave grating spectrograph. D. L. MACADAM (J. Opt. Soc. Amer., 1933, 23, 178—181).—A method for mounting a 21-ft. concave grating and slit so that the focus will lie on a previously determined track is based on a precise knowledge of the nature of the general focal curve. C. W. G.

Moving film cameras in X-ray analysis. B. W. ROBINSON (J. Sci. Instr., 1933, **10**, 165—169).—In one type the film is wrapped around a cylinder which rotates at the same speed as the crystal about an axis perpendicular to the *X*-ray beam and to the axis of rotation of the crystal. In the other a cylindrical film moves parallel to its own axis, which is also the axis of rotation of the crystal. C. W. G.

Exact focussing *X*-ray spectrometer. T. JOHANSSON (Z. Physik, 1933, **82**, 507—528). A. B. D. C.

Concave grating spectrograph. J. E. MACK and J. R. STEHN (J. Opt. Soc. Amer., 1933, **23**, 184—185; cf. *ibid.*, 1932, **22**, 245).—A graph from which the optimum width of a concave grating may be found for any practical case is given. C. W. G.

Uranium as a source of continuous ultraviolet radiation. S. J. LEWIS (Chem. and Ind., 1933, 464—465).—A spark between U electrodes provides a continuous spectrum down to 2100 Å. The advantage of this over a line spectrum (W steel) in absorption spectrum work is illustrated by means of photographs of the spectrum of C_6H_6 in C_6H_{14}. D. R. D.

Preparation of test plates for the microscope. L. C. MARTIN (J. Sci. Instr., 1933, **10**, 187—188).—Directions for obtaining a uniform film of realgar on glass are given. C. W. G.

Thiel's method of absolute colorimetry. E. LANDT (Z. Elektrochem., 1933, **39**, 310—312; cf. A., 1932, 1225).—The grey solutions described by Thiel have an extinction coeff. < 0·5 for red light. The solutions lack the stability and freedom from sensitivity to light which were claimed. H. J. E.

Absolute colorimetry with grey solutions. A. THIEL (Z. Elektrochem., 1933, **39**, 312—316).—A reply (cf. preceding abstract). Further details of technique are given. A new and more stable solution is described. H. J. E.

Crystalline quartz double monochromator. W. E. FORSYTHE and B. T. BARNES (Rev. Sci. Instr., 1933, [ii], **4**, 289—294).—Settings on a spectral line can be repeated to 0·1 Å. at 3000 Å. C. W. G.

Durable glass electrode. D. A. MACINNES and D. BELCHER (Ind. Eng. Chem. [Anal.], 1933, **5**, 199—200).—The electrode and liquid junction device described give results for p_H which are in good agreement with accepted vals. E. S. H.

Technique of the glass electrode. T. F. G. HEPBURN (J. Soc. Leather Trades Chem., 1933, **17**, 268—270).—The apparatus can be made efficient only in the absence of H_2O, low temp., and electrical disturbances. The results are affected by the proximity of other metallic apparatus. Other necessary precautions are detailed D. W.

One-valve amplifier for p_H determinations with glass electrode. R. NORDBØ (Tidsskr. Kjemi, 1933, **13**, 62—66).—An amplifier of simple construction has been devised, based on the work of Dubois and Stadie (A., 1929, 1262; 1931, 58), which can be employed in potentiometric measurements in conjunction with either a glass or a quinhydrone electrode. H. F. H.

High-capacity hydrogen electrodes. A. EUCKEN and K. BRATZLER (Ber. Ges. Kohlentech., 1933, **4**, 290—304).—Measurements of H electrode potential using a Pt net against suitable Hg electrodes in acid and alkaline solutions of varying concns. and for varying c.d. are recorded and compared with those calc. It is shown that in both acid and alkaline solution up

to a c.d. of 1·25 amp. per sq. dm. the current strength is determined by the rate of diffusion of $H^{\cdot}$. The alkaline solution is only slightly inferior to the acid in current yield so that cheaper electrode materials than Pt are possible. With a platinised C cylinder, the alkaline solution was markedly inferior. In neither case did stirring make much difference. The C electrode deteriorated with use probably through adsorption except in strongly acid solution. C. I.

Radioactive contamination of ionisation chamber materials. J. A. BEARDEN (Rev. Sci. Instr., 1933, 4, [ii], 271—275).—Cold-rolled steel was least contaminated, followed, in order, by amber, brass, and Cu. Surfaces once cleaned should be kept in an atm. of MeBr, CO_2, or N_2. C. W. G.

Micro-fractionating column for liquids having low heat of vaporisation. P. E. WESTON (Ind. Eng. Chem. [Anal.], 1933, 5, 179—180).—The apparatus may be used with 10—15 c.c. of liquid. Total condensation occurs at the head of the column and all the vapour must flow past the bulb of the thermometer. E. S. H.

Head for laboratory fractionating columns. E. C. WAGNER and J. K. SIMONS (Ind. Eng. Chem. [Anal.], 1933, 5, 183—184).—An all-glass apparatus is described. E. S. H.

Apparatus and methods for precise fractional-distillation analysis. IV. Standardisation of low-temperature fractionation-analysis apparatus and method of using automatic recording and control. W. J. PODBIELNIAK (Ind. Eng. Chem. [Anal.], 1933, 5, 171—178; cf. A., 1931, 704).—The apparatus formerly described has been improved by using an automatic recording and control mechanism, with further development and standardisation of the fractionating unit. E. S. H

Determination of osmotic pressures by isothermal distillation. II. M. ULMANN (Z. physikal. Chem., 1933, **164**, 318—326).—The apparatus previously described (A., 1931, 1367) has been modified so as to make it suitable for use with solutions in AcOH. Measurements with dil. solutions of maltose octa-acetate and glucose penta-acetate (I) have shown the apparatus to be satisfactory. With (I) there is appreciable association even in 0·2% solution. R. C.

Continuous extractor of large capacity. C. M. MCCAY (Ind. Eng. Chem. [Anal.], 1933, 5, 213).—The apparatus takes a 10—45 kg. charge of material. E. S. H.

Device for removing "frozen" glass stoppers from reagent bottles. C. WIRTH (Ind. Eng. Chem. [Anal.], 1933, 5, 217). E. S. H.

Burette with greaseless stopcock. W. A. LALANDE, jun. (Rev. Sci. Instr., 1933, [ii], 4, 296).—The liquid contained in the burette acts as a lubricant for a plunger ground at the lower end and actuated by a screw. C. W. G.

Micro-burette. M. MALMY (J. Pharm. Chim., 1933, [viii], **17**, 469—474).—The attachment of a fine glass tip to the jet of a micro-burette allows very small drops to be delivered. F. O. H.

Laboratory screw clamp. W. A. SPERRY (Ind. Eng. Chem. [Anal.], 1933, 5, 188). E. S. H.

Air pressure for blast lamps. G. W. THIESSEN and J. E. WERTZ (Ind. Eng. Chem. [Anal.], 1933, 5, 201).—A vac. cleaner may be adapted. E. S. H.

Windshield for Saybolt viscosimeter. F. J. VITOVEC, jun. (Ind. Eng. Chem. [Anal.], 1933, 5, 212).—A glass screen is described. E. S. H.

Use of the slide rule in calculating hydrogen-ion concentration and p_H values. M. C. SANZ (Ind. Eng. Chem. [Anal.], 1933, 5, 218). E. S. H.

Collodion membrane filters. I, II. I. ASHESHOV (J. Bact., 1933, **25**, 323—337, 339—357).—The prep. and uses of graduated membrane filters are described. A. G. P.

Regulating the air supply of microburners. C. A. DALY (Science, 1933, **77**, 413).—Details of a satisfactory method are described. L. S. T.

Buchner filters with heating jackets. W. GURR (Chem. Fabr., 1933, 6, 248—249).—(1) A Buchner filter may have a simple steam jacket; (2) the filter and jacket may be double the usual depth; (3) the steam may also be led through the filter plate by passages, so reducing the filtration area. The last arrangement allows the temp. in the cake to be raised from 70° to 90° and in many cases the more rapid filtration more than compensates for the loss of filtration area. C. I.

Bar rider for accurate weighing. L. RAMBERG (Arkiv Kemi, Min., Geol., 1933, **11 A**, No. 7, 24 pp.).—In order to attain an accuracy of 0·001 mg. in weighings made on a microbalance, the position of the rider on the notch of the beam must be reproducible to 0·007 mm., and its angle of inclination from the vertical should not exceed 0·2°. A special rider, consisting of a short rod of quartz glass, permits much greater accuracy than the usual form. It is placed horizontally in the notches of the beam by means of a special transporter. The importance of calibrating the beam of a microbalance before employing a rider is also emphasised. H. F. H.

Priestley as a practical chemist. T. S. PATTERSON (Nature, 1933, **131**, 690).—A criticism. L. S. T.

Priestley as a practical chemist. A. N. MELDRUM (Nature, 1933, **131**, 801).—A reply (cf. preceding abstract). L. S. T.

Geochemistry.

Formaldehyde in dew. N. R. DHAR and A. RAM (Nature, 1933, **131**, 800; cf. A., 1932, 1106).—Dew from Allahabad contains approx. 0·0015 g. of CH_2O (I) per litre. It appears to be obtained from air in contact with grass, leaves, and soil. The origin of (I) is discussed. L. S. T.

Oceanography and geochemistry. V. J. VERNADSKY (Tsch. Min. Petr. Mitt., 1933, **44**, 168—192).—A lecture. L. J. S.

Boric acid in sea-water and its effect on the carbon dioxide equilibrium. K. BUCH (Nature, 1933, **131**, 688).—Ocean-H_2O contains 15 g. B_2O_3 per cu.m. as against 0·7 usually quoted. The ratio B : Cl is $0·237—0·248 \times 10^{-3}$. The effect of H_3BO_3 on the CO_2 equilibrium of sea-H_2O is discussed. L. S. T.

Temperature and salinity of the deeper waters of the Bay of Bengal and Andaman Sea. R. B. S. SEWELL (Mem. Asiatic Soc. Bengal, 1932, **9**, 357—423). CH. ABS.

Chloride as indicator in detecting the inflowing into an inland-water lake of underground water possessing special physico-chemical properties. S. YOSHIMURA (Proc. Imp. Acad. Tokyo, 1933, **9**, 156—158).—Variation of Cl′ content with depth in lake H_2O is the best indicator of the inflow of underground H_2O with special physico-chemical properties. J. W. S.

Algal sediments of Andros Island, Bahamas. M. BLACK (Phil. Trans., 1933, **B**, **222**, 165—192).—Algal deposits of characteristic structure, consisting of $CaCO_3$ sediment mechanically entrapped, are described. The structure is best developed in regions of lower salinity than that of open ocean. J. S. A.

Mineral springs of Chechnya (Caucasus). G. A. MAXIMOVICH (J. Appl. Chem., Russia, 1932, **5**, 1066—1077).—Results of analyses are recorded. CH. ABS.

Activity of non-pathogenic bacteria utilising mineral matter in the thermal water of Aix-les-Bains and Aix-Burtscheid. I. A. SCHLOEMER (Z. Unters. Lebensm., 1933, **65**, 470—476).—The content of Fe is 1000 times, of Ca and SiO_2 many times, higher in the slimy sediment of the Kaiserbad spring at Aix than in the H_2O. This is due to the action of Fe-, Ca-, and Brussoff's SiO_2-bacteria. The sediment is also richer in Al, which was not found by Feder (*ibid.*, 1923, **46**, 339) in the H_2O, but is now shown to be present. E. C. S.

Corrections and additions to the diagram for the determination of felspars by Fedorov's method. V. V. NIKITIN (Tsch. Min. Petr. Mitt., 1933, **44**, 117—167).—The crystallographic directions of a series of felspars are plotted on a stereographic projection with reference to the axes of the optical ellipsoid, and the results given by extinction angles on certain faces and section planes are tabulated. Several new chemical analyses are given of felspars of which the optical data are determined. L. J. S.

Position of the cotectic line between potash felspar and plagioclase and their relations. H. L. ALLING (Amer. J. Sci., 1933, [v], **25**, 471—576).—A discussion of the views of Doggett (J. Geol., 1929, **37**, 712), Vogt (Norsk. Videnskaps Akad., 1926, 58; 1931, 225), and Harker ("Natural History of Igneous Rocks," 1909, 250). C. W. G.

Intrusive igneous rocks of the Muswellbrook–Singleton district. II. Savoy Sill. H. G. RAGGATT and H. F. WHITWORTH (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 194—233).—The Savoy intrusion is partly of the simple sill type and partly phacoidal, and is of tertiary age. Analyses of the constituent dolerite and syenite are given. C. W. G.

Composition and structure of artificial spherulites. H. W. MORSE, J. D. H. DONNAY, and E. OTT (Amer. J. Sci., 1933, [v], **25**, 494—498).—Each spherulite fibre is probably an aggregate of variously oriented crystals, each 10^{-3} to 10^{-5} cm. (cf. A., 1932 564). C. W. G.

Occurrence of sulphur, organic matter, nitrogen, and water in phosphate rock. W. L. HILL, H. L. MARSHALL, and K. D. JACOB (J. Assoc. Off. Agric. Chem., 1933, **16**, 260—276).—The determination of org. C by the dry combustion of rocks has been employed as a standard, and the results obtained have been compared with those by other methods. Colorimetric methods with sugar give high results and those obtained by comparison with tannic acid are probably high, although they agree fairly well for certain types of rock with those obtained by the combustion of actual org. matter extracted from the rock. Colorimetric methods are unsatisfactory for rocks such as Tennessee brown or blue rock, or Idaho phosphate. Results obtained by the direct ignition of the rock are affected by the oxidation of sulphides and org. S, whilst some of the S is expelled. Results are given for the org. C, N, S, and H_2O contents of 29 samples of natural phosphates. T. McL.

Granulite containing riebeckite and a calcareous detrital rock in the Niari basin (French Congo). R. C. SABOT (Compt. rend., 1933, **196**, 1517—1519).—Riebeckite, largely transformed into antigorite, occurs in a granulite that forms slabs in the river Bamaga near Bendé. C. A. S.

Eruptive massif of Cavallo (Constantine). L. GLANGEAUD (Compt. rend., 1933, **196**, 1515—1517).—The tertiary eruptive rock in the neighbourhood of Cavallo (west of Jijelli, Algeria) consists, to the N.E., of microgranodiorites and quartziferous microdiorites containing phenocrysts of plagioclase (30—54% anorthite) and 5—23% of quartz; that in the centre of dacites and dacitoids containing colourless augite, with breccias of various materials. Both also contain green polychroic hornblende, and (especially the microgranodiorites) are traversed by veins of Ag- and Au-containing Cu, Pb, Zn, and Fe minerals, the rock in the neighbourhood of the veins being damouritised, kaolinised, or propylitised to considerable distances. Chlorites also abound. C. A. S.

β-Cristobalite in Australian opals. F. P. DWYER and D. P. MELLOR (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 378—382).—*X*-Ray evidence is adduced. C. W. G.

Age of a Canadian cyrtolite. O. B. MUENCH (Amer. J. Sci., 1933, [v], **25**, 487—493).—Average contents are U 0·529, Pb 0·04308, Th 0·0799%, whence the age is calc. to be 571×10^6 years. C. W. G.

Gypsum deposits of the Stopini–Salaspils–Nāvessala districts. E. ROSENSTEIN (Latvij. Univ.

Raksti, 1933, **2**, 241—288).—Dolomite inclusions (I) occur in deposits of cryst. but not of fibrous gypsum (II). Clay, if present, occurs only in (I), whilst bitumen is found in both (I) and (II). (I) is often intercalated with micro-crystals of (II). R. T.

Fibre structure and optical properties of chalcedony. C. W. CORRENS and G. NAGELSCHMIDT (Z. Krist., 1933, **85**, 199—213; cf. A., 1922, ii, 304).—Chalcedony consists of quartz, which is capable of fibre-like growth in two crystallographic directions. The double refraction, n_D 1·532 along, and 1·538 across, the direction of the fibres, is distinctly < that of quartz, which is attributed to the fibre aggregate possessing a double refraction of form of opposite sense to that of quartz. Density and H_2O content indicate opal as the cementing material, with free H_2O in one case. C. A. S.

Antimony tetroxide and antimonates. G. NATTA and M. BACCAREDDA (Z. Krist., 1933, **85**, 271—296; cf. A., 1932, 450).—$Pb_2Sb_2O_7$, $Ca_2Sb_2O_7$, Sb_2O_4, and the corresponding minerals romeite, bindheimite, and stibiconite are all cubic, space-group O_h^7, with a 10·44, 10·25, 10·24, 10·25, 10·37—10·43, and 10·26 Å., and 8, 8, 16, 8, 8, and 16 mols. in the unit cell, respectively. Sb_2O_4 is best written $Sb^{III}{}_2Sb^{V}{}_2O_8$, the positions of Sb^{III} and Sb^{V} being distinguishable in the lattice; the position of one O remains unoccupied in the pyroantimonates. The H_2O in stibiconite (Sb_2O_4,H_2O) has noi nfluence on the structure; this also holds for that in the CaO-containing group of Sb ochres, $CaO,Sb_2O_5,3H_2O$ and $3CaO,2Sb_2O_5,8H_2O$, which have the same structure as romeite, and are designated hydroromeites. Similarly the $PbCO_3$ often present in bindheimite is an impurity removable by acid, and without effect on the structure. Analyses of hydroromeite (2), stibiconite, cervantite, and bindheimite (2) are given. C. A. S.

Molybdenite at Azegur (Morocco). R. E. GROSCLAUDE (Arch. Sci. phys. nat., 1933, [v], **15**, 93—126).—Molybdenite occurs at Azegur 80 km. south of Marrakesh, as lamellæ 0·5—3 cm. across, disseminated through a garnet hornfels (containing in places diopside, duparcite, and idocrase), which forms lenses in cryst. Cambrian limestone and schists, and is strongly metamorphosed by intrusive granite. This has mineralised the hornfels to distances dependent on the volatility of the mineral, molybdenite occurring nearest, then chalcopyrite, and furthest blende, with hæmatite, pyrite, pyrrhotite, galena, and mispickel as accessories. Analyses of 12 associated rocks are given. The molybdenite is best separated by pulverising to pass through a no. 200 sieve, and flotation with cresol, a little H_2SO_4 being added. The concentrates contain 2·1—3% MoS_2. In places the molybdenite is oxidised to molybdite. C. A. S.

Mineralogy of Volhynian topaz deposits. L. L. IVANOV (Bull. Acad. Sci. U.S.S.R., 1933, 421—444).—Topaz occurs in association with orthoclase, biotite, muscovite, smoky quartz, amethyst, and beryl in pegmatite veins of red Korosten granite, and in the products of their weathering. R. T.

Formation of syngenite. J. CHLOUPEK (Chem. Listy, 1933, **27**, 197—199).—Syngenite is pptd. as follows: $Ca(IO_3)_2,6H_2O+2K_2SO_4=CaSO_4,K_2SO_4,H_2O+2KIO_3+5H_2O$. R. T.

Plagioclase in the trachydolerite of Pauliberg, Burgenland. H. WIESENEDER (Tsch. Min. Petr. Mitt., 1933, **44**, 199—204).—The plagioclase of this extrusive igneous rock shows frequent twinning on (001), which is ascribed to the alkali content of the rock. L. J. S.

Petrography of the Čista-Jechnitz granite massif, Bohemia. A. ORLOV (Tsch. Min. Petr. Mitt., 1933, **44**, 205—210).—The acid granite and oligoclase-granodiorite forming this mass were derived by crystallisation-differentiation from the same magma. Chemical analyses of the rocks are given. L. J. S.

Composition and genesis of the alkali-rocks of South Africa. S. J. SHAND (Tsch. Min. Petr. Mitt., 1933, **44**, 211—216).—Occurrences of alkali-rocks in the Bushveld, Transvaal, give support to Daly's hypothesis of the origin of such rocks. A granitic magma has assimilated the limestone into which it was intruded, and the heavier lime silicates have separated, leaving alkalis in excess of the ratio $R_2O : Al_2O_3 : SiO_2 = 1 : 1 : 6$. L. J. S.

Genesis of colloidal pyrrhotite and other minerals in the Bottino mine. C. L. SAGUI and A. JOURDAN (Compt. rend., 1933, **196**, 1424—1426).—In the narrower parts of the vein in the Bottino mine (near Florence), where cooling would be more rapid, galena is replaced by pyrites and pyrrhotite. In the light of Stevens' results (cf. Econ. Geol., 1933, **28**, 1) this is explicable and due to the increased proportion of Na in the later solidifying portions of the magma, giving rise to Na sulphides, which in turn would convert PbS into the more fusible Na_2S,PbS (cf. A., 1926, 494), causing it to be carried on more readily past a cooler place, and at the same time convert Fe into pyrrhotite. This on removal of the Na sulphide by H_2O would be deposited in colloidal form, and be converted into pyrites by excess of S. C. A. S.

Alkali metals in minerals. R. BOSSUET (Compt. rend., 1933, **196**, 1381—1383; cf. this vol., 363).—The method previously described shows the presence of Li, Na, K, Rb, and Cs in 17, 29, 27, 21, and 14, respectively, of the 29 alkali-containing minerals examined. Rb and Li occur in both orthose and microcline (cf. A., 1911, ii, 122); Rb and Cs chiefly in minerals containing K. C. A. S.

Beryllium and helium. (LORD) RAYLEIGH (Nature, 1933, **131**, 724).—The richest of about 40 different beryls contains 29·2 cu. mm. of He per g. of beryl, *i.e.*, 1 He to $2·41\times10^4$ Be. Beryls from the younger rocks contain little He, whilst those from older rocks contain a relatively large amount, supporting the view that the He has accumulated as the result of at. disintegration of Be. Using the He-rich mineral a possible α-activity of beryl was estimated at $\geqslant 1·47\times10^7$ α-particles per g. per annum requiring $5·43\times10^{10}$ years for the observed He to accumulate. Be–Al foil gave an activity of $1·55\times10^8$ α-particles per g. per annum requiring a period of $1·05\times10^{11}$ years; both of these periods are too long, and hence the He in beryl cannot be related to existing emission of α-

particles. The α-ray activity of Be found by Lange and Raitt (Physical Rev., 1933, [ii], **43**, 585) also will not account for the He in beryl. L. S. T.

James coal of New Zealand. W. PENSELER (Fuel, 1933, **12**, 166—181).—Geologically the James coal marks a transition stage from fresh-H_2O to marine beds. It is black, dull, hard, and tough, has a conchoidal fracture, and is resistant to weathering. Its composition (H_2O 6·0, volatile matter 51·5, fixed C 38·0, ash 4·5, S 4·5%) approaches that of a cannel coal. Microscopical examination of thin sections (illustrated) shows that the coal contains an abnormal amount of resistant plant entities, mainly cuticle and suberised tissue, but the absence of spore material distinguishes it from ordinary cannel coal. The evidence suggests that the coal has been formed from forest offal which had drifted into brackish H_2O in a sheltered region of an estuary. A. B. M.

Lignin theory of the origin of coal. P. FISCHER. —See B., 1933, 496.

Refractive index of agriculturally important compounds and changes under the influence of potassium chloride. J. H. HELLMERS and R. KÖHLER (Z. Pflanz. Düng., 1933, **29**, A, 309—320).—Changes in n of $Al(OH)_3$, $Fe(OH)_3$, kaolin, humic material, etc. after treatment with KCl are recorded and the utilisation of optical methods in the examination of the course of weathering of minerals is discussed. A. G. P.

Investigation and classification of soils on physicochemical lines. P. VAGELER and F. ALTEN (Ernähr. Pflanze, 1933, **29**, 121—132).—The authors' views on, and methods of examining, the nutrient balance of soils are summarised. A. G. P.

Soil zones of Australia. J. A. PRESCOTT (Soil Res., 1933, **3**, 133—145).—A general survey. A. G. P.

Red soils of the Tripolitanian plateau. A. COMEL (Soil Res., 1933, **3**, 126—132).—Chemical and mineralogical data are presented and the formation of these soils is discussed. A. G. P.

Principles and scheme of a general soil system. A. A. J. DE 'SIGMOND (Soil Res., 1933, **3**, 103—126).—Modifications of existing systems are proposed. A. G. P.

Soil survey of the Nyah, Tresco, Tresco West, Kangaroo Lake (Vic.), and Goodnight (N.S.W.) settlements. J. TAYLOR, F. PENMAN, T. J. MARSHALL, and G. W. LEEPER (Comm. Australia, Counc. Sci. Ind. Res., Bull. No. 73, 1933, 47 pp.).

Organic Chemistry.

Relation between physical properties of organic molecules and their constitution and configuration. J. TIMMERMANS (Inst. int. Chim. Solvay, Conseil Chim., 1931, **4**, 191—237; Chem. Zentr., 1933, i, 201—203).

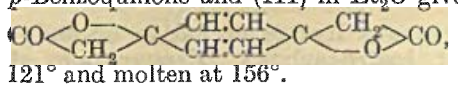
Free radicals. W. SCHLENK (Inst. int. Chim. Solvay, Conseil Chim., 1931, **4**, 503—515; Chem. Zentr., 1933, i, 203).

Catalytic oxidation of organic compounds in the vapour state. G. CHARLOT.—See this vol., 680.

Thermal decomposition of *iso*butane into primary products. L. F. MAREK and M. NEUHAUS (Ind. Eng. Chem., 1933, **25**, 516—519).—Expressed as mols. per 100 mols. of *iso*butane decomposed in a SiO_2 vessel, the proportions of products at 571° were H_2 and butylene 63·0, CH_4 and propylene 34·5, and C_2H_6 2·5; at 617° the corresponding figures were 63·0, 36·0, and 1·5. As calc. by Rice the ratio of CH_4 to H_2 should be 0·91 at 600° instead of 0·56 found. A. G.

Configurative relationship of hydrocarbons. V. Optical rotations of hydrocarbons of the *iso*propyl series. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1933, **100**, 769—773; cf. A., 1931, 709).—l-α*β*-*Dimethyldecane*, b.p. 112°/20 mm., $[M]_D^{25}$ −0·51°, is prepared by the action of MeI in dry Et_2O on Et *d*-methylheptylacetate followed by dehydration with $H_2C_2O_4$ and subsequent catalytic hydrogenation. l-β-iso*Propylpentane*, b.p. 113—114°/760 mm., $[M]_D^{25}$ −1·05°, is prepared in a similar manner from $CHMePr^{\alpha}\cdot CO_2H$. In the series $R\cdot CHMePr^{\beta}$ the direction of rotation is independent of the weight of R. A. L.

Causes of the simultaneous production of Δ^{α}- and Δ^{β}-butene by catalytic dehydration of butyl alcohol by alumina. C. MATIGNON, H. MOUREAU, and M. DODÉ (Compt. rend., 1933, **196**, 973—977).—Dehydration of BuOH with an Al_2O_3 catalyst (I) at 330—380° affords 85% of Δ^{α}- (II) and 15% of Δ^{β}-butene (III) if (I) is pptd. and washed with dil. alkali. Preps. of (I) containing traces of acidic substances cause isomerisation of (II) to (III), and yield 90% of the latter. After being heated to 650° such catalysts again give (II). A. C.

Condensation of isoprene. H. VON EULER and L. AHLSTRÖM (Arkiv Kemi, Min. Geol., 1932, **11** A, No. 2, 18 pp.).—Isoprene (I) and $AlCl_3$ in $CHCl_3$ give an amorphous *complex*, $C_{10}H_{16},2SbCl_3$, m.p. > 300°, from which (I) could not be regenerated [showing rapid condensation of (I)]. Dipentene similarly gives a *complex*, $C_{10}H_{16},3SbCl_3,7SbOCl$. (I) is polymerised by varying amounts of $SbCl_3$ at 110°; removal of Sb from the resultant products by hot dil. HCl gives amorphous substances. Polymerisation of (I) is retarded by $(NPh)_3$, carotene, quinol, AcCl, or Cu wire; little retardation occurs with $(NPh)_2$+amyl nitrate (II). The variable rate (due to unknown impurities) of self-polymerisation of (I) is not compensated by a definite amount of a catalyst such as (II). The product from (I) and $CO(NH_2)_2$ at 110° is N-free. Coloured and gummy products are formed from (I) and keten (III) at 60—70° and 75—105°. *p*-Benzoquinone and (III) in Et_2O give the *dilactone*  , decomp. from 121° and molten at 156°. H. B.

Direct oxidation of acetylene by air. P. MONDAIN-MONVAL and R. WELLARD (Compt. rend., 1933, **196**, 1226—1228).—The concn. zones of mixtures of air and C_2H_2 at atm. pressure which will undergo inflammation at a mean temp. of 310° when heated at const. vol. narrows from 17—85% of C_2H_2 by vol. at a heating rate of 40° per min. to 35—70% at 25° per min. Outside this zone, a faint green luminescence and lowering of pressure, not due to polymerisation of C_2H_2, are observed. An oil is formed which responds to Schiff's reagent and is similar to that obtained from saturated hydrocarbons (A., 1930, 167). Similar phenomena with mixtures at an initial pressure of 4 atm. are described. A. C.

Polymerisation and rupture of hydrocarbons under the influence of electric discharge. R. V. DE SAINT-AUNAY (Chim. et Ind., 1933, **29**, 1011—1025).—Hydrocarbons are submitted to a high-frequency silent electric discharge so that the primary products are rapidly removed and condensed, and thus the effect of temp. and p.d. are studied. Three main types of reaction are observed: (*a*) polymerisation due to activation of the C·H linking, (*b*) dehydrogenation due to a greater degree of activation of this linking which becomes more important the more saturated is the initial hydrocarbon, and (*c*) the rupture of C·C linkings and subsequent union of the radicals to more complex compounds. With C_2H_2 only (*a*) occurs, rapid condensation affording gaseous products (4% of the condensed C_2H_2), H_2, C_2H_4, and C_2H_6, the yields of which increase to a max. and then diminish to 0 as the time of reaction is prolonged. The liquid products, b.p. 10°/23 mm., contain $(C_2H_2)_3$ (partly crystallises at −60°; *Ag* derivative $C_6H_4Ag_2,2AgNO_3$) in which $CHMe(C{:}CH)_2$, $(\cdot CH_2\cdot C{:}CH)_2$, and $(:C\cdot CH{:}CH_2)_2$ are present, since cold 5%$KMnO_4$ affords HCO_2H, $EtCO_2H$, and H_2CO_3, and O_3 gives $(\cdot CH_2\cdot CO_2H)_2$, CH_2O, and HCO_2H, but no MeCHO or AcOH. With C_2H_4 the gaseous products consist of H_2 and C_2H_2 (*b*) from which C_2H_6, C_4H_8, and C_6H_{14} are obtained, and fractionation of the liquid products affords Δ^{α}-butene and Δ^{α}-hexene (*a*). C_2H_6 affords (*a*) C_2H_4, C_2H_2, and H_2, and by hydrogenation of these or by (*c*), CH_4 and higher saturated hydrocarbons. CH_4 gives H_2, C_2H_6, C_2H_4, and a little C_2H_2. With C_6H_6 the gaseous product (produced regularly throughout) contains H_2 52, C_2H_2 32·8, C_2H_4 7·2, C_2H_6 7·2, higher ethylenic hydrocarbons 0·8%. In the liquid products, b.p. 105—145°/14 mm., (*a*) gives dihydrodiphenyl whence by (*b*) Ph_2 and H_2 are obtained, Ph_2 alone being formed with a more intense discharge. The gaseous products from PhMe are H_2 58, C_2H_2 etc. 10, C_2H_4 8, C_2H_6 4, CH_4 14, higher olefines 3%, the liquid products, b.p. 110—145°/18 mm., containing dihydroditolyls, b.p. 130—136°/17 mm., and $(\cdot CH_2Ph)_2$ (crystallises at −30°). C_6H_{14} gives H_2 43, C_2H_6 6, C_2H_4 21, CH_4 12, C_3H_6 11, C_3H_8 6% ($C_3H_6 \longrightarrow CH_4+C_2H_2$; $C_3H_8 \longrightarrow CH_4+C_2H_4$), the liquid products, b.p. 45—120°/15 mm., containing Δ^{α}-hexene and saturated hydrocarbons $>C_9$. J. W. B.

Action of gaseous hydrogen iodide on iodo-derivatives of hydrocarbons. Preparation of ethylidene and vinyl iodides and ααα-tri-iodoethane. G. EMSCHWILLER (Compt. rend., 1933, **196**, 1028—1030).—Cold gaseous HI has no action on alkyl iodides, CH_2I_2, $CHMeI_2$ (I), CHI_3, $CMeI_3$ (II), or C_2H_4. CI_4 is reduced to CHI_3, and $(\cdot CH_2I)_2$ to (I). Vinyl iodide (III) adds HI yielding (I), but no reaction occurs with conc. aq. HI. The primary product from $(CHI{:})_2$ and HI (1 mol.) is ααβ-tri-iodoethane (IV), but a mixture of this with (I), (III), and I is obtained. The yield of (III) is 70% if (IV) is heated. The sole product from 2 mols. HI is (I). $(CI_2{:})_2$ and HI yield (II), probably through the intermediate $CHI_2\cdot CI_3$. A. C.

Conjugated systems. XII. Addition of bromine, hydrogen bromide, and hypobromous acid to α-bromobutadiene. I. E. MUSKAT and L. B. GRIMSLEY (J. Amer. Chem. Soc., 1933, **55**, 2140—2145).—α-Bromobutadiene (I) and Br (1 mol.) in light petroleum, $CHCl_3$, or AcOH at −20° to about 50° give *ααδ-tribromo-Δ$^{\beta}$-butene*, b.p. 94°/8 mm., oxidised by O_3 to $CH_2Br\cdot CO_2H$, $H_2C_2O_4$, and $CHO\cdot CO_2H$ (qual. test), and by $KMnO_4$–$COMe_2$ to $CH_2Br\cdot CO_2H$. (I) and dry HBr afford *αα-dibromo-Δ$^{\beta}$-butene*, b.p. 71—72°/24 mm. (ozonolysis products, AcOH and $H_2C_2O_4$), which with Br in $CHCl_3$ gives *ααβγ-tetrabromobutane*, b.p. 148—150°/25 mm. These results are contrary to those of Ingold and Smith (A., 1931, 1391), who state that γδ-addition of Br and HBr to (I) occurs, but agree with the principles previously developed (A., 1930, 1553). (I) absorbs 1 mol. of HOBr to give *αδ-dibromo-α-hydroxy-Δ$^{\beta}$-butene* (ozonolysis products, $CH_2Br\cdot CO_2H$ and $H_2C_2O_4$). H. B.

Direct iodination of monosubstituted acetylenes. T. H. VAUGHN and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1933, **55**, 2150—2153).—CI:CR are prepared from CH:CR and I in liquid NH_3. When R=Ph, tolyl, or vinyl, iodination occurs rapidly at −34° and the yields are almost quant., but when R=alkyl, reaction is slow and incomplete at −34° [but at 25° (in an autoclave), the yields are 15—50%; the reaction, $3I_2+8NH_3 \longrightarrow 6NH_4I+N_2$, also occurs]. CNa·CR reacts instantaneously with I in liquid NH_3. The following are prepared: α-iodo-Δ$^{\alpha}$-butinene, b.p. 83—85°/156 mm., *-hexinene*, b.p. 52·5°/6 mm., 75°/20 mm., -heptinene, b.p. 93°/21 mm., m.p. −37° to −35° (also prepared using I in Et_2O–NH_3), and -noninene, b.p. 105—107°/4 mm.; α-iodo-β-phenyl-, decomp. when heated, and -tolyl-, b.p. 135—141°/16 mm., -acetylenes. H. B.

Acetylene polymerides and their derivatives. XI. βγ-Dichloro- and αβγ-trichloro-Δ$^{\alpha\gamma}$-butadienes. G. J. BERCHET and W. H. CAROTHERS. **XIII. Action of chlorine on divinylacetylene.** D. D. COFFMAN and W. H. CAROTHERS. **XIV. Dihydrochloride of divinylacetylene.** D. D. COFFMAN, J. A. NIEUWLAND, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1933, **55**, 2004—2008, 2040—2047, 2048—2051).—XI. βγδ-Trichloro-Δ$^{\alpha}$-butene or αβγδ-tetrachlorobutane and MeOH–KOH give *βγ-dichloro-Δ$^{\alpha\gamma}$-butadiene* (I), b.p. 39—41°/80 mm., 98°/760 mm., whilst αβγγδ-pentachlorobutane and MeOH–KOH afford *αβγ-trichloro-Δ$^{\alpha\gamma}$-butadiene* (II), b.p. 33—34°/7 mm., and *αββγ-tetrachloro-Δ$^{\gamma}$-butene*, b.p. 41—42°/7 mm. (oxidised by aq. $KMnO_4$ to ααβ-

trichloropropionic acid). Condensation products of (I) with naphthaquinone or maleic anhydride could not be prepared. (I) polymerises much more readily than chloroprene (β-chloro-$\Delta^{\alpha\gamma}$-butadiene) (III); the polymeride is an opaque, non-plastic, hard mass which is almost entirely devoid of rubber-like properties. The ease of spontaneous polymerisation of the various chlorobutadienes is (I) (III) (II) > α-chloro-$\Delta^{\alpha\gamma}$-butadiene αβγδ-tetrachloro-$\Delta^{\alpha\gamma}$-butadiene.

XIII. Divinylacetylene (I) and Cl_2 (1·22 mols.) in CCl_4 at −50° give 25% of *αδ-dichloro-$\Delta^{\beta\gamma\epsilon}$-hexatriene* (II), b.p. 38°/1 mm., 45—46°/3 mm., also formed in small yield from (I) and aq. HOCl, which is oxidised (aq. $KMnO_4$) to $CH_2Cl{\cdot}CO_2H$, is reduced (H_2, PtO_2, EtOAc) to *n*-hexane, contains 1 active Cl (aq. Na_2CO_3), and with Cl_2 (1·18 mols.) in CCl_4 at 5—10° affords *αγδζ-tetrachloro-$\Delta^{\beta\delta}$-hexadiene* (III), b.p. 84—89°/2 mm. (oxidation product, $CH_2Cl{\cdot}CO_2H$). (II) and MeOH–KOH or –NaOMe yield *γ-chloro-$\Delta^{\alpha\gamma\delta\epsilon}$-hexatetraene*, b.p. 55°/54 mm., 82°/163 mm. [reduced (as above) to *n*-hexane; oxidation product, $H_2C_2O_4$], whilst (II), HCl (*d* 1·18), and CuCl at 27° afford *αδδ-trichloro-$\Delta^{\beta\epsilon}$-hexadiene*, b.p. 100—103°/4 mm. (oxidation product, $CH_2Cl{\cdot}CO_2H$). (I) and Cl_2 (1·6 mols.) at −50° to −40° give (III), which is chlorinated further to *αβγοεζ-hexachloro-Δ^{γ}-butene* (IV), b.p. 110—112°/2 mm., m.p. 58—59°, and is converted by MeOH–KOH into *αγδ-trichloro-$\Delta^{\beta\delta\epsilon}$-hexatriene*, b.p. 50°/1 mm., and *γδ-dichloro-$\Delta^{\alpha\beta\delta\epsilon}$-hexatetraene* (V), b.p. 38—40°/8 mm. Saturation (apparent) of (I) with Cl_2 in CCl_4 gives about 10% of (IV) and (mainly) a viscous syrup (*M* 360—370) of the composition $C_6H_6Cl_6$. (IV) is not attacked by O_3 and hot HNO_3 but is completely destroyed by alkaline $KMnO_4$. Of the above Cl-derivatives, (V) only shows any marked tendency to polymerise spontaneously and gives a dark brown brittle resin. (II) polymerises slowly when kept to a viscous syrup; the polymerisation is greatly accelerated by pressure.

XIV. Divinylacetylene, 12*N*-HCl, and CuCl at 0° or room temp. give 53% of (probably) *αγ-dichloro-$\Delta^{\beta\delta}$-hexadiene*, b.p. 80—82°/17 mm. (oxidation products, AcOH and $CH_2Cl{\cdot}CO_2H$), converted by MeOH–KOH and NaOAc–AcOH into *γ-chloro-α-methoxy-*, b.p. 88—92°/30 mm., and *γ-chloro-α-acetoxy-*, b.p. 84—85°/3 mm., *-$\Delta^{\beta\delta}$-hexadiene*, respectively; the use of $CaCl_2$ for CuCl reduces the yield to 6·8%. The (intermediate) monohydrochloride is produced in poor yield and has not yet been obtained pure.

H. B.

Acetylene polymerides and their derivatives. XII. Addition of *p*-thiocresol to divinylacetylene. W. H. Carothers (J. Amer. Chem. Soc., 1933, **55**, 2008—2012).—Divinylacetylene (I) (1 mol.) and *p*-$C_6H_4Me{\cdot}SH$ (2 mols.) give (after 10 days at room temp. or in 5 hr. when irradiated by light from a mercury arc) about 80% of *αζ-di-p-tolylthiol-Δ^{γ}-hexinene*, m.p. 74·5—75·5° (*γδ-dibromide*, m.p. 46—47·5°), which is oxidised by $KMnO_4$ in $COMe_2$ to β-*p*-toluenesulphonylpropionic acid, by $KMnO_4$ and dil. H_2SO_4 in cold CCl_4 to *αζ-di-p-toluenesulphonyl-hexane-γδ-dione*, m.p. 200—201° (softens at 197—200°), and by $KMnO_4$ and dil. H_2SO_4 in cold $CHCl_3$ to *αζ-di-p-toluenesulphonyl-Δ^{γ}-hexinene* (II), m.p. 157—158° (*γδ-dibromide*, m.p. 172·5—173·5°). (II) and conc. H_2SO_4 afford *αζ-di-p-toluenesulphonylhexan-γ-one*, m.p. 134—135°. The above reactions confirm the structure of (I).

H. B.

Chromic oxide as a catalyst for the decomposition of methyl alcohol. G. F. Huttig and K. Strial [with H. Kittel].—See this vol., 681.

Catalytic activity of zinc oxide [in the decomposition of methyl alcohol. O. Kostelitz and G. F. Huttig.—See this vol., 681.

Reactions and properties of boron fluoride in methyl alcohol. L. A. O'Leary and H. H. Wenzke (J. Amer. Chem. Soc., 1933, **55**, 2117—2121).—The v.-p. curve of the system BF_3–MeOH indicates that the equilibrium, $BF_3+MeOH \rightleftharpoons MeOH,BF_3$ (I), exists. The conductivity curve indicates that on dilution (I) decomposes to $OMe{\cdot}BF_2$ and HF. *Hg methoxyfluoborate* (II), $Hg(OMe,BF_3)_2$, is prepared from (I) and HgO; (I) and NH_3 give the *compound*, BF_3,NH_3. The existence of (II) probably explains the role of HgO in catalysing acetal formation, for which a possible mechanism (cf. Nieuwland *et al.*, A., 1930, 745, 1160; 1931, 1404) is suggested. The acid characteristics of org. compounds containing a donor atom and an ionisable H are greatly increased by addition of BF_3.

H. B.

Dehydration of tertiary alcohols by anhydrous copper sulphate. A. Meyer and M. Tuot (Compt. rend., 1933, **196**, 1231—1233).—βδ-Dimethylhexan-δ-ol, βε-dimethylhexan-δ-ol, ββδ-dimethylheptan-δ-ol, βε-dimethylheptan-ε-ol, ββδζ-trimethylheptan-δ-ol, *βγε-trimethylhexan-γ-ol*, b.p. 72°/21 mm., *βδ-dimethyloctan-δ-ol*, b.p. 97°/27 mm., and *βδη-trimethyloctan-δ-ol*, b.p. 100°/17 mm., are dehydrated by anhyd. $CuSO_4$ yielding *βο-dimethyl-Δ^{δ}-heptene* (?), *βε-dimethyl-Δ^{β}-hexene*, *βδ-dimethyl-Δ^{δ}-heptene*, *βε-dimethyl-Δ°-heptene*, *ββδζ-trimethyl-Δ^{γ}-heptene*, *βγε-trimethyl-Δ^{β}-hexene*, *βδ-dimethyl-Δ^{δ}-octene*, and *βοη-trimethyl-Δ^{δ}-octene*, respectively.

A. C.

Action of phosphorus pentachloride on ethers. F. C. Whitmore and D. P. Langlois (J. Amer. Chem. Soc., 1933, **55**, 1518—1520).—The action of PCl_5 on ethers (various types) and acetals, $CH_2(OR)_2$, is studied. Di*iso*amyl ether (1 mol.) and PCl_5 (1 mol.) at 100° (bath) give HCl (approx. 0·5 mol.), liquid products, b.p. 50—168°, but no *iso*amyl chloride; Pr^{β}_2O (1 mol.) and PCl_5 (2 mols.) at 110° afford $Pr^{\beta}Cl$ (24%), much HCl, and material, b.p. 36—130°; dibenzyl ether boiled with PCl_5 yields CH_2PhCl (I), $CHPhCl_2$ (II), $CPhCl_3$ (III), and (probably) a benzyl phosphate; $CH_2Ph{\cdot}OBu$ similarly furnishes BuCl (19%), (probably) impure $CHPrCl_2$, and traces of (I), (II), and (III); benzyl amyl ether gives *n*-amyl chloride (18%), (I), and (II); benzyl *sec.*-amyl ether affords impure β-chloropentane (39%); diphenylene oxide yields a *chlorodiphenylene oxide*, m.p. 94—96° (80%); $CH_2(OBu)_2$ furnishes BuCl (23%), $CH_2Cl{\cdot}OBu$ (?), and Bu chlorobutyl ether (?); *formaldehyde di-neopentyl acetal*, b.p. 176—177·5°/737 mm. (cf. Conant *et al.*, A., 1929, 680) gives traces of amyl (mainly *tert.*) chlorides.

H. B.

Cyclic acetals. II. Formation of cyclic acetals of δε-dihydroxy-$\Delta^{\beta\zeta}$-octadiene. C. P. Burt, D. R.

CORCORAN, and I. V. KOERBER (J. Amer. Chem. Soc., 1933, **55**, 2068—2070; cf. A., 1930, 319).—The following *ethers* of δε-dihydroxy-$\Delta^{\beta\zeta}$-octadiene (I) are prepared from (I) and the requisite aldehyde or ketone at about 70° using a little 40% H_2SO_4 as the catalyst: iso*butylidene*, b.p. 101°/14 mm. (86% yield), *amylidene*, b.p. 110—111°/5 mm. (65%), iso*amylidene*, b.p. 106°/4 mm. (77%), β-*phenylpropylidene*, b.p. 160—161°/4 mm. (79%), and *diethylmethylene*, b.p. 100—101°/4·5 mm. (57%). Ethers could not be obtained from (I) and Me hexyl ketone, COMeBu$^\gamma$, methylheptenone, citral, COPhMe, $COPh_2$, Ph styryl and styryl Me ketones, *p*-tolylbenzophenone, *o*-$C_6H_4Cl\cdot CHO$, *o*-$NO_2\cdot C_6H_4\cdot CHO$, *o*-$OH\cdot C_6H_4\cdot CHO$, and *p*-$OMe\cdot C_6H_4\cdot CHO$. H. B.

Decomposition of glycol diacetate by alcohol in feebly alkaline medium. E. M. BELLET (Compt. rend., 1933, **196**, 1506—1508).—Glycol diacetate (I) (0·1 mol.), EtOH (100 c.c.), and *N*-EtOH–KOH (II) (6 c.c.) heated at 100° (bath)/3 hr. gives EtOAc = decomp. of 32% of (I). Addition of (II) in 6 portions of 1 c.c. at intervals of 1 hr. under the same conditions gives EtOAc = 55% of (I), indicating that decomp. is not solely a function of the amount of (II) used, but is a function of the time during which alkalinity persists H. B.

Action of periodic acid on α- and β-glycerophosphoric acids. P. FLEURY and R. PARIS (Compt. rend., 1933, **196**, 1416—1418).—α-Glycerophosphoric acid (I) is oxidised rapidly (10 min. at 20—22°) to CH_2O (1 mol.) and (probably) $CHO\cdot CH_2\cdot O\cdot PO_3H_2$ (Ba salt), whilst the β-isomeride (II) is practically unaffected during 24 hr. The amount of (I) in mixtures of (I) and (II) can thus be determined. H. B.

Chlorides of alkylsulphurous acids. P. CARRE and D. LIBERMANN (Compt. rend., 1933, **196**, 1419—1421).—The following reactions occur between $CH_2R\cdot OH$ and $SOCl_2$: (i) $CH_2R\cdot OH + SOCl_2 \longrightarrow CH_2R\cdot O\cdot SOCl + HCl$; (ii) $CH_2R\cdot O\cdot SOCl + CH_2R\cdot OH \longrightarrow SO(O\cdot CH_2R)_2 + HCl$; (iii) $SO(O\cdot CH_2R)_2 + SOCl_2 \longrightarrow 2CH_2R\cdot O\cdot SOCl$; (iii) is the slowest reaction. Addition of 1 mol. of EtOH to 1·15 mols. of $SOCl_2$ gives (after 48 hr. at room temp.) 95% of EtO·SOCl; the following are similarly prepared: Me, Pr$^\alpha$, Bu$^\beta$, *iso*amyl, *Bu*$^\alpha$, b.p. 88°/45 mm., β-*chloroethyl*, b.p. 100—101°/300 mm., n-*heptyl* (I), and n-*decyl* (II) *chlorosulphites*. (I) and (II) decompose on distillation and are converted into *Pr*$^\alpha$ *heptyl*, b.p. 148—150°/18 mm., and *Et* n-*decyl*, b.p. 188—190°/30 mm., *sulphite*, respectively. Chlorosulphites could not be prepared from $SOCl_2$ and *sec.*- or *tert.*-alcohols. Contrary to Voss and Blanke (A., 1931, 462), Pr$^\beta$OH and $SOCl_2$ give Pr$^\beta$Cl, C_3H_6 (partly polymerised), and a little $SO(OPr^\beta)_2$. *Pr*$^\beta$, b.p. 71—73°/75 mm., sec.-*Bu*, b.p. 75—77°/60 mm., and cyclo*hexyl*, decomp. when distilled, *chlorosulphites* are prepared from $SO(OR)_2$ and $SOCl_2$. Treatment of SO(OR)(OR′) with $SOCl_2$ gives RO·SOCl and R′O·SOCl; *allyl*, b.p. 32°/40 mm., *benzyl*, not distillable, and *Bu*$^\gamma$, unstable, *chlorosulphites* are thus prepared. cyclo*Hexyl Pr*$^\alpha$, b.p. 175—178°/60 mm., *benzyl Me*, b.p. 137—138°/18 mm., and *Pr*$^\alpha$ *Bu*$^\gamma$, b.p. 99—100°/30 mm., *sulphites* are described. H. B.

Reaction of mercaptans with carbon tetrachloride. H. J. BACKER and P. L. STEDEHOUDER (Rec. trav. chim., 1933, **52**, 437—453).—Mercaptans, CCl_4, and NaOEt in EtOH give, not substances, $C(SR)_4$ (A., 1877, 294), but mixtures of disulphides and trithio-orthoformic esters. In this way are prepared Me_3, Et_3, *Pr*$^\alpha_3$, b.p. 158—160°/12 mm., *Bu*$^\alpha_3$ (I), b.p. 188—189°/12 mm., *Bu*$^\gamma_3$ (II), m.p. 64·5°, b.p. 115—117°/4 mm. [previously (A., 1932, 830) believed to be $C(SBu^\gamma)_4$], and $(CH_2Ph)_3$ *trithio-orthoformate*, and the corresponding disulphides. $SHBu^\gamma$, however, gives also O-*Et* S-*Bu*$^\gamma_2$ *dithio-orthoformate* (III), b.p. 118—120°/12 mm., oxidised by HNO_3 to $Bu^\gamma SO_3H$ (see below) and by acid $KMnO_4$ to *ethoxymethylenedi*(tert.-*butylsulphone*), $OEt\cdot CH(SO_2Bu^\gamma)_2$, m.p. 85°, and decomposed by alkali. Oxidation of the trithio-esters by H_2O_2 and AcOH gives the sulphonic acids, but acid $KMnO_4$ gives the following *methylenedi*(*alkylsulphones*), $CH_2(SO_2\cdot R)_2$: Me_2-, Et_2-, *Pr*$^\alpha_2$- (IV), m.p. 90° (*Br*$_2$-derivative, m.p. 88°), *Bu*$^\gamma_2$- (V), m.p. 156—156·5°. *Di*-(n-*propylthiol*)*methane*, b.p. 94—95°/13 mm., prepared from $SHPr^\alpha$, NaOEt, and CH_2Cl_2 in EtOH, with acid $KMnO_4$ gives (IV). *Di*(tert.-*butylthiol*)*methane*, b.p. 99—101°/13 mm., m.p. —4° (*HgI*$_2$ complex, decomp. > 120°), similarly prepared, gives (V). (I) and acid $KMnO_4$ gives anomalously *tri*-n-*butylsulphonylmethane*, m.p. 229—230°, unaffected by Br. $CS(NH_2)_2$, $Bu^\gamma Br$, and H_2O give tert.-*butylthiocarbamide*, cryst. BuCl gives in one operation an excellent yield of $Bu^\gamma SH$, which with boiling HCO_2H, HCO_2Et, and dry HCl, or $CHCl_3$ and NaOEt in EtOH, gives (II), some (III) being also formed by the last method. *Na* n-*butylsulphonate*, $+H_2O$, and tert.-*butylsulphonic acid*, m.p. (anhyd.) about 97—100°, ($+H_2O$) 114—116°, ($+2H_2O$) about 99° after softening at 78° (*Na*, $+1·5H_2O$, *K*, $+H_2O$, *Tl*, *Ba*, anhyd. and $+H_2O$, *Pb*, $+3H_2O$, *Cu*, $+6H_2O$, and *brucine* salts), are described. Dibenzyl disulphide and MeI at 100° give after several hr. SMe_3I. The CCl_4 condensation with allyl mercaptan gives diallyl disulphide and polymerised mercaptan, and with αγ-dithiolpropane a spongy mass, oxidised by HNO_3 to Na trimethylenedisulphonate. R. S. C.

Behaviour of trimethylene sulphide in heptane and naphtha. R. W. BOST and M. W. CONN (Ind. Eng. Chem., 1933, **25**, 526—528).—The following *products* were obtained from trimethylene sulphide, $(C_3H_6S)_x$, in heptane and naphtha: $C_3H_6S,HgCl_2$, m.p. 92—95°, C_3H_6S,MeI, m.p. 98—100°, $C_3H_6SBr_2$. Oxidation with $KMnO_4$ or H_2O_2 yields the *sulphone*, $C_3H_6SO_2$, m.p. 75°. No stable compound was obtained with HgI_2, and HNO_3 and HCl cause polymerisation. The behaviour of Et_2S is contrasted. A. G.

Oxidation of disulphides to sulphonic acids with hydrogen peroxide. Synthesis of taurine. A. SCHÖBERL (Z. physiol. Chem., 1933, **216**, 193—202).—Oxidation of dithiodiacetic acid with H_2O_2 gives sulphoacetic acid. Cystine (I) with H_2O_2 affords cysteic acid, cystamine (II) yields taurine (III) [phenylcarbamido-derivative, decomp. 195°, and its Ba salt ($+H_2O$)]. The oxidation of (I) to (III) *in vivo* probably occurs by way of (II). J. H. B.

Cholesterol as a microchemical reagent for fatty acids. G. DENIGES (Compt. rend., 1933, **196**,

1504—1506).—Cholesterol hydrate (I) (< 1 mg.) is moistened with the acid (*e.g.*, AcOH) (aq. or EtOH solutions of $CH_2Cl{\cdot}CO_2H$ and $CCl_3{\cdot}CO_2H$ are used) and the crystals formed (*e.g.*, $C_{27}H_{46}O$,AcOH) are examined microscopically; if (I) dissolves in the acid, the solution is first evaporated. HCO_2H does not give defined crystals. $PrCO_2H$ can be distinguished from $Pr^{\beta}CO_2H$. H. B

Catalytic decomposition in the gaseous phase of esters of fatty acids by pumice and sulphuric acid. J. B. Senderens (Compt. rend., 1933, **196**, 979—982).—Decomp. of $EtCO_2H$ vapour by pumice–H_2SO_4 does not occur below 195°. Esters of fatty acids are catalytically decomposed at 160—170° into acid (I), which is recovered, and alcohol which is converted into the ethylenic hydrocarbon (II). The gaseous product consists of 90% of (II) with small proportions of CO and CO_2. At higher temp. the formation of (II) is accompanied by decomp. of (I) with increasing production of CO and CO_2. $EtCO_2Pr$ gives at 210° a gas containing CO 41, CO_2 34·5, and C_3H_6 24·5%. Similar results are recorded for PrOAc and Et *iso*butyrate. A. C.

Ether-like compounds. X. Rate of reaction of aliphatic acid halides. M. H. Palomaa and R. Leimu (Ber., 1933, **66**, [*B*], 813—815; cf. this vol., 491).—The rates of reaction of AcCl (I), EtCOCl (II), $Pr^{\alpha}COCl$ (III), ClCOCl (IV), $CH_2Cl{\cdot}COCl$ (V), $OEt{\cdot}COCl$ (VI), $OEt{\cdot}CH_2{\cdot}COCl$ (VII), and AcBr (VIII) with $CH_2Cl{\cdot}CH_2{\cdot}OH$ in dioxan have been measured at 5°, 15°, 25°, and 35°. For (I)—(III) the rate is in agreement with the avidities of the acids, but differs from the sequence of acid hydrolysis of the esters. In the series (I—III)⟶(V)⟶(IV) the rate increases greatly, whereas great retardation is observed in the sequence (I—III)⟶(VII)⟶(VI), Cl and OEt having therefore marked opposed influences. H. W.

Alkamine esters of aliphatic acids. Novocaine analogues. IV. H. C. Brill and T. A. Bulow (J. Amer. Chem. Soc., 1933, **55**, 2059—2061).—The following β-*diethylaminoethyl ester hydrochlorides* are prepared: butyrate, m.p. 115°, valerate, m.p. 118°, *iso*valerate, m.p. 92°, hexoate, m.p. 127°, heptoate, m.p. 123°, nonoate (I), m.p. 131°, laurate, m.p. 107°, myristate, m.p. 110°, palmitate, m.p. 111°, and stearate, m.p. 133°. The narcotic effect (on goldfish) increases up to (I); above (I), the esters are very toxic. H. B.

αβ-Dimethylvaleric acid. A. E. Tschitschibabin and M. M. Katznelson (Bull. Acad. Sci. U.S.S.R., 1933, 267—271).—Et sodiomethylmalonate and *sec.*-BuBr in EtOH give *Et methyl-sec.-butylmalonate*, b.p. 236·5—238·5°/748 mm., hydrolysed to the acid, m.p. 118—119°, converted on heating into αβ-*dimethylvaleric acid*, b.p. 210·5—210·8°/750 mm. (*Me* ester, b.p. 155—158°/743 mm.; *chloride*, b.p. 110—113°/193 mm.; *amide*, m.p. 101—103°; *anilide*, m.p. 71—72°; p-*bromoanilide*, m.p. 115—117°). The occurrence of the theoretically possible stereoisomerides was not observed. G. A. R. K.

Highly polymerised compounds. LXXX. Polyacrylic acids. IV. Mol. wt. of polyacrylic acids and esters. H. Staudinger and E. Trommsdorff (Annalen, 1933, **502**, 201—223).—Polymerisation of Et acrylate by heating a solution in BuOAc at 100—200° for 4—25 days gives esters of mol. wt. 2200—41,000 (calc. from viscosity measurements). The lower members (*M* 2200—7800) dissolve in C_6H_6 to slightly viscous solutions which obey the Hagen–Poiseuille law, are difficult to purify, and are hydrolysed by EtOH–NaOH (without alteration in chain-length). Solutions of the resulting acids (*M* up to 12,000) in EtOH–NaOH do not undergo any appreciable change when shaken for 5 days, since the sp. viscosities remain almost const. The sp. viscosities of the acids in 2*N*-NaOH are the same as in 2*N*-NaOH containing 20% of NaCl. The sp. viscosities (1·4%) of the acids in 2*N*-NaOH are about 1·5 as great as those of the corresponding esters in BuOAc or C_6H_6 (the same relationship is found for an impure Et polyacrylate prepared from the Ag salt of the acid and EtI in Et_2O). The high vals. for the acids are considered to be due to co-ordinatively bound H_2O (2 mols. per 1 mol. of acrylic acid); if this is taken into account, almost identical vals. are obtained for the acids in 2*N*-NaOH and the esters in BuOAc. The viscosity of a solution of a heteropolar "mol. colloid" in excess of NaOH is solely a function of chain-length as in the case of a homopolar "mol. colloid" in org. solvents. H. B.

Salts of lævulic acid. A. Proskouriakoff (J. Amer. Chem. Soc., 1933, **55**, 2132—2134).—The *Ca*, *Mg*, *Cd*, *Ni*, and *Mn* salts are described. H. B.

Course of alkylation of enolates. F. Adickes, G. von Hessling, and S. von Müllenheim (Ber., 1933, **66**, [*B*], 826—828).—Alkylation of the Na derivative of $CH_2(CO_2Et)_2$ with MeI or of that of $CH_2(CO_2Me)_2$ with EtI followed by hydrolysis does not afford MeOH or EtOH, respectively, thus indicating the improbability of the intermediate production of $CO_2R{\cdot}CH{:}C(OMe){\cdot}OEt$. Similar observations are made with $CH(CO_2Et)_3$ and MeI. H. W.

Action of ammonia on ethyl malonate and ethyl malonamate. K. C. Bailey (Proc. Roy. Irish Acad., 1933, **41 B**, 161—167; cf. A., 1931, 315).—*K* (calc. for a third-order reaction) for reaction between $CH_2(CO_2Et)_2$ and NH_3 in EtOH–H_2O decreases with increasing EtOH concn. and varies when the concns. of reactants are varied, although when $CH_2(CO_2Et)_2$ is in large excess, after an initial period of high *K* (1), a fairly good second-order coeff. is obtained. (I) is increased by alkali and diminished by acid, which also retards the reaction as a whole; *o*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ exert a more powerful effect than H_2SO_4 or AcOH, indicating that the uncombined acid has a sp. retarding influence. Interaction of $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ and NH_3 in H_2O–EtOH is accompanied by an initial rapid reaction due to the catalytic effect of OH′ on hydrolysis; acids retard the reaction. J. L. D.

Methylation of ethyl αβ-dimethylglutaconate. J. Packer and J. D. Sargent (J.C.S., 1933, 556—557).—"Labile" Et_2 αβ-dimethylglutaconate is not methylated under Thorpe and Wood's conditions (*ibid.*, 1913, **103**, 1759), but with MeI and Na powder

in hot Et_2O gives Et, ααβ-trimethylglutaconate, hydrolysed by acid or alkali to a mixture of *cis*- and *trans*-acids. R. S. C.

Fehling's solution and isomerism of tartaric acids. H. Sobotka (J. Amer. Chem. Soc., 1933, **55**, 2164).—The oxidising power of Fehling's solution towards glucose is the same whether Na K *d*- or meso-tartrate is used in its prep. H. B.

Nature of racemates. V. N. Belov (J. Gen. Chem. Russ., 1933, **3**, 7—12).—Theoretical. The phenomenon of racemisation is interpreted on the assumption of the formation of "homochemical" compounds (A., 1921, ii, 324). This involves the approach of three like groups when optical antipodes form such a complex, whilst only two like groups can approach one another in the case of identical asymmetric mols.; this explains the greater stability of the racemic compound. In some cases both forms of complex exist and are at equilibrium under certain conditions (*e.g.*, Na NH_4 tartrate at 27°). It is suggested that racemates should possess a higher viscosity than their single constituents. G. A. R. K.

Constitution of ascorbic acid. W. N. Haworth (Chem. and Ind., 1933, 482—485).—A lecture. H. W.

Constitution of vitamin-*C*. IV. F. Micheel and K. Kraft (Z. physiol. Chem., 1933, **216**, 233—238; cf. this vol., 489).—Ascorbic acid (I) with CH_2N_2 gives cryst. *Me methylascorbate* (II), m.p. 63°, $[\alpha]_D$ +38° in EtOH. Hydrolysis of the ozonisation product (III) (*loc. cit.*) gives *l*-threonic acid, $[\alpha]_D^{20}$ +17·2° in H_2O (phenylhydrazide, m.p. 157—158°, $[\alpha]_D^{20}$ +30° in H_2O). *Me dinitrobenzoyl*-l-*threonate*, m.p. 137°, is obtained by partial hydrolysis of (III). From the similarity of the absorption curves of (I) and (II), (I) exists in EtOH solution chiefly in the enol form. J. H. B.

Constitution of dehydroascorbic acid. P. Karrer, H. Salomon, and K. Schopp (Nature, 1933, **131**, 800).—Dehydroascorbic acid (I) is probably an inner peroxide (this vol., 490). The view that oxidation of ascorbic acid to (I) should lead to the formation of a new OH group (this vol., 489) is erroneous. L. S. T.

Vitamin-*C* and related substances. H. von Euler and M. Malm.—See this vol., 756.

Vitamin-*C*. P. Karrer, H. von Euler, and H. Hellstrom.—See this vol., 756.

Derivatives of glycuronic acid. II. Acetylation of glycuron. W. F. Goebel and F. H. Babers (J. Biol. Chem., 1933, **100**, 743—748).—*α-Triacetylglycuron*, m.p. 194—195°, $[\alpha]_D^{23}$ +84·1° in $CHCl_3$, and *β-triacetylglycuron*, m.p. 110—112°, $[\alpha]_D^{24}$ +203·6° in $CHCl_3$, are prepared by acetylation with Ac_2O and C_5H_5N and also with Ac_2O and $ZnCl_2$, separation being accomplished by crystallisation from EtOH and AcOH. Results of a crystallographic study of the two isomerides are included. A. L.

Chemical nature of heparin. II. Preparation of pure heparin. III. Constitution of heparin. A. Schmitz and A. Fischer (Z. physiol. Chem., 1933, **216**, 264—273, 274—280; cf. A., 1932, 1054).—II. Heparin (I), $C_{18}H_{22}O_{17},6H_2O$, decomp. 250° [cryst. *brucine* salt $C_{18}H_{32}O_{17}(C_{23}H_{26}O_4N_2),4H_2O$, m.p. 255° (decomp.); *Na* and *Ba* salts], was obtained pure after a long fractionation.

III. (I) is a monobasic acid, K ~ $2{\cdot}0\times10^{-4}$, probably a carbohydrate derivative. It has $[\alpha]_D^{20}$ +41·6° in aq. HCl [*bromophenylosazone* (?), m.p. 300—310°]. The acid group carrier is probably a uronic acid. The fission products are lævorotatory. (I) absorbs light only in the extreme ultra-violet. J. H. B.

Thioketonic esters. II. S. M. Mitra. **III. Alkylation of ethyl thioacetoacetate.** P. C. Ray, S. K. Mitra, and N. N. Ghosh (J. Indian Chem. Soc., 1933, **10**, 71—74, 75—79).—II. $CH_2Ac{\cdot}CO_2Et$ in EtOH saturated with HCl at 0° affords with H_2S during several hr. Et thioacetoacetate (A., 1931, 1398) free from a by-product, now identified as *Et β-thiodicrotonate*, b.p. 155°/15 mm. Similarly, $CO(CH_2{\cdot}CO_2Et)_2$ affords *Et thioacetonedicarboxylate* (I), b.p 128°/15 mm. (decomp.). The Na derivative of (I) in boiling C_6H_6–EtOH with Pr^{n}I or EtBr during 4 hr. affords, respectively, *Et* n-*propyl*-, b.p. 220°/30 mm., and *Et ethyl-thioacetonedicarboxylate*, b.p. 175°/17 mm.

III. The following *S*-alkyl derivatives of Et β-thiolcrotonate are prepared: *Et*, b.p. 114—117°/15 mm., hydrolysed by cold 12% EtOH–KOH to *β-ethylthiolcrotonic acid*, m.p. 86° (and by boiling dil. H_2SO_4 to $COMe_2$, CO_2, and Et_2S_2), which may be a mixture of the cis- and trans-*forms*, m.p. 112° and 92°, respectively; n-*Pr*, b.p. 117—120°/15 mm. (*β-n-propylthiolcrotonic acid*, m.p. 70°); n-*amyl*, b.p. 126—128°/15 mm.; *benzyl*, m.p. 68° (*β-benzylthiolcrotonic acid*, m.p. 134°); *benzoylmethyl*, m.p. 85°. When boiled with $NHPh{\cdot}NH_2$, these compounds afford a *dehydropyrazolone*, m.p. 330° (decomp.). J. L. D.

Photolysis of acetaldehyde. P. A. Leighton and F. E. Blacet.—See this vol., 682.

Determination of methylglyoxal. T. Takahashi (J. Biochem. Japan, 1933, **17**, 299—305).—The methods of Fischler and Boettner (A., 1928, 870), of Friedemann (A., 1927, 648), and of Neuberg and Kobel (A., 1929, 354) are the most trustworthy, whilst those of Ariyama (A., 1928, 796) and of Barrenscheen and Dreguss (A., 1931, 825) also give accurate results. Improvements in technique are suggested for some of the above methods. F. O. H.

Generalisation of the method of condensation of ketones by mixed amino-magnesium derivatives. J. Colonge (Compt. rend., 1933, **196**, 1414—1416).—The formation of hydroxy-ketones by the action of $NHPh{\cdot}MgBr$ or $NPhMe{\cdot}MgBr$ (I) on aliphatic ketones (cf. A., 1932, 499) occurs only when there are $\not<$ 3 H atoms in the immediate neighbourhood of the CO group. Thus, γ-methyl-γ-ethylpentan-β-one (II) and δ-methylhexan-γ-one condense readily, whilst ββ- and βδ-dimethylpentan-γ-one give traces of condensation products. The following are prepared as previously described (*loc. cit.*): *κ-methylheneicosan-κ-ol-μ-one*, m.p. 23°, in 70% yield from Me nonyl ketone; *γδη-trimethyl-γη-diethylnonan-δ-ol-ζ-one* (61%), b.p. 135—136°/6 mm., from (II); 1-*hydroxy*-1-2′-*keto*cyclo*pentyl*cyclo*pentane* (40%), b.p.

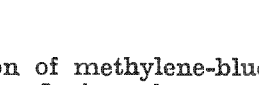
98—99°/3 mm., m.p. 31°, and some di*cyclo*pentylidene-*cyclo*pentanone (*oxime*, m.p. 78°) from *cyclo*pentanone; 1-*hydroxy*-1-2′-*keto*cyclo*hexyl*cyclo*hexane* (50%), b.p. 116—119°/5 mm., m.p. 56° (*oxime*, m.p. 113°), from *cyclo*hexanone; βδ-*diphenylbutan*-β-*ol*-δ-*one*, m.p. 63°, from COPhMe. Treatment of the product from $COPh_2$ and (I) with $COMeBu^{\gamma}$ gives 35% of αα-*diphenyl*-δδ-*dimethylpentan*-α-*ol*-γ-*one*, m.p. 102°. H. B.

Copper–iodometric reagents for sugar determination. P. A. Shaffer and M. Somogyi (J. Biol. Chem., 1933, **100**, 695—713).—In iodometric Cu reagents for sugar determination, the lower is the ratio Na_2CO_3 : $NaHCO_3$, the slower is the rate of sugar oxidation, but the higher the amount of Cu reduced. A comparison of the rates of reduction of various sugars by several reagents indicates that no single reagent is best for all sugars. The influence of I′ and IO_3' is considered. A. L.

Reduction by sugar derivatives. H. von Euler and E. Klussmann (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 8, 6 pp.).—When aldo- and keto-sugars are warmed with moderately dil. alkali (hydroxide) or $Ba(OH)_2$, substances are produced (in 1·4—8% yield) which, like vitamin-*C* (Szent-Gyorgyi, A., 1929, 98), reduce phenolindophenol and $KMnO_4$, $Fe^{\cdots}$ salts, and Cu salts in acid solution. H. B.

Highly reducing intermediates (reductones) in the alkaline rearrangement of simple sugars. H. von Euler and E. Klussmann (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 12, 6 pp.).—2% glucose (20 c.c.) warmed with 2*N*-NaOH (2 c.c.) at 77° for 10 min. gives a solution which reduces phenolindophenol and methylene-blue (I) (in N_2); the reducing power disappears when the solution is kept. (I) is similarly reduced by $CO(CH_2{\cdot}OH)_2$ and AcCHO in alkaline solution. H. B.

Glucoreductone. H. von Euler and C. Martius (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 14, 4 pp.).—Details are given (cf. this vol., 596) for the isolation of *glucoreductone* (I), $(C_3H_4O_3)_x$, chars 200—220° (mono-*Me* derivative, m.p. 67°, by the action of CH_2N_2; carbamide derivative, decomp. 200—220°), which has many of the reducing properties of ascorbic acid (II), reduces 2 : 6-dichlorophenolindophenol to a greater extent than (II), is a weak acid, and with $NHPh{\cdot}NH_2$ in AcOH gives the di- and tri-phenylhydrazones of $CO(CHO)_2$. (I) is considered to be OH·CH:C(OH)·CHO, *i.e.*, the enol form of $OH{\cdot}CH_2{\cdot}CO{\cdot}CHO$ or $OH{\cdot}CH(CHO)_2$. The properties of (II) are best explained by the structure



H. B.

Reduction of methylene-blue by products of the alkaline fission of sugars. H. von Euler and E. Klussmann.—See this vol., 680.

Action of oxygen on reducing sugars. (Mme.) N. Mayer-Reich (Compt. rend., 1933, **196**, 1337—1339).—30% solutions of glucose, xylose, and fructose in 0·1*N*-NaOH, buffered by phosphates, absorb O_2 (pure or from air) and evolve CO_2 faster in alkaline than in acid solutions. Heavy metals catalyse the reaction, since KCN and $K_4P_2O_7$ reduce the velocity by forming complexes with the catalyst. It is believed that the catalyst acts by activating (*a*) the O_2 and (*b*) the " mobile " H atom of the sugar. R. S. C.

Influence of sodium borate on the reaction between alkali cyanides and reducing sugars. J. Bougault, Z. Hardy, and A. Pinguet.—See this vol., 680.

Oxidation of α- and β-glucose, and isomeric forms of the sugar in solution. H. S. Isbell and W. Pigman (Bur. Stand. J. Res., 1933, **10**, 337—356).—Oxidation of α- or β-glucose with excess of aq. Br in presence of $BaCO_3$ and CO_2 gives δ-gluconolactone directly, without intermediate formation of the acid (cf. Irvine and McGlynn, A., 1932, 255). The oxidation of the β-form is approx. 35 times as great as that of the α-form (53 if mutarotation is allowed for), and in an equilibrium mixture of α- and β-forms the latter oxidises first, and a sudden change in the rate of oxidation then occurs, the results indicating the composition 64% of β- and 36% of α-forms. H. A. P.

Calcium chloride modifications of mannose and gulose. H. S. Isbell (J. Amer. Chem. Soc., 1933, **55**, 2166—2167).—Oxidation of the compound, $C_6H_{12}O_6,CaCl_2,4H_2O$ (I), from *d*-mannose (Dale, A., 1929, 1280) with cold Br–H_2O in presence of $BaCO_3$ gives largely γ-mannonolactone, indicating that (I) contains a 1 : 4-ring. More prolonged oxidation affords a considerable amount of δ-mannonolactone, which probably arises from α-*d*-mannose [formed from (I) by the mutarotation reaction]. The mutarotation of the compound, $C_6H_{12}O_6,CaCl_2,H_2O$, of α-*d*-gulose is probably more complex than the reversible interconversion of two isomerides. A new *compound*, $(C_6H_{12}O_6)_2,CaCl_2$, obtained from gulose, has $[\alpha]^{20}$ (in H_2O) +34° (1·4 min. after dissolution)⟶ −167° (const.). H. B.

Preparation of crystalline β-*l*-allose, a new aldohexose, from *l*-ribose by the cyanohydrin reaction. W. C. Austin and F. L. Humoller (J. Amer. Chem. Soc., 1933, **55**, 2167—2168).—*l*-Ribose is converted (cf. Levene and Jacobs, A., 1911, i, 14) into *l*-altronic acid (as Ca salt) and *l*-allonolactone (I), m.p. 130°, $[\alpha]^{25}$ +6·3° in H_2O. Reduction (Na–Hg) of (I) gives β-*l*-*allose*, m.p. 128—129°, $[\alpha]_D^{20}$ (in H_2O) −2·88° (4 min. after dissolution)⟶ −8·13° (34 min.) —— −13·88° (const.). H. B.

Crystalline 6-β-*d*-galactosido-*d*-glucose. B. Helferich and G. Sparmberg (Ber., 1933, **66**, [*B*], 806—807; cf. A., 1926, 386).—Improvements in technique lead to the isolation of cryst. 6-β-*d*-galactosido-*d*-glucose, m.p. 174—176° (decomp.), $[\alpha]_D^{18}$ +30·7° (final) in H_2O [*phenylosazone*, m.p. 188—189° (decomp.), $[\alpha]_D^{18}$ −74·5° (initial) in C_5H_5N], which in many respects resembles *allo*lactose (Polonovski *et al.*, A., 1932, 406, 1031). H. W.

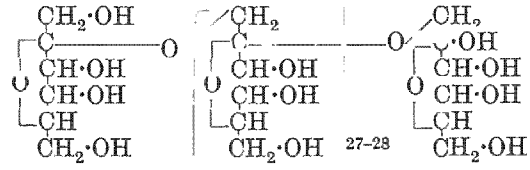
[Determination of] structure of heterosides by their absorption spectra. (Mme.) Ramart-Lucas and Rabate (Compt. rend., 1933, **196**, 1493—1495).—Sugars in neutral solution are transparent to light of > 2200 Å., whether alone or combined to form a

heteroside, provided that the prosthetic group is aliphatic or attached through an aliphatic group; thus the absorption spectrum of phenylethyl-β-glucoside is identical with that of $CH_2Ph{\cdot}CH_2{\cdot}OH$, but if the sugar is attached directly to an aryl nucleus the spectra are different. Thus esterification of a phenol by a sugar shifts the absorption spectrum towards the ultra-violet. C. A. S.

***Digitalis* glucosides. VII. Isomeric dihydrogitoxigenins.** W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1933, **100**, 671—683).—Gitoxigenin when rapidly hydrogenated in aq. EtOH gives 70% *α-dihydrodigitoxigenin* (I), $C_{23}H_{36}O_5$, m.p. 212—213°, $[\alpha]^{20}$ +42° in C_5H_5N, and on slow hydrogenation, *β-dihydrodigitoxigenin* (II), $C_{23}H_{36}O_5$, m.p. 242—244°, $[\alpha]_D$ −57° in MeOH, both substances showing mutarotation to give the same equilibrium mixture. (I) and (II) give on hydrolysis the same *dihydrogitoxigeninic acid*, $C_{23}H_{38}O_6$, m.p. 170° and after resolidifying 235°, $[\alpha]_D$ +22° in EtOH, whereas BzCl in C_5H_5N gives *α-dihydrogitoxigenin dibenzoate*, $C_{37}H_{44}O_7$, m.p. 250°, $[\alpha]_D$ +52° in C_5H_5N, and *β-dihydrogitoxigenin dibenzoate*, $C_{37}H_{44}O_7$, m.p. 233°, $[\alpha]_D^{20}$ −45° in C_5H_5N, respectively. Ac_2O in C_5H_5N gives with (II) the usual diacetate, but with (I) only *α-dihydrogitoxigenin monoacetate*, $C_{25}H_{38}O_6$ (III), m.p. 213° (softens at 206—208°), $[\alpha]_D^{23}$ +35° in C_5H_5N, is formed. (III) could be isomerised with *β-dihydrogitoxigenin monoacetate*, $C_{25}H_{38}O_6$, m.p. 224—226°, $[\alpha]_D^{23}$ −82° in C_5H_5N. (I) and (II) with Ac_2O and $ZnCl_2$ yield respectively *anhydro-α-* (IV), $C_{27}H_{38}O_6$, m.p. 208°, $[\alpha]_D^{22}$ +82° in C_5H_5N, and *anhydro-β-dihydrogitoxigenin diacetate* (V), $C_{27}H_{38}O_6$, m.p. 157°, $[\alpha]_D$ −34° in C_5H_5N. Attempts to hydrogenate the double linking of (IV) and (V) were unsuccessful. (II) with CrO_3 in AcOH, unlike the α-derivative, does not give α-oxodihydrogitoxigenin as the main yield, but the compound $C_{23}H_{32}O_6$ previously obtained, and a new *substance*, $C_{23}H_{34}O_5$, m.p. 228°, $[\alpha]^{20}$ −42° in $COMe_2$. It is suggested that the unsaturated lactonic group of gitoxigenin is attached through an intermediate C atom having a $OH{\cdot}CH_2$ branched chain. A. L.

Modifications of F. Schardinger's α-dextrin. K. HESS, C. TROGUS, and M. ULMANN (Z. physikal. Chem., 1933, **B**, **21**, 1—6; cf. A., 1932, 604).—*X*-Ray investigation shows the existence of at least 10 modification, but whether these are structural isomerides or merely polymorphic modifications is undecided. Their formation depends on the nature of the solvent, whether reaction is homogeneous or heterogeneous, and the temp. of separation. The conditions of interconversion are stated. R. C.

Methylation and constitution of inulin. (SIR) J. C. IRVINE and T. N. MONTGOMERY (J. Amer. Chem. Soc., 1933, **55**, 1988—1994).—Trimethylinulin (improved prep. given; cf. J.C.S., 1920, **117**, 1474; 1922, **121**, 1060) is hydrolysed by aq. EtOH–$H_2C_2O_4$ (cf. Haworth and Learner, A., 1928, 510) to 3 : 4 : 6-trimethyl-γ-fructose (I) (87—88·5%), tetramethyl-γ-fructose (II) (1·7—2·7%), *trimethylanhydro-γ-fructose* (III) (4·5—4·6%), b.p. 180—190° (bath)/0·06 mm., $[\alpha]_D$ +45·1° in $CHCl_3$, trimethylglucose (IV) (1—3·3%), and ω-methoxy-5-methylfurfuraldehyde (V) (1·5—2·5%). The uniformity of (I) is proved by the nature of its condensation product with $COMe_2$. The production of (IV) is due to a secondary reaction involving the transformation (I)⟶(IV); it is shown that small amounts of (IV), (V), and an anhydro-derivative, b.p. 170—180°/0·04 mm., $[\alpha]_D$ +62·7° in $CHCl_3$ [similar to (III)], are formed from (I) and aq. EtOH–$H_2C_2O_4$. The ideal yields of (I) and (II) are considered to be 95 and 4%, respectively; the following constitution is suggested (from these results) for inulin.



27-28

H. B.

Methylene esters of cellulose and their acetates. P. SCHORIGIN and J. RYMASCHEVSKAJA (Cellulosechem., 1933, **14**, 81—83).—Viscose silk is partly acetylated and partly methylenated by Ac_2O, AcOH, and $CH_2(OMe)_2$ (I) at 100°. Cellulose, pretreated with AcOH–H_2SO_4 (7·5%), and then with (I) and Ac_2O at 40°, gives a product which probably contains chains of $\cdot O{\cdot}C_6H_7O(OH)(OAc)(O{\cdot}CH_2{\cdot}OH){\cdot}O$ groupings. If the Ac_2O is omitted, the product contains up to 4·25% CH_2O_2. Cellulose, mercerised by 33% NaOH, with warm (I) gives products containing up to 3·95% of CH_2O_2. CH_2I_2 and alkali-cellulose give very slightly methylenated or decomposed products. R. S. C.

Preparation of amines by catalytic hydrogenation of derivatives of aldehydes and ketones. C. F. WINANS and H. ADKINS (J. Amer. Chem. Soc., 1933, **55**, 2051—2058).—Good yields of NH_2R are often obtained by reduction of oximes with H_2 and a Ni–kieselguhr catalyst in Et_2O, EtOH, or methyl*cyclo*hexane, usually at 100—125°/100—150 atm.; there is, however, considerable variation in the yields and proportions of NH_2R and NHR_2 according to the structure of the original aldehyde or ketone. Thus, $CMe_2{:}N{\cdot}OH$ gives NH_2Pr^{β} (67%) and $NHPr^{\beta}_2$ (10%); *n*-valeraldoxime affords *n*-amylamine (62%) (*p-bromobenzenesulphonyl* derivative, m.p. 60—61°) and di-*n*-amylamine (27%) (*hydrochloride*); *n*-heptaldoxime yields *n*-heptylamine (61%) and di-*n*-heptylamine (20%) (*hydrochloride*); cinnamaldoxime furnishes γ-phenylpropylamine (32%) and di-γ-phenylpropylamine (12%), also obtained in 48 and 43% yield, respectively, from γ-phenylpropaldoxime; $CPh_2{:}N{\cdot}OH$ gives 95% of $CHPh_2{\cdot}NH_2$; camphoroxime affords 94% of bornylamine; p-$NO{\cdot}C_6H_4{\cdot}OH$ yields 85% of p-$NH_2{\cdot}C_6H_4{\cdot}OH$; benzoinoxime furnishes β-amino-αβ-diphenylethyl alcohol (64%) and tetraphenylpyrazine (I) (20%); *syn*-benzildioxime gives $(\cdot CHPh{\cdot}NH_2)_2$ (44·5%) and (I) (51%); α-$CHPh{.}N{\cdot}OH$ affords $CH_2Ph{\cdot}NH_2$ (73—77%) and $NH(CH_2Ph)_2$ (19—20%). Reduction of various phenylhydrazones, azines, azo-compounds, hydroamides, dihydroglyoxalines, and aldimines is effected by the above method. Thus, $(:NPh)_2$ gives 95% of NH_2Ph at 90° and NH_2Ph (21%), *cyclo*hexylamine (22%) (*benzenesulphonyl* derivative, m.p. 88—89°), and di*cyclo*hexylamine (48%) at 200°;

CHPr:N·NHPh affords NH_2Ph (95%), NH_2Bu (57%), and $NHBu_2$ (40%), showing that fission of the N·N linking must have preceded reduction of the C:N linking; benzaldazine yields $CH_2Ph·NH_2$ (68%), $NH(CH_2Ph)_2$ (26%), and $N(CH_2Ph)_3$ (2%) (this is the only *tert.*-amine isolated during the investigation); trifurfurylidenediamine (hydrofuramide) furnishes tetrahydrofurfurylamine (88%) (*phenylcarbamyl* derivative, m.p. 147—147·5°) and ditetrahydrofurfurylamine (90%) (*picrate*, m.p. 104—105°); tri(trimethylethylidene)diamine (hydropinalamide) gives *tert.*-butylcarbinylamine (79%) and di*tert.*-butylcarbinylamine (62%) (p-*bromobenzenesulphonyl* derivative, m.p. 128—129°); triheptylidenediamine (hydroheptoamide) affords *n*-heptylamine (43%) and di-*n*-heptylamine (49%); polymeric hexahydrobenzaldimine yields hexahydrobenzylamine (61%) and dihexahydrobenzylamine (33%) (*hydrochloride*, m.p. 298—299°); polymeric $CHPr^{\beta}$:NH furnishes NH_2Bu^{β} (70%) and $NHBu^{\beta}_2$ (24%); OH·CHPr·NH_2 (as hydrate) gives NH_2Bu (32%), $NHBu_2$ (13%), and 3 : 5-diethyl-2-*n*-propylpyridine (II) (26%); heptaldehyde-ammonia affords *n*-heptylamine (32%) and di-*n*-heptylamine (12%); PrCHO+EtOH–NH_3 yields NH_2Bu (32%), $NHBu_2$ (21%), and (II) (26%); triacetoneamine yields 4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine (81%); 2 : 4 : 5-triphenyl-4 : 5-dihydroglyoxaline furnishes the 2 : 4 : 5-tri*cyclo*hexyl derivative; 2 : 4 : 5-trifuryl-4 : 5-dihydroglyoxaline (furfurin) gives 2 : 4 : 5-tritetrahydrofuryl-4 : 5-dihydroglyoxaline (*picrate*, m.p. 202—203°); 2 : 4 : 5-tristyryl-4 : 5-dihydroglyoxaline affords 2 : 4 : 5-tri-β-phenylethyl-4 : 5-dihydroglyoxaline (*picrate*, m.p. 130—132°).

H. B.

Influence of poles and polar linkings on the course of elimination reactions. XV. Dynamics of the elimination of olefines from quaternary ammonium compounds. E. D. Hughes and C. K. Ingold. **XVI. Mechanism of the thermal decomposition of quaternary ammonium compounds.** E. D. Hughes, C. K. Ingold, and C. S. Patel. **XVII. Thermal decomposition of phosphonium ethoxides.** L. Hey and C. K. Ingold. **XVIII. Thermal decomposition of sulphonium hydroxides.** C. K. Ingold, J. A. Jessop, K. I. Kuriyan, and (in part) A. M. M. Mandour (J.C.S., 1933, 523—526, 526—530, 531—533, 533—537; cf. this vol., 262).—XV. The decomp. of $CH_2Ph·CH_2·NMe_3·OH$ [iodide, m.p. about 225° (decomp.)] is bimol. and proportional to the concn. of each ion. The decomp. of β-p-*nitrophenylethyltrimethylammonium iodide* (I), m.p. 199° (decomp.) [corresponding *picrate*, m.p. 147° (decomp.)], and of the *bromide*, m.p. 222°, is unimol., and independent of the halide concn., both reactions having the same k; the corresponding hydroxide in H_2O at room temp. gives NMe_3 and *p*-nitrostyrene, whilst (I) gives NMe_3 and a glassy *polymeride* of *p*-nitrostyrene. Reaction is retarded by acids and accelerated by bases, and is slower in $Pr^{\alpha}OH$ than in H_2O.

XVI. Theoretical. Recognition of the fact that both modes of decomp. of quaternary ammonium compounds (to give olefines or alcohols) may be either uni- or bi-mol. explains previous anomalies. Von Braun's conception of the decomp. is criticised.

XVII. Decomp. of $PMe_4·OEt$ at 100—140° gives C_3H_8 and PMe_3O only. $PEt_4·OEt$ gives *n*-C_4H_{10} and PEt_3O only. β-Phenylethyltriethylphosphonium ethoxide gives 90% of *n*-butylbenzene and PEt_3O, with a little $CHPh.CH_2$ and PEt_3. Triphenyl-ββ-diphenylethylphosphonium ethoxide (from the corresponding *chloride*) gives 5% of *αα-diphenyl-n-butane*, b.p. about 170—175°/15 mm., and PEt_3O, and 95% of PEt_3 and $CH_2{:}CPh_2$. The close similarity in the modes of decomp. of corresponding ethoxides and hydroxides is unexpected and its theoretical aspect is discussed.

XVIII. The following were prepared from mercaptans and sulphides: *dimethyl-ethyl-* (I), m.p. about 110° (decomp.), hygroscopic, *-n-propyl-* (II), cryst., hygroscopic, *-n-butyl-* (III), m.p. 82° (decomp.), *-isobutyl-* (IV), m.p. 88—90° (decomp.), and *-isopropyl-* (V), cryst., hygroscopic, *-sulphonium iodide*. $SEtPr^{\alpha}$, b.p. 115—117°, and MeI in cold $MeNO_2$ led to *methylethylisobutylsulphonium iodide* (VII). SEt·$[CH_2]_2$·Ph, b.p. 113—115°/10 mm. (from SEtNa and $CH_2Ph·CH_2Cl$), gives β-*phenylethylmethylethylsulphonium iodide* (VIII), m.p. 84—85°. $SEtPr^{\beta}$, b.p. 102—104° (from SEtNa and $Pr^{\beta}I$ in EtOH), led to *methylethylisopropylsulphonium picrate* (IX), m.p. 173—175°. $SHPr^{\beta}$, b.p. 57—60°, gives $SMePr^{\beta}$, b.p. 93—95°, which with $Bu^{\beta}I$ and Ag_2SO_4 in $MeNO_2$ at 80—90° led to *methylisopropylisobutylsulphonium picrate* (X), m.p. 49—50°. The corresponding hydroxides at 120—130° give the following yields of olefines: (I) 27; (II) 7·7; (III) 3·8; (IV) 1·5; (VI) 63%. Decomp. of the hydroxides corresponding with (VI), (VII), and (VIII) gives mixtures of olefines containing 80, 93, and 3% of C_2H_4, respectively, whilst that of (IX) and (X) gives mixtures of olefines containing 75 and 94% of propylene, respectively. The regularities and irregularities of these results exactly parallel those in the ammonium series (except that elimination of MeOH is more facile from the S bases) and justify the application of the same reaction mechanism to both reactions. The non-formation of paraffins is probably due to the instability of the S atom with a decet of electrons (except when, as in the sulphones, some of the linkings are semi-polar).

R. S. C.

Organic bromine compounds of therapeutic value, and hexamethylenetetramine hydrobromide. G. Aurisicchio (L'Ind. Chimica, 1933, 8, 442—444).—When $(CH_2)_6N_4$,HBr is prepared directly from the base and the acid, some hydrolysis takes place, and MgO is therefore added, the resulting $MgBr_2$ remaining in the product, which gives solutions of p_H 8 or even higher. Methods are suggested of obtaining a product as free as possible from $MgBr_2$.

Condensation of αγ-dibromohydrin with NMe_3, $NHEt_2$, and NH_2Et, respectively, yields *αγ-di(dimethylamino)propan-β-ol dimethobromide*, *αγ-di(diethylamino)propan-β-ol dihydrobromide*, and *αγ-di(ethylamino)propan-β-ol dihydrobromide*.

T. H. P.

Synthesis of 2-thiolhistidine; experiments towards the synthesis of ergothioneine. C. R. Harington and J. Overhoff (Biochem. J., 1933, 27, 338—344).—Certain proposed routes to ergothioneine have proved impracticable. Et α-chloro-β-glyoxaline-4(or 5)-propionate cannot be benzoylated. Treat-

ment of 2-thiol-4(or 5)-aminomethylglyoxaline with I in order to obtain the disulphide yields a complex product. 2-Thiol-4(or 5)-phenoxyglyoxaline (synthesis outlined) cannot be converted into the 4(or 5)-OH- or -Br-compounds. Condensation of phthalimidohalogenoacetones with Et sodiochloromalonate yields resins.

Acetylaspartic acid (I), m.p. 142—143°, $[\alpha]^{20}_{61}$ +5·9° in H_2O, is obtained from aspartic acid (II) with Ac_2O and aq. NaOH or with keten in aq. NaOH. Boiling Ac_2O converts (I) or (II) into the *azlactone* (III), m.p. 145—146°, to which Bergmann *et al.* (A., 1926, 1236) assigned the structure of acetamidosuccinic anhydride (IV). A *product*, m.p. 175°, probably (IV), is obtained from moist (I) and Ac_2O at 95°. (III) and PCl_5 in AcCl yields the *acid chloride*, which, treated with CH_2N_2, followed by HCl and EtOH, yields *Et δ-chloro-α-acetamido-γ-ketovalerate*, m.p. 128°, converted into the *δ-phthalimido*-compound (V), m.p. 175°, which yields with 20% HCl under reflux *αδ-diamino-γ-ketovaleric acid monohydrochloride*, yellows at 175°, blackens at 210°, which is converted by NaCNS into dl-2-*thiolhistidine* [2HCl, m.p. 204—206° (decomp.)], oxidised by $Fe_2(SO_4)_3$ to *dl*-histidine. *α-Amino-α-phthalimido-γ-ketovaleric acid* (VI), m.p. 165—166° (decomp.), is obtained from (V) by refluxing with *N*-HCl; it cannot be methylated, but yields only NMe_3 and an unsaturated acid. Treatment of (VI) in 3*N*-H_2SO_4 with KBr and $NaNO_2$ yields the *α-bromo*-compound, m.p. 185—186° (decomp.), hydrolysis of which yields a non-basic oil. R. K. C.

Electrolytic oxidation of glutamic acid. Y. Takayama.—See this vol., 681.

Acyl derivatives of aminomethanesulphonic acids. H. J. Backer and H. Mulder (Rec. trav. chim., 1933, **52**, 454—468).—The constitution of Reinking's aminomethanesulphonic acid (I) (A., 1905, i, 261) is confirmed by its transformation by NOCl into chloromethanesulphonic acid. Differentiation of sulphonic acids from alkyl sulphites by cleavage by KCN, supposed to be typical of the latter, is invalid, since some sulphonic acids, *e.g.*, (I) and its SO_2Ph derivative (II), are thus cleaved, whereas acylation by other acids and *N*-nitration or -nitrosation of (II) gives stable substances. In the cases marked * below the free acid was not isolated. (I), Ac_2O, and aq. NaOH give *acetamidomethanesulphonic acid*, $+H_2O$ (*Na* and *K* salts; *nitrate*, $+H_2O$); Na_2CO_3 and the chloroformate give the *carbomethoxy-* and *carbethoxy-*derivatives * of (I) (*Na* salts), and KCN the *carbamyl* derivative (carbamidomethanesulphonic acid), $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}SO_3H$ (*K* salt). CH_2O, aq. $NaHSO_3$, and the appropriate amine give *N-methyl-* * (*Na*, decomp. 80°, and *K* salts; *nitrate* of *K* salt; *K* salt of *Ac* derivative), *-tert.-butyl-* * [*Na* salt, $+H_2O$ (*nitrate*)], *-dimethylamino-* * (*Na* salt) and *-phenyl-aminomethanesulphonic acid* [*Na* salt, $+H_2O$; *Na* salt (III) of the *Ac* derivative; *Na* salt of the N-*NO*-derivative]. NH_2Bz gives similarly *benzamidomethanesulphonic acid* (*K*, $+H_2O$, and *Na*, $+2H_2O$, salts). The last and also the following derivatives * of (I) are prepared by the Schotten–Baumann method: *SO_2Ph-* (*Na* salt), *o-* (*Na* salt), and *p-toluenesulphonyl-* [*K* salt; *K* salts of *NO-* and *NO_2-* (IV) *-*derivatives]. The action of KCN on the salt of the appropriate acid gives *tert.-butylamino-*, b.p. 83—88°/14 mm., *dimethylamino-*, *benzenesulphonamido-*, m.p. 77°, and *o-toluenesulphonamido-* (V), m.p. 63·5°, *-acetonitrile*. (V) with H_2O_2 and NaOH in EtOH at 50° gives *o*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$, and with EtOH and dry HCl in cold Et_2O gives the *hydrochloride* of the *imino-ether*, *o*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$, which with H_2O affords *Et o-toluenesulphonylglycine*, an oil. (IV) with conc., aq. NH_3 at 100° gives *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$. R. S. C.

Thiocarbamyl chloride. M. Battegay and E. Hégazi (Compt. rend., 1933, **196**, 1030—1032).—The action of dry HCl (I) on HCNS (II) in Et_2O yields *thiocarbamyl chloride* (65%), decomp. 75—80°. H_2O decomposes it into (I) and (II), alcohols into thiourethanes, $NH_2{\cdot}CS{\cdot}OR$. A. C.

Organic compounds of boron. T. Thomson and T. S. Stevens (J.C.S., 1933, 556).—Attempts to prepare compounds of the type $[BR_4]M$ by heating BMe_3 or BPh_3 with LiEt, LiPh, NaMe, NaEt, or Na·CH_2Ph in a neutral solvent failed. LiEt or NaEt in ligroin at 120° gives a solid which on hydrolysis yields H_2, corresponding with 50% of LiH. R. S. C.

Action of arsines with halogenoarsines. W. Steinkopf (J. Amer. Chem. Soc., 1933, **55**, 2165; cf. Blicke and Powers, A., 1932, 1049).—The results of Steinkopf and Smie (Ber., 1926, **59**, *B*, 1459) have been shown to be incorrect by Steinkopf and Dudek (A., 1929, 1471). H. B.

Action of arsines with halogenoarsines. F. F. Blicke and L. D. Powers (J. Amer. Chem. Soc., 1933, **55**, 2165—2166).—A reply to Steinkopf (preceding abstract). H. B.

Existence of metal ketyls in the aliphatic series. A. E. Favorsky and J. N. Nazarow (Compt. rend., 1933, **196**, 1229—1231).—Na with $CO(CMe_3)_2$ (I) produces a deep red solution which is decolorised on exposure to air with the appearance of reactions for H_2O_2. In Et_2O slow association of the metal ketyl produces the pinacol alcoholate $[ONa{\cdot}C(CMe_3)_2]_2$, decomposed by H_2O into *tetratert.-butylethylene glycol*, m.p. 85—86°, b.p. 156°/13 mm., which with cold conc. H_2SO_4, affords *ββεε-tetramethyl-δδ-ditert.-butylhexan-γ-one*, b.p. 135—136°/20 mm., which gives a violet colour with Na. $CMe_3{\cdot}COPr^{\beta}$ reacts with Na similarly to (I). Pinacolin does not give a coloration with Na. Treatment of the reaction product with H_2O leads to the isolation of *βγ-ditert.-butyl-Δ^{α}-buten-γ-ol*, b.p. 105—107°/15 mm. (II), and *ββδ-trimethyl-δ-tert.-butylpentan-γ-one*, b.p. 200—202°, reduced to the corresponding *alcohol*, b.p. 99°/15 mm. (*benzoate*, m.p. 48—49°). (II) is dehydrated by anhyd. $H_2C_2O_4$ to *βγ-ditert.-butylbutadiene*, b.p. 168—170°, which gives, with maleic anhydride, a *ditert.-butyltetrahydrophthalic anhydride*, m.p. 128—129°. A. C.

Reaction of monobromoamine with Grignard reagents. G. H. Coleman, H. Soroos, and C. B. Yager (J. Amer. Chem. Soc., 1933, **55**, 2075—2080).—NH_2Br (method of prep. given; cf. Moldenhauer and Burger, A., 1929, 897) treated with MgRX (R=

Bu^{α}, Bu^{γ}, *sec.*-Bu, $\cdot CH_2Ph$, $\cdot C_2H_4Ph$, and Ph; X= Cl, Br, I) in Et_2O at −5° to 0° gives N_2 (5—15%), NH_3 (22—89%), and NH_2R (3—63%). The yield of NH_2R is greatest with MgRCl and smallest with MgRI; smaller yields are obtained than with NH_4Cl (A., 1928, 622; 1929, 431). H. B.

Thermal decomposition of *cyclo*hexane and *cyclo*hexene in presence of silica gel. A. Mailhe (Chim. et Ind., 1933, **29**, 759—765; cf. A., 1932, 729).—Thermal decomp. of *cyclo*hexene (I) in presence of SiO_2 commenced at about 500°, was slight below 600°, whereas at 600—700° increasing quantities of C_6H_6 were formed with varying amounts of C_2H_4 and its homologues (C_3H_6 in general preponderating). Above 700°, PhMe, $C_6H_4Me_2$, $C_{10}H_8$, and anthracene were formed (in addition to C_6H_6). *cyclo*Hexane began to decompose at about 600°; the primary reaction at this and higher temp. was apparently simple dehydrogenation to (I), the reaction products being the same as were obtained with the latter. A. B. M.

Preparation of hydrocarbons with a hemicyclic double linking. N. K. Alexandrovitsch (J. Gen. Chem. Russ., 1933, **3**, 48—51).—*cyclo*Hexylcarbinol is converted by Na and CS_2 in Et_2O into *Me* cyclo*hexyl xanthate*, m.p. 165° (*amide*, m.p. 75—76°), pyrolysed above 200° to methylene*cyclo*hexane. 4-Methyl*cyclo*hexylcarbinol similarly affords *Me* 4-*methyl*cyclo*hexyl xanthate* (*amide*, m.p. 104—105°), pyrolysed to methylene-4-methyl*cyclo*hexane. G. A. R. K.

Carotenoids. IV. Degradation of carotene and β-ionone with ozone. R. Pummerer and L. Rebmann (Ber., 1932, **66**, [*B*], 798—801; cf. A., 1931, 491).—Ozonisation of β-ionone followed by fission with warm H_2O and separation of the products with steam gives a 15·2% yield of neutral oil and a 23·8% yield of non-volatile acids, among which ε-keto-αα-dimethylheptoic and αα-dimethyladipic acids were identified. Geronaldehyde is accompanied by an unidentified trimethyl*cyclo*hexanone (*semicarbazone*, m.p. 206°). The p-*nitrophenylhydrazones* of β- and α-ionone have m.p. 173° and 113°, respectively. H. W.

Oxidation of β-carotene. P. Karrer, H. von Euler, H. Hellstrom, and E. Klussmann (Arkiv Kemi, Min., Geol., 1932, **11 B**, No. 3, 5 pp.).—Oxidation of β-carotene (I) occurs slowly when a colloidal aq. solution is kept in vac. or (more rapidly) in air at 39°; oxidation with H_2O_2 (large excess) proceeds much more rapidly to completion in a similar manner. Carotene oxide, m.p. 161°, from (I) and Bz_2O_2H in $CHCl_3$, has an absorption spectrum which differs from that of (I), β-hydroxycarotene (Kuhn and Brockmann, A., 1932, 749), and β-carotenone (*loc. cit.*); it exhibits marked growth-promoting properties towards rats. H. B.

Apparent anomalous lability of the 2-nitro-group in 2 : 3-dinitrotoluene. Example of the reversed-field effect. H. H. Hodgson and E. W. Smith (J.C.S., 1933, 500—501).—3-Nitro-*o*-toluidine (modified prep.) and K_2SO_4 in H_2SO_4–EtOH–H_2O give 3 : 3′-*dinitro*-2 : 2′-*azoxytoluene*, m.p. 121°, oxidised by HNO_3 (*d* 1·5) at < 20° to 2 : 3-dinitrotoluene. This with NaOH gives 3-nitro-*o*-cresol, with Na_2S in aq. $COMe_2$ 3 : 3′-dinitro-2 : 2′-ditolyl sulphide, m.p. 152° (lit. 150°) [oxidised (without isolation) by $K_3Fe(CN)_6$ to 3 : 3′-*dinitro*-2 : 2′-*ditolyl disulphide*, m.p. 145°], and with Na_2S_2 in aq. $COMe_2$ to 3 : 3′-*diamino*-2 : 2′-*ditolyl disulphide*, m.p. 123° (Ac_2 derivative, m.p. 167°; *dipicrate*, m.p. 158°). The above and similar replacement reactions of the 2-NO_2-group are examples of the reversed-field effect. R. S. C.

Relative stability of penta-arylethanes. I. Preparation of penta-arylethanes. W. E. Bachmann (J. Amer. Chem. Soc., 1933, **55**, 2135—2139).—The following are prepared from CPh_3·MgBr and the appropriate $CHAr_2Br$ in Et_2O–C_6H_6 and N_2: penta-phenyl-, m.p. 182—185° (in N_2; the m.p. quoted in N_2 are all with decomp. and are > in air, probably owing to oxidation taking place in the latter case), ααα-*triphenyl*-β-*diphenylene*-, m.p. 248—256° (in N_2), ααaβ-*tetraphenyl*-β-p-*tolyl*-, m.p. 183—185° (in N_2), ααα-*triphenyl*-ββ-*di*-p-*tolyl*-, m.p. 170—180° (in N_2), ααaβ-*tetraphenyl*-β-*anisyl*-, m.p. 172—176° (in N_2), ααα-*triphenyl*-ββ-*dianisyl*-, m.p. 168—176° (in N_2), ααaβ-*tetraphenyl*-β-p-*diphenylyl*-, m.p. 166—175° (in N_2), ααα-*triphenyl*-ββ-*di*-p-*diphenylyl*-, m.p. 180—190° (in N_2), and ααaβ-*tetraphenyl*-β-α′-*naphthyl*-, m.p. 194—196° (in N_2), -*ethane*. The $CHAr_2Br$ used are prepared from $CHAr_2$·OH, HBr, and AcBr in AcOH; the 4 : 4′-*dimethyl*-, m.p. 48·5—49°, and p-*phenyl*- (I), m.p. 104°, -*benzhydryl bromides* are new. (I) is also prepared from *p*-phenyldiphenylmethane and Br at 185°. p-*Methoxybenzhydryl chloride*, m.p. 64° (the bromide could not be prepared), is obtained from the hydrol and dry HCl in C_6H_6+$CaCl_2$.

9-Bromo-9-phenylfluorene and CPh_3·MgBr give $(\cdot CPh_3)_2$ and αβ-diphenyl-αβ-di(diphenylene)ethane (II), m.p. 254° (in N_2). 9-Chloro-9-phenylfluorene and MgPhBr afford a mixture of 9 : 9-diphenylfluorene and (II) (cf. A., 1930, 1279, and Schmidt-Nickels, A., 1929, 695). H. B.

Dissociation into free radicals of tetradiphenyldi*tert.*-butylethane. J. B. Conant and R. F. Schultz (J. Amer. Chem. Soc., 1933, **55**, 2098—2104).—Li *p*-diphenylyl (I) (from Li and *p*-bromodiphenyl in Et_2O and N_2) and CMe_3·CO_2Et in Et_2O give *di*-p-*diphenylyl*tert.-*butylcarbinol*, m.p. 129—130°, which with $SOCl_2$ at −15° (and then at room temp.) affords the *chloride* (II), m.p. 105—106°. Crystallisation of (II) from hot C_6H_6 gives a considerable amount of an isomeric *chloride*, m.p. 181°, also formed in appreciable amount from the carbinol and $SOCl_2$ at 25°. (II) and 40% Na–Hg in Et_2O yield Na di-*p*-diphenylyl*tert.*-butylmethyl (III), converted by CO_2 into *di*-p-*diphenylyl*tert.-*butylacetic acid*, m.p. 178—181°, and by moist Et_2O into *di*-p-*diphenylyl*-tert.-*butylmethane*, m.p. 178—179°. (III) and *s*-$C_2Me_4Br_2$ give s-*tetra*-p-*diphenylyldi*tert.-*butylethane* (IV), light orange, m.p. (in N_2) 136—137° (becoming red; the colour fades at 145—150°), resolidifying with m.p. 160—175°, which absorbs O_2 instantaneously in PhBr giving di-*p*-diphenylyl ketone, and is cleaved by 40% Na–Hg to (III). Solutions of (IV) in PhMe are orange-red at room temp. and the intensity of the colour is diminished by cooling; at 80°, disproportionation occurs. The *Me ether*, m.p. 141·5—142·5°, of cyclo*hexyldi*-p-*diphenylylcarbinol*, m.p. 126—

127° [from (I) and Me hexahydrobenzoate], and 40% Na–Hg in Et_2O give a violet Na derivative, which with *s*-$C_2Me_4Br_2$ yields an orange-coloured solution of *s*-di*cyclo*hexyltetra-*p*-diphenylylethane (not isolable owing to rapid disproportionation). H. B.

[4 : 4′-Derivatives of diphenyldidiphenylyl and didiphenylyl.] R. Pummerer (Ber., 1933, **66**, [*B*], 802; cf. A., 1931, 1406).—An acknowledgment of the work of Kuhn (A., 1929, 1435). H. W.

Preparation of chloromethylnaphthalenes and 1 : 5-dimethylnaphthalene. A. R. Anderson and W. F. Short (J.C.S., 1933, 485).—1-$C_{10}H_7$·CH_2Cl (I) (modified prep.) and alkaline Na_2SO_3 give 1-$C_{10}H_7$·CH_2·SO_3Na, which gives a very little 1-$C_{10}H_7Me$ (II) when distilled with NaOH. (I) with Na and EtOH gives a mixture of (II) and its reduction products, dehydrogenated by S at 220°, and with Zn needles and dry HCl in EtOH at 0° a 68% yield of (II). (I) and NH_2Ph at 100° give 1-naphthylmethylaniline (77% yield) (NO-derivative, m.p. 57°), oxidised by $KMnO_4$ in $COMe_2$ at 0° to naphthylideneaniline (poor yield) and smoothly hydrolysed to $C_{10}H_7$·CHO, obtained in 60% yield from (II) and $(CH_2)_6N_4$ in EtOH. (I), paraform, $ZnCl_2$, and dry HCl in ligroin at 60—65° give a mixture of $C_{10}H_6(CH_2Cl)_2$, oxidised by $K_3Fe(CN)_6$ to 1 : 5-$C_{10}H_6(CO_2H)_2$, and reduced by Zn and HCl–EtOH to a mixture of $C_{10}H_6Me_2$ (crude picrate, m.p. 139—140°), containing some of the 1 : 5-isomeride (picrate, m.p. 138—139°). R. S. C.

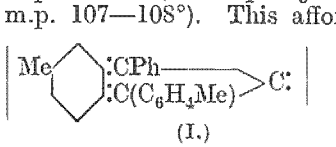
Reaction between naphthalene-2-sulphonyl chloride and some thiol compounds. B. C. Saunders (Biochem. J., 1933, **27**, 397—402).—Both glutathione (I) and its oxidation product (presumably the disulphide) reduce 2-$C_{10}H_7$·SO_2Cl (II) to 2-$C_{10}H_7$·SO_2H. Since (I) reduces 1·5 mols. of (II), it appears that glutathione disulphoxide is formed, but a pure product could not be isolated. No *N*-sulphonyl derivative of glutathione is formed. Analogously, cysteine yields di(naphthalene-2-sulphonyl)-cysteine (*Na* derivative, decomp. 214°, isolated at p_H 8·8) and 2-$C_{10}H_7$·SO_2H. *S*-Benzylcysteine, however, yields N-*naphthalene*-2-*sulphonyl*-S-*benzylcysteine*, m.p. 132°, without formation of 2-$C_{10}H_7$·SO_2H. Thiolacetic acid yields dithioglycollic acid and 2-$C_{10}H_7$·SO_2H. R. K. C.

Stereochemistry of dicyclic ring systems. VIII. $\Delta^{1:9}$-Octahydronaphthalene. W. Huckel and H. Naab (Annalen, 1933, **502**, 136—155).—Successive treatment of the Na derivative of *trans*-decahydro-α-naphthol, m.p. 63°, with CS_2 and MeI in Et_2O affords the Me xanthate, which decomposes at 180—210°/vac. to give 30—40% of a mixture (*A*) of $\Delta^{1:9}$-octahydronaphthalene (I) (about 80%), b.p. 196·5—198·5° [bimol. *nitrosochloride*, colourless, m.p. 127°; nitrolpiperidide, m.p. 179° (decomp.)], and *trans*-$\Delta^{1:2}$-octahydronaphthalene (II) (about 20%). Oxidation (O_3, AcOH) of (*A*) gives (mainly) γ-2-*keto*-cyclo*hexylbutyric acid* (III), m.p. 60—61° (*semicarbazone*, m.p. 189°; *oxime*, m.p. 101—103°), which is oxidised (alkaline $KMnO_4$) further to δ-ketosebacic acid; (III) arises from (I). Oxidation ($KMnO_4$) of (*A*) affords (III), δ-ketosebacic, *trans*-3-2-carboxy-*cyclo*hexylpropionic, succinic, and liquid acids, and a trace of non-cryst. glycols. The *Me xanthate*, m.p. 86°, from *cis*-decahydro-α-naphthol (IV), m.p. 93°, similarly decomposes to (mainly) *cis*-$\Delta^{1:2}$-octahydronaphthalene (V) and a little (I) [(III) is not isolated on ozonolysis], whilst the *p*-toluenesulphonate of (IV) and Na_2CO_3 in boiling MeOH afford (I) (about 80%), (V) (about 20%), and a trace of $\Delta^{9:10}$-octahydronaphthalene (VI). The *p*-toluenesulphonate of *trans*-decahydro-α-naphthol, m.p. 49°, similarly gives (I) (about 80%), (II) (about 20%), and a trace of (VI). (I) is largely isomerised to (VI) by *p*-C_6H_4Me·SO_3H in MeOH. The N-*Me* derivative, b.p. 119—122°/22 mm., of *trans*-decahydro-α-naphthylamine, m.p. −1°, MeI, and MeOH–KOH give trans-*decahydro-α-naphthyltrimethylammonium iodide*, decomp. partly from 180°; thermal decomp. of the hydroxide affords almost 100% of (II), which is oxidised by BzO_2H to a *glycol* (VII), $C_{10}H_{18}O_2$, m.p. 184—186°, and by $KMnO_4$ to *trans*-3-2-carboxy*cyclo*hexylpropionic acid. The mol. heats of combustion of (I) and (VI) are 1452—1454 and 1455—1456 kg.-cal., respectively, and are approx. the same as that of *trans*-Δ^2-octahydronaphthalene (VIII) (A., 1930, 76), thus indicating the absence of strain in (I).

[With E. Baertich and (in part) A. Gercke.] Oxidation (BzO_2H) of a specimen of (VIII) which contains about 10% of *trans*-Δ^1-octahydronaphthalene gives the oxide, b.p. 91—92°/10 mm., hydrated to a mixture of a glycol (IX), m.p. 163°, and a little (VII). (IX) is the sole product when (VIII) is first regenerated from its dibromide, m.p. 85° (during the prep. of which an *isomeride*, m.p. 49—50°, is also formed), with Mg; about 50% of decahydronaphthalene is produced during this treatment. *Di*-trans-*decahydro-β-naphthyl ethers*, m.p. 52—54° and 62—65°, are by-products in the prep. of (VIII) from *trans*-decahydro-β-naphthol, m.p. 75° (cf. *loc. cit.*).

[With A. Gercke and A. Gross.] Oxidation (CrO_3, AcOH) of (VI) gives *trans*-9 : 10-dihydroxydecahydronaphthalene, m.p. 96° (cf. *loc. cit.*) (*monoacetate*, m.p. 132°), and 1-keto-$\Delta^{9:10}$-octahydronaphthalene, b.p. 128—130°/12 mm. (*semicarbazone*, m.p. 243°); the latter is reduced (H_2, Pd–C, MeOH) to 1-keto-decahydronaphthalene. H. B.

Dissociable organic oxides. The dissociable oxide of 1 : 1′-di-*p*-tolyl-3 : 3′-diphenyl-5 : 5-dimethylrubene. C. Dufraisse and J.-A. Monier (Compt. rend., 1933, **196**, 1327—1329).—Et phenylpropiolate and *p*-C_6H_4Me·MgBr yield γ-*phenyl*-αα-*di*-p-*tolylpropinen*-α-*ol*, m.p. 87—88° (giving a *Me ether*, m.p. 75—76°, and *phenyl* ββ-*di*-p-*tolylvinyl ketone*, m.p. 107—108°). This affords 1 : 1′-*di*-p-*tolyl*-3 : 3′-



(I.)

diphenyl-5 : 5′-*dimethylrubene* (I), m.p. (anhyd.) 242° (+0·33BuOAc 194°), giving the *peroxide*, $C_{46}H_{36}O_4$, m.p. 210° (anhyd.), which decomposes quantitatively at 170°. R. S. C.

Nitration of alkyl oxanilates. G. Tierie (Rec. trav. chim., 1933, **52**, 420—424).—Et oxanilate affords good yields of the *p*-NO_2- (by HNO_3, *d* 1·45, at 0°), 2 : 4-*di*-, m.p. 143° (by abs. HNO_3 at 0°), and

2 : 4 : 6-*trinitro*-, m.p. 105° (by abs. HNO_3 and H_2SO_4 at < 35°), -derivatives. Mc oxanilate gives similarly the *p*-, m.p. 232° (also obtained from *p*-nitroaniline and $Me_2C_2O_4$ at 100°), 2 : 4-*di*-, m.p. 181°, and 2 : 4 : 6-*trinitro*-, m.p. 132—134°, -derivatives. R. S. C.

Nitrosation of methylaniline. J. C. Earl and N. F. B. Hall (J.C.S., 1933, 510—512).—Interaction of NHPhMe,HCl and HNO_2 in MeOH studied in a dilatometer (A., 1932, 1125) shows that at 8° vol. contraction occurs during the initiatory period (I) followed by a sudden expansion (II) and then contraction to const. vol. (II) is due to a sudden rise in temp. of about 1°. Reaction probably occurs as a result of the formation of $NPhMe^{\cdot}$ followed by an accumulation of $H^{\cdot}$ which catalyses the reaction. This explanation finds strong support in conductivity measurements on the reaction mixture, and in the fact that the greater is the acid concn. the shorter is (I). J. L. D.

Influence of the nitroso-group on the formation of [complex salts of] amines. R. Rascanu (Ann. Sci. Univ. Jassy, 1933, **17**, 130—148).—The following *salts* are prepared: (*a*) $[UO_2,B]X_2$; B = *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and *p*-$NO{\cdot}C_6H_4{\cdot}NEt_2$; X = NO_3, OAc, and $0{\cdot}5C_2O_4$; (*b*) $[UO_2,B_2]X_2$; B as above; X = NO_3, Cl, Br, and $0{\cdot}5SO_4$. They are stable in air, decomposed by dil. acids, and give reactions for UO_2. $NPhMe_2$ and $NPhEt_2$ do not form such salts. The NO-group is thus probably responsible for complex formation, and its position appears to influence the readiness with which it takes place. However, antipyrine forms a salt, and the NO-derivative gives a salt containing 3 mols. of base. R. S. C.

Reductions with lead–sodium [alloys]. F. Fichter and H. Stenzl (Helv. Chim. Acta, 1933, **16**, 571—573; cf. A., 1932, 49).—An aq. solution of $NPhMe_3{\cdot}SO_4Me$ is reduced by 30% Na–Pb alloy to NMe_3 and C_6H_6; the alloy behaves qualitatively and quantitatively like a Pb cathode. Na–Hg is without action. F. L. U.

Alkylanilines with tertiary alkyl groups. W. J. Hickinbottom (Nature, 1933, **131**, 762—763).—Pure *tert.*-butyl- (I), -amyl- (II), and -hexylaniline (III) have been obtained by a modification of Nef's method. The *tert.*-alkyl group is removed by heating the amines with dil. mineral acid, and this type of fission occurs more readily with the arylsulphonyl derivatives. With hot, dil. H_2SO_4 the readiness with which the alkyl group is eliminated is in the order (I) < (II) < (III). The freo amines do not readily react with Ac_2O or arylsulphonyl chlorides. MeI readily reacts with (I). L. S. T.

Aromatic compounds of fluorine. XIV. Reaction of *p*-fluorophenylhydrazine; *N*-alkylated fluoroanilines. G. Schiemann and W. Winkelmuller (Ber., 1933, 66, [*B*], 727—732; cf. A., 1932, 1247).—Diazotisation of *p*-$C_6H_4F{\cdot}NH_2$ in HCl followed by reduction with $NaHSO_3$ gives *p*-fluorophenylhydrazine (I), b.p. 129·2°/21 mm., m.p. 39°, in 74% yield (cf. Rinkes, A., 1914, i, 679, 1200). The *hydrochloride* volatilises with decomp. without melting. (I) smoothly yields *salicylaldehyde*-p-*fluorophenylhydrazone*, m.p. 166·5°, *glucose*-p-*fluorophenylosazone*, decomp. 187—188°, and *benzoylacetyl*-p-*fluorophenylhydrazone*, m.p. 179·5°. (I) and $COMe_2$ in presence of $ZnCl_2$ at 100° afford 5-*fluoro*-2-*methylindole*, m.p. 102°. Treatment of (I) with $CH_2Ac{\cdot}CO_2Et$ in boiling 50% AcOH leads to impure 1-p-*fluorophenyl*-3-*methylpyrazol*-5-*one*, transformed by boiling $COMe_2$ into a mixture of 4 : 4′-iso*propylidenedi*-1-p-*fluorophenyl*-3-*methylpyrazol*-5-*one* (II), m.p. 141·5°, and 1-p-*fluorophenyl*-3-*methyl*-4-iso*propylidenepyrazol*-5-*one* (III), m.p. 136°. (II) is partly transformed into (III) in boiling $COMe_2$.

[With R. Pillarsky.] *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ is diazotised and converted into the *diazonium fluoborate*, decomp. 151°, which when heated with sand gives *p*-fluorodimethylaniline, b.p. 78—79·5°/16 mm., m.p. 25° (hygroscopic *hydrochloride*, m.p. 118°; *picrate*, m.p. 151·5°), in 17·2% yield. Similarly, p-*diethylaminophenyldiazonium fluoborate*, decomp. 113°, gives *p*-$C_6H_4F{\cdot}NEt_2$, b.p. 92·5°/12 mm. (*picrate*, m.p. 150·5°), in 20% yield. H. W.

Action of heat on β-naphthyl*iso*propylamine hydrochloride. T. Heap (J.C.S., 1933, 495—496).—β-$C_{10}H_7{\cdot}NH_2$, and $Pr^{\beta}Br$ in a sealed tube at 180° during 6 hr. afford $NHPr^{\beta}{\cdot}C_{10}H_7$-β (*Bz* derivative, m.p. 96—98°; p-*toluenesulphonamide*, m.p. 119—120°; *hydrochloride*, m.p. 209—210°), which when heated under pressure at 300—320° for 6 hr. decomposes completely into propylene and β-$C_{10}H_7{\cdot}NH_2$. At 200—220° some $NH(C_{10}H_7\text{-}\beta)_2$ (I) is formed, the amount depending on the time of heating. (I) is formed similarly from β-$C_{10}H_7{\cdot}NH_2$,HCl (cf. A., 1885, 990). J. L. D.

Heteropolarity. XXI. *NN*′-Diphenyl-*p*-phenylenediamine and triphenylmethyl chloride. W. Dilthey and G. Escherich (Ber., 1933, **66**, [*B*], 782—783; cf. A., 1932, 263).—The increase in the intensity of colour developed by the gradual addition of Br_2 in AcOH to the "blue" chloride confirms the constitution $[NHPh{\cdot}C_6H_4{\cdot}NHPh]^+Cl,C_{18}H_{18}N_2$ previously assigned. *NN*′-Diphenyl-*p*-phenylene-diamine and -imine do not appear to yield a chemical compound comparable with a quinhydrone. H. W.

Ditolyl series. V. Resolution into optical antipodes of *dl*-2-iodo-2′-amino-6 : 6′-dimethyldiphenyl. A. Angeletti (Gazzetta, 1933, **63**, 145—151).—The NO_2-compound (A., 1932, 152) is reduced ($SnCl_2$) to dl-2-*iodo*-2′-*amino*-6 : 6′-*dimethyldiphenyl*, m.p. 46—47° (I) (*hydrochloride*, m.p. 203—204°), from which the d-*bromocamphorsulphonates*, m.p. 167—168° (decomp.), $[\alpha]_D^{20}$ +48·0°, and m.p. 125° (decomp.), $[\alpha]_D^{20}$ +39·33°, respectively, of the d- and l-*isomerides* yield the *hydrochlorides*, each of m.p. 202—203°, $[\alpha]_D^{20}$ +2·33°, and −2°, respectively. From (I), or from 2 : 2′-diamino-6 : 6′-dimethyldiphenyl, 2 : 2′-*di*-*iodo*-6 : 6′-*dimethyldiphenyl*, m.p. 92—93°, is obtained, with an insol. product. E. W. W.

Action of bromine on nitrobenzeneazoacetoacetates and related compounds. F. D. Chattaway and D. R. Ashworth (J.C.S., 1933, 475—479; cf. A., 1932, 1125).—*p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ (I) and cold $CH_2Ac{\cdot}CO_2Et$ afford *Et* p-*nitrobenzeneazoacetoacetate* (II), m.p. 127°. *Et* 2-*bromo*-4-*nitro*-, m.p.

130°; *Et* 2 : 6-*dibromo*-4-*nitro*-, m.p. 135°; *Et* o-*nitro*-, m.p. 93°, and *Et* m-*nitro-benzeneazoacetoacetate*, m.p. 128°, are similarly prepared. (I) with $CH_2Ac{\cdot}CO_2H$ in aq. NaOAc at 0° affords α-*ketopropaldehyde*-p-*nitrophenylhydrazone* (III), m.p. 217°. α-*Ketopropaldehyde*-2-*bromo*-4-*nitro*-, m.p. 187°; -2 : 6-*dibromo*-4-*nitro*-, m.p. 151°; -o-*nitro*-, m.p. 128°; -m-*nitro*-, m.p. 152°, and -4-*bromo*-2-*nitro-phenylhydrazone*, m.p. 176°, are similarly prepared. (II) (1 mol.) and Br (1 mol.) in AcOH containing excess of NaOAc in the cold afford *Et* α-*bromoglyoxylate*-p-*nitrophenylhydrazone*, m.p. 203°, which with NH_3–EtOH affords *Et* α-*aminoglyoxylate*-p-*nitrophenylhydrazone*, m.p. 181°. The following are prepared similarly: *Et* α-*bromoglyoxylate*-2-*bromo*-4-*nitro*-, m.p. 126° (α-*amino*-compound, m.p. 124·5°); -2 : 6-*dibromo*-4-*nitro*-, m.p. 144° (α-*amino*-compound, m.p. 191°); -o-*nitro*-, m.p. 137° (α-*amino*-compound, m.p. 123°); -m-*nitro-phenylhydrazone*, m.p. 149°. (I) with $CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ in aq. EtOH–NaOAc during 6 hr., or Br (1 mol.) and (II) (1 mol.) in hot AcOH, affords *Et* p-*nitrobenzeneazo*-γ-*bromoacetoacetate* (IV), m.p. 163°. The following are prepared similarly: *Et* 2-*bromo*-4-*nitro*-, m.p. 138°; *Et* 2 : 6-*dibromo*-4-*nitro*-, m.p. 118°; *Et* o-*nitro*-, m.p. 145°; *Et* m-*nitro-benzeneazo*-γ-*bromoacetoacetate*, m.p. 122°. (II) (1 mol.) with Br (2 mols.) in boiling AcOH affords *Et* p-*nitrobenzeneazo*-γγ-*dibromoacetoacetate* (V), m.p. 134°. The following are prepared similarly: *Et* 2-*bromo*-4-*nitro*-, m.p. 167°; *Et* 2 : 6-*dibromo*-4-*nitro*-, m.p. 153°; *Et* o-*nitro*-, m.p. 116°; *Et* m-*nitro-benzeneazo*-γγ-*dibromoacetoacetate*, m.p. 117°. (II) (1 mol.) with Br (3 mols.) in boiling AcOH affords ββω-*tribromo*-α-*ketopropaldehyde*-p-*nitrophenylhydrazone*, m.p. 194°. The following are prepared similarly: -2-*bromo*-4-*nitro*-, m.p. 186°; -2 : 6-*dibromo*-4-*nitro*-, m.p. 128°; -m-*nitro*-, m.p. 158°; -o-*nitro*-, m.p. 145·5°; -4-*bromo*-2-*nitrophenylhydrazone*, m.p. 160°. (III) (1 mol.) with Br (1 mol.) in cold AcOH in 1 hr. affords ω-*bromo*-α-*ketopropaldehyde*-p-*nitrophenylhydrazone*, m.p. 233°, which with saturated EtOH–NH_3 affords the ω-*amino*-compound, m.p. 240° (decomp.); ω-*anilino*-compound, m.p. 167°. The following are prepared similarly: -2-*bromo*-4-*nitro*-, m.p. 162°; -2 : 6-*dibromo*-4-*nitro*-, m.p. 156°; -o-*nitro*-, m.p. 185°; -m-*nitrophenylhydrazone*, m.p. 214°. (III) with Br (2 mols.) in AcOH at 90° affords βω-*dibromo*-α-*ketopropaldehyde*-p-*nitrophenylhydrazone*, m.p. 228°, and similarly are prepared the -2-*bromo*-4-*nitro*-, m.p. 177°, -2 : 6-*dibromo*-4-*nitro*-, m.p. 136°, and -o-*nitro-phenylhydrazone*, m.p. 175° (ω-*amino*-compound, m.p. 174°; ω-*anilino*-compound, m.p. 140°). (III) with excess of Br affords the nitrophenylhydrazino-derivatives of ββγ-tribromo-α-ketopropaldehyde. (IV) in boiling EtOH with KOAc affords 4-*hydroxy*-3-*carbethoxy*-1-(4′-*nitrophenyl*)*pyrazole*, m.p. 220° (*Ac* derivative, m.p. 167°), brominated in boiling AcOH to 5-*bromo*-4-*hydroxy*-3-*carbethoxy*-1-(4′-*nitrophenyl*)*pyrazole*, m.p. 163° (*Ac* derivative, m.p. 126°), also obtained by the interaction of KOAc in boiling EtOH with (V). The following are prepared similarly: 4-*hydroxy*-3-*carbethoxy*-1-(2′-*bromo*-4′-*nitrophenyl*)*pyrazole*, m.p. 189° [*Ac* derivative, m.p. 138·5°; 5-*Br*-derivative, m.p. 218° (*Ac* derivative, m.p. 108°)]; -1-(2′ : 6′-*dibromo*-4′-*nitrophenyl*)*pyrazole*, m.p. 170° [*Ac* derivative, m.p. 148°; *Bz* derivative, m.p. 143°; 5-*Br*-derivative, m.p. 209·5° (*Ac* derivative, m.p. 126°)]; -1-(2′-*nitrophenyl*)*pyrazole*, m.p. 153° [*Ac* derivative, m.p. 115°; 5-*Br*-derivative, m.p. 161° (*Ac* derivative, m.p. 111°)]; -1-(3′-*nitrophenyl*)*pyrazole*, m.p. 199° (*Ac* derivative, m.p. 140·5°; 5-*Br*-derivative, m.p. 167°). J. L. D.

Action of bromine on arylazobenzoylacetones. F. R. Chattaway and R. J. Lye (J.C.S., 1933, 480—482; cf. preceding abstract).—Benzeneazobenzoylacetone (I), m.p. 90—95° (lit., 99°) (1 mol.), and Br (2 mols.) in cold AcOH containing NaOAc afford ω-*bromophenylglyoxal*-p-*bromophenylhydrazone*, m.p. 197° (converted by NH_2Ph in boiling EtOH into the ω-*anilino*-compound, m.p. 165°), further brominated in hot AcOH to ω-*bromophenylglyoxal*-2 : 4-*dibromophenylhydrazone* (II), m.p. 122° (ω-*anilino*-compound, m.p. 137°). The following analogues of (I) are described: 2 : 4-*dibromobenzene*- (III), m.p. 160° (*Ac* derivative, m.p. 171°), which with 1 equiv. Br affords (II); 2 : 4 : 6-*tribromobenzene-azobenzoylacetone*, m.p. 112° (*Ac* derivative, m.p. 159°), which with Br (1 mol.) in cold AcOH–NaOAc affords ω-*bromo*-, m.p. 132°, and with Cl_2 in AcOH affords ω-*chloro-phenylglyoxal*-2 : 4 : 6-*tribromophenylhydrazone*, m.p. 142° (ω-*anilino*-derivative, m.p. 118°). (I) (1 mol.) with Br (3 mols.) in AcOH at about 40° affords δδ-*dibromo*-αβγ-*triketo*-α-*phenylbutane*-β-p-*bromophenylhydrazone*, m.p. 177° (decomp.) (the intermediate stages being difficult to realise). (III) (1 mol.) with Br (1 mol.) in boiling AcOH affords δ-*bromo*-αβγ-*triketo*-α-*phenylbutane*-β-2 : 4-*dibromophenylhydrazone* (IV), m.p. 170° (decomp.), whereas more extensive bromination gives the δδ-*dibromo*-compound (V), m.p. 187° (decomp.). δ-*Bromo*- (VI), m.p. 158° (decomp.), and δδ-*dibromo*-αβγ-*triketo*-α-*phenylbutane*-β-2 : 4 : 6-*tribromophenylhydrazone* (VII), m.p. 156° (decomp.), are similarly prepared. (IV) when boiled with EtOH containing excess of KOAc affords 4-*hydroxy*-3-*benzoyl*-1-(2′ : 4′-*dibromophenyl*)*pyrazole*, m.p. 171°, brominated to a 5-*Br*-derivative, m.p. 127°, also obtained by the cyclisation of (V). (VI) is similarly cyclised to 4-*hydroxy*-3-*benzoyl*-1-(2′ : 4′ : 6′-*tribromophenyl*)*pyrazole*, m.p. 206° (*Ac* derivative, m.p. 140°), brominated to a 5-*Br*-derivative, m.p. 178° [*Ac* derivative, m.p. 117° (decomp.)], also obtained from (VII). J. L. D.

Demethylating phenol ethers. E. A. Tzofin and K. A. Tschchkivadze (Khim. Farm. Prom., 1932, **10**, 376).—By a modification of Klemens' method, in which salts of aromatic amines are used together with dry HCl at 160—170°, 94% yields are obtained. Ch. Abs.

Iodination of phenol under anhydrous conditions. W. H. Hunter and T. T. Budrow (J. Amer. Chem. Soc., 1933, **55**, 2122—2125).—Iodination of PhONa (from PhOH and Na) in dry xylene proceeds almost as rapidly as in presence of H_2O; approx. 1 mol. of I is consumed and the products formed are (mainly) o-$C_6H_4I{\cdot}OH$, small amounts of $C_6H_3I_2{\cdot}OH$ and $C_6H_2I_3{\cdot}OH$, and a trace of a halogen-free non-phenolic substance, m.p. 116—118°. Coffman's postulation (J.C.S., 1919, **115**, 1040) of HOI as the active iodinating agent cannot apply in this case.

Behaviour of mixed halogenated phenols in the Zincke method of nitration. L. C. RAIFORD and G. R. MILLER (J. Amer. Chem. Soc., 1933, **55**, 2125—2131).—*4-Chloro-2-bromophenol*, b.p. 121—123°/10 mm., m.p. 33—34° (from *p*-C_6H_4Cl·OH and Br in CS_2) (*benzoate*, m.p. 99—100°), is nitrated by $NaNO_2$ and AcOH (the Zincke method) to its 6-NO_2-derivative (I), whilst 2 chloro-4-bromophenol, b.p. 233—234°, m.p. 48—49° (lit. 50—51°) (from *o*-C_6H_4Cl·OH), similarly gives its 6-NO_2-derivative (II) and 2-chloro-4-nitrophenol. 2 : 4-Dichloro-6-bromo- and 2 : 6-dichloro-4-bromo-phenols similarly afford 2 : 4-dichloro-6-nitro- and 2 : 6-dichloro-4-nitro-phenols, respectively; 4-chloro-2 : 6-dibromophenol yields (I), whilst 2-chloro-4 : 6-dibromophenol furnishes (II) and 2-chloro-6-bromo-4-nitrophenol. 5-Chloro-3 : 4 : 6-tribromo-*o*-cresol (from 5-chloro-*o*-cresol and an excess of Br containing about 1% Al) is oxidised (fuming HNO_3 at 0°) to 3 : 4 : 6-tribromotoluquinone, m.p. 238—240° (lit. 232°), and nitrated to ɔ-*chloro*-4 : 6-*dibromo*-3-*nitro*-o-*cresol*, m.p. 149—150° (*benzoate*, m.p. 131—132°), whilst 3-chloro-4 : 5 : 6-tribromo-*o*-cresol, m.p. 214—216° (lit. 209—211°), is nitrated to 3-*chloro*-4 : 6-*dibromo*-5-*nitro*-o-*cresol*, m.p. 182—183°. When both *o*- and *p*-positions are substituted by Cl and the other positions by Br, no replacement of halogen occurs (even with 2 mols. of $NaNO_2$).

3-*Chloro*-ɔ-*bromo*-p-*cresol* (III), b.p. 127—128°/5 mm., m.p. 30° (by chlorination of the bromocresol), is nitrated to 3-chloro-5-nitro-*p*-cresol, whilst 3-*chloro*-5 : 6-*dibromo*-p-*cresol*, m.p. 80—81° [from (III) and Br in $CHCl_3$ containing a little I and Fe powder], gives 3-*chloro*-6-*bromo*-5-*nitro*-p-*cresol*, m.p. 109—110°, and 3-*chloro*-2 : 5 : 6-*tribromo*-p-*cresol*, m.p. 197—198° [from (III) and excess of Br containing Al], affords 3-*chloro*-2 : 6-*dibromo*-5-*nitro*-p-*cresol*, m.p. 157—158° (*Na* salt). 6-Chloro-4-bromo-*m*-cresol is nitrated to its 2-NO_2-derivative, m.p. 103—104°, and 6-*chloro*-4-*nitro*-m-*cresol* (IV), m.p. 133—134°, whilst 6-chloro-2 : 4-dibromo-*m*-cresol gives 6-*chloro*-2-*bromo*-4-*nitro*-m-*cresol*, m.p. 87°, also prepared by bromination of (IV). Cl is not replaced by NO_2 under the conditions now used.

5-*Chloro*-3-*amino*-o-*cresol*, m.p. 107° (ON-Ac_2, m.p. 195—196°, N-*Ac*, m.p. 110°, O-*Ac*-N-*Bz*, m.p. 159°, and N-*Bz*, m.p. 203°, derivatives), 6-*chloro*-4-*bromo*-2-*amino*-m-*cresol*, m.p. 131—132° (ON-Ac_2, m.p. 215°, N-*Ac*, m.p. 184—185°, O-*Ac*-N-*Bz*, m.p. 166—167°, and N-*Bz*, m.p. 247°, derivatives), 6-*chloro*-2-*bromo*-4-*amino*-m-*cresol*, m.p. 111—112° [ON-Ac_2, m.p. 220°, N-*Ac*, m.p. 180° (decomp.), O-*Ac*-N-*Bz*, m.p. 189°, N-*Bz*, m.p. 192—193°, and ON-Bz_2, m.p. 191°, derivatives], and 3-*chloro*-6-*bromo*-5-*amino*-p-*cresol*, m.p. 146—147° (ON-Ac_2, m.p. 194—195°, N-*Ac*, m.p. 149—149·5°, O-*Ac*-N-*Bz*, m.p. 220—221°, and N-*Bz*, m.p. 178°, derivatives), are prepared by reduction of the corresponding NO_2-derivatives by the method previously described (A., 1911, i, 993). Only one (*O*-)Ac-(*N*-)Bz derivative can be prepared from a substituted *o*-aminophenol regardless of the order of introduction of the groups. H. B.

Synthesis of chloromethyl derivatives of *p*-bromoanisole and the nitroanisoles. R. QUELET (Compt. rend., 1933, **196**, 1411—1413; cf. A., 1932, 943).—*p*-C_6H_4Br·OMe, $(CH_2Cl)_2O$ [or, more conveniently, OMe·CH_2Cl (I)], and $ZnCl_2$ at room temp. give about 45% of 5-bromo-2-methoxybenzyl chloride; a larger proportion of 5 : 5′-dibromo-2 : 2′-dimethoxydiphenylmethane is formed with (I). With *o*-NO_2·C_6H_4·OMe (II), reaction begins at about 40°, is rapid at 70°, and gives a good yield of 3-nitro-4-methoxybenzyl chloride (III); *p*-NO_2·C_6H_4·OMe (IV) reacts more slowly, whilst *m*-NO_2·C_6H_4·OMe (V) affords a trace only of condensation product. With $SnCl_4$ for $ZnCl_2$, (II) gives a quant. yield of 3 : 3′-dinitro-4 : 4′-dimethoxydiphenylmethane (VI), m.p. 168°, which is oxidised (CrO_3) to 3 : 3′-dinitro-4 : 4′-dimethoxybenzophenone, m.p. 190°; (IV) similarly affords the CH_2Cl derivative. Saturation of suspension of $(CH_2O)_3$ and $ZnCl_2$ in (II) with dry HCl gives 80% of (III) and a little (VI); (IV) similarly gives 70% of 5-nitro-2-methoxybenzyl chloride, whilst (V) affords a trace of 4-nitro-2-methoxybenzyl chloride, m.p. 90°. H. B.

Physico-chemical properties of *p*-aminophenol methosulphate. V. LUCAS (Bol. assoc. brasil. pharm., 1932, **12**, 214).—The substance gives with $FeCl_3$ a wine-red colour on boiling, reduces hot Fehling's solution and Nessler reagent, and gives ppts. with basic Pb acetate, $BaCl_2$, and Br–H_2O.

CH. ABS.

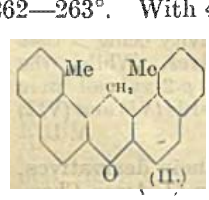
Antiseptic activity and chemical constitution of the xylenols and their monohalogen derivatives. G. LOCKEMANN and T. KUNZMANN (Angew. Chem., 1933, **46**, 296—301).—The following monohalogeno-xylenols are prepared by the action of SO_2Cl_2 and Br on the corresponding xylenols and from the corresponding nitro-xylenols by reduction and diazotisation in presence of I, KI, and Cu powder, respectively: 6-*chloro*-, m.p. 98°, 6-*bromo*-, m.p. 92°, 6-*iodo*-, m.p. 84°, -o-3-; 5-*chloro*-, m.p. 87°, ɔ-*bromo*-, m.p. 84°, 5-*iodo*-, m.p. 71°, -o-4-; 5-*chloro*- (I), m.p. 72°, 5-*iodo*- (II), m.p. 68°, -m-2-; 5-*iodo*-m-4- (III), b.p. 108°; 2-*bromo*-, m.p. 82°; 2-*iodo*-, m.p. 74°, -m-5-; 5-*chloro*- (IV), and ɔ-*iodo*-p-2-*xylenol*. Action of the xylenols on *B. coli* (V), *Staphylococcus pyogenes aureus* (VI), and *B. typhosus* (VII) was not appreciably affected by the position of the Me and OH groups, but the effect of the position of halogen substitution was very marked. Whereas of the Cl-derivatives (I) and (IV) were most active against (V), the activity of the corresponding Br- and I-derivatives was much less, although still > that of the xylenols. (II) and (III) and the corresponding Br-derivatives were the most active of these two series, their activity being > that of the corresponding Cl-derivatives. Whilst the halogen derivatives of *m*-2- and *p*-2-xylenol were similar in activity towards (V), towards (VI) and (VII) the latter was much more active. A. L.

Nitro*cyclo*hexylphenols and their derivatives. J. F. BARTLETT and C. E. GARLAND (J. Amer. Chem. Soc., 1933, **55**, 2064—2068).—*o-cyclo*Hexylphenol (I) and HNO_3 (*d* 1·5) in EtOAc containing P_2O_5 at <—15° and then at 0°, give a NO_2-derivative, b.p. 144—146°/3—4 mm.; at 0—5° and then at room temp., a $(NO_2)_2$-derivative, m.p. 106·5—107·5° [reduced (H_2, PtO_2, Ac_2O) to the Ac_3 derivative, m.p. 200—202°,

of the $(NH_2)_2$-compound], results. *p-cyclo*Hexylphenol (II) similarly affords a NO_2-derivative, b.p. 140—142°/2 mm. (*Me ether*, b.p. 148—152°/4 mm.; *Et ether*, b.p. 146—150°/4 mm.), which is reduced (as above) to the Ac_2 derivative, m.p. 173—174°, of the NH_2-compound, and a $(NO_2)_2$-derivative (III), m.p. 84—85° (*Me ether*, b.p. 204—208°/7 mm.; *Et ether*, m.p. 83—84°), which is reduced (as above) to the Ac_3 derivative, m.p. 212—213°, of the $(NH_2)_2$-compound. It is probable that in the prep. of the ethers of (III) by Drew's method (J.C.S., 1920, **117**, 1618), *aci*-ethers are first formed; these subsequently rearrange. (I) and (II) are prepared from *cyclo*hexanol and PhOH in presence of P_2O_5, $ZnCl_2$, or conc. H_2SO_4 at 100° (bath) for 2—3 days. H. B.

Butyl and amyl ethers of naphthols and some of their derivatives. S. D. Wilson, C. M. Ma, and Y. L. T'ien (J. Chinese Chem. Soc., 1933, **1**, 11—16).—*n*-Bu and *n*-amyl bromides with K naphthoxides by an improved process give (50—65% yield) the following: 1-*chloro*-, m.p. 28°, 1-*bromo*-, m.p. 29·5°, and 1-*nitro*-β-*naphthyl Bu*^{a} *ether*, m.p. 55°, and α-*naphthyl*, m.p. 29·5—30·0°, β-*naphthyl*, m.p. 24·0—24·5°, and 1-*chloro*-, m.p. 31·0—31·5°, 1-*bromo*-, m.p. 25·5°, and 1-*nitro*-β-*naphthyl* n-*amyl ether*. α- and β-Naphthyl Bu^a ethers have m.p. 24° and 34·5—35·0°, respectively. A. A. L.

7-Hydroxy-1-methylnaphthalene. V. Vesely and F. Šturša (Coll. Czech. Chem. Comm., 1933, **5**, 170—178).—Reduction of the 7-NO_2-derivative (Schroeter and Laves, A., 1930, 1039) of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (prepared by a modification of Hock and Susemihl's method, this vol., 153) affords the 7-NH_2-derivative, from which by diazotisation is obtained the 7-*OH*-compound, m.p. 166°, b.p. 213—215°/12 mm., the *Me ether*, m.p. 67—68°, of which with MeMgI affords the *tert.*-alcohol, which loses H_2O at 100—110° giving 7-*methoxy*-1-*methyl*-3 : 4-*dihydronaphthalene*, b.p. 154—156°/12 mm. This is dehydrogenated by S at 220° to the *Me ether*, m.p. 47—48°, b.p. 152—153°/10 mm., of 7-*hydroxy*-1-*methylnaphthalene* (I), m.p. 69—70°, b.p. 176°/10 mm. (*Bz* derivative, m.p. 88—90°), which is obtained by demethylation with HBr (*d* 1·49). (I) is converted by conc. aq. NH_3+$(NH_4)_2SO_3$ at 170° into 7-*amino*-1-*methylnaphthalene*, m.p. 85—86° (Ac derivative, m.p. 157—158°, identical with a specimen prepared from 7-nitro-1-methylnaphthalene), and couples with diazotised *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ to give 8-p-*nitrobenzeneazo*-1-*methyl*-7-*naphthol*, m.p. 262—263°. With 40% CH_2O in 50% AcOH (I) gives the *dimethyldinaphthopyran* (II), m.p. 216—217°, and with $FeCl_3$ it affords 7 : 7-*dihydroxy*-1 : 1-*dimethyl*-8 : 8′-*dinaphthyl*, m.p. 238—239°. The m.p. of (I) and its related compounds differ from those obtained by Dziewoński and Waszkowski (A., 1930, 336). J. W. B.



(II.)

Bromo-derivatives of benzylphenols. I. Mono-, di-, and tri-bromo-derivatives of *o*- and *p*-benzylphenols. R. C. Huston, A. Neeley, B. L. Fayerweather, H. M. D'Arcy, F. H. Maxfield, M. M. Ballard, and W. C. Lewis (J. Amer. Chem. Soc., 1933, **55**, 2146—2149).—Br-derivatives of 2- and 4-hydroxydiphenylmethanes are prepared from benzyl (and the bromobenzyl) chloride and PhOH (and its Br-derivatives) by the Claisen method (A., 1925, i, 656) or by condensation with $AlCl_3$. The presence of Br in the ring of CH_2PhCl favours ether formation with $AlCl_3$, and affects the yield in the Claisen reaction (the retarding influence increases in the order: *p*-, *o*-, *m*-Br). Ethers are not produced from the bromophenols, CH_2PhCl, and $AlCl_3$. The Br_3-derivatives described are also prepared by bromination of the corresponding Br-compounds in the cold. The following derivatives are described: (*a*) of 2-hydroxydiphenylmethane: 3-, b.p. 150—153°/2 mm. (*benzoate*, m.p. 89·5—90°; *p-toluenesulphonate*, m.p. 85—85·5°), 5-, m.p. 55—56°, 2′-, m.p. 47—48° (*benzoate*, m.p. 39—40°), 3′-, b.p. 167—169°/3 mm. (*benzoate*, m.p. 69—70°), and 4′-, m.p. 72—73° (*benzoate*, m.p. 50—51°), -*Br*-derivatives; 3 : 5-Br_2-derivative, m.p. 90—91°; 3 : 5 : 2′-, m.p. 41·5—42·5°, 3 : 5 : 3′-, m.p. 76—77° (*benzoate*, m.p. 90—91°), and 3 : 5 : 4′-, m.p. 80—81° (*benzoate*, m.p. 115—116°), -Br_3-derivatives; (*b*) of 4-hydroxydiphenylmethane: 3-, b.p. 148—150°/2 mm. (*benzoate*, m.p. 63—64°; *benzenesulphonate*, m.p. 56—57°), 2′-, m.p. 71—73° (*benzoate*, m.p. 64—65°), 3′-, b.p. 169—171°/3 mm. (*benzoate*, m.p. 97—98°), and 4′-, m.p. 82—83° (*benzoate*, m.p. 118—120°), -*Br*-derivatives; 3 : 5-Br_2-derivative, m.p. 56—57°; 3 : 5 : 2′-, m.p. 78—80°, 3 : 5 : 3′-, m.p. 106—107° (*benzoate*, m.p. 131·5—132·5°), and 3 : 5 : 4′-, m.p. 81—82° (*benzoate*, m.p. 144—145°), -Br_3 derivatives. The following *ethers* are prepared: 2 : 4-*dibromophenyl benzyl*, m.p. 67—68°; o-, b.p. 142—144°/2 mm., and p-, m.p. 60—61°, -*bromophenyl benzyl*; *Ph* o-, m.p. 34—36°, m-, m.p. 36—37°, and p-, m.p. 92·5—93·5°, -*bromobenzyl*; 2 : 4-*dibromophenyl* o-, m.p. 62—64°, m-, m.p. 49—50°, and p-, m.p. 86—87°, -*bromobenzyl*. In some cases the yield of hydroxydiphenylmethane in the Claisen reaction is much increased by addition of the corresponding Ph benzyl ether. H. B.

Derivatives of dihydroeugenol and pharmacological properties of some of the compounds. D. E. Levin [with A. Lowy] (J. Amer. Chem. Soc., 1933, **55**, 1995—2000).—Reduction (H_2, PtO_2, EtOH) of eugenol [5-NO_2-derivative (I), m.p. 42·8—43·4° (*K* salt)] gives dihydroeugenol (II), b.p. 94—95°/1 mm., 126—127°/15 mm. (*acetate*, b.p. 115°/2 mm.; *benzoate*, m.p. 73°), which with HNO_3 (*d* 1·5) in Et_2O at 23—26° affords *o-nitro*-4-*hydroxy*-3-*methoxypropylbenzene*, m.p. 33·8—34·2° (*K* salt). This is reduced (as above) to 5-*amino*-4-*hydroxy*-3-*methoxypropylbenzene* (III), m.p. 83—84° (*hydrochloride*, decomp. 191—192°; ON-Ac_2, m.p. 155°, ON-Bz_2, m.p. 162°, and p-*nitrobenzylidene*, m.p. 133—134°, derivatives), also prepared by similar reduction of (I). *Dyes* are prepared from diazotised (III) and β-$C_{10}H_7{\cdot}OH$, 1 : 8-aminonaphthol-3 : 6-disulphonic acid, 2-hydroxy-3-naphthanilide, and α-naphthol-4-sulphonic acid. 2-*Methoxy*-4-*propylphenoxyacetic acid*, m.p. 104°, is obtained from (II), $CH_2Cl{\cdot}CO_2H$, and aq. KOH. The effects of many of the above compounds on mucous membrane, cardiac muscle, turtle heart (*in situ*), blood pressure, and respiration are given. H. B.

Action of cyanogen on phenols and naphthols. II. Trihydroxybenzenes. III. Naphthols. G. MACHEK (Monatsh., 1933, **62**, 195—205; cf. A., 1932, 1245).—The following additive *compounds* are prepared by interaction of gaseous $(CN)_2$ with the appropriate OH-compound in H_2O or EtOH at 0°: 2[1 : 2 : 3-$C_6H_3(OH)_3$],$(CN)_2$, decomp. 125—135°; β-$C_{10}H_7$·OH,$(CN)_2$, decomp. 109—110°; 3[2 : 3-$C_{10}H_6(OH)_2$],$(CN)_2$, m.p. 150—180° (decomp.); 3[2 : 3-$C_{10}H_6(OH)_2$],2$(CN)_2$, decomp. 220—230°; 2 : 7-$C_{10}H_6(OH)_2$,$(CN)_2$, decomp. 135°. PhOH reacts with $(CN)_2$ in H_2O, but not in EtOH or CS_2, to give a very unstable additive compound that could not be isolated pure on account of its ready loss of $(CN)_2$. Negative results were also obtained with 1 : 2 : 4- and 1 : 3 : 5-$C_6H_3(OH)_3$, α-$C_{10}H_7$·OH, and 1 : 3- and 1 : 4-$C_{10}H_6(OH)_2$. H. A. P.

Podophyllin. III. W. BORSCHE and J. NIEMANN (Annalen, 1933, **502**, 264—272).—Veratraldehyde, Na methylsuccinate, and Ac_2O at 115—125° give γ-3 : 4-dimethoxyphenyl-α-methyl-Δ^{β}-butenoic acid, the Me ester of which when reduced catalytically and subsequently warmed with conc. H_2SO_4 affords 1-*keto*-6 : 7-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I), m.p. 129—130° [2 : 4-*dinitrophenylhydrazone*, m.p. 259—260° (decomp.)]. Clemmensen reduction of (I) and dehydrogenation (Se at 250—280°) of the product gives 6 : 7-*dimethoxy*-2-*methyl naphthalene* (II), m.p. 98—99° (*picrate*, m.p. 118—120°), which is identical with phyllomerol Me_2 ether (A., 1932, 1258). Veratrole, methylsuccinic anhydride, and $AlCl_3$ in $PhNO_2$ give β-3 : 4-*dimethoxybenzoylbutyric acid* (III), m.p. 107—108° [*Me* ester, m.p. 74—75° (2 : 4-*dinitrophenylhydrazone*, m.p. 155—156°)], and non-cryst. material (*A*). Clemmensen reduction of (III) affords some γ-3 : 4-*dimethoxyphenyl*-β-*methylbutyric acid*, b.p. 200—220°/15 mm., which with conc. H_2SO_4 yields 1-*keto*-6 : 7-*dimethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 120—121° [2 : 4-*dinitrophenylhydrazone*, m.p. 200—201° (decomp.)], convertible [as (I)] into (II). Esterification (MeOH) of (*A*) gives a *Me* ester, $C_{14}H_{18}O_5$, b.p. 218—220°/12 mm., whilst reduction (Clemmensen) affords 6 : 7-*dihydroxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (?), m.p. 76—80°, and *tetrahydrophyllomerol Me*, m.p. 98—101°, and Me_2 ethers. Phyllomeronic acid is converted partly into podophyllomeronic acid (*loc. cit.*) when heated with CH_2I_2 and MeOH–NaOMe at 100°/20 hr. The optical activity of *apo*picropodophyllin is confirmed; vals. of $[\alpha]_D^{15}$ +99·6° and $[\alpha]_D^{15}$ +107° are found for preps. obtained using Ac_2O–H_2SO_4 and PCl_5, respectively. H. B.

Reaction of halogen-substituted aryl alkyl and dialkyl sulphides with benzylamine. I. T. P. DAWSON (J. Amer. Chem. Soc., 1933, **55**, 2070—2075).—The following are prepared [generally by methods already described (lit.)]: Et, b.p. 63—65°/47 mm., Pr$^{\alpha}$, b.p. 43—45°/2 mm., Bu$^{\alpha}$, b.p. 58—59°/1 mm., *iso*amyl, b.p. 68°/1 mm., Ph, b.p. 88—89°/0·637 mm., and benzyl, b.p. 113—115°/1·01 mm., β-chloroethyl sulphides; CH_2Br·CH_2·SEt, b.p. 57—58°/6 mm.; di-β-, b.p. 94—95°/7 mm., and di-γ-, b.p. 111—112°/7 mm., -chloropropyl sulphides; Et β-chloropropyl, b.p. 60°/17 mm., and *Et γ-chloropropyl*, b.p. 72°/17 mm., sulphides; $S(CH_2Cl)_2$, b.p. 51°/11 mm.; di-β-chloroethyl disulphide, b.p. 124—127°/10 mm.; β-chloroethyl chlorovinyl sulphide (mixture), b.p. 83—84°/4 mm.; β-chloroethyl αβ-dichlorovinyl sulphide, b.p. 79·5—80·5°/4 mm.; *Et allyl sulphide*, b.p. 115—116°. The following are prepared from CH_2Ph·NH_2, the appropriate alkyl (aryl) chloro- (or bromo-)alkyl sulphide, and Na_2CO_3 in EtOH: *Et*, b.p. 162—164°/13 mm. (*hydrochloride*, m.p. 214—215°), Pr$^{\alpha}$, b.p. 167—169°/13 mm. (*hydrochloride*, m.p. 175°), Bu$^{\alpha}$, b.p. 172—230°/13 mm. (*hydrochloride*, m.p. 152—153°), iso*amyl*, b.p. 190—250°/17 mm. (*hydrochloride*, m.p. 161—162°), *Ph*, decomp. when heated (*hydrochloride*, m.p. 152—153°), *chlorovinyl* (mixture), decomp. when heated (*hydrochloride*, m.p. 211—212°), and αβ-*dichlorovinyl*, decomp. when heated (*hydrochloride*, m.p. 174—176°), β-*benzylaminoethyl sulphides*; *Et* γ-*benzylaminopropyl sulphide*, b.p. 163—165°/12 mm. (*hydrochloride*, m.p. 172°); 3-*benzyl*-1 : 3-*thiazetidine*, b.p. 175—185°/16 mm. (*hydrochloride*, m.p. 201—203°); *di*-β-*benzylaminopropyl sulphide*, decomp. when heated (*hydrochloride*, m.p. 239—240°); *ai*-β-*benzylaminoethyl disulphide*, decomp. when heated (*hydrochloride*, m.p. 269°). Numerous other physical data are given. H. B.

Preparation and properties of 2 : 4-dimethoxyphenyl alkyl sulphides. C. M. SUTER and H. L. HANSEN (J. Amer. Chem. Soc., 1933, **55**, 2080—2082).—*m*-$C_6H_4(OMe)_2$ and conc. H_2SO_4 give 2 : 4-dimethoxybenzenesulphonic acid [p-*toluidine* salt, m.p. 191—192° (corr.); *acid chloride* (I), m.p. 70·5° (softens at 69°); *amide*, m.p. 166—167°], the K salt of which with Cl_2 in H_2O affords 4 : 6-dichlororesorcinol Me_2 ether. Reduction (cf. Org. Synth., 1921, **1**, 71) of (I) gives 2 : 4-dimethoxythiophenol (II), b.p. 115—117°/5 mm. (*Pb* salt). 2 : 4-*Dimethoxyphenyl Me*, b.p. 115—118°/4 mm., m.p. 38—39°, *Et*, b.p. 140—142°/7 mm., Pr$^{\alpha}$, b.p. 157—160°/8 mm., and Bu$^{\alpha}$, b.p. 148—151°/6 mm., *sulphides* are prepared from (II) by the method previously described (A., 1932, 1244); the mol. refractions of these show considerable exaltation. Demethylation of these sulphides did not give the expected $(OH)_2$-compounds. H. B.

Factors giving rise to the abnormal iodine value of cholesterol. J. O. RALLS (J. Amer. Chem. Soc., 1933, **55**, 2083—2094).—When cholesterol (I) is treated with IBr or C_5H_5N sulphate dibromide (II) in AcOH the main reaction is the formation of the dihalide; this loses HHal at 0° and 25° (the elimination is facilitated by C_5H_5N) to give dehydrocholestan-4-ol-7-one (III) (Windaus, A., 1904, i, 49) [dinitrophenylhydrazone, m.p. 257° (decomp.)]. (I) is also oxidised by IBr or (II) in AcOH at 25° to cholestenone (IV) (2 : 4-dinitrophenylhydrazone, m.p. 231—232°). Elimination of HHal does not occur when IBr in CCl_4 is used at 25°; the amount of IBr consumed is more than is required for one double linking owing to concurrent substitution; at 0°, the theoretical val. is obtained. The reaction products from (I) and (II) or the Hanus reagent give the Lifschütz reaction (A., 1908, ii, 233) indicating that substances other than the dibromide of (I), (III), (IV) and its dibromide are formed. H. B.

Dehydrogenation of cholesterol. J. W. Cook and C. L. Hewett (Chem. and Ind., 1933, 451—452).—The dehydrogenation product of cholesterol, $C_{10}H_{18}$ (Diels *et al.*, A., 1927, 241), is probably impure 1 : 2-*cyclo*pentenophenanthrene, m.p. 152—153° (picrate, m.p. 133—134·5°; *s*-trinitrobenzene derivative, m.p. 165·5—166·5°); the impurity may be the corresponding indene derivative. F. R. S.

Constitution of cholesterol, and a new isomeride. R. de Fazi (Atti R. Accad. Lincei, 1933, [vi], **17**, 166—172).—The literature on the constitution of cholesterol is discussed. The hydrochloride, m.p. 136—137° (A., 1932, 511), gives an *isomeride* of cholesterol, m.p. 141—143° (possibly a mixture of two *iso*cholesterols, m.p. 138—139° and 142—144°). Another *hydrochloride*, m.p. 124—126°, is formed on treating cholesterol, in EtOH or Et_2O, with gaseous HCl. The following conclusions are reached: the double linking of cholesterol is in the 6 : 7-position and that of *meta*cholesterol at 5 : 6 or 7 : 8; for Diels' cholesterol, *allo*cholesterol, and the new isomeride (or isomerides), m.p. 141—143°, the double linkings are in the 12 : 13-, 13 : 1-, 1 : 2-, and 2 : 3-positions, but it cannot be stated which is which. T. H. P.

***iso*Cholesterol. I. Lanosterol and a new method for its preparation.** C. Doree and D. C. Garratt (J.S.C.I., 1933, **52**, 141—143T).—Lanosterol (I) is obtained from a "neutral wool grease" extracted from sheep's wool with H_2O. The grease is saponified in Et_2O solution with NaOEt, the optically inactive alcohols are removed by treatment with $COMe_2$, and (I) is separated from cholesterol by crystallisation from a 1 : 2-vol. mixture of MeOH and $COMe_2$ in which it is sparingly sol. Agnosterol (Windaus and Tschesche, A., 1930, 1179) was not present in the samples of wool grease employed, 1 kg. of which gave 40 g. of pure (I). Attempts to prepare "*iso*cholesterol" from S. African rubber, the latex of *Euphorbia* species (Cohen, A., 1908, i, 884), gave negative results.

Preparation of *allo*cholesterol hydrochloride. O. Wagner (Biochem. Z., 1933, **261**, 64—65).—The yield of this hydrochloride obtained by Mauthner's method (A., 1906, i, 579) is increased to 75% and the product is purer by working in $CHCl_3$. W. McC.

Coprosterol and lithobilianic acid. R. Langer (Z. physiol. Chem., 1933, **216**, 189—192).—The dicarboxylic acid (I), m.p. 250°, obtained by oxidation of coprosterol (or cholesterol) gives on oxidation with CrO_3 lithobilianic acid (II). The observation by Windaus and Riemann that *iso*lithobilianic acid (III) is produced was made with impure (I) containing isomerides which could give a mixture of (II) and (III). J. H. B.

Action of αγ-dichloropropylene on sodium derivatives of arylaliphatic alcohols. P. C. Dorier (Compt. rend., 1933, **196**, 1325—1327).—αγ-Dichloropropylene and the appropriate Na alkoxide at 130° in PhMe give *benzyl* (I), b.p. 123°/13 mm., β-*phenylethyl*, b.p. 135°/13 mm., and γ-*phenylpropyl* γ-*chloroallyl ether* (II), b.p. 146°/13 mm. The Cl of these ethers is unreactive. (II) with Br liberates HBr which hydrolyses the ether to CH_2PhBr. γ-Chloroallylbenzene does not react with Na phenoxides. R. S. C.

Sterically hindered *tert.*-carbinols. 2 : 4 : 6-Tribromotriphenylcarbinol. A. A. Morton and L. V. Peakes, jun. (J. Amer. Chem. Soc., 1933, **55**, 2110—2112).—2 : 4 : 6-$C_6H_2Br_3$·CO_2Me and MgPhBr in Et_2O–PhCl give 28% of 2 : 4 : 6-*tribromotriphenylcarbinol* (I), m.p. 116·5—117·5°; none is produced in Et_2O alone and a trace only is obtained from 2 : 4 : 6-tribromobenzophenone and MgPhBr. No reaction occurs between *s*-$C_6H_3Br_3$, CPh_2Cl_2, and $AlCl_3$ in CS_2. (I) and PCl_5 in CCl_4 give a product, which with Ag in Et_2O affords a yellowish-orange solution (becoming red when heated) which is decolorised by exposure to air. H. B.

Heteropolarity. XXII. Constitution and colour. W. Dilthey (Ber., 1933, **66**, [*B*], 825—826; cf. A., 1932, 1127).—A reply to Burawoy (this vol., 208). H. W.

The two diastereoisomeric αβγ-triphenyl-*n*-propyl alcohols. Exclusive preparation of each from stilbene and *iso*stilbene oxides. F. Kayser (Compt. rend., 1933, **196**, 1127—1129).—Stilbene oxide, obtained by oxidation of stilbene with BzO_2H, reacts with CH_2Ph·MgCl affording r-"β"-αβγ-*triphenyl*-n-*propyl alcohol* (I), m.p. 87° (*phenylurethane*, m.p. 121·5°; *acetate*, m.p. 89°). *iso*Stilbene oxide from *iso*stilbene, obtained by catalytic hydrogenation of tolane, similarly yields r-"α"-αβγ-*triphenyl*-n-*propyl alcohol* (II), m.p. 92° (*phenylurethane*, m.p. 125°; *acetate*, m.p. 70°). Both (I) and (II) yield benzyldeoxybenzoin on oxidation with CrO_3–AcOH. A. C.

Dissymmetric influence exercised by an asymmetric carbon atom during the action of an organo-magnesium compound on an aldehyde group. Production of a single diastereoisomeride. M. Tiffeneau, (Mlle.) J. Lévy, and F. Kayser (Compt. rend., 1933, **196**, 1407—1408).—*dl*-αβ-Diphenylpropaldehyde and MgPhBr give α-*dl*-αβγ-triphenylpropyl alcohol, m.p. 92° (cf. preceding abstract), whilst reduction (Na–Hg) of CH_2Ph·CHPh·COPh affords β-*dl*-αβγ-triphenylpropyl alcohol, m.p. 87° (cf. *loc. cit.*). H. B.

Derivatives of *p*-xylylene glycol. R. Quelet (Bull. Soc. chim., 1933, [iv], **53**, 222—234).—ωω'-Dichloro-*p*-xylene (I), m.p. 100°, b.p. 135°/16 mm., is obtained in 40% yield [calc. on $(CH_2O)_x$] by interaction of CH_2PhCl, $(CH_2O)_x$, and gaseous HCl in presence of $ZnCl_2$; a little *ωω'-dichloro-o-xylene*, m.p. 55°, b.p. 130—135°/19 mm., is formed at the same time. With KOH in EtOH (I) gives, not (II) (below) alone (cf. Grimaux, Bull. Soc. chim., 1870, **14**, 193), but mainly p-*xylylene glycol Et$_2$ ether*, b.p. 134°/15 mm., 252°/760 mm.; this and some *Et ether* (II), b.p. 154°/16 mm., are prepared in better yield by use of NaOEt in EtOH. The *Me*$_2$, b.p. 124°/18 mm., 235°/1 atm.; *Pr$^\alpha$*$_2$, b.p. 148°/15 mm.; *Pr$^\beta$*$_2$, b.p. 145°/15 mm.; *Bu$^\alpha$*$_2$, b.p. 180°/15 mm.; *di*-iso*amyl*, b.p. 185°/15 mm., and *dibenzyl ether*, m.p. 67°, are similarly prepared.

p-Xylylene glycol, m.p. 114°, is best prepared from (I) and aq. Na_2CO_3 in an autoclave at 150°, allowing the CO_2 to escape from time to time, otherwise the white insol. polymeride is formed. Its monoalkyl ethers are obtainable from the Na deriv-

ative and alkyl halides, but are better prepared by action of AcCl on an excess of the dialkyl ether in presence of $ZnCl_2$ and hydrolysing the resulting half-chloride: $C_6H_4(CH_2\cdot OR)_2 + AcCl \longrightarrow AcOR + C_6H_4(CH_2\cdot OR)\cdot CH_2Cl$. The *Me ether*, b.p. 152°/16 mm. [*phenylurethane*, m.p. 62°; *acetate*, b.p. 150°/16 mm. (from chloride and NaOAc)], and (II) are thus prepared. The method does not work well with the higher ethers, but gives difficultly separable mixtures containing much (I). From the half-chloride and hexamethylenetetramine p-*methoxymethylbenzaldehyde*, b.p. 125°/16 mm. [*semicarbazone*, m.p. 186° (block)], is prepared, and converted by the Cannizzaro reaction into p-*methoxymethylbenzoic acid*, m.p. 123°. H. A. P.

Iodo-silver benzoate complex; its application to the oxidation of ethylenic compounds to α-glycols. C. Prévost (Compt. rend., 1933, **196**, 1129—1131).—AgOBz and I combine to form the complex $AgI(OBz)_2$ (I), which liberates I from KI, oxidises EtOH to a mixture of aldehydes, $Fe^{\cdot\cdot}$ to $Fe^{\cdot\cdot\cdot}$, S_2O_3'' to SO_4'', and is decomposed by H_2O into BzOH, AgI, and O_2. Unsaturated compounds, $R\cdot CH{:}CH_2$, are converted by (I) *in situ* into α-glycol dibenzoates in accordance with the equation (I) + $R\cdot CH{:}CH_2 \longrightarrow AgI + R\cdot CH(OBz)\cdot CH_2\cdot OBz$. The mechanism of the reaction is not regarded as addition of 2I to the double linking followed by reaction of the iodide with AgOBz. The reaction is applicable to the synthesis of erythritols and substituted glycerols. Stycerol, $OH\cdot CHPh\cdot CH(OH)\cdot CH_2\cdot OH$, is obtained cryst., m.p. 99·5°. A. C.

α-*cyclo*Pentylpropionic acid. A. E. Tschitschibabin and S. I. Korjagin (Bull. Acad. Sci. U.S.S.R., 1933, 273—276).—Et sodiomethylmalonate and *cyclo*pentyl bromide in EtOH afford *Et* cyclo*pentylmethylmalonate*, b.p. 138—145°/12 mm., hydrolysed to the *acid*, m.p. 150—151° (decomp.), which when heated gives α-cyclo*pentylpropionic acid*, b.p. 238·5—240° (*chloride*, b.p. 107°/49 mm.; *Me* ester, b.p. 189·5—191°; *amide*, m.p. 136·5—137°; *anilide*, m.p. 115—116°; p-*nitroanilide*, m.p. 167—168°). G. A. R. K.

Effect of the medium "metallic nitrate–acetic anhydride" on the orientation of the nitro-group [introduced into] aromatic compounds. G. Bacharach, A. H. Haut, and (Miss) L. Caroline (Rec. trav. chim., 1933, **52**, 413—419).—Quinoline and $LiNO_3$ with a trace of $Cu(NO_3)_2$ in Ac_2O give 7-nitroquinoline. $Al(NO_3)_3$ is less effective, and heavy metal nitrates are ineffective. $CH_2Ph\cdot CO_2H$ with $Cu(NO_3)_2$ and Ac_2O gives *m*- (50%) and *o*- (10%) $-NO_2$-derivatives. The former result is explained on electronic grounds by co-ordination of the Ac_2O with the N atom. The latter confirms the views of Porter *et al.* (A., 1932, 511). R. S. C.

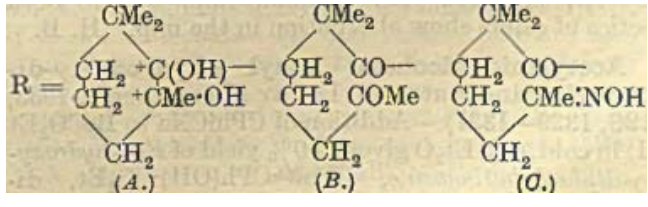
Degradation of optically active carboxylic acids by azoimide and sulphuric acid. J. von Braun and E. Friehmelt (Ber., 1933, **66**, [*B*], 684—685).—Addition of 10% HN_3 in $CHCl_3$ to optically active α-benzylpropionic acid in conc. H_2SO_4 at 40—42° affords α-benzylethylamine hydrochloride, m.p. 146°, $[\alpha]_D^{21}$ +16·1° (cf. Jones and Wallis, A., 1926, 279). The fenchelylamine hydrochloride obtained similarly from fencholic acid is identical with that derived from *d*-fenchone through fencholamide. With optically active acids this method of degradation can replace the Br–alkali or azide method. H. W.

Alkamine esters of cinnamic acid and derivatives. Novocaine analogues. V. H. C. Brill and C. F. Cook (J. Amer. Chem. Soc., 1933, **55**, 2062—2064).—The *hydrochlorides* of β-diethylaminoethyl cinnamate, β-phenylpropionate, and phenylpropiolate, and of γ-diethylaminopropyl αβ-dibromo-β-phenylpropionate have m.p. 135°, 111°, 163°, and 148°, respectively. The narcotic effects (on goldfish) of these are compared with that of γ-diethylaminopropyl cinnamate (apothesin). H. B.

Condensation of aromatic aldehydes and cyanoacetic acid. V. M. Rodionov and A. M. Fedorova (Arch. Pharm., 1933, **271**, 292—296).—Benzhydramide and $CN\cdot CH_2\cdot CO_2H$ (I) in EtOH give α-cyanocinnamic acid in 96% yield. (I) and the appropriate aldehyde in EtOH–NH_3 give the following substituted α-cyanoacrylic acids in the yield stated: β-piperonyl-, 80·3; β-*p*-hydroxy-*m*-methoxyphenyl-, 78; β-*p*-anisyl-, 57; and β-furyl-, 58%. R. S. C.

Constitution of azafrin. R. Kuhn and A. Deutsch (Ber., 1933, **66**, [*B*], 883—892).—Further analyses of azafrin (I) and its Me ester (II) after purification by crystallisation and chromatographically coupled with determinations of the equiv. of tetradecahydroazafrin (III) lead to alteration of the formula of (I) from $C_{28}H_{40}O_4$ to $C_{27}H_{38}O_4$. Cautious oxidation of (I) with CrO_3 (O=1) leads to *azafrinone* (IV), $C_{27}H_{36}O_4$, m.p. 191° (corr., Berl). (IV) catalytically absorbs $7H_2$ readily and a further $2H_2$ with greater difficulty. It is optically inactive. The absorption spectrum of (IV) lies more toward the region of longer wave-length than that of (I); hence one OH of (I) is in immediate proximity to the system of conjugated double linkings and the CO formed by its oxidation is optically involved in the polyene system. Hence (I) is a glycol in which both OH groups are attached to a C ring. They are immediately proximate to the polyene chain, and the optical activity of (I) depends on the C atoms to which the OH groups are attached. (I) is a di-*tert.*-glycol, since tetradecahydroazafrin reacts quantitatively with 1 mol. of $Pb(OAc)_4$ and the tetradecahydroazafrinone has no aldehydic properties. Oxidation of (I) with $KMnO_4$ affords geronic [δ-acetyl-αα′-dimethyl-*n*-valeric] acid [semicarbazone, m.p. 163° (corr.) after softening] and considerable amounts of αα′-dimethylglutaric acid. The saturated ring system is therefore closely related to that of β-carotene. Drastic oxidation of (I) with CrO_3 affords 3·5 mols. of AcOH. To (I), (IV), and *azafrinonemonoxime*, m.p. 194° (corr., Berl), the constitutions *A*, *B*, and *C* are respectively assigned.

$R\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot CH{:}CH\cdot CH{:}CMe\cdot CH{:}CH\cdot CO_2H$



Azafrinone Me ester, m.p. 110° (corr., Berl), is reduced by Zn and AcOH in C_5H_5N to a dihydro-compound, this behaviour being characteristic of carotenoids containing CO at each end of the chain. (I) has $[\alpha]^{20}_{1}$ −75·0° in EtOH, −72·5° in EtOH with 1% of $B(OH)_3$, whereas (II) has $[\alpha]^{20}_{Cd}$ −32°, −73°, −158°, and −210° to −193° (*c*=0·56 to 0·07) in $CHCl_3$, EtOH, $PhNO_2$, and C_5H_5N, respectively. H. W.

The monoamide of salicylacetic acid. E. A. Tzofin and K. A. Tschchikvadze (J. Gen. Chem. Russ., 1933, **3**, 17—20).—Salicylamide (I) and $CH_2Cl{\cdot}CO_2Et$ condense in presence of NaOEt to *Et salicylamidoacetate* (II), m.p. 130—131°, hydrolysed with cold alkali to the *acid*, m.p. 213—215°, also obtained from (I) and $CH_2Cl{\cdot}CO_2H$. (II) is therefore isomeric with Merriman's compound, m.p. 164—165° (J.C.S., 1911, **99**, 911; 1913, **103**, 1838), which is shown to be *o*-carbethoxyphenylglycollamide by synthesis from Et salicylate and $CH_2Cl{\cdot}CO{\cdot}NH_2$. Unlike this compound, (II) can be allylated to an ester hydrolysable in the cold to *salicyl-N-allylamidoacetic acid*, m.p. 120—121°, also obtained from salicyl-*N*-allylamide, $CH_2Cl{\cdot}CO_2Et$, and NaOEt. G. A. R. K.

Hydrate of *m*-5-xylenoxyacetic acid. A. R. Albright (J. Amer. Chem. Soc., 1933, **55**, 1736—1737).—*m*-5-Xylenoxyacetic acid has m.p. 111·2°, whilst the monohydrate has m.p. 81° (corr.); discrepancies in the m.p. (lit.) are thus explained. The acid is volatile in steam. H. B.

Configuration of natural (−)-tyrosine. S. Goldschmidt and G. Freyss (Ber., 1933, **66**, [*B*], 784—785).—The lævo-configuration of (−)-tyrosine is established by the observation that (+)-benzoyltyrosine is oxidised by $KMnO_4$ to the Bz derivative of *l*(+)-aspartic acid, m.p. 181°, $[\alpha]_D$ +38·5° in KOH–H_2O. H. W.

Condensation of oxalic esters with benzyl cyanide. G. S. Skinner (J. Amer. Chem. Soc., 1933, **55**, 2036—2039).—The following data are reported: Et, m.p. −40·2°, Pr$^{\alpha}$, b.p. 78—80°/3 mm., m.p. −46·3°, Bu$^{\alpha}$, b.p. 95—97°/2 mm., m.p. −30°, *n*-amyl, b.p. 131—132°/5 mm., m.p. −12·8°, *n*-hexyl, b.p. 135—136°/2·5 mm., m.p. −9°, *n*-heptyl, b.p. 142—144°/2 mm., m.p. 12·5°, and *n*-octyl, b.p. 167—169°/3 mm., m.p. 11·2°, oxalates; the higher esters (C_5—C_8) are prepared by heating $H_2C_2O_4,2H_2O$ and the alcohol in vac. $Alk_2C_2O_4$, $CH_2Ph{\cdot}CN$, and Na in Et_2O give the alkyl β-cyano-β-phenylpyruvates; the following are prepared: *Me*, b.p. 152—154°/3 mm., m.p. 115°; Et, b.p. 158—160°/4 mm., m.p. 130°; *Pr*$^{\alpha}$, b.p. 161—163°/3 mm., m.p. 93°; *Bu*$^{\alpha}$, b.p. 167—169°/3 mm., m.p. 95°; n-*amyl*, b.p. 173—175°/3 mm., m.p. 88°; n-*hexyl*, b.p. 181—183°/4 mm., m.p. 94°; n-*heptyl*, b.p. 200—205°/8 mm., m.p. 91·5°; and n-*octyl*, b.p. 195—197°/2 mm., m.p. 97·5°. Both series of esters show alternation in the m.p. H. B.

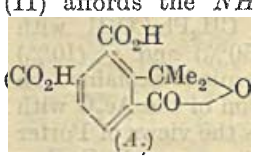
Acetylenic alcohols. Ethyl α-hydroxy-αγ-diphenylbutinenoate. M. Loury (Compt. rend., 1933, **196**, 1329—1331).—Addition of CPh·CNa to $BzCO_2Et$ (I) in cold, dry Et_2O gives a 50% yield of *Et α-hydroxy-αγ-diphenylbutinenoate*, $CPh{:}C{\cdot}CPh(OH){\cdot}CO_2Et$, dimorphous, m.p. 55—56° and 80—81°, sol. in conc. alkalis and giving with hot 5% KOH CPh:CH, BzOH, and HCO_2H. $COBz{\cdot}C{:}CPh$ is not formed. R. S. C.

3 : 5-Dihydroxy-*p*-toluic acid. Y. Asahina and J. Asano (Ber., 1933, **66**, [*B*], 687—688).—*p*-Toluic acid is transformed by fuming H_2SO_4 (50% SO_3) at 170—180° into the 3 : 5-disulphonic acid [Ba salt, $C_8H_6O_2(SO_3)_2Ba,H_2O$], the K salt of which is converted by molten KOH at 250—270° into 3 : 5-dihydroxy-*p*-toluic acid (I), m.p. 262° after darkening (lit., m.p. 175—176°). (I) with KOH–Me_2SO_4 and subsequently with Ag_2O–MeI affords *Me* 3 : 5-*dimethoxy*-p-*toluate*, m.p. 105°. H. W.

Dehydrogenation of cholatrienic acid. II. H. Raudnitz, F. Petru, and A. Stadler (Ber., 1933, **66**, [*B*], 879—882; cf. A., 1932, 944).—Cholic acid is converted at about 300° into cholatrienic acid, which is mixed with Zn dust and distilled over Zn–pumice at a low red heat under slight vac. The presence of chrysene (I) in the distillate is placed beyond doubt; very probably picene is present also in the solid portion. The liquid distillate gives the reactions of indene. The formation of (I) is attributed to the enlargement of the 5-membered fourth ring of cholesterol and the bile acids. H. W.

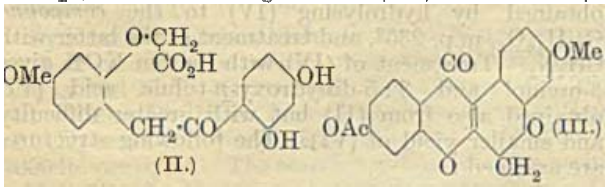
Bile acids. III. Enolisation of dehydrocholic acid and experiments on the structure of the acid. S. Minovici and M. Vanghelovici (Bul. Soc. Chim. Romania, 1933, **14**, 171—178).—Dehydrocholic acid does not condense with $CH_2(CO_2Et)_2$, showing the absence of the CHO group, but gives Ac_2, m.p. 201°, and Bz_2 derivatives, m.p. 115°, of the di-enol form of the acid. F. R. S.

Bitter substances. V. Constitution of picrotoxin. K. F. W. Hansen (Ber., 1933, **66**, [*B*], 849—854).—Oxidation of picrotoxin, picrotin, or picrotoxinin with MnO_2 and boiling 57% H_2SO_4 yields an *acid*, $C_{12}H_{10}O_6,H_2O$ (I), m.p. 286° after anhydride formation, and 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$, m.p. 240—241° (Me_4 ester, m.p. 131—132°). (I) is converted by CH_2N_2 into the Me_2 ester, m.p. 103° (also obtained from MeI and the *Ag* salt); the Et_2 ester has m.p. 93°. It is not affected by PhNCO, acetylation, or benzoylation. When heated at 250° or boiled with AcCl (I) yields the *anhydride* $C_{12}H_8O_5$, m.p. 286°, transformed by $CO(NH_2)_2$ into the *imide* $C_{12}H_9O_4N$ (II), m.p. 325—327°. The Hofmann degradation of (II) affords the NH_2-acid $C_{11}H_{11}O_4N$, m.p. 219—220°, transformed by diazotisation and treatment with boiling EtOH into the monocarboxylic *acid*, $C_{11}H_{10}O_4$, m.p. 202—203°. Decarboxylation of (I) by Cu powder in boiling quinoline yields dimethylphthalide. (I) has probably the constitution *A*. H. W.



Synthesis of rotenone and its derivatives. III. The dehydrorotenone nucleus. A. Robertson (J.C.S., 1933, 489—493; cf. A., 1932, 751).—4-*O*-Methylresorcylaldehyde, $CH_2Br{\cdot}CO_2Et$, and K_2CO_3 in $COMe_2$ during 2 hr. afford *Et 2-aldehydo-5-methoxyphenoxyacetate*, m.p. 64° (*semicarbazone*, m.p. 222°),

which condenses with hippuric acid to give the *azlactone*, m.p. 128—129°, hydrolysed by boiling NaOH for 6 hr. and then heated with excess of dil. HCl for 3 hr. to give *5-methoxyphenoxyacetic-2-pyruvic acid*, m.p. 250—251° (decomp.) [*oxime* (I), anhydro-form, m.p. 128—130° and at 152—153° after solidifying at 140—145°]. Interaction of (I) with Ac_2O affords *5-methoxy-2-cyanomethylphenoxyacetic acid*, m.p. 156°, the *Me* ester, m.p. 88°, of which with resorcinol in Et_2O containing $ZnCl_2$ and HCl, followed by hydrolysis with H_2O, affords *5-methoxy-2-2′:4′-dihydroxybenzoylmethylphenoxyacetic acid* (II) (+H_2O, m.p. 193°; *Me* ester, m.p. 89—90°). Cyclisation of (II) by boiling Ac_2O containing NaOAc during 10 min. affords *7-hydroxy-7′-methoxychromeno-*(3′:4′:2:3)*-chromone acetate* (III), m.p. 195°, hydrolysed by EtOH–HCl to the *hydroxychromone*, m.p. 258—260° (decomp.). With boiling NaOH (III) reverts to (II).



This reaction is identical with the formation of derrisic acid and deguelic acid from dehydrorotenone and dehydrodeguelin, respectively. Salicylaldehyde, $CH_2Br·CO_2Et$, and K_2CO_3 in $COMe_2$ during 2 hr. afford *Et 2-aldehydophenoxyacetate*, m.p. 34—35° (*semicarbazone*, m.p. 178°), which affords with hippuric acid an *azlactone*, m.p. 131°, converted into *2-cyanomethylphenoxyacetic acid*, m.p. 136° [*Me* ester (IV), m.p. 68°], by hydrolysis of the azlactone to a pyruvic acid, followed by the action of Ac_2O on its oxime. (IV) and resorcinol after the procedure of Hoesch afford 2-2′: *-dihydroxybenzoylmethylphenoxyacetic acid* (V), m.p. 206°, cyclised by Ac_2O and NaOAc to *7-acetoxychromeno-*(3′:4′:2:3)*-chromone*, m.p. 178°, hydrolysed to (V) by NaOH. 3-Hydroxycoumarin when boiled with NaOH affords with NH_2OH,HCl the *oxime*, m.p. 126° (decomp.), of 2-hydroxyphenylpyruvic acid, which with Ac_2O affords 2-hydroxyphenylacetonitrile, m.p. 122° (lit., 117—119°). Diacetylresorcylaldehyde and 2-acetyl-4-*O*-methylresorcylaldehyde condense with hippuric acid to give *azlactones*, m.p. 130° and 150°, respectively.

J. L. D.

Bile acids. XXXIX. M. Schenck (Z. physiol. Chem., 1933, 217, 68—74; cf. this vol., 609).—Catalytic hydrogenation of the NO-compound $C_{24}H_{31}O_8N$ (I) (A., 1928, 764) gives bilianic acid oxime lactam (II), indicating the probability of a double linking between C_7 and C_8 in (I). With HNO_3 the oximinoamino-acid $C_{24}H_{38}O_9N_2$ does not form the aminonitrile $C_{24}H_{36}O_{10}N_2$ (III) and the aminoamide $C_{24}H_{38}O_{11}N_2$ given by (I) and (II), but gives first a NO-compound (green coloration) and then as gel a tribasic *acid*, $C_{24}H_{36}O_9N_2$, decomp. 195°, which evolves a gas (? N_2) on treatment with aq. NaOH in excess. Probably in the production of (III) from (I) or (II) the reaction at the NO- or :N·OH group is first completed before the lactam ring is opened (if this occurs).

J. H. B.

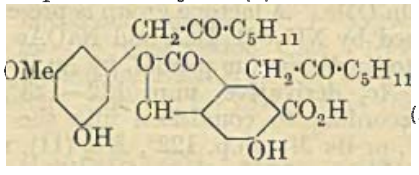
Lichen acids. V. Synthesis of methyl *O*-tetramethylgyrophorate. F. W. Canter, A. Robertson, and R. B. Waters (J.C.S., 1933, 493—495; cf. A., 1932, 1258).—Carbomethoxy*iso*evernic acid (prepared by methylation of *p*-monocarbomethoxyorsellinic acid) and PCl_5 in $CHCl_3$ afford a chloride (*anilide*, m.p. 149—150°), which with Me *iso*evernate in C_5H_5N at room temp. during several days affords *Me O-dimethyl-lecanorate* (I), m.p. 142°. Interaction of orcylaldehyde Me_2 ether and $KMnO_4$ in warm $COMe_2$ affords orsellinic acid Me_2 ether, m.p. 145—146° (decomp.) (lit. 64—65°), converted by PCl_5 into a gummy chloride (II) (*anilide*, m.p. 131°). Interaction of (I) and (II) in dry C_5H_5N during 3 days affords Me gyrophorate Me_4 ether, m.p. 195° (cf. A., 1932, 851). *iso*Evernaldehyde (prep. described) with Ac_2O and NaOAc during 3 hr. affords 2:4-*diacetoxy*-6-*methylbenzylidene diacetate*, m.p. 95—96°, which with $KMnO_4$ did not yield *O*-diacetylorsellinic acid.

J. L. D.

Lichen substances. XIX. Alectoronic acid, a new component of pale-coloured *Alectoria* species. Y. Asahina and A. Hashimoto. **XX. Collatolic acid, an alectoronic acid methyl ether.** Y. Asahina, Y. Kanaoka, and F. Fuzikawa. **XXI. Salazic acid. I.** Y. Asahina and J. Asano [with M. Fuse and K. Okami]. **XXII. Cetraric acid.** Y. Asahina and Y. Tanase (Ber., 1933, **66**, [*B*], 641—649, 649—655, 689—699, 700—703).—XIX. Extraction of *A. japonica*, Tuck., with Et_2O and concn. of the extract leads to *l*-usnic acid, m.p. 203°, $[\alpha]_D^{18}$ −482·1° in $CHCl_3$, and *alectoronic acid* (I), $C_{29}H_{34}O_9$, m.p. 193° (*monohydrate*, m.p. 120—121°), which is optically inactive and does not contain OMe. A lactone group is present. (I) is transformed by NH_2OH, HCl, and NaOAc in anhyd. EtOH into its *dioxime*, m.p. 194°, by Ac_2O at 80—90° into the Ac_3 derivative, m.p. 122—123°, and by CH_2N_2 according to conditions into the *Me* ester, m.p. 160°, or its *Me*, m.p. 122°, Me_2 (II), m.p. 136°, or Me_3 (III), m.p. 114°, *ether*. Conditions are given for the formation of (II) or (III) from (I), Ag_2O, and MeI. Treatment of (I) with boiling HCO_2H affords *alectorone* [*alectoronolactone*] (IV), $C_{29}H_{32}O_8$, m.p. 198°. The Ac_3 derivative, m.p. 157—158°, from (I) or (IV), NaOAc, and boiling Ac_2O, the *oxime*, m.p. 226°, and the Me_3 *ether* (V), m.p. 185°, from (IV) and an excess of CH_2N_2, or Ag_2O and MeI, or from (III) and boiling HCO_2H, are described. The *oxime* of (V) had m.p. 180°. Treatment of (V) or (III) with KOH or of (I) with Me_2SO_4 and KOH leads to the dicarboxylic *acid*, $C_{32}H_{42}O_{10}$, m.p. 119—120° (Me_2 ester, m.p. 68—70°). Treatment of (I) with molten KOH affords *n*-hexoic acid (anilide, m.p. 98°), orcinol, 5-hydroxy-*m*-xylene, and 3-hydroxy-5-methylbenzoic acid. The presence of 3 OH, 2 CO, CO_2H, one lactone group, an orcinol and a *m*-cresol nucleus, and probably 2 $CO·C_5H_{11}$ groups is established. The ready formation of an enol-lactone suggests that CO_2H is vicinal to $CO·C_5H_{11}$. (I) is not a depside. (I) and *l*-usnic acid are also obtained from *A. japonica* from Sakhalin and from *A. sarmentosa*, Ach., from Europe. *A. ochrolenea* contains *d*-usnic and diffractaic acid (VI); the barbatinic acid reported by Zopf was probably crude (VI).

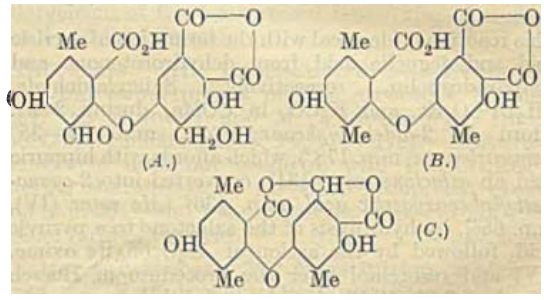
XX. Maceration of the thalli of *Cetraria collata*,

Nyl., with cold Et_2O leads to the isolation of atranorin, m.p. 196°, α-collatolic acid, $C_{30}H_{36}O_9$ m.p. 124—125°, or +aq. m.p. 90—95°, and traces of *β-collatolic acid* (II), m.p. 162° (see below). (I) is optically inactive, contains 1OMe and a lactone ring, and yields a *disemicarbazone*, m.p. 212° (decomp.). Regulated treatment with CH_2N_2 transforms (I) into the Me ester (III), m.p. 122°, identical with Me alectoronate Me ether (see above), and thence into Me alectoronate Me_2 (IV), m.p. 136°, and Me_3, m.p. 114°, ether. (I) and 95% HCO_2H at 130° afford *collatolone* [*collatololactone*], $C_{30}H_{34}O_8$ (V), m.p. 142°, also obtained from (III). From (V) are derived a *monoxime*, m.p. 175°, and Ac_2 derivative (VI), m.p. 105°, prepared from (V) and cold Ac_2O containing H_2SO_4, and an *Ac* compound, m.p. 151°, prepared similarly from (I) and transformed into (VI) by NaOAc and boiling Ac_2O. Treatment of (IV) with boiling HCO_2H affords *collatololactone Me ether* (VII), m.p. 185°. Collatololactone Me_2 ether (VIII), m.p. 185°, identical with alectorolactone Me_3 ether (see above), is obtained from (V) or (VII) with excess of CH_2N_2 or from (V), Ag_2O, and MeI in Et_2O. (VIII) is hydrolysed by KOH–EtOH to the dicarboxylic acid $C_{32}H_{42}O_{10},0{\cdot}5H_2O$, m.p. 125° ($Me_2$ ester, m.p. 72°), identical with that derived from alectorolactone Me_3 ether (see above). Hydrolysis of (III) with dil. KOH–EtOH leads to β-collatolic acid, m.p. 162° (see above), readily transformed into (V) by HCO_2H. Preservation of (I) in cold C_5H_5N causes formation of *γ-collatolic acid* (IX), $C_{30}H_{36}O_9$, m.p. 140—141°, converted by HCO_2H into (V). Oxidation of (IX) by $KMnO_4$ in $COMe_2$ affords olivetonide Me ether, m.p. 57°, and (?) a little hexoic acid. The constitution *A* is advanced provisionally for (I).



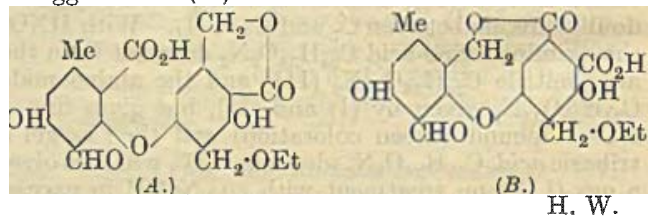
(*A.*)

XXI. Extraction of *Parmelia conspersa* (Ehrh.), Ach., *var. hypoclysta*, Nyl., with Et_2O gives about 1% of *d*-usnic acid and traces of a colourless acid, m.p. 205° (decomp.), and subsequent treatment with $COMe_2$ affords about 3% of salazic acid (I, *A*). Similar treatment of *P. cetrata*, Arch., var. *sorediifera*, Wain, gives atranorin, m.p. 195°, (?) cetratic acid, m.p. 178—180°, and (I). (I), $C_{18}H_{12}O_{10}$ (also $+1H_2O$ and +1MeOH), decomposes at about 260° after becoming discoloured at 240°. (I) is converted by boiling Ac_2O into the Ac_3 derivative, m.p. 206—207°, and by cold Ac_2O containing H_2SO_4 into the Ac_6 compound, m.p. 178°, which does not give a colour with $FeCl_3$ and contains 2Ac as an aldehydediacetate. With NH_2Ph and $NHPh{\cdot}NH_2$ in $COMe_2$ it affords the *dianil* $C_{30}H_{22}O_8N_2$, decomp. 280° after darkening at 240°, and *diphenylhydrazone*, $C_{30}H_{24}O_8N_4$, decomp. 295° after blackening at 270°, respectively, indicating 2CO. Dry distillation or distillation with Zn dust affords atranol. Molten KOH converts (I) into orcinol and α-resorcylic acid. Catalytic hydrogenation of (I) (Pd–C) gives the *product* $C_{18}H_{14}O_8$ (II, *B*), decomp. about 280° after becoming discoloured at 240°, which yields an *NH_2Ph* salt and gives β-orcinol when dry distilled. It is transformed by CH_2N_2 into the *compound* $C_{18}H_{11}O_5(OMe)_3$ (III), m.p. 165°, which does not contain an active H. Acidification of (III) after short treatment with KOH–MeOH yields the *substance* $C_{18}H_{12}O_5(OMe)_4$, converted by CH_2N_2 into the *compound* $C_{18}H_{11}O_4(OMe)_5$, m.p. 146°, obtainable in poor yield directly from (II). Reduction therefore causes the transformation of CHO into Me in the atranol nucleus and of C·OH into Me in the second nucleus. Prolonged hydrogenation of (I) in warm solution or, preferably, short treatment of (II) with hot AcOH and Zn dust yields the *substance* $C_{18}H_{14}O_7$ (IV, *C*), m.p. about 300° (also $+1COMe_2$), converted by CH_2N_2 into the *Me_2 ether* $C_{18}H_{12}O_5(OMe)_2$ (V), m.p. 283°, which does not contain an active H. When warmed with KOH–MeOH (V) gives an *acid*, $C_{18}H_{13}O_5(OMe)_3$, m.p. 178°, transformed by CH_2N_2 into the *compound* $C_{18}H_{12}O_4(OMe)_4$, m.p. 111°, also obtained by hydrolysing (IV) to the *compound* $C_{18}H_{16}O_8$, m.p. 235°, and treatment of the latter with CH_2N_2. Treatment of (IV) with molten KOH gives β-orcinol and 3 : 5-dihydroxy-*p*-toluic acid (VI) obtained also from (II) but with greater difficulty and smaller yield of (VI). The following structures are assigned :



(*B.*)

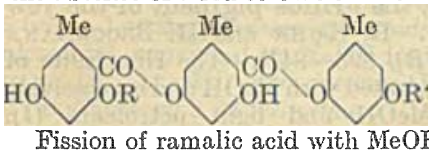
XXII. Thermal decomp. of fumarprotocetraric acid (I) yields atranol. (I), obtained by extraction of *Cetraria islandica*, Ach., with $COMe_2$, is converted into cetraric acid (II), decomp. 255° after darkening at 220°, by Simon's method (*anil*, decomp. about 250°). Treatment of (II) with KOH at 250—310° yields orcinol and α-resorcylic acid. Catalytic hydrogenation (Pd–C) of (II) is accompanied by loss of OEt (therefore acetal form) and production of the *compound* $C_{18}H_{16}O_7$, m.p. 242° (decomp.) after becoming discoloured at 215°, which yields a *Me_3* derivative (III), m.p. 170°, in which active H is not present. (III) and molten KOH afford β-orcinol, 3 : 5-dihydroxy-*p*-toluic acid, and small amounts of a *phenol*, $C_{16}H_{18}O_4$, m.p. 218—219°. The structure *A* or *B* is suggested for (II) :



H. W.

Umbilicaric and ramalic acids. G. Koller and G. Pfeiffer (Monatsh., 1933, **62**, 241—251).—Umbilicaric acid, m.p. 203° (decomp.) [Ac_3 derivative,

decomp. 197° (in vac.) (*Me* ester, decomp. 206—207°)], is converted by CH_2N_2 into a Me_3 ether Me ester, m.p. 196°, identical with Me tetramethylgyrophorate; it is therefore a Me ether of gyrophoric acid. Fission with 30% NaOH in H_2 gives lecanoric, orsellinic, and *iso*evernic acids; the last-named is identified by mixed m.p. of its Me ester and decarboxylation to orcinol. It is therefore represented by formula (I) or (II), (I) being preferred on account of the absence of a red coloration with $Ca(OCl)_2$.



(I) R=Me, R′=H
(II) R=H, R′=Me

Fission of ramalic acid with MeOH at its b.p. gives Me rhizonate, m.p. 103°, therefore it is identical with obtusatic acid (cf. A., 1932, 613). H. A. P.

Synthesis of benzaldehyde from benzene and carbon monoxide under pressure. J. H. Holloway and N. W. Krase (Ind. Eng. Chem., 1933, **25**, 497—502).—PhCHO is formed by direct combination of C_6H_6 and CO in presence of $AlCl_3$ at 25—50°/500—2000 lb. per sq. in. The reaction is dependent on rapid and thorough stirring to bring about intimate admixture of the gaseous and liquid phases and is accelerated by added PhCHO and by small amounts of H_2O or HCl. Above 25° the conversion decreases with rising temp., and at > 50° oils of high b.p. form in increasing amounts; the conversion increases rapidly with pressure up to 700—1000 lb. per sq. in. and then more slowly. With 1 mol. $AlCl_3$: 1 mol. C_6H_6 : 0·12 mol. H_2O at 25°/1000 lb. per sq. in. a yield of 65·4% of theory is realised in 2 hr. H. A. P.

Reimer–Tiemann reaction. D. E. Armstrong and D. H. Richardson (J.C.S., 1933, 496—500).—The Reimer–Tiemann reaction carried out with many phenols, substituting $CCl_3{\cdot}CO_2H$ for $CHCl_3$, resulted in no improvement in the yields of aldehyde. Evidence is adduced of the formation of an acetal in the above reaction. Interaction of *p*-chlorophenol and $CCl_3{\cdot}CO_2H$ in KOH solution affords tri-*p*-chlorophenyl orthoformate and di(chlorosalicylaldehyde) and an acetal indicated by (*a*) the formation of a *p*-nitrophenylhydrazone after removal of aldehydes and subsequent hydrolysis with $NaHCO_3$, (*b*) reaction with MeMgI, and (*c*) methylation with Me_2SO_4. Analyses of the resinous products obtained indicate the existence of $CHPh_3$ derivatives. J. L. D.

Action of phenylcarbimide on aromatic amino-oximes. C. V. Gheorghiu (Ann. Sci. Univ. Jassy, 1933, **17**, 188—194).—Two mols. of aryl-carbimide react with 1 mol. of amino-oximes, whereas only 1 mol. of -thiocarbimide reacts. This difference may be due to the difference in electronic structure, viz., R·N:C:O and  , disclosed by Raman spectra.

ON-*Dicarbanilido*-derivatives are prepared from the following substances and have the m.p. quoted: *p*- [176—177° (decomp.)] and *m*-aminobenzaldoxime, 171° (decomp.); 3-amino-*p*-anisaldoxime (CH:N·OH =1), 170—171° (decomp.); p- [178—179° (decomp.)] and m- (I) *-aminoacetophenoneoxime* [175—176° (decomp.)]. (I), m.p. 129—130°, is prepared by reduction of *m*-nitroacephenoneoxime with $(NH_4)_2S$. *o*-Aminobenzaldoxime and PhNCO in Et_2O give *4-carbanilidohydroxylamino-2-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline* (II) (or ON-*dicarbanilido-o-aminobenzaldoxime*), m.p. (anhyd.) 195—196° (decomp.), (? $+Et_2O$) · 148° (decomp.); the cyclic structure $NH<^{C_6H_4(o)}_{CO\cdot NPh}>CH\cdot NH\cdot O\cdot CO\cdot NHPh$ for (II) is probable, since the substance has pale green fluorescence in H_2SO_4. R. S. C.

Action of chlorides of the type XCl_3 on vanillin and methyl anthranilate. G. Sollazzo (Officina, 1932, 5, 270—273).—Condensation in presence of XCl_3–Et_2O affords compounds probably having the constitution $(R{\cdot}NH_2R{\cdot}CHO)XCl_2$. $AsCl_3$ gives a reddish-yellow substance, m.p. 143° (decomp.); $AlCl_3$ gives a citron-yellow substance, m.p. 178°. Ch. Abs.

Lignin content of cellulose products. A. G. Norman and S. H. Jenkins (Nature, 1933, **131**, 729).—A pentose on treatment with cold 72% H_2SO_4 and then boiling with dil. H_2SO_4 gave a quantity of material as resistant as lignin and determined as such by accepted methods. About 25% of the apparent lignin content of celluloses from cereal straws is secondarily produced from the cellulosan fraction, but there is some true lignin or other equally acid-resistant material present. The determination of lignin by the 72% H_2SO_4 method should be critically examined. L. S. T.

Lignin reactions. P. Klason (Arkiv Kemi, Min., Geol., 1932, **11 A**, No. 1, 12 pp.; No. 3, 4 pp.).—A discussion of the composition and reactions of lignin and ligninsulphonic acid. Freudenberg's view that the aliphatic part of lignin contains a no. of linked alcohol groups is refuted, as 50% of his material certainly contained a free CHO group. H. F. H.

Carbon rings. XXIII. Parachor and compressibility of multi-membered ring compounds. L. Ružicka, H. A. Boekenoogen, and H. J. Edelman (Helv. Chim. Acta, 1933, **16**, 487—492; cf. this vol., 230).—Vals. for the parachor of *cyclo*octane, *cyclo*octanone, methyl*cyclo*pentadecane, 1-methyl*cyclo*pentadecan-3-one, and Δ^9-*cyclo*heptadecen-1-one, and for the compressibility coeff. of *cyclo*hexane, *cyclo*hexanone, methyl*cyclo*pentadecane, and 1-methyl*cyclo*pentadecan-1-one, are given. Rings with more than about 8 members behave like aliphatic compounds with respect to both properties. U

Selective catalytic reduction of ketones. N. D. Zelinski, K. Packendorff, and L. Leder-Packendorff (Ber., 1933, **66**, [*B*], 872—874).—Hydrogenation of COPhMe in EtOH in presence of 10% Pt-C activated with Pd at room temp. and pressure affords PhEt. Homologues of COPhMe behave similarly, whereas the CO of *cyclo*pentanone, *cyclo*hexanone, hexahydroacetophenone and its homologues, and of ketones in which CO is separated from the C_6H_6 ring by at least one CH_2 remains unaffected. It is thus possible to separate aromatic ketones from cyclic ketones or those which do not contain CO in the α-position to the C_6H_6 ring. Accumulation of negative groups in the neighbourhood of CO does not

with AcO_2H); by H_2 and Cu chromite to a βζ-di- facilitate its reduction, since $COPh_2$ is not reduced. Change proceeds $>CO \longrightarrow >CH\cdot OH \longrightarrow >CH_2$, since OH·CHPhBz affords successively OH·CHPh·CHPh·OH and $(CH_2Ph)_2$ (also obtained from COPhBz). $CH_2Bz\cdot OMe$ affords $CH_2Ph\cdot CH_2\cdot COMe$ exclusively. H. W.

Chlorination product obtained by condensation of methyl ethyl ketone with benzaldehyde [in presence of hydrogen chloride]. G. Massara (Gazzetta, 1933, **63**, 199—206).—The interaction of COMeEt, PhCHO, and HCl (cf. A., 1902, i, 295) yields the hydrochloride of dibenzylidenebutanone (A., 1916, i, 372), which is reduced (Zn–AcOH) to *β-phenylethyl α-benzylethyl ketone*, m.p. 47—48° (*oxime*, m.p. 129—130°; *semicarbazone*, m.p. 215—216°). E. W. W.

Synthesis of αβ-aminoketones. A. Skita, F. Keil, and E. Baesler (Ber., 1933, **66**, [*B*], 858—866; cf. A., 1928, 1120; 1929, 808).—The catalytic action of Pd in the hydrogenation of αβ-diketones in the presence of bases is more selective than that of Pt and by suitable adjustment of the amount of metal the NH_2-ketone (I) can be readily prepared, whereas with larger amounts the NH_2-alcohol is obtained. By use of very small amounts of Pt, (I) can be prepared. *sec.*-Amines can be used in place of primary amines in the synthesis of (I) if base and ketone have low mol. wt. NH_2-ketones, if liquid, are usually unstable and readily give viscous, red substances. Details are given for the reduction of AcBz in presence of NH_2Me and Pd or Pt to ephedrine (*loc. cit.*) or β-methylamino-α-phenylpropan-α-one, b.p. 120—121°/11 mm. (hydrochloride, m.p. 180°; picrate, m.p. 138°; chloroplatinate, m.p. 191—192°). The following are described: β-cyclo*hexylamino*-, b.p. 185—195°/15 mm., m.p. 178° (*picrate*, m.p. 154°); β-β′-*hydroxyethylamino*-, m.p. 78° (*hydrochloride*, m.p. 159—160°), and β-*anilino*-α-*phenylpropan*-α-*one*, m.p. 100—101° (*hydrochloride*, m.p. 191°); β-*anilino*-α-*phenylpropan*-α-*ol*, m.p. 122° (*hydrochloride*, m.p. 184°); β-*methylamino*-, b.p. 160°/11 mm. (*picrate*, m.p. 179—180°), β-cyclo*hexylamino*-, m.p. 110° (*hydrochloride*, m.p. 193—194°), and β-p-*toluidino*-α-p-*anisylpropan*-α-*one*, m.p. 83° (*hydrochloride*, m.p. 182—183°); β-cyclo*hexylamino*-, m.p. 107—108° [*hydrochloride*, m.p. 235—237° (decomp.)], and β-α′-*ethylpropylamino*-αβ-*diphenylethan*-α-*one*, b.p. 200—201°/11 mm. (*picrate*, m.p. 148°); β-cyclo*hexyl*-, b.p. 128—130°/13 mm. (*hydrochloride*, m.p. 176°), β-*methyl*-, b.p. 70—71°/18 mm. (*picrolonate*, m.p. 183—184°), -*hydroxyethyl*-, b.p. 142—144°/14 mm., m.p. 68° (*picrolonate*, m.p. 217—218°), and β-p-*ethoxyphenyl*-*aminohexan*-γ-*one*, b.p. 189—190°/15 mm. (*hydrochloride*, m.p. 148—149°); β-cyclo*hexylamino*-, b.p. 118°/12 mm. (*hydrochloride*, m.p. 157—158°), and β-*methylanilino*-*pentan*-γ-*one*, b.p. 148—150°/14 mm. (*picrolonate*, m.p. 182—183°); β-*dimethylaminohexan*-γ-*one*, b.p. 89—90°/25 mm. (*picrolonate*, m.p. 163—164°). H. W.

Bromination of enols and enol ethers. T. Fjader (Suomen Kem., 1933, **6**, 60—61).—Bromination of the appropriate 3-diketone by Toivonen's method (in suspension in cold AcOH in presence of KOAc) affords the *Br*-derivatives of 4-methyl-, m.p. 103—104°, 4-ethyl-, m.p. 40—41°, and 4-*iso*propyl-, m.p. 80—81°, -menthone, 4-phenyl-1-methyl*cyclo*hexane-2 : 6-dione, m.p. 55—56°, and $CHAc_2Me$, b.p. 63°/11 mm., the appropriate enol ethers similarly giving 2-*bromo*-3-*methoxy*-, m.p. 103—104°, -3-*ethoxy*-, m.p. 112—113°, and -3-iso*propoxy*-, m.p. 89—90°, -5 : 5-*dimethyl*-Δ^2-cyclo*hexenone*. J. W. B.

Rhodoxanthin, the arillus pigment of the yew (*Taxus baccata*). R. Kuhn and H. Brockmann (Ber., 1933, **66**, [*B*], 828—841).—The ripe fruits of *T. baccata* are dehydrated with MeOH and successively extracted with MeOH and light petroleum (I). Isolation by repeated distribution between 90% MeOH and (I) leads to rhodoxanthin (II), $C_{40}H_{50}O_2$, m.p. 219° (corr., vac., Berl), bluish-black in colour, unusually stable to air. It is not acidic and does not give the supposed alkali salts. It is unchanged by CH_2N_2. With MgMeI it evolves rather more than 1 mol. of CH_4, but the presence of the indicated OH is not confirmed by the action of Ac_2O in C_5H_5N. It is indifferent towards KOH–EtOH. With NH_2OH in presence of a little NaOH it affords the *dioxime* (III), $C_{30}H_{52}O_2N_2$, m.p. 227—228° (corr., vac., Berl). The absorption spectra of (II) and (III) show the CO groups to be in conjugation with a system of conjugated double linkings. The difficulty of reaction with NH_2OH proves the presence of CO not CHO in (II). Catalytic hydrogenation of (II) [Pt–kieselguhr] causes rapid absorption of $12H_2$ and ultimate absorption of $14H_2$ showing the presence of 12 double linkings and reduction of CO to CH·OH. The parent hydrocarbon and its perhydro-compound have therefore the formulæ $C_{40}H_{54}$ and $C_{40}H_{78}$, requiring the presence of two C rings. Reduction of (II) with Zn dust and AcOH yields *dihydrorhodoxanthin* (IV), $C_{40}H_{52}O_2$, m.p. 219° (corr., vac., Berl), which absorbs catalytically $13H_2$ and differs from (II) mainly in colour and absorption spectrum. With NH_2OH it yields a *dioxime* (V), $C_{40}H_{54}O_2N_2$, m.p. 226—227° (corr., vac., Berl). The optical identity of (IV) and (V) shows that the conjugation of the CO groups is broken by the absorption of the two H atoms. Addition of NaOH–EtOH to (IV) in C_5H_5N in high vac. gives a dark violet solution immediately, yielding (II) on exposure to air; reduction is therefore reversible. Oxidation of (II) with CrO_3 affords 5·5 mols. of AcOH, whilst treatment with I yields about 0·2 mol. of $COMe_2$. To (II) and (IV) the following constitutions are assigned.

(II.) $\left(\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot CH{:}C\langle\begin{matrix}CMe_2\cdot CH_2\\CMe{=}CH\end{matrix}\rangle CO\right)_2$

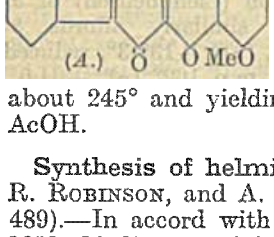
(IV.) $\left(:[CH\cdot CH{:}CMe\cdot CH{:}]_2CH\cdot C\langle\begin{matrix}CMe_2\cdot CH_2\\CMe{-}CH_2\end{matrix}\rangle CO\right)_2$

Rhodoxanthin is the first representative of a new type of polyene colouring matter, the polyene-ketone type.

Aromatic cyanohydrins and their transformation into quinomethide derivatives. I. Gorski and S. Makarov (Ber., 1933, **66**, [*B*], 674—680).—Treatment of *o*-methoxybenzaldehyde cyanohydrin in abs. Et_2O with $SOCl_2$ affords *chloro*-*o*-*methoxy*-

phenylacetonitrile, b.p. 132—133°/9 mm., m.p. 43—44°. Vanillin (I) is transformed by anhyd. HCN in presence of a little KOH or KCN into the corresponding *cyanohydrin* (II), m.p. 80°, converted into its components by boiling KOH–EtOH and into homoprotocatechuic acid (III), m.p. 127°, by boiling HI (*d* 1·7). (II) in Et_2O is transformed by PCl_3, PCl_5, or PBr_5 into m-*methoxycyanoquinomethide* (IV), 1 : 2 : 4-O:C_6H_3(OMe):CHCN, decomp. after incipient melting at 138°, transformed by 10% NaOH or dil. H_2SO_3 into (I) and HCN. Br in $CHCl_3$ transforms (IV) into *o-bromo-3-methoxycyanoquinomethide*, m.p. 172—174° (decomp.), converted by NaOH into 5-bromovanillin, m.p. 163·5°. (IV) and boiling HI (*d* 1·7) yield 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxy*-ωω′-*dicyanostilbene*, m.p. 231—232°, whence, by protracted action of HI, 3 : 3′ : 4 : 4′-*tetrahydroxystilbene*-ωω′-*dicarboxylic acid*, m.p. 204—212° (decomp.). The production of homovanillic acid and (III) from (IV) is described. H. W.

Condensation of *p*-benzoquinone with cresols and veratrole. R. Pummerer, M. Dally, and S. Reissinger [with, in part, G. Huppmann] (Ber., 1933, **66**, [*B*], 792—798).—Addition of a suspension of *p*-benzoquinone (I) in CS_2 to a solution of $AlCl_3$ in CS_2 and *o*-C_6H_4Me·OH at 0° yields a quinol derivative, oxidised by $FeCl_3$ in AcOH to 2 : *o-di*-6′-*hydroxy*-m-*tolyl*-p-*benzoquinone* [*diacetate*, m.p. 238—239°; *Et*$_2$ *ether*, m.p. 200° (from *o*-C_6H_4Me·OEt)]. (I), $AlCl_3$, *m*-C_6H_4Me·OH, and CS_2 afford 2 : 5-*di*-5′-*hydroxy*-p-*tolylquinol*, m.p. 310—313° (under CO_2) [*Ac*$_4$ derivative, m.p. 186—187°), oxidised with unusual difficulty by $FeCl_3$ in boiling AcOH to the corresponding *quinone*, incipient decomp. 260—270° (?+PhOMe). *p*-C_6H_4Me·OH does not afford a homogeneous condensation product, whereas its Me ether yields (?) 2 : 5-*di*-2′-*methoxy*-5′-*methyl*-*phenylquinol*, m.p. 138°. (I) and veratrole appear to yield the *substance A*, darkening about 245° and yielding a vat dye with NH_2Ph in AcOH. H. W.



Synthesis of helminthosporin. H. Raistrick, R. Robinson, and A. R. Todd (J.C.S., 1933, 488—489).—In accord with Shah and Alimchandani (A., 1931, 1053), γ-coccinic acid Me ether is inaccessible by the method of Schleussner and Voswinckel (A., 1921, i, 111). 3-Methoxy-5-methylphthalic anhydride (modified prep. of acid; cf. Meldrum, J.C.S., 1911, **99**, 1712), *p*-$C_6H_4(OMe)_2$, and $AlCl_3$ in boiling CS_2 during 24 hr. affords a *compound*, m.p. 222—225° (suggested constitution), which with conc. H_2SO_4 at 150° during 0·5 hr. affords 4 : 5 : 8-*trihydroxy*-2-*methylanthraquinone*, m.p. 226—227°, identical with helminthosporin, m.p. 225—226°. J. L. D.

Sugar-beet sapogenin. II. Oleanolic acid. V. Prelog (Coll. Czech. Chem. Comm., 1933, 5, 165—169; cf. A., 1932, 46).—The substance $C_{31}H_{46}O_4$ obtained by CrO_3 oxidation of the sapogenin $C_{30}H_{48}O_2$ (A., 1930, 1044; all formulæ there given now having CH_2 less) is actually a diketolactone $C_{30}H_{44}O_4$ (identical with that obtained by Kitasato and Sone, A., 1932, 1035), since it affords a *dioxime*, m.p. 222—223° (decomp.), and a *monosemicarbazone*, decomp. 292—294°. Me oleanolate (*oxime*, m.p. 239°) also gives 1 mol. of CH_4 by Zerevitinov's method, due to enolisation of the CO group. Partial formulæ for these derivatives are given. J. W. B.

Menthenes and menthadienes. R. Gachard (Bull. Inst. Pin, 1933, 42—48, 67—72, 79—87, 97—102).—The products described below are identified mainly by their Raman spectra. Menthol, dehydrated by the xanthate method, gives a mixture of Δ^2- and Δ^3-menthenes, also obtained similarly, with carvomenthene, from carvomenthol, and, possibly with $\Delta^{4(8)}$-menthene, from menthyl chloride by EtOH–KOH or NH_2Ph. This chloride, prepared by PCl_5, is entirely the 4-Cl-compound, formed by rearrangement. Ozonisation and determination of the CH_2O formed is not an accurate method of determining the CH_2: group. Turpentine and 50% H_2SO_4 below 50° give cymene, limonene, camphene, dipentene, α- and γ-terpinene, terpinolene, 1 : 4-cincole, and 3 unidentified substances. R. S. C.

"Terpinolene." Attempts to obtain pure terpinolene. (Mlle.) R. Marot (Bull. Inst. Pin, 1933, 38—41, 61—66).—Commercial terpinolene (I) contains 80% of cineole. Dipentene (II), α- (III) and γ- (IV) -terpinene, and terpinolene (V) are readily identified by their Raman spectra, the principal frequencies being: (II), 765, 1647, and 1676; (III), 876 and 1615; (IV), 1640; (V), 1672 and 1681. Pure terpinene dihydrochloride (from cineole) and NH_2Ph give much (III) and traces of (V). The crude hydrochloride from (I) gives similarly much (II), some (III), and probably a little (V). Commercial terpineol and Al_2O_3 give (II), (III), and much (V). Distillation at 12 mm. of the crude acetate from pinene gives limonene, (III), and (V). *iso*Cineole (VI) [$H_4Fe(CN)_6$ compound, regenerates (VI) with cold KOH, but, when heated, gives also some hydrocarbon] is stable to cold 40% H_2SO_4 and hot CrO_3–dil. H_2SO_4, fairly stable to cold, conc. HNO_3, polymerised by conc. H_2SO_4, oxidised by $KMnO_4$ to cineolic acid, m.p. 203—204° (lit. 156°), and dehydrated by $H_2C_2O_4$ to (III) and (IV). R. S. C.

Isomerisation of α-pinene to an aliphatic terpene. I, II. Examination of the aliphatic terpene. B. A. Arbusov (J. Gen. Chem. Russ., 1933, 3, 21—27, 28—34).—I. When α-pinene (I) is passed over Cu chromite (A., 1931, 598) at 300°, some 80% of (I) is recovered and 20% of an aliphatic terpene (II). At 375°, 23% of (I), 42% of dipentene, and 31% of (II) are produced, and at 400—410°, 20% of (I), 23% of dipentene, 20% of (II), and 36% of an unidentified monocyclic terpene $C_{10}H_{16}$. Dipentene is not isomerised under these conditions. (II) may be identical with the product obtained from (I) with an Al catalyst (B., 1932, 376). A Co–Th catalyst at 380° gives similar products in comparable yield.

II. (II), b.p. 87—87·5°/16 mm., d_0^{15} 0·8162, n_D 1·5448, $[\alpha]_0$ 0, closely resembles *allo*ocimene; it is readily oxidised in the air to a viscous product with the properties of a peroxide. (II) is reduced by Na and EtOH to a *dihydro*-compound, b.p. 168·5—170°/760 mm., containing two double linkings (titration

methyloctene, b.p. 165—166°/760 mm., and with H_2 and Ni to *dl*-βζ-dimethyloctane, b.p. 159·5°. (II) combines with maleic anhydride to an *anhydride*, $C_{14}H_{18}O_3$ (III), m.p. 81—82°, hydrated to an *acid*, $C_{14}H_{20}O_4$, m.p. 154·5—155·5°, which is isomerised by HBr to an *acid*, m.p. 189—190°, dehydrated by Se to a compound, m.p. 77·5—80° (?=III). (II) and citraconic anhydride give an *anhydride*, $C_{15}H_{20}O_3$, m.p. 82°. G. A. R. K.

Homologues in the camphor group. VIII. *tert.*-Propylborneol and its reactions. S. S. Nametkin and A. I. Schavrygin (J. Gen. Chem. Russ., 1933, **3**, 35—42).—$MgPr^aBr$ does not yield the expected *tert.*-alcohol with camphor, but reduction (H_2–Pt) of *tert.*-allylborneol gives a good yield of tert.-*propylborneol* (I), m.p. 34—36°. Dehydration of (I) with $NaHSO_4$ gives a *hydrocarbon*, b.p. 100—101°/22 mm., oxidised by $KMnO_4$ to camphoric acid. The hydrocarbon is only partly hydrated by AcOH–H_2SO_4, the greater part remaining unchanged and probably consisting of *propylidenecamphane*. The hydration product on hydrolysis gives 4-*propyl*iso-*borneol*, m.p. 57—58°, oxidised by HNO_3 to 4-*propyl*-*camphor*, m.p. 61—62° (*semicarbazone*, m.p. 203—204°); this in turn is oxidised by $KMnO_4$ to *propyl*-*camphoric acid*, m.p. 177—178° (with elimination of H_2O). The dehydration of (I) therefore proceeds for the most part without isomerisation, although a part undergoes the " Nametkin " change. G. A. R. K.

Hydrocarbons corresponding with particular camphor-like substances. III. Hydrocarbons from dichlorides of the camphor series. G. Komppa and T. Hasselstrom (Annalen, 1933, **502**, 272—281).—Reduction (Na, EtOH) of camphor dichloride (I), m.p. 155—156°, or chlorocamphene [from (I) and NH_2Ph] gives a mixture of camphene, bornylene, and a little tricyclene. *dl*-Fenchone and PCl_5 at 105—110° afford *fenchone dichloride* (II), b.p. 105—107°/11 mm., and a little *chlorofenchene*, m.p. 45—46° (cf. Gardner and Cockburn, J.C.S., 1896, **73**, 704). (II) is reduced (Na, EtOH) to a mixture of β-, γ-, and δ-fenchenes and *cyclo*fenchene. The *chloro*-*fenchene*, b.p. 84—87°/6·5 mm., from *dl-iso*fenchone and PCl_5 in the cold, is similarly reduced to β- and δ-fenchenes. dl-α-*Fenchocamphorone dichloride*, b.p. 71—74°/22 mm., is reduced (Na, EtOH) to *apo*bornylene and (probably) a little *apo*cyclene (III), whilst β-*fenchocamphorone dichloride*, b.p. 87—92°/15 mm., similarly gives *apoiso*fenchene and a little (III). The constitutions of the hydrocarbons are determined by oxidation ($KMnO_4$). H. B.

New diterpene, γ-camphorene. K. Kafuku, T. Oyamada, and M. Nishi (Bull. Chem. Soc. Japan, 1933, **8**, 144—148).—Myrcene at 240—260° is partly converted into a monocyclic terpene (not isolated pure) and a mixture of α- (I), b.p. 178°/4·5 mm., d_4^{21} 0·8864, n_D^{21} 1·4998, and γ-*camphorene* (II), b.p. 176—178°/4·5 mm., d_4^{19} 0·8875, n_D^{19} 1·5030, separated by the solubility in ligroin of the *tetrahydrochloride*, m.p. 96—98° (decomposed by hot EtOH), of (II), whence (II) is obtained by 10% KOH–EtOH (cf. A., 1913, i, 377). (I) and (II) give *tetrahydrobromides*, m.p. 133—134° and 111—114°, respectively; the latter is unstable in hot EtOH. Both hydrocarbons form an *octabromide*, m.p. indefinite, 70—80°. R. S. C.

Ionic theory of organic reactions. III. Ring-chain tautomerism and conception of " syn-ionie." A. Kirrmann and C. Prévost (Bull. Soc. chim., 1933, [iv], **53**, 253—260; cf. A., 1931, 670; 1932, 11).—The ionic theory is applied to ring-chain tautomerism and a no. of reversible and irreversible changes of similar type in the terpene series. H. A. P.

Essential oil from the wood of *Eremophila Mitchelli* (Bentham). A. E. Bradfield, A. R. Penfold, and J. L. Simonsen. **Essential oils of three species of *Geijera* and the occurrence of a new hydrocarbon. II.** A. R. Penfold and J. L. Simonsen.—See B., 1933, 445.

Saponin series. XII. Parent hydrocarbons of the triterpene group. A. Winterstein and G. Stein (Annalen, 1933, **502**, 223—236).—α-Amyrin and PCl$_5$ in light petroleum give α-amyrilene I, m.p. 133—135° (all m.p. are corr.), reduced (H_2, PtO_2, AcOH–methyl*cyclo*hexane) to α-*amyrene* I, m.p. 96—97·5°, $[\alpha]_D^{19}$ +72·2° (all rotations are in $CHCl_3$), which is probably identical with the dihydro-α-amyrilene of Ruzicka *et al.* (A., 1932, 517, 1254). β-Amyrin similarly gives β-amyrilene I, m.p. 170—175°, reduced (as above) to a mixture of β-*amyrene* I, m.p. 89—91·5°, $[\alpha]_D^{19}$ +77·6° [probably identical with the dihydro-β-amyrilene of Ruzicka *et al.* (*loc. cit.*)], and β-*amyrene* Ia, m.p. 209—210°, $[\alpha]_D^{19}$ +115°. Decomp. of benzoyl-α-amyrin at 270—300° gives α-*amyrilene* II, m.p. 119—120°, $[\alpha]_D^{19}$ +136·6°, reduced (as above) to a non-homogeneous α-amyrene II (fractions of m.p. 111—112° and 120—122° are isolated), $[\alpha]_D$ +88·8° to +98·9°, which is also produced by reduction (Clemmensen) of α-amyrone. Benzoyl-β-amyrin similarly affords β-*amyrilene* II, m.p. 148—150°, $[\alpha]^{19}$ +139·3°, reduced (as above) to β-*amyrene* II (*A*), m.p. 162°, $[\alpha]_D^{19}$ +94·6°. Reduction (Clemmensen) of β-amyrone gives β-*amyrene* III (*B*), m.p. 187—189·5°, $[\alpha]_D^{19}$ −22°, whilst the use of Zn and AcOH–conc. HCl affords β-*amyrene* IV (*C*), m.p. 159—161°, $[\alpha]_D^{18}$ +57·3°. (*A*) and (*C*) are converted into (*B*) by Zn–Hg and AcOH–conc. HCl, whilst (*C*) is produced from (*A*) by the action of HCl or Zn+HCl.

Oleanol and PCl$_5$ give *oleanylene* I, m.p. 145—149°, $[\alpha]_D^{22}$ +78·9°, reduced catalytically to *oleanene* I, m.p. 113—116°, whilst Clemmensen reduction of oleanone, m.p. 168—172°, $[\alpha]_D^{20}$ +95·8°, affords *oleanone* III (*D*), m.p. 225—226°, $[\alpha]_D^{20}$ +30·1°. Oleanylene II (A., 1932, 61), Zn–Hg, and AcOH–conc. HCl give oleanylene III, m.p. 178—182°, which is reduced catalytically to (*D*). Oleanene II (*loc. cit.*) rearranges to (*D*) when treated with the Clemmensen reagents. Decomp. of dibenzoylhederagenol, m.p. 179—182°, gives resinous material and the *benzoate* of *anhydrohederagenol*, $C_{29}H_{16}O$, m.p. 193—195° (after sintering).

Reduction (Zn, AcOH–conc. HCl) of ergosterol gives a product, $[\alpha]_D^{17}$ +48·5°, whilst Clemmensen reduction affords a product, $[\alpha]_D^{19}$ +56·2°; neither of these is pptd. by digitonin. Similar reductions of cholesterol

give products, $[\alpha]_I^{19}$ +5·2° and +23·2°, respectively; the amounts pptd. by digitonin are 12 and 0·2%, respectively. H. B.

Friedel–Crafts reaction with phenols and furoyl chloride. H. GILMAN and J. B. DICKEY (Rec. trav. chim., 1933, **52**, 389—394).—PhOH, furoyl chloride (I), and $AlCl_3$ in $PhNO_2$ or CS_2–$PhNO_2$, first at room temp. and then at 60—65°, give p-*furoylphenol* [p-*hydroxyphenyl 2-furyl ketone*] (II), m.p. 163—164° (*Me ether*, m.p. 60°, giving *p*-anisic acid when oxidised) (24—32% yield), and Ph furoate. In CS_2 alone much p-*furoylphenyl furoate*, m.p. 84° [also obtained from (I) and (II)], is also formed. PhOBz gives a poor yield of (II). Resorcinol similarly gives 2-*furoylresorcinol*, m.p. 123—124°, in 80% yield. Quinol gives p-*hydroxyphenyl furoate*, m.p. 193—195°. R. S. C.

Furanpolycarboxylic acids. II. Furan-2 : 3 : 5-tricarboxylic acid. T. REICHSTEIN and A. GRUSSNER (Helv. Chim. Acta, 1933, **16**, 555—557).—7-Hydroxycoumarone-2-carboxylic acid (synthesis later) is oxidised (H_2O_2, 10% KOH) to *furan*-2 : 3 : 5-*tricarboxylic acid* [*Me* ester, b.p. 130—131°/0·3 mm., m.p. 76° (corr.)], which when heated to 250° gives furan-2 : 4-dicarboxylic acid. H. B.

2 : 2′-Di(furylmethyl) ether. T. ISEKI (Z. physiol. Chem., 1933, **216**, 130—132).—5-Hydroxymethylfurfuraldehyde yields 2 : 2′-di(furylmethyl) ether 5 : 5′-dialdehyde (I) more readily in presence of $AcCO_2H$. When heated with Ac_2O and NaOAc, (I) gives 2 : 2′-*di*(*furylmethyl*) *ether* 5 : 5′-*diacrylic acid*, m.p. 190°. (I) is oxidised in the animal organism to 2 : 2′-*di*(*furylmethyl*) *ether* 5 : 5′-*dicarboxylic acid*, m.p. 206°. J. H. B.

Synthesis of *dl*-hydroxymethylfurylalanine. T. ISEKI (Z. physiol. Chem., 1933, **216**, 127—129).—5-Hydroxymethylfurfuraldehyde heated with hydantoin and NaOAc gives 5-*hydroxymethylfurfuraldehydehydantoin* (I), m.p. 247°, which on reduction with Na–Hg in aq. NaOH affords ɔ-*hydroxymethylfurfurylhydantoin* (II), m.p. 167°. Hydrolysis of (II) with aq. $Ba(OH)_2$ yields dl-5-*hydroxymethylfurylalanine*, m.p. 295°. J. H. B.

α- and β-Cinenic acids. H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1933, **16**, 505—514).—An improved method of separation (cf. A., 1909, i, 7) of α-cinenic acid (I) (A., 1905, i, 409) (p-*bromophenacyl* ester, m.p. 98—99°) and β-cinenic acid (II) (A., 1901, i, 578) (p-*bromophenacyl* ester, m.p. 66°) is given. The Me esters of (I) and (II) form compounds with $H_3Fe(CN)_6$ and $H_4Fe(CN)_6$ (in 50—64% yield) indicating that they are oxido-compounds. (II) is converted [as is (I)] by cold conc. H_2SO_4 into (mainly) δ-acetyl-αα-dimethylvaleric acid and the lactone, m.p. 51°, previously described (A., 1908, i, 390). (I) and (II) give the same Br-derivative (A., 1909, i, 7) when treated with aq. HBr (saturated at 0°); this with $MgCO_3$ and H_2O affords cinogenic (αε-dihydroxy-αε-dimethylheptoic) acid, which when distilled gives (I). H. B.

***iso*Benzpyrylium ferrichloride.** B. K. BLOUNT and R. ROBINSON (J.C.S., 1933, 555—556).—Homophthalaldehyde, obtained by oxidation of *trans*-1 : 2-hydrindenediol, gives with HCl and $FeCl_3$ *isobenzpyrylium ferrichloride*, decomp. 205—208°, which forms *iso*quinoline with NH_3. F. R. S.

Dye of *acacia* wood. K. C. GULATI and K. VENKATARAMAN (J. pr. Chem., 1933, [ii], **137**, 53—56).—Treatment of synthetic 3 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone (Badhwar *et al.*, A., 1932, 621) with Ac_2O and C_5H_5N and crystallisation of the product from MeOH gives an Ac_5 derivative (I), m.p. 225°, identical with that obtained by Brass *et al.* (this vol., 103) from natural source. Crystallisation from MeOH–H_2O and finally from C_6H_6 yields the Ac_5 compound, m.p. 177—178°, described previously (*loc. cit.*). Dimorphism is assumed. Hydrolysis of (I) leads to a product, m.p. 310—312° (decomp.) which could not be raised to 325—330°. H. W.

Comparison of the directive powers of elements having consecutive atomic numbers. V. Nitration of 9-phenylxanthylium perchlorate. R. J. W. LE FEVRE and J. PEARSON (J.C.S., 1933, 482—484).—Xanthylium ferrichloride is unaffected by HNO_3 of a concn. which dinitrates xanthone. 9-Phenylxanthylium perchlorate, m.p. 274—275°, is nitrated to the 9-p-NO_2-derivative, m.p. 257—258°, which gives the corresponding 9-p-*nitrophenylxanthenol*, m.p. 116—118°. The Grignard reaction on *p*-C_6H_4ClBr and xanthone affords 9-p-*chlorophenylxanthenol*, m.p. 164° (*perchlorate*, m.p. 280—281°), and on *p*-$C_6H_4Br_2$ forms the 9-*Br*-compound, m.p. 132—133° (*perchlorate*, m.p. > 300°). 9-*Phenyl*-10-*methylacridinium perchlorate* (?), m.p. 244—245° (hydrochloride, m.p. 161—162°; picrate, m.p. 169—170°), is nitrated to the NO_2-derivative, m.p. 257—262° (decomp.). F. R. S.

Synthesis of diflavones. J. ALGAR, (MISS) I. B. MCCARTHY, and (MISS) E. M. DICK (Proc. Roy. Irish Acad., 1933, **41 B**, 155—160; cf. A., 1915, i, 707).—Diacetoresorcinol (I), Bz_2O, and NaOBz at 190—200° afford 3 : 3′-*dibenzoyldiflavone*, m.p. 292°, hydrolysed by EtOH–KOH to 4 : 6-*dibenzoylacetoresorcinol* (II), m.p. 203—204°, converted by boiling EtOH–HCl into diflavone. (II) is cyclised by boiling Ac_2O–NaOAc to 2 : 2′-*dimethyl*-3 : 3′-*dibenzoyldichromone*, m.p. 263—264°. Interaction of (I) with anisic anhydride and Na_2CO_3 at 190—200° affords the *anisate*, m.p. 233—235°, of 7-hydroxy-4′-methoxy-6-anisoylaceto-3-anisoylflavone, hydrolysed (EtOH–KOH) to 4 : 6-*dianisoylacetoresorcinol*, m.p. 203—204°, converted by boiling EtOH–HCl into 4′ : 4″-*dimethoxydiflavone*, m.p. 321—322°, different from the substance obtained by Gulati and Venkataraman (A., 1931, 1305). J. L. D.

Preparation of *dl*-proline. A. HEYMONS (Ber., 1933, **66**, [*B*], 846—848).—Treatment of piperidone (I) with PCl_5 in $C_6H_4Me_2$ at 100° and subsequently at 120° affords the imido-chloride, hydrolysed by conc. HCl to αα-dichloro-δ-amino-*n*-valeric acid hydrochloride (II), whence the free acid (III) is isolated in 60% yield by cold 2*N*-Na_2CO_3. Treatment of (I) with 1 mol. of PCl_5 in C_6H_6 and subsequently with 2 mols. of Br followed by hydrolysis affords *dibromopiperidone*, m.p. 172—173°, whence *αα-dibromo-δ-amino*-n-*valeric acid*, m.p. 191° (decomp.).

Treatment of (II) with EtOH affords (III), which when heated alone or with *tert.* bases causes lactamisation with ultimate production of 2-pyridone. In acid medium (III) is reduced to δ-amino-*n*-valeric acid under very mild conditions, whereas with Na–Hg it affords pyrrolidine-2-carboxylic acid in 47% yield. H. W.

Amino-acids and related compounds. II. Electrolytic oxidation of pyrrolidonecarboxylic acids. Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, **8**, 137—143; cf. this vol., 681).—By determining changes in NH_2-N it is shown that equilibrium exists between glutamic (I) and pyrrolidone-2-carboxylic acid (II) in *N*-H_2SO_4 at 35°. Electrolytic oxidation of (II) affords much succinimide and a little succinic acid, whilst (I) gives a little succinamic acid. R. S. C.

Action of alkali hypoiodites on pyrrolealdehydes. P. PRATESI (Atti R. Accad. Lincei, 1933, [vi], **17**, 173—177).—Towards KOI, pyrrole-2- and -3-aldehydes behave like phenol-*o*- and -*p*-aldehydes and naphtholaldehydes. Thus, Et 3-formyl-2 : 4-dimethylpyrrole-5-carboxylate gives Et 3-iodo-2 : 4-dimethylpyrrole-5-carboxylate; Et 3-formyl-2-methylpyrrole-5-carboxylate gives *Et* 3 : 4-*di-iodo*-2-*methylpyrrole*-5-*carboxylate*, m.p. 185°; pyrrole-2-aldehyde gives heptaiododipyrryl (A., 1922, i, 763); Et 3-iodo-2 : 4-dimethylpyrrole-5-carboxylate gives *Et* 3-*iodo*-2-*formyl*-4-*methylpyrrole*-5-*carboxylate*, m.p. 172·5 (*aldazine*, m.p. 232°), and Et 3-iodo-2-formyl-4-methylpyrrole-5-carboxylate a *compound*, m.p. 189°. T. H. P.

Hypnotic action of mixed ketones containing different types of aromatic nuclei. H. GILMAN, L. W. ROWE, and J. B. DICKEY (Rec. trav. chim., 1933, **52**, 395—398).—Mg pyrryl bromide and Et furoate give *furoylpurrole* [*furyl pyrryl ketone*] (I), m.p. 69—70°, b.p. 141—144°/1·5 mm. (18% yield), also obtained (in 42% yield) from Mg pyrryl iodide and furoyl chloride (II). Thiophen, (II), and $SnCl_4$ in C_6H_6 give *furoylthiophen* [*thienyl pyrryl ketone*] (III), b.p. 134—136°/3 mm., in 66% yield. The following are hypnotic in large doses: COPhMe, acetyl- (slightly) and benzoyl-pyrrole, and (I). The following are not hypnotic: acetyl-thiophen and -furan, furoyl-thiophen, and benzoylfuran. The inhibition of hypnotic properties by the furan and thiophen nuclei may be due to the super-aromatic nature of these nuclei. R. S. C.

***N*-3-Nitropyridylpyridinium chloride.** E. KOENIGS and G. JUNG (J. pr. Chem., 1933, [ii], **137**, 157—160).—4-Chloro-3-nitropyridine hydrochloride and C_5H_5N (with or without 4-aminopyridine) at 40—50° give N-3-*nitropyridylpyridinium chloride*, m.p. 175° (corresponding *chloroaurate*, m.p. 171—172°). In contrast to *N*-pyridylpyridinium chloride this is monobasic and more readily disrupted. With hot, dil. HCl, or better hot H_2O, it gives C_5H_5N and 3-nitro-4-hydroxypyridine, and with NH_2Ph at 100° glutacondianil. With cold aq. NH_3 it affords the substance $C_{10}H_9O_3N_3$, m.p. 161° (A., 1904, i, 448), probably δ-3-nitro-4-pyridylpentadienaldehyde (*hydrochloride*, m.p. 171°; *phenylhydrazone*, m.p. 147°). R. S. C.

4 : 4′-Dipyridylamine and its derivatives. E. KOENIGS and G. JUNG (J. pr. Chem., 1933, [ii], **137**, 141—156).—4-Aminopyridine (I) and PCl_3 in C_5H_5N give 4 : 4′-dipyridylamine (II) (72% yield) [*hydrochloride*, m.p. > 300°; *picrate*, m.p. 235° (decomp.)] and a little *tri*-N-4-*aminopyridylphosphine*, $P(NH{\cdot}C_5H_4N)_3$, m.p. 305—308°. In quinoline or α-picoline a poorer yield of (II) is obtained. The substances, m.p. about 130°, previously (A., 1926, 178) believed to be (II), contained much (I). 4 : 4′-Dipyridylamine-2 : 6-dicarboxylic acid, when prepared as described (*loc. cit.*), contains much of its (I) salt; when freed therefrom by crystallisation from HCl, it has m.p. 305° (decomp.); when distilled, it is partly decomposed into (I). (I) does not react with PCl_3 alone, $POCl_3$, or $POCl_3$–C_5H_5N. (II) does not react with HNO_2, BzCl–aq. NaOH, or EtI–EtOH. Addition of the *nitrate*, m.p. 226° (decomp.), of (II) to H_2SO_4 at 110—120° gives 3-*nitro*-4 : 4′-*dipyridylamine*, $+H_2O$, m.p. 96° and (anhyd.) 122—123° [*nitrate*, m.p. 210° (decomp.)], which with Br and NaOAc in AcOH at 80—100° gives 5 : 3′ : 5′-*tribromo*-3-*nitro*-4 : 4′-*dipyridylamine*, m.p. 181° (neutral), and is reduced by Na_2S at 70° to 3-*amino*-4 : 4′-*dipyridylamine*, m.p. 239° [*nitrate*, m.p. 195° (decomp.); *picrate*, m.p. 224°; reduces $HAuCl_4$], the constitution of which is proved by formation of 4′-*pyridyl*-3 : 4-*pyridotriazole*, m.p. 183° (*chloroaurate*, m.p. 249°; *picrate*, m.p. 197—198°), by HNO_2. With HNO_3 (*d* 1·52) and oleum (60% SO_3) at 100° (II) gives 3 : 3′-*dinitro*-4 : 4′-*dipyridylamine*, m.p. 195—196° [*nitrate*, m.p. 187—188° (decomp.); *picrate*, m.p. 202°; *Na* salt, red], which with Br and NaOAc in hot AcOH gives 5 : 5′-*dibromo*-3 : 3′-*diamino*-4 : 4′-*dipyridylamine*, m.p. 222—223° (neutral), and with Na_2S at 70° affords 3 : 3′-*diamino*-4 : 4′-*dipyridylamine*, m.p. 244—245° (decomp.) [*dinitrate*, m.p. about 300° (decomp.); *dipicrate*, m.p. 238° (decomp.)], the constitution of which is proved by (i) formation of 3′-*amino*-4′-*pyridyl*-3 : 4-*pyridotriazole*, m.p. 244° (*picrate*, m.p. 192°; can be diazotised), by HNO_2 and (ii) transformation of the *dihydrochloride* at 215° into *di*-3 : 4-*pyridodihydrophenazine*, m.p. 310° (*dioxalate*, *dihydrochloride*, and *dinitrate*, m.p. 310°; *picrate*, decomp. 300—301°), oxidised by H_2O_2 to *di*-3 : 4-*pyridopyrazine*, m.p. about 290—300°, a feeble base. Bromination of (II), best with Br and NaOAc in hot AcOH, affords only 3 : 5 : 3′ : 5′-*tetrabromo*-4 : 4′-*dipyridylamine*, m.p. 222° (neutral). R. S. C.

***N*-Hydroxyethyl-2-pyridone and some of its derivatives.** J. A. GAUTIER (Compt. rend., 1933, **196**, 1124—1127).—1-Hydroxyethylpyridinium chloride, m.p. 128—129° (lit. 125—126°), is converted by Decker's reaction into 1-*hydroxyethyl*-2-*pyridone*, m.p. 92°. The following derivatives are described: *hydrochloride*; *chloroaurate* (+2EtOH), m.p. 92°; *chloroplatinate*, m.p. 205° (decomp.); *picrate*, m.p. 103°; *phenylurethane*, m.p. 132° [*hydrochloride*; *chloroplatinate* (+2EtOH), m.p. 150° (decomp.)]; *benzoate*, m.p. 118° [*chloroplatinate* (+2EtOH), m.p. 225° (decomp.)]. A. C.

Mechanism of C. Mayer's triphenylpiperidone synthesis. E. MACOVSKI and A. SILBERG (J. pr. Chem., 1933, [ii], **137**, 131—140).—Benzylideneaniline (I) and H_2O_2 in boiling $COMe_2$ give β-*anilino*-β-

phenylethyl Me ketone (II), m.p. 91°, also obtained from NH_2Ph, PhCHO, and H_2O_2 in boiling $COMe_2$. The constitution of (II) is proved by (i) hydrolysis by hot HCl or cold, conc. H_2SO_4 to NH_2Ph and benzylideneacetone (III), (ii) formation of 1 : 5-dimethylpyrazoline by NH_2·NHPh in hot AcOH [by preliminary hydrolysis to (III)], (iii) formation of tribromoaniline and a *substance*, m.p. 115°, by Br in $CHCl_3$, and (iv) synthesis from (III) and NH_2Ph in EtOH, best with addition of a little NaOH. (II) is presumed to be formed by hydrolysis of (I) to NH_2Ph and PhCHO, synthesis of (II), and subsequent addition of NH_2Ph. Similarly, formation of triphenylpiperidone from (I) and $COMe_2$ is assumed to occur by hydrolysis of (I), formation of (II), and direct two-fold addition of unchanged (I) to (II); this view is supported by formation of styryl β-anilino-β-phenylethyl ketone [obtained by single addition of (I) to (II)] as a by-product. Objections are raised to previously suggested mechanisms. R. S. C.

Oxidation of magnesylindoles by hydrogen peroxide. G. Ingraffia (Gazzetta, 1933, **63**, 175—182).—The reaction of Oddo and Binaghi (A., 1922, i, 314) is extended. With 100-vol. H_2O_2 in theoretical proportion, Mg indole gives 1-*hydroxyindole*, m.p. 160°, Mg 2- and 3-methylindole give 3-*hydroxy*-2-, m.p. 40° (*picrate*, m.p. 128°; 2-*methylindole picrate* has m.p. 139°), and 1-*hydroxy*-3-*methylindole*, m.p. 120° (no picrate obtained), respectively. Colour reactions of the products are described. E. W. W.

Indole series. I. Synthesis of 2-benzylindoles. P. L. Julian and J. Pikl (J. Amer. Chem. Soc., 1933, **55**, 2105—2110).—Et *N*-methylanilinoacetate, CH_2Ph·CN, and EtOH–NaOEt give γ-N-*methylanilino*-α-*phenylacetoacetonitrile* (I), CN·CHPh·CO·CH_2·NPhMe, m.p. 121°, hydrolysed (90% H_2SO_4 at 125°) to γ-N-*methylanilino*-α-*phenylacetoacetamide*, m.p. 141°, which is hydrolysed (5% HCl) to *benzyl* N-*methylanilinomethyl ketone* (II), m.p. 37° (*oxime*, m.p. 119°), and a little of a compound (III), m.p. 245°; (III) is the main product from (I) and conc. HCl. (I) and MeOH–HCl afford *Me* γ-N-*methylanilino*-α-*phenylacetoacetate*, m.p. 73° (*hydrochloride*, m.p. 158°), also hydrolysed (5% HCl) to (II) and (III). (II) heated with NH_2Ph and NH_2Ph,HCl gives 2-*benzylindole*, m.p. 86° (*picrate*, m.p. 115°), and a little 3-*benzyl*-1-*methylindole*, m.p. 61° (*picrate*, m.p. 120—121°) (also prepared from β-phenylpropaldehydephenylmethylhydrazone and $ZnCl_2$ at 170—180°). Similarly, (II), NHPhMe, and NHPhMe,HCl afford 2-*benzyl*-1-*methylindole*, m.p. 65° (*picrate*, m.p. 97°). The following are prepared by reactions similar to the above: γ-N-*methylanilino*-α-3 : 4-*dimethoxyphenyl-acetoacetonitrile*, m.p. 110° (this and following m.p. are corr.), and -*acetoacetamide*, m.p. 156° (accompanied by a substance, m.p. 214°); 3 : 4-*dimethoxybenzyl* N-*methylanilinomethyl ketone*, m.p. 79·5° (*oxime*, m.p. 120°); 2-3 : 4-*dimethoxybenzylindole*, m.p. 146° (*picrate*, m.p. 101°), and its 1-*Me* derivative, m.p. 96° (*picrate*, m.p. 97°). H. B.

Spectroscopic study and assay of histamine. B. Lewis, E. von Gebauer-Fuelnegg, and C. J. Farmer (J. Amer. Chem. Soc., 1933, **55**, 2025—2027).—Histamine can be determined spectroscopically in concns. of 0·00367—1·82 g./100 c.c. H. B.

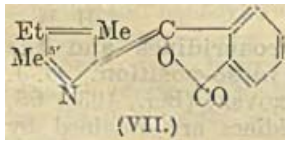
Complex salts of 8-hydroxyquinoline. A. Ablov (Bull. Soc. chim., 1933, [iv], **53**, 234—240).—The complex *salt* $Co(C_9H_6ON)_3$ is prepared by addition of H_2O_2 to a solution of a Co^{II} salt and 8-hydroxyquinoline (I), or by direct combination of (I) with hydrated Co_2O_3. It is also formed from cobaltammines, *e.g.*, $[Co(NH_3)_5]Cl_2$, *trans*-$[Co\ en_2\ Cl_2]Cl$, or $[Co(NH_3)_6]Cl_3$ and (I), there being no evidence of the formation of a cobaltammine containing (I). *Co* salts are also prepared from 5-chloro- and 5 : 7-dibromo-8-hydroxyquinoline, and the *salt* $Cr(C_9H_6ON)_3$ from (I) and $[Cr\{CO(NH_2)_2\}_6]Cl_3$. H. A. P.

Quinoline derivatives. IX. Photochemical oxidation of methylated 2-phenylquinolines. H. John and G. Behmel (Ber., 1933, **66**, [*B*], 844—845; cf. A., 1926, 622).—Irradiation of 2-phenyl-3-methylquinoline (I) leads to dark resins, about 3% of 2-phenylquinoline-3-carboxylic acid, and 47% of unchanged (I). 2-Phenyl-6-methylquinoline yields amorphous products, and about 8% of 2-phenylquinoline-6-carboxylic acid, whereas 2-*p*-tolylquinoline gives no acid, resin, and 37·5% of unchanged base. H. W.

Ring-chain conjugation in the quinoline series. A. Hoffman, M. W. Farlow, and R. C. Fuson (J. Amer. Chem. Soc., 1933, **55**, 2000—2004).—2-Styrylquinoline (I) and MgPhBr in Et_2O give 70% of 2-ββ-*diphenylethylquinoline* (II), m.p. 121—121·5° (*Br*-derivative, m.p. 131·5—132·5°; *picrate*, decomp. >200°), also obtained from (I), C_6H_6, and $AlCl_3$. 2-p-*Chlorostyrylquinoline* (III), m.p. 139·5° (*dibromide*, m.p. 175°), from 2-methylquinoline, *p*-C_6H_4Cl·CHO, and $ZnCl_2$ at 140—160°, and MgPhBr afford 64% of 2-β-*phenyl*-β-p-*chlorophenylethylquinoline*, m.p. 91·5—92·5°. (III), C_6H_6, and $AlCl_3$ give (II); reaction does not occur when the reagents are kept free from moisture, but does take place when dry HCl is passed into the reaction mixture (indicating that condensation involves the hydrochloride of the base). H. B.

Formation of *meso*chloroacridines and the mobility of chlorine in the *meso*-position. O. J. Magidson and A. M. Grigorovski (Ber., 1933, **66**, [*B*], 866—872).—9-Chloroacridines are obtained by heating the requisite diphenylaminecarboxylic acid with $POCl_3$, removal of excess of the latter under diminished pressure, suspending the residue in PhMe or $C_6H_4Me_2$, and decomposing with H_2O at 0°. Thus are prepared: 9-chloroacridine, m.p. 119—120°, 2-ethoxy-, m.p. 142—144°, 6-*nitro*-2-*ethoxy*- (I), m.p. 187—188°, and 7-nitro-2-ethoxy- (II), m.p. 365—370°, -9-chloroacridine. The rates of hydrolysis of the acetates in AcOH have been measured. (I) is transformed by PhOH at 80° into 6-*nitro*-9-*phenoxy*-2-*ethoxyacridine*, m.p. 173—174°, and by NH_3–EtOH at 130—135° into 6-*nitro*-9-*amino*-2-*ethoxyacridine*, m.p. 310°. Similar treatment of (II) yields 7-nitro-2-ethoxyacridone, but a modified procedure leads to 7-*nitro*-9-*phenoxy*-2-*ethoxyacridine*, m.p. 152—153°, and 7-*nitro*-9-*amino*-2-*ethoxyacridine*, m.p. >300°. H. W.

Dipyrryl ketones. II. H. FISCHER and H. ORTH (Annalen, 1933, **502**, 237—264).—$COCl_2$ in PhMe converts the product from Et_2O–MgEtBr and 2-methyl-, 2-ethyl-, 2 : 4-diethyl-, 2-methyl-4-ethyl-, 5-methyl-3 : 4-diethyl-, 4-methyl-2 : 3-diethyl-, 2 : 3-dimethyl-4-propyl-, 2 : 4-dimethyl-3-propyl-, 2 : 3-dimethyl-, and 2 : 3 : 4-trimethyl-pyrroles into *di*-(5-*methyl*-2-*pyrryl*), m.p. 250°, *di*-(5-*ethyl*-2-*pyrryl*), m.p. 175°, *di*-(3 : ɔ-*diethyl*-2-*pyrryl*) (I), m.p. 140°, *di*-(5-*methyl*-3-*ethyl*-2-*pyrryl*) (II), m.p. 186°, *di*-(5-*methyl*-3 : 4-*diethyl*-2-*pyrryl*) (III), m.p. 156°, *di*-(3-*methyl*-4 : 5-*diethyl*-2-*pyrryl*), m.p. 182°, *di*-(4 : 5-*dimethyl*-3-*propyl*-2-*pyrryl*) (IV), m.p. 160°, *di*-(3 : 5-*dimethyl*-4-*propyl*-2-*pyrryl*) (V), m.p. 177° (*azine*, m.p. 229°), *di*-(4 : 5-*dimethyl*-2-*pyrryl*), m.p. 275° [*hydrazone*, m.p. 173° (not sharp)], and *di*-(3 : 4 : 5-*trimethyl*-2-*pyrryl*) (VI), m.p. 252° (*hydrazone*, m.p. 174°; *azine*, m.p. 267°), *ketones*, respectively. (I), AcCl, and $AlCl_3$ in CS_2 give *di*-(4-*acetyl*-3 : ɔ-*diethyl*-2-*pyrryl*) *ketone*, m.p. 180—181°, whilst (II) similarly gives *di*-(4-*acetyl*-5-*methyl*-3-*ethyl*-2-*pyrryl*) *ketone*, m.p. 250°, which with Br in AcOH affords the *di*-(5-*bromomethyl*) derivative, m.p. 205° (decomp.) (darkens at 195°). (III) and 20% $COCl_2$ in PhMe give 5 : 5′-*dimethyl*-3 : 4 : 3′ : 4′-*tetraethyl*-ms-*chloropyrromethene hydrochloride*, m.p. 152° (*Zn* salt, sinters at 180°); 4 : 5 : 4′ : 5′-*tetramethyl*-3 : 3′-*dipropyl*-, m.p. 245° [*hydrochloride*, m.p. 155—156° (*Zn* salt, m.p. 165°)], 3 : 5 : 3′ : 5′-*tetramethyl*-4 : 4′-*dipropyl*-, m.p. 105° [*hydrochloride*, m.p. 90—93° (*Zn* salt, darkens at 125°)], and 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethyl*-, unstable (hydrochloride, m.p. 148°), -ms-*chloropyrromethenes* are similarly prepared from (IV), (V), and (VI), respectively. The *Zn* salt, darkens and sinters at 171°, of 3 : 5 : 3′ : 5′-tetramethyl-4 : 4′-diethyl-*ms*-chloropyrromethene hydrochloride (A., 1931, 1168) is also described. Di-(3 : 5-dimethyl-4-ethyl-2-pyrryl) ketone (*loc. cit.*) undergoes fission when treated with *o*-$C_6H_4(CO)_2O$ and AcOH at 180—190° to give cryptopyrrolephthalide (VII) (cf. A., 1913, i, 93), which is also similarly prepared from Et 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate. (VII) and Br in AcOH afford the



(VII.)

5′-*bromomethyl* derivative, m.p. 192°, converted by boiling MeOH into a *OMe*-derivative, m.p. 157°, and by NH_2Ph into an *anilino*-derivative, m.p. 170°. Et 2 : 4-diethylpyrrole-5-carboxylate, AcCl, and $AlCl_3$ in CS_2 give the *Et* ester, m.p. 106° (*oxime*, m.p. 164°), of 3-*acetyl*-2 : 4-*diethylpyrrole*-5-*carboxylic acid*, m.p. 205°; the ester is reduced (Wolff–Kishner) to 2 : 3 : 4-triethylpyrrole, b.p. 103—104°/12 mm., which is converted (as above) into *di*-(3 : 4 : 5-*triethyl*-2-*pyrryl*) *ketone*, m.p. 134° (*hydrazone*, m.p. 130°), and with HCO_2H and HBr affords 3 : 4 : 5 : 3′ : 4′ : ɔ′-*hexaethylpyrromethene hydrobromide*, m.p. 155° (free *base*, m.p. 123°). *Di*-(4-*carbethoxy*-5-*methyl*-2-*pyrryl*) *ketone*, m.p. 216° (decomp.), and *Me xanthopyrrolecarboxylate picrate*, m.p. 102°, are described. *Di*-(3-*methyl*-5-*ethyl*-2-*pyrryl*) *ketone* (VIII), m.p. 150° (*azine*, m.p. 171°; *Ac* derivative, m.p. 136°, of hydrazone), prepared (as above) from xanthopyrrole, is brominated to the 4 : 4′-*Br*$_2$-derivative, sinters at 163°, converted by $COCl_2$ into 4 : 4′-dibromo-3 : 3′-dimethyl-5 : 5′-diethyl-*ms*-chloropyrromethene hydrochloride, m.p. about 150°. (VIII), AcCl, and $AlCl_3$ in CS_2 give the 4 : 4′-*Ac*$_2$ derivative, m.p. 237°, which with Br (2 mols.) in AcOH affords *di*-(4-*acetyl*-3-*methyl*-5-β-*bromoethyl*-2-*pyrryl*) *ketone*, darkens at 182° and sinters at 196°, converted by boiling EtOH into the *di*-ɔ-β-*ethoxyethyl* derivative, m.p. 216—217° (decomp.). *Di*-(4-*acetyl*-3 : 5-*dimethyl*-2-*pyrryl*) *ketone* (IX), m.p. 271° (*dioxime*, m.p. 269°), is brominated to the *di*-5-*bromomethyl* derivative, darkens at 180°, converted into the *di*-ɔ-*methoxy*-, m.p. 218—219°, *di*-5-*ethoxy*-, m.p. 222° (sinters at 209°), and *di*-ɔ-*acetoxy*-, m.p. 260° (darkens at 206°), -*methyl* derivatives by the action of MeOH–KOH, EtOH–KOH, and AcOH–AgOAc, respectively. (IX) and SO_2Cl_2 in Et_2O give a *compound*, $C_{17}H_{12}O_3N_2Cl_8$, m.p. 224—227°.

Me opsopyrrolecarboxylate and $COCl_2$ in Et_2O afford 3-methyl-4-β-carbomethoxyethylpyrrole-2-carboxylic chloride (corresponding *anilide*, m.p. 141°), which with 3-acetyl-2 : 4-dimethylpyrrole (X) and $AlCl_3$ in CS_2 gives 4′-*acetyl*-3 : 3′ : 5′-*trimethyl*-4-β-*carbomethoxyethyldi*-2-*pyrryl ketone*, m.p. 156°. The acid chloride (XI) from $COCl_2$ and Me β-2 : 4-dimethyl-3-pyrrylpropionate with Et 2 : 4-dimethylpyrrole-3-carboxylate and $AlCl_3$ in CS_2 affords 4-*carbethoxy*-3 : 5 : 3′ : 5′-*tetramethyl*-4′-β-*carbomethoxyethyldi*-2-*pyrryl ketone*, m.p. 173—174°. Et 2-methylpyrrole-3-carboxylate (XII) and (XI) similarly give 4-*carbethoxy*-5 : 3′ : 5′-*trimethyl*-4′-β-*carbomethoxyethyldi*-2-*pyrryl ketone*, m.p. 188°, whilst 4-*acetyl*-3 : 5 : 3′ : 5′-*tetramethyl*-4′-β-*carbomethoxyethyldi*-2-*pyrryl ketone*, m.p. 186°, is prepared from (XI) and (X). The chloride from Me hæmopyrrolecarboxylate and $COCl_2$ with (X) and (XII) gives 4-*acetyl*-3 : 5 : 4′ : 5′-*tetramethyl*-, m.p. 153°, and 4-*carbethoxy*-ɔ : 4′ : ɔ′-*trimethyl*-, m.p. 170°, -3′-β-*carbomethoxyethyldi*-2-*pyrryl ketone*, respectively. An improved method of prep. (cf. Hess and Anselm, A., 1921, i, 881) of di-2-pyrryl ketone (XIII) (*Br*$_4$-derivative, darkens at 255°) is given. (XIII) and SO_2Cl_2 in Et_2O afford (probably) *di*-(3 : ɔ-*dichloro*-2-*pyrryl*) *ketone*, m.p. 296—297° (sinters at 275°). Pyrrole-2-aldoxime, Ac_2O, and NaOAc give 2-*cyano*-ɔ-*acetylpyrrole*, m.p. 74—75°.

H. B.

New metallic complexes of cyanogen compounds. J. FOUCRY (J. Pharm. Chim., 1933, [viii], **17**, 432—433).—Unstable coloured complex salts are pptd. when a solution of Fe–antipyrine [antipyrine + $Fe_2(SO_4)_3$] is added to NaSCN or $Na_2Fe(CN)_5NO$. The reaction is sp. for antipyrine, but similar ppts. are obtained with UO_2, Zn, Mn, or Cu^{II} in place of Fe.

J. W. B.

Glyoxaline derivatives. III. Occurrence of 4-hydroxymethylglyoxaline. T. YABUTA and K. KAMBE (J. Agric. Chem. Soc. Japan, 1932, **8**, 815—820).—In presence of O_2, a solution of fructose and NH_3 in presence of $Cu(OH)_2$ afford 4-hydroxymethylglyoxaline (I), which is also obtained from fructose, CH_2O, NH_4 phosphate, and aq. NH_3, or fructose, CH_2O, aq. NH_3, and methylene-blue, in presence of O_2. Hydroxygluconic acid, $Cu(OH)_2$, and aq. NH_3 afford (I) and glyoxaline-4-carboxylic acid.

CH. ABS.

Hydro-orotic acid. M. BACHSTEZ (Gazzetta, 1933, **63**, 206—210).—Maleic acid heated with

$CO(NH_2)_2$ at 132° gives a small yield of *hydro-orotic acid* (*hydrouracil-4-carboxylic acid*), m.p. 247° (corr.), K $6{\cdot}19\times10^{-3}$. E. W. W.

Action of triphenylmethyl perchlorate on substituted barbituric acids. H. Aspelund (J. pr. Chem., 1933, [ii], **137**. 1—8).—The action of CPh_3ClO_4 on Na 5-ethyl- (I) or 5-benzyl- (II) -barbiturate in $CHCl_3$ or Et_2O does not lead to the expected derivatives. CPh_3 is recovered as $CHPh_3$ or $CPh_3{\cdot}OH$, whilst (I) and (II) are recovered with a small amount of the corresponding dialuric acid. (II) is partly transformed into a *substance*, m.p. (indef.) 183—184°. CPh_3ClO_4 and Na 5 : 5-diethyl- (III) and 5-ethyl-ɔ-allyl- (IV) -barbiturate afford 1 : 3-*ditriphenylmethyl*-5 : 5-*diethyl*-, m.p. 220°, according to rate of heating, and 1 : 3-*ditriphenylmethyl*-5-*ethyl*-ɔ-*allyl*-, m.p. 192—196°, -*barbituric acid*, respectively, insol. in H_2O and alkali and very readily hydrolysed with much unchanged (III) and (IV) and $CPh_3{\cdot}OH$. (III) in $CHCl_3$ at 40° gives the *compound* $C_{16}H_{24}O_6N_4,NaClO_4$, m.p. 229°. (IV) is obtained in 85% yield from (I) suspended in H_2O and allyl chloride (V) (20% excess) at 40°. 5 : 5-Diallylbarbituric acid results in 65% yield from Na barbiturate and (V) at 70—80°. H. W.

Interaction of *cyclo*hexene oxide with piperazine and piperidine. T. S. Kusner (Ukrain. Chem. J., 1932, **7**, [Sci.], 179—183).—On warming an aq. suspension of piperazine and *cyclo*hexene oxide (I), *NN'*-bis-(2-hydroxy*cyclo*hexyl)piperazine, m.p. 208—208·5°, is produced (picrate, m.p. 232°; *dihydrochloride*, darkens about 270°, carbonises at 276—280°; *dihydrochloride* of *dibenzoate*, darkens at 250—260°) (cf. A., 1932, 404). $C_5H_{11}N$ and (I) yield N-(2-*hydroxy*cyclo*hexyl*)*piperidine*, b.p. 142—143°/21 mm., m.p. 34° [*hydrochloride*, m.p. 268° (decomp.); *hydrochloride* of *benzoate*, m.p. 265—266° (decomp.)]. Both the benzoates possess local anæsthetic properties. G. A. R. K.

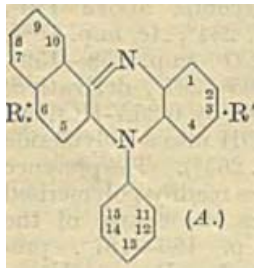
Constitution of polypeptides and [action of] proteolytic enzymes. I, II. J. Matsui (J. Biochem. Japan, 1933, **17**, 163—169, 253—258).—I. Treatment of glycyltyrosine Et ester with fumaryl chloride in $CHCl_3$ yields *fumaryldi*(*glycyltyrosine*) *Et ester*, hydrolysed to *fumaryldi*(*glycyltyrosine*), m.p. 159—160°, which with aq. NH_3 at 100° under pressure affords asparagyldi(glycyltyrosine), m.p. 183°, hydrolysed by trypsin-enterokinase (I), but not by pepsin (II), erepsin, (III), or non-activated trypsin (IV). Thus glycyltyrosine is no longer a substrate for (III) when the NH_2 group is linked with aspartic acid, but becomes a substrate for proteases such as (I).

II. Et aminomalonate in Et_2O solution shaken with $CH_2Cl{\cdot}COCl$ and aq. Na_2CO_3 yields *Et chloroacetamidomalonate*, m.p. 98°. The corresponding *acid*, m.p. 113°, on treatment with NH_3 etc. affords *glycylaminomalonic anhydride*, m.p. 193°, which has a diketopiperazine structure, is hydrolysed by (IV) and, to a greater extent, by (I) but not by (II) or (III). F. O. H.

Enzymic degradation of diketopiperazine rings. T. Ishiyama (J. Biochem. Japan, 1933, **17**, 285—297).—The anhydride of Et glycylaspartate (A., 1904, i, 31) is hydrolysed with $Ba(OH)_2$ to yield *diketopiperazinediacetic acid*, m.p. 270°. Et glutamate hydrochloride is converted into the free base and treated with $CH_2Cl{\cdot}COCl$ to give Et chloroacetylglutamate, which with NH_3-saturated EtOH yields *diketopiperazinepropionamide*, m.p. 248—250° (decomp.), and with 0·93N-NH_3 in EtOH yields *Et glycylglutamate anhydride*, m.p. 140°. The latter with $Ba(OH)_2$ affords *diketopiperazinepropionic acid*, m.p. 225°. The action of trypsin and of trypsin-kinase on these and other diketopiperazine derivatives indicates that glycylglutamic acid on anhydride (diketopiperazine) formation is no longer hydrolysable by trypsin, but becomes a sp. substrate for trypsin. Diketopiperazine and pyrrolidone-2-carboxylic acid and its amide are not hydrolysed by trypsin. F. O. H.

Quinazolines. VI. Alkylation of benzoylenecarbamide [2 : 4-diketotetrahydroquinazoline]. N. A. Lange and F. E. Sheibley (J. Amer. Chem. Soc., 1933, **55**, 2113—2116).—*o*-$NHEt{\cdot}C_6H_4{\cdot}CO_2H$ (I) and KNCO in AcOH give 2 : 4-*diketo*-1-*ethyltetrahydroquinazoline*, m.p. 215—217°, also obtained from (I) and $CO(NH_2)_2$ at 150°, which is ethylated (EtI and EtOH–KOH; Et_2SO_4 and N-NaOH) to the 1 : 3-Et_2 derivative, m.p. 110—111° [this could not be prepared by Bogert and May's method (A., 1909, i, 329)], and methylated (MeI, MeOH–KOH) to 2 : 4-*diketo*-3-*methyl*-1-*ethyltetrahydroquinazoline*, m.p. 138—139°. Ethylation (EtI; cf. Bogert and Scatchard, A., 1920, i, 184) of 2 : 4-diketotetrahydroquinazoline gives the 3-Et derivative, m.p. 197·5—198·5°, which is methylated (Me_2SO_4, N-NaOH) to 2 : 4-*diketo*-1-*methyl*-3-*ethyltetrahydroquinazoline*, m.p. 133—134° (softens at about 110°). All m.p. are corr. H. B.

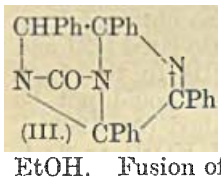
Analysis of azine dyes. R. Bass (Helv. Chim. Acta, 1933, **16**, 403—418).—Naphthophenosafranines (*A*, where R and R' are basic groups) are hydrolysed by heating with AcOH–conc. HCl under pressure (cf. Fischer and Arntz, A., 1907, i, 94) to well-defined OH-derivatives. Thus, Wool Fast Blue BL (By) (I) and Novazol Acid Blue G. L. (Gy) (II) give compounds resembling (appearance; position of main absorption band) naphthosafranol (*A*, R=O, R'=OH); that from (II) has the composition $C_{22}H_{14}O_3N_2$, and contains 2 OH groups (Zerevitinov in PhOMe). Neutral Blue (C) (III) similarly gives a violet compound (the main absorption band of which differs from that of *iso*rosindone), whilst Basle Blue R (DH) (IV) and dimethyl*iso*rosindulines containing a substituent in position 13 afford non-homogeneous products. Prolonged heating with 60—70% H_2SO_4 causes the elimination of the 6-substituent; thus, (I) gives the *compound* (*A* with R=O, R'=NHPh, and SO_3Na at position 4 or 7), (II) affords the *compound* (*A* with R=O, R'=NEt_2, Me at 11, and an undetermined SO_3Na group), whilst Indocyanine BF (A) yields a substance, the spectrum of which resembles that of dimethylnaphthosafraninone (*A*, R=O, R'=NMe_2). (III) is unaffected by 60—70% H_2SO_4



at 140—160°, whilst (IV) gives a non-homogeneous product. No useful information is obtained by reduction (Sn, HCl) of the dyes. The above methods of degradation give some idea of the constitutions, but do not establish the structures of the dyes.

H. B.

Heterocyclic compounds obtained by the interaction of benzoins and hydrazine hydrochloride. II. J. VAN ALPHEN (Rec. trav. chim., 1933, **52**, 478—486; cf. this vol., 286).—The following derivatives of Δ^2-1 : 3 : 4 : 6-tetraphenyl[dehydro]trimidine (I) are prepared: 5 : 7-*Me*$_2$-, m.p. 189°, and -*Et*$_2$-, m.p. 135°; 5- or 7-β-*bromoethyl*-, m.p. 158° [reduced to (I) by Zn dust in hot AcOH], a *complex* (II) of the 5 : 7-*oxalylo*-derivative with 0·5$(COCl)_2$, m.p. about 240°; 5 : 7-*carbonylo*- (III), m.p. about 335° [*complex* with 0·5$COCl_2$, m.p. 158°, gives (I) at 250°]; 5 : 7-*sulphono*-, decomp. > 280° (by conc. H_2SO_4 at 160°), gives (III) when boiled with 50% H_2SO_4. PhI, KOH, and Cu-bronze in boiling $PhNO_2$ give Δ^2-1 : 3 : 4 : 5 : 6 : 7-*hexaphenyl*[*dehydro*]*trimidine*, m.p. 283°. Addition of ligroin to a C_6H_6 solution of (II) or boiling (II) with NaOAc–EtOH gives the 5 : 7-*oxalylo*-derivative (IV), m.p. 268—269° (decomp.), which rapidly affords (I) when boiled with KOH–EtOH. Fusion of (II) or (IV) gives (III).



R. S. C.

Polymerisation of alkylated indoles. O. SCHMITZ-DUMONT and K. H. GELLER (Ber., 1933, **66**, [*B*], 766—774; cf. A., 1931, 1165, 1429).—*Di*-7-*methylindole hydrochloride* (I) is obtained by passing HCl into 7-methylindole (II) in C_6H_6 or by rapid addition of fuming HCl to (II) in EtOH at −10°. (I) and KOH yield *di*-7-*methylindole*, m.p. 88°, which contains 2 active H but affords only monoacyl derivatives. It is smoothly depolymerised at 225—240° vac. to (II). The *picrate*, decomp. above 130°, *phenylcarbamide* derivative, m.p. 234°, *Ac*, m.p. 186°, ·CO_2Et, m.p. 195—196°, CCl_3·CO·, m.p. 158—159°, decomp. 160°, and *Bz*, m.p. 265—267°, derivatives are described. (II) is not affected by 0·25*N*-HCl, but is converted by HCl in H_2O–EtOH into a polymeride (*Ac* derivative, $C_{33}H_{33}O_3N_3$, m.p. 263°). The presence of the 7-Me in (II) renders (II) less readily polymerised than indole and also influences the course of the change. *Tri*-7-*methylindole*, m.p. 186—187°, prepared by the prolonged action of $SnBr_4$ on (II) in $C_6H_4Me_2$, contains 3 active H, is depolymerised to (II) at 240°/vac., and gives an *Ac* derivative, m.p. 250—251°. 1-Methylindole (III) in C_6H_6 is converted by HCl into *tri*-1-*methylindole* (IV), m.p. 178—179° (*hydrochloride*), in very poor yield, the main reaction following a different course. (III) in EtOH is transformed by fuming HCl at −10° into *di*-1-*methylindole*, m.p. 133—135° (*hydrochloride*), a little (IV), and much other material. Increase in size of the alkyl groups diminishes the tendency towards polymerisation; 3-ethyl-, unlike 3-methyl-indole, is not polymerised.

H. W.

Chlorophyll. XXXII. Neophæoporphyrin a_6, hydroxymethylphæophorbide and its dihydro-derivative, and *allo*phæoporphyrin a_7. H. FISCHER and W. HAGERT (Annalen, 1933, **502**, 41—74).—Allomerisation of phæophorbide *a* (I) with O_2 in AcOH and subsequent esterification (CH_2N_2) give *Me* esters, $C_{36}H_{38}O_6N_4$, m.p. 253° (previous sintering), and $C_{36}H_{38}O_5N_4$, m.p. 228° (previous sintering). Similar allomerisation of phæophytin and subsequent reduction (HI–AcOH at 60°) affords chloroporphyrin e_6 (II), phæoporphyrin a_6 (III), phæoporphyrin a_5 (IV) (*Me*$_2$ ester, m.p. 279°), phylloerythrin (V), and porphyrins of the *b*-series. Reduction (HI–AcOH) of chlorophyllide *a* and *b* gives only (V); when solution in AcOH is kept under O_2 for 35 days and then reduced, 75% of (III) is produced (similar results are obtained using benzoquinone in N_2 for O_2). Hydrolysis (MeOH–KOH–C_5H_5N) of the more sol. fraction from allomerised (I) gives a chlorin (*Me* ester, $C_{37}H_{42}O_6N_4$, m.p. 212°). (II) is converted by O_2 in 3% HCl into some (III) and by O_2 in conc. H_2SO_4 into (IV), whilst (IV) and O_2 in AcOH give (V). Esterification (MeOH–HCl; CH_2N_2; Me_2SO_4) of (III) affords the *Me*$_2$ ester, m.p. 250—258° (according to method of prep.), of *allophæoporphyrin* a_7 (VI), $C_{35}H_{36}O_7N_4$, also formed when (III) is kept for 1 year or treated with EtOH–C_5H_5N or EtOH–NH_3. (VI) is unaffected by benzoquinone in 4% HCl and N_2 and is converted by conc. H_2SO_4 into (III). Short reduction (HI–AcOH) of allomerised (O_2–AcOH) (I) and subsequent hydrolysis (HCl) give (IV) and (after esterification with CH_2N_2) *dihydrohydroxymethylphæophorbide* (VII), $C_{36}H_{40}O_6N_4$, m.p. 272° (sinters at 263°), and phæoporphyrin 658 (VIII), $C_{36}H_{40}O_6N_4$, m.p. 221—228° (blackens at 190°) (characterised by an absorption max. at 658 mμ); (VIII) is obtained also by further reduction (HI) of (VII) and is converted by 12—14% HCl or 10% aq. NH_3 into (III). Reduction of the allomerised (I) under slightly differing conditions gives (IV), (VII), (VIII), and *neophæoporphyrin* a_6 (*Me* ester, $C_{36}H_{36(38)}O_6N_4$, m.p. 270—272°; *oxime*), which is hydrolysed (7% HCl) to (III). Phæoporphyrin a_6 ester is hydrolysed (MeOH–KOH in EtOH–C_5H_5N and N_2) to (VI). Hydrolysis of allomerised (I) to chlorins and esterification of the fraction sol. in 10% HCl gives a *compound* (IX), $C_{37}H_{42}O_7N_4$, m.p. 300°. (I) heated with AcOH affords (V) and a more basic porphyrin [the Me ester of which is identical with (IX)]. Details of the prep. of phæophorbides *a* and *b* from methylchlorophyllide by extraction with HCl in N_2 are given. Structures are suggested for most of the above new compounds.

H. B.

Ultra-violet absorption of porphyrins. A. TREIBS (Z. physiol. Chem., 1933, **217**, 38; cf. this vol., 76).—The work of Bois (A., 1928, 345) and van der Bom is acknowledged.

J. H. B.

Relations between constitution and spectra of porphyrins. Fluorescence of ætioporphyrin. H. HELLSTRÖM (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 11, 5 pp.).—Irradiation of ætioporphyrin (I) in C_5H_5N with light of the same wave-lengths as the absorption bands causes variations in the intensities of the non-equiv. fluorescence bands; this does not occur in Et_2O. The former results are due to the production of photoporphyrin [obtained when a conc.

solution of (I) in C_5H_5N is exposed to sunlight], which is altered by 25% HCl and 14% HCl–Et_2O, and is probably formed by dehydrogenation of (I). H. B.

Production of urobilin by the action of ultra-violet rays on chlorophyll and porphyrins. B. GOUZON (Compt. rend., 1933, **196**, 1542—1544).—Urobilin is formed when solutions of chlorophyll and hæmato-, oo-, and proto-porphyrins in $CHCl_3$ or $CHCl_3$–C_5H_5N are exposed to ultra-violet rays at $< 40°$. H. B.

Bile pigments. XII. Dihydromesobilirubin. H. FISCHER and H. BAUMGARTNER (Z. physiol. Chem., 1933, **216**, 260—263; cf. A., 1932, 627).—An intermediate product in the reduction of mesobilirubin to mesobilirubinogen is *dihydromesobilirubin*, blackens at 250°, m.p. 278—284° (decomp.). J. H. B.

Formation of hydrindones from unsaturated ketones. K. VON AUWERS and E. RISSE (Annalen, 1933, **502**, 282—299).—*p*-Xylene, cinnamoyl chloride (I), and $AlCl_3$ in CS_2 give 3-*phenyl*-4 : 7-*dimethyl*-α-*hydrindone*, b.p. 198—202°/11 mm., m.p. 94—95° [*oxime*, m.p. 218—219° (*Ac* derivative, m.p. 127—127·5°); *phenylhydrazone*, m.p. 193—194°; *semicarbazone*, m.p. 232°], also obtained when p-*xylyl styryl ketone*, m.p. 41—42° (from aceto-*p*-xylene, PhCHO, and MeOH–KOH), is treated with $AlCl_3$ in CS_2. *p*-Xylene and crotonyl chloride (II) similarly give a mixture (*A*) of *p*-xylyl propenyl ketone (III) (not obtained pure) and 3 : 4 : 7-*trimethyl*-α-*hydrindone* (IV), b.p. 142°/12 mm., m.p. 32—33° [*oxime*, m.p. 144·5° (*Ac* derivative, m.p. 74—75°); p-*nitrophenylhydrazone*, m.p. 195°; *benzylidene* derivative, m.p. 90·5—91·5°]; (IV) is isolated from the product from (*A*) and $AlCl_3$ in CS_2. Aceto-*p*-xylene, $CH_2Br{\cdot}CO_2Et$, and Zn in C_6H_6 give Et β-hydroxy-β-*p*-xylylbutyrate, b.p. 140—155°/12 mm., dehydrated by 90% HCO_2H to the Et ester, b.p. 150—154°/20 mm., of β : 2 : 5-*trimethylcinnamic acid*, m.p. 68° (which is probably the *trans*-form); the acid is reduced (Na–Hg, aq. Na_2CO_3) to β-p-*xylylbutyric acid*, m.p. 111—112°, the chloride of which with $AlCl_3$ in CS_2 gives (IV). αβ-*Dibromobutyryl*-p-*xylene*, m.p. 62—63° (from *p*-xylene, $CHMeBr{\cdot}CHBr{\cdot}COCl$, and $AlCl_3$ in CS_2), and EtOH–KI also afford impure (III). (IV) is also produced during the condensation of β-chlorobutyryl chloride and *p*-xylene.

m-Xylene and (I) give m-4-*xylyl styryl ketone*, b.p. 218—219°/11 mm., m.p. 71—72°, which does not yield an oxime, semicarbazone, or phenylhydrazone, and is unaffected by $AlCl_3$; in one condensation, a little 3-*phenyl*-5 : 7-*dimethyl*-α-*hydrindone*, m.p. 101° (*semicarbazone*, m.p. 195—197°), was produced. m-4-*Xylyl propenyl ketone*, b.p. 144—146°/15 mm., formed using (II), is polymerised by $AlCl_3$. *o*-Xylene and (I) afford o-4-*xylyl styryl ketone*, m.p. 72—73° (*dibromide*, m.p. 87—88°), which with NH_2OH,HCl in EtOH gives o-*phenyl*-3-3′ : 4′-*dimethylphenyl*-isooxazoline, m.p. 179·5—180·5°; and with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ yields 5-*phenyl*-1-p *nitrophenyl*-3-3′ : 4′-*dimethylphenylpyrazoline*, m.p. 172—173°. o-4-*Xylyl propenyl ketone*, b.p. 138—140°/12 mm., polymerises readily. PhMe and (I) give *p*-tolyl styryl ketone and a saturated additive compound (not isolated); with (II), p-*tolyl propenyl ketone*, b.p. 132—134°/11 mm., results. m-*Tolyl styryl ketone*, b.p. 214—216°/11 mm. (from *m*-$C_6H_4Me{\cdot}COMe$ and PhCHO), is converted by $AlCl_3$ at 100° into 3-*phenyl*-6-*methyl*-α-*hydrindone*, b.p. 210—220°/11 mm. (p-*nitrophenylhydrazone*, m.p. 236—238°). The production of Ph ββ-diphenylethyl ketone and 3-phenyl-α-hydrindone from C_6H_6 and (I) is confirmed. C_6H_6 and (II) give Ph propenyl ketone, b.p. 124—128°/14 mm. (cf. A., 1921, i, 466). 3-Methyl-α-hydrindoneoxime has m.p. 99—100° (lit. 141·5°). The ring closures show that the *o*-H in PhMe is more reactive than the *p*-H atom, which is more reactive than a H in C_6H_6, which is more reactive than the *m*-H in PhMe (cf. von Braun *et al.*, A., 1929, 562). H. B.

[Hydroxylamine derivatives of ketones.] II. Derivatives of benzylideneacetone, ethylideneacetophenone, and benzoylacetone. III. *iso*-Oxazolines and *iso*oxazoles. K. VON AUWERS and H. MULLER (J. pr. Chem., 1933, [ii], **137**, 81—101, 102—130; cf. this vol., 611).—Styryl Me ketone does not form an oximino-oxime; the normal oxime, m.p. 116°, with HCl gives an isomeride, which usually has m.p. 105—106°, but often lower. The second oxime, when pure, gives by the Beckmann change acetylstyrylamine, but, when impure, methylcinnamamide. Ethylideneacetophenone does not form a simple oxime; with NH_2OH and a drop of HCl in hot abs. EtOH it gives β-*hydroxylaminobutyrophenoneoxime* (I), m.p. 151—152° (*Bz*$_2$ derivative, m.p. 124—125°), and a little "*B-iso*oxazole," 3-*phenyl*-5-*methyl*-isooxazole (II), m.p. 43°. (I) is stable to hot, dil., or conc. HCl, and cold NH_3–MeOH; when boiled for a day with 2*N*-H_2SO_4, it gives NH_2OH and the "*A-iso*-oxazole," 5-*phenyl*-3-*methyl*isooxazole (III), m.p. 68°; when heated above the m.p., or boiled for 15 min. with AcOH, it gives (II); when kept in cold NaOH or oxidised by $K_3Fe(CN)_6$, it gives benzoylacetonedioxime (IV); when boiled for a few min. with HCO_2H, it forms NH_3 and β-N-*formylhydroxylaminobutyrophenone* (*propiophenone*-β-*formhydroxamic acid*) (V), m.p. 95—96° (*Cu* salt; *Ac* derivative, m.p. 96°), and some (III); when boiled for 15 min. with HCO_2H, (V) yields (III), also formed almost exclusively by similar treatment of (II). With hot NaOH (V) gives COPhMe and (?) CH_2O. CH_2BzAc (VI) and cold NH_2OH (2 mols.) in aq. EtOH give *benzoylacetoneoxime* (VII), an oil (*Bz*$_2$ derivative, m.p. 68—70°); when heated, however, (III) is formed (cf. A., 1926, 406); (III) is also obtained if NH_2OH,HCl (3 mols.) and KOH (1·5 mols.) in cold aq. MeOH are used. (VI), NH_2OH (2 mols.), and NaOH (2 mols.) in cold aq. EtOH give (II) and (VII); when this solution is boiled, (II), (IV), and COPhMe are obtained. Hot or cold $K_3Fe(CN)_6$ oxidises (VII) to BzOH. (VI), NH_2OH (3 mols.), and NaOH (3 mols.) in cold aq. EtOH give (IV), m.p. 86—87° or 95° (*Bz* derivative, m.p. 148—149°, unchanged by PCl_5), oxidised by $K_3Fe(CN)_6$ to (II). O-*Benzoylacetophenoneoxime*, m.p. 98—100°, is also stable to PCl_5. With boiling HCO_2H or cold, dil. HCl (IV) gives (III), but with aq. NaOH more slowly (II). The constitutions of (IV) and (VII) are supported by refractometric data.

III. Ph styryl ketone (VIII) (1 mol.), NH_2OH,HCl (1 mol.), and NaOEt (1·5 mol.) in cold EtOH give

3 : 5-diphenyl*iso*oxazoline (IX); the oxime of (VIII), however, is unchanged by excess NaOH, with or without NH_2OH, in hot or cold solvents. *NN'*-Di-(α-phenyl-β-benzoylethyl)hydroxylamine is entirely or mostly unchanged by NH_2OH in cold EtOH, cold EtOH–NaOH, or hot, conc. HCl, but in hot EtOH–NaOH gives (II) and a little COPhMe. Styryl Me ketoxime (either isomeride) is stable to alkali, but with cold, conc. H_2SO_4 gives *5-phenyl-3-methyliso-oxazoline*, b.p. 151—152°/13 mm. This method gives a good yield of pure (IX) from (VIII), but fails with *Bz-* or α-substituted derivatives. Crotonylbenzene in cold EtOH–NaOH yields *3-phenyl-5-methylisooxazoline* (X), m.p. 49—50° (completely degraded by CrO_3–AcOH), but in hot solution a trace of oxamino-oxime is also formed. β-Chloropropionic acid (XI) and NaOAc or KOAc in hot AcOH afford a little Ph vinyl ketone (XII) and much *β-acetoxypropionic acid*, m.p. 53—54° [hydrolysed by KOH to (XII)], which with NH_2OH and excess of hot KOH–EtOH gives *3-phenylisooxazoline*, m.p. 66—67° (degraded by CrO_3), also obtained similarly from (XI) together with *NN'-di-(β-benzoylethyl)hydroxylaminedioxime*, m.p. 154—155°. The dioxime reduces warm Fehling's solution, is sol. in acids and alkalis, and is also formed with the *iso*oxazoline in the cold; with hot HCl (1 : 1) it gives *NN'-di-(β-benzoylethyl)hydroxylamine*, m.p. 140°, which with NH_2OH in cold EtOH–NaOH gives a mixture of *iso*oxazolines, containing a substance, m.p. 58—59°, probably *5-phenylisooxazoline*. β-Chlorobutyryl chloride, b.p. 51—53°/21 mm. (from the acid, b.p. 108—110°/11 mm.), $AlCl_3$, and C_6H_6 in CS_2 give a mixture of Ph propenyl ketone and β-phenylbutyrophenone. The former ketone and HCl in AcOH give *β-chlorobutyrophenone*, m.p. 24—25°. This, when kept with NH_2OH,HCl (3 mols.) and KOH (1·5 mols.) in cold EtOH for a day, gives (I), but after 2 days some (III) is also formed; with excess of NaOH in the cold (I) and (X) are obtained. Acetylacetonedioxime is unchanged by PCl_5 in Et_2O; with $K_3Fe(CN)_6$ it gives 3 : 5-dimethyl*iso*oxazole. The configurations of the *iso*oxazolines are supported by refractometric data, only those substances having a N:CPh grouping giving a large exaltation. From the above and previously recorded data it is concluded that *iso*oxazolines are not formed by direct ring-closure of *syn*-oximes, but by way of either oxamino-oximes or disubstituted hydroxylamines, which, however, must be more reactive in the "nascent" state than after isolation. The mechanism of the formation of *iso*oxazoles is discussed. R. S. C.

Dioximes. XCIX. G. Ponzio and F. Biglietti (Gazzetta, 1933, **63**, 159—171).—Dioximes of the type $CAr(:NOH)\cdot C<^{CAr(:NOH):N}_{N\text{———}O}$ when heated with dil. NaOH, or even alone, isomerise to those of the type $CAr(:NOH)\cdot C(:NOH)\cdot C<^{CAr:N}_{N\text{—}O}$. Thus, when Ar=Ph, 3 : 4-dibenzoyl-1 : 2 : 5-oxadiazoledioxime (*Ac*$_2$, m.p. 95°, and *Bz*$_2$, m.p. 148—149°, derivatives), of which the peroxide (A., 1927, 1207) is reduced by $SnCl_2$, gives rise to the *α-dioxime* (I) of 3-benzoylformyl-4-phenyl-1 : 2 : 5-oxadiazole, m.p. 203—204° (decomp.) (*Ac*$_2$, m.p. 102—103°, and *Bz*$_2$, m.p. 119—120°, derivatives), and to the *β-dioxime* (II), m.p. 189—190° (*Ac*$_2$, m.p. 113—114°, and *Bz*$_2$, m.p. 118—119°, derivatives), isolated through its *Ni* salt, m.p. 262—263° (decomp.). (I) is partly converted into (II) when heated; with N_2O_4 or HNO_3 both give *peroxides*, m.p. 135—136° and 131—132°, respectively. With $POCl_3$ (II) yields *3 : 4'-diphenyl-5 : 3'-(1 : 2 : 4-oxadiazolyl)-1' : 2' : 5'-oxadiazole*, m.p. 100—101°. Another product of heating (I) or of reducing the peroxides of (I) or (II) is *4 : 4'-diphenyl-3 : 3'-di-1 : 2 : 5-oxadiazolyl*, m.p. 136—137°. When Ar = *p*-C_6H_4Me, the *α-dioxime*, m.p. 218—219° (decomp.), of 3-*p*-toluoylformyl-4-*p*-tolyl-1 : 2 : 5-oxadiazole is separated from the *β-dioxime*, m.p. 199—200°, through the *Ni* salt of the latter. *4 : 4'-Di-p-tolyl-3 : 3'-di-1 : 2 : 5-oxadiazolyl* has m.p. 147—148°. E. W. W.

Naphthathiazole series. I. Constitution of the bromo-additive compounds of bromo-substituted alkylamino-β-naphthathiazoles obtained in the bromination of *s*-α-naphthylalkylthiocarbamides. C. Hasan and R. F. Hunter (J. Indian Chem. Soc., 1933, **10**, 81—89).—Extensive bromination of *s*-α-naphthylmethylthiocarbamide (I) in boiling $CHCl_3$ affords *8-bromo-2-methylamino-β-naphthathiazole hydropentabromide* (II), m.p. 135° (decomp.), which easily loses Br to give the *hydrotribromide* (III), m.p. 163° (decomp.) (cf. A., 1927, 263), and is further reduced by SO_2 to *8-bromo-2-methylamino-β-naphthathiazole*, m.p. 194—195° (*Ac* derivative, m.p. 208°). 4-Bromo-α-naphthylamine in $CHCl_3$ and $CSCl_2$ in H_2O afford *4-bromo-α-naphthylthiocarbimide*, m.p. 90°, which with NH_2Me in aq. EtOH affords *s-4-bromo-α-naphthylmethylthiocarbamide*, m.p. 179°, converted into (II) when boiled with Br in $CHCl_3$ during 5 min., and by less vigorous bromination into (III) [also obtained from (I)], which is further brominated to (II). Less exhaustive bromination of (I) affords *8-bromo-2-methylamino-β-naphthathiazole hydrodibromide*, m.p. 195° (decomp.) (cf. A., 1930, 483), also obtained by keeping (III) over KOH. *s*-α-Naphthylethylthiocarbamide similarly gives rise to *8-bromo-2-ethylamino-β-naphthathiazole hydropentabromide* (IV), m.p. 93° [also obtained from *s-4-bromo-α-naphthylethylthiocarbamide* (V), m.p. 82° (prep. as above)], and a *hydrotribromide*, m.p. 204° [also obtained from (IV) and (V)], both reduced by SO_2 to *8-bromo-2-ethylamino-β-naphthathiazole*, m.p. 147° (*Ac* derivative, m.p. 172—173°). Similarly, *s*-α-naphthyl*iso*amylthiocarbamide gives rise to *8-bromo-2-isoamylamino-β-naphthathiazole hydropentabromide* (VI), m.p. 79—80° [also obtained from *s-4-bromo-α-naphthylisoamylthiocarbamide* (VII), m.p. 128°], and a *hydrotribromide*, m.p. 121° [also obtained from (VI)], reduced by SO_2 to *8-bromo-2-isoamylamino-β-naphthathiazole*, m.p. 126°. J. L. D.

Constitution of the so-called dithiourazole of Martin Freund. V. Isomerism of hydrazodithiodicarbonamides, iminothiolthiodiazoles, and di-R-iminothiodiazoles. VI. Isomerism of hydrazomonothiodicarbonamides, iminothiodiazolones, and monothiourazoles. S. L. Jannıah and P. C. Guha (J. Indian Inst. Sci., 1933, **16 A**, 11—18, 19—27).—V. Hydrazodithiodicarbon-di-

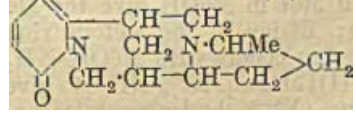
methyl-, -mono- and -di-phenyl- (I), and -*o*-tolyl- (II) -amide when boiled with 2*N*-HCl afford *isomerides*, m.p. 198°, 162° (III), 173°, and 178°, respectively (cf. A., 1931, 369). (III) is converted by HCl into iminothiolthiodiazole or *endo*iminothiolthiodiazole according to the concn. of the acid. (I) with boiling HCl (*d* 1·16) affords the alkali-sol. 5-*anilo*-4 : 5-*dihydro*-2-*thiol*-1 : 3 : 4-*thiodiazole*, m.p. 219° (cf. A., 1895, i, 400), and some PhNCS, whereas with HCl (*d* 1·19) alkali-insol. 2 : 5-dianilo-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole (IV), m.p. 249° (decomp.) [Ac_2 derivative (V), m.p. 224°], identical with that of Guha (A., 1923, i, 607), is obtained. Hydrolysis of (V) with dil. HCl affords (IV), whereas HCl (*d* 1·19) affords PhNCS and 2-*anilino*-2 : 5-endo*anilo*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m.p. 208°. (II) and boiling HCl (*d* 1·16) afford some thiocarbimide and 5-*o*-*tolylimino*-4 : 5-*dihydro*-2-*thiol*-1 : 3 : 4-*thiodiazole*, m.p. 195° (oxidised by I to a disulphide), whereas with boiling HCl (*d* 1·19) it affords 2 : 5-*di*-*o*-*tolylimino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole* (VI), m.p. 217° (decomp.) (not oxidised by I). The Ac_2 derivative of (VI), m.p. 262°, with boiling dil. HCl affords (VI), whereas with HCl (*d* 1·19) it affords 2-*o*-*tolylimino*-2 : 5-endo-*o*-*tolylimino*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m.p. 133°.

VI. Hydrazomonothiodicarbonamide (I) with boiling 2*N*-HCl affords only $NH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$,HCl (see above), but with boiling 5*N*-HCl cyclises to 2 : 5-*endo*oxy-1 : 3 : 4-triazole (II) (A., 1927, 784). Boiling HCl (*d* 1·19) with (I) affords both (II) and 2-*imino*-5-*keto*-1 : 3 : 4-*thiodiazole* (III), m.p. 177° [*Ac* derivative (IV), m.p. 295°]. (IV) is hydrolysed by boiling conc. HCl to 2-amino-2 : 5-*endo*oxy-2 : 3-dihydro-1 : 3 : 4-thiodiazole, an isomeride of (III), previously obtained by Guha (A., 1923, i, 607). Hydrazomonothiodicarbon-phenyl- (V), -methyl- (VI), and -allyl-amide (VII) are isomerised (see above) by boiling dil. HCl to *substances*, m.p. 175°, 168°, and 192°, respectively. (V) with boiling HCl (*d* 1·19) affords 2-*thiol*-2 : 5-endo*oxy*-1-*phenyl*-2 : 3-*dihydro*-1 : 3 : 4-*triazole* (VIII), m.p. 184° [*disulphide*, m.p. 196°; S-*Me ether*, m.p. 90—91°; Ac_2 derivative, hydrolysed (conc. HCl) to a product, m.p. 206°, identical with that obtained by Guha and Chakravarti (A., 1929, 582) and now assigned the structure 2-anilino-2 : 5-*endo*oxy-2 : 3-dihydro-1 : 3 : 4-thiodiazole]. Similarly, (VI) and (VII) with boiling HCl (*d* 1·19) afford 2-*thiol*-2 : 5-endo*oxy*-1-*methyl*-, m.p. 182° (*disulphide*, m.p. 265°; *Ac* derivative, m.p. 196—197°, hydrolysed by conc. HCl to 2-*methylamino*-2 : 5-endo*oxy*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m.p. 232°), and 2-*thiol*-2 : 5-endo*oxy*-1-*allyl*-2 : 3-*dihydro*-1 : 3 : 4-*triazole* (*disulphide*, m.p. 174°; *Ac* derivative, m.p. 171°, hydrolysed by boiling conc. HCl to 2-*allylamino*-2 : 5-endo*oxy*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m.p. 210—211°), respectively. J. L. D.

Alkaloids of *Heliotropium lasiocarpum*. II. Degradation of heliotridine to heliotridane. G. Menschikov (Ber., 1933, **66**, [*B*], 875—878; cf. A., 1932, 865).—The presence of 2OH in heliotridine (I) is established by the isolation of the Bz_2 derivative as *hydrochloride*, m.p. 180°; NMe is not present. (I) is mainly resinified by red P and HI at 200—210°. Cautious treatment of (I) with $SOCl_2$ causes replacement of 2OH by 2Cl and the unstable product is catalytically reduced (PtO_2) to *chloroheliotridane* (II), $C_8H_{14}NCl$, b.p. 84—85°/10 mm., $[\alpha]_D$ −133·5° [*picrate*, m.p. 242° (decomp.)], which, rapidly when heated, slowly when preserved, becomes cryst. and then contains ionisable Cl. (II) is stable to Zn and HI and to H_2 (Pd–$CaCO_3$) but is transformed by NaOEt in boiling EtOH into *heliotridine* $C_8H_{13}N$, b.p. 54—55°/12 mm., $[\alpha]_D$ −10·5°, reduced by Na and EtOH followed by H_2 (PtO_2) to *heliotridane* $C_8H_{15}N$, b.p. 169—170°, $[\alpha]_D$ −68° [*methiodide*, decomp. 240—250°; *picrate*, m.p. 236° (decomp.)]. H. W.

Alkaloids of *Salsola Richteri*. A. Orekhov and N. Proskurnina (Ber., 1933, **66**, [*B*], 841—843).—Percolation of the foliage of *S. Richteri* with EtOH containing 2% of AcOH, evaporation of the solution to dryness, and treatment of the residue with 2% HCl in C_6H_6 followed by K_2CO_3 and $CHCl_3$ leads to *salsoline* (I), $C_{11}H_{15}O_2N$, m.p. 218—211°, optically inactive (*hydrochloride* (+1·5H_2O), m.p. indef. 141—152°; Bz_2, m.p. 166—168°, and N-*Bz*, m.p. 172—174°, derivatives). (I) and MeI in MeOH yield *methylsalsoline methiodide*, m.p. 232—235° (*Bz* derivative, m.p. 249—253°). (I) is therefore $OH{\cdot}C_{10}H_{10}(NH){\cdot}OMe$. H. W.

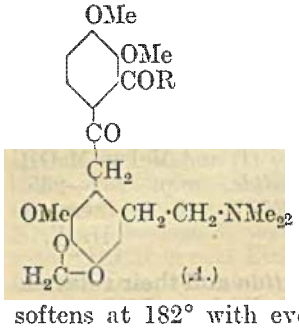
Alkaloids of *Anagyris fœtida* and their relation to the lupin alkaloids. H. R. Ing (J.C.S., 1933, 504—510).—Improved separation from the mixed alkaloids is described; anagyrine is more readily extracted by C_6H_6 from aq. solution than is cytisine, and *anagyrine perchlorate*, decomp. 270°, is less sol. in H_2O than *cytisine perchlorate*. Anagyrine, $C_{15}H_{20}ON_2$ (I), has not been obtained cryst., has $[\alpha]_D^{20}$ −165·3°, and forms a Br_2-derivative, m.p. 202—203°, which does not lose HBr with KOH. (I) is oxidised with $Ba(MnO_4)_2$ to *anagyramide*, m.p. 201—202° (cf. Litterscheid, A., 1900, i, 514, "anagyrine oxide"), which with HI and P gives *anagyramine*, m.p. 98—99° (*Ac* derivative, m.p. 134—135°; *NO*-derivative, m.p. 127—128°), and is ozonised to a *lactam*, m.p. 258° (*benzenesulphonyl* derivative, m.p. 141°). Anagyrine methiodide, m.p. 264° (decomp.), affords the methohydroxide, which is reduced (Pd–H_2) to *dihydromethylanagyrine*, b.p. 180—190°/1 mm.; two further degradations give *hexahydroanagyryline*, $C_{15}H_{23}ON$, b.p. 155—160°/4 mm., ozonised to a *lactam*, $C_{11}H_{21}ON$, b.p. 140—150°/4 mm., which is hydrolysed and subsequently oxidised by $KMnO_4$ to an *acid*, $C_{11}H_{20}O_4$, b.p. 180—200°/4 mm. This acid is converted through the anhydride into α-*methyl*-α′-n-*amylglutarimide*, m.p. 53—54°, identical with the synthetic specimen obtained from the corresponding -*glutaric acid*, b.p. 180—200°/4 mm.



(I) is derived from cytisine with the addition of a new methylpyrrolidine ring. Anagyrine hydrochloride is reduced (Pd–H_2) to *tetrahydroanagyrine*, b.p. 186—190°/1 mm., $[\alpha]_D^{20}$ −61·45°, identical with *l*-lupinane (*perchlorate*, m.p. 210°). Electrolysis of (I) in 50% aq. H_2SO_4 gives *hexahydrodeoxyanagyrine*, b.p. 130—135°/1 mm.,

$[\alpha]_D^{19}$ +10·9° (*monoperchlorate*, m.p. 169—170°), which appears to be identical with *d*-sparteine (*l-sparteine monoperchlorate*, m.p. 171—172°). Lupinane must be (I) with the N ring fully hydrogenated and sparteine is derived from it by replacing CO by CH_2. F. R. S.

Narcotine and hydrastine. Mechanism of their conversion into narceine, methylhydrasteine, and their derivatives. C. R. Addinall and R. T. Major (J. Amer. Chem. Soc., 1933, **55**, 2153—2163).—The *Me* ester *hydriodide*, m.p. 181—182°, hydrochloride, m.p. 150—151°, and *Me H sulphate*, m.p. 213—214°, of narceine (I) (*A*, R=OH) are obtained when narcotine methiodide (II), methochloride (III), and methosulphate (IV), respectively, are boiled with MeOH in dry NH_3; the *Et* ester *hydriodide*, m.p. 212—213°, and *hydrochloride*, m.p. 208—210°, the Pr^{β} ester *hydriodide*, m.p. 224—225°, and the *Bu* ester *hydriodide*, m.p. 185—186°, of (I) are similarly prepared from the requisite quaternary salt. (II) boiled with H_2O containing a little C_5H_5N gives (I), also formed by hydrolysis of (III) and (IV) with boiling H_2O. (II) and liquid NH_3 give the *hydriodide* (V), softens at 182° with evolution of gas and melts at 216—218° to a red gum, of *narceinamide* (VI) (*A*, R=NH_2); the hydrochloride of (VI) is similarly prepared from (III). Repeated crystallisation of (V) from H_2O gives *narceinimide hydriodide*, m.p. 228°, whilst boiling MeOH converts it into an *imide hydriodide* (+MeOH), m.p. 216° (decomp.). (II) heated with 28% aq. NH_3 affords (I) and (VI) (m.p. 178°); (VI) is also produced from (IV) and cold 28% aq. NH_3 and from (II) or (IV) and aq. EtOH–NH_3. The *diethylaminoethyl* ester (+MeOH), m.p. 203°, of (I) is obtained by heating (II) with an excess of $NEt_2{\cdot}C_2H_4{\cdot}OH$ and dilution with H_2O. Hydrastine methiodide (VII) boiled with H_2O gives *methylhydrasteine hydriodide*, m.p. 216—217°; with liquid NH_3, *methylhydrastamide hydriodide*, m.p. 233—235° (converted by dil. aq. NH_3 into methylhydrastimide), results. (VII) and 28% aq. NH_3 afford methylhydrastamide, which is also obtained from methylhydrastine and 28% aq. NH_3 in presence or absence of dioxan. (VII) boiled with EtOH in NH_3 gives the *Et* ester *hydriodide* (VIII), m.p. 235—236°, of methylhydrasteine. Mechanisms are advanced which explain the above changes.



(A.)

Methylnarcotine (IX) is obtained by Rabe and McMillan's procedure (A., 1911, i, 77), but could not be prepared by Tambach and Jaeger's method (A., 1906, i, 879). (IX) and MeI in MeOH give the Me ester methiodide of (I); fission of the lactone ring first occurs. Similar fission occurs with MeOH–NH_3 [to give the Me ester of (I)] and aq. 28% NH_3 [to give (VI)]. Methylhydrastine (X) is hydrolysed by aq. NaOH (not by H_2O) to methylhydrasteine (XI); with MeOH–NH_3, the *Me* ester, m.p. 175°, of (XI) results. Contrary to Schmidt (A., 1890, 1167), (X) and aq. EtOH do not give the *Et* ester, m.p. 194—195° [*chloroplatinate*, m.p. 210° (decomp.)], of (XI), which is obtained from (X) and EtOH–NH_3. The *hydriodide*, m.p. 257—258°, of (X) is unaffected by liquid NH_3 or boiling with H_2O or EtOH; EtOH–NH_3 converts it into (VIII). Narcotine heated with BzCl gives *benzoylnornarceine* (+MeOH), m.p. 174—175° (*A*, R=OH, and NMe_2=NMeBz). H. B.

Amine oxides of alkaloids. IX. Action of hydrogen peroxide on narcotimethine and hydrastimethine. Stereochemistry of hydrastine and narcotine. Max Polonovski and Michel Polonovski (Bull. Soc. chim., 1933, [iv], **53**, 268—276).—Action of H_2O_2 in $COMe_2$ on *hydrastimethine* (I) (the base from hydrastine methiodide), m.p. 157° (*hydrochloride*, m.p. 249°), gives *hydrasteimethine N-oxide* (II), m.p. 213° [*hydrochloride*, m.p. 230°], and a small amount of its *anhydro-base* (III), m.p. 186° (*hydrochloride*, m.p. 230°; *nitrate*, m.p. 235°). (III) is also formed by repeated evaporation of (II) with dil. HCl and treatment of the yellow insol. salt thus formed with dil. NaOH; on warming with NaOH it is reconverted into (II). SO_2 in $COMe_2$ or H_2O converts (II) into *hydrasteimethine O-sulphate*, m.p. 249°, but is without action on (III); similarly, (II) gives with Ac_2O at 100° *acetylnorhydrastimethine*, m.p. 200°, and an amorphous Ac_n derivative: (II) and (III) are therefore considered to be OH-acid and lactone, respectively.

Reduction of (I) with Na–Hg in dil. NaOH gives *dihydrohydrasteimethine* (IV), m.p. 174°, readily converted by acids, even by SO_2, into *dihydrohydrastimethine*, which is delactonised to (IV) by NaOH or H_2O_2 without formation of an *N*-oxide in the latter case. The difference in behaviour between (I) and narcotimethine (cf. A., 1931, 969) is attributed to geometrical isomerism about the meconic acid–*iso*-quinoline double linking. H. A. P.

Alkaloids of fumaraceous plants. IV. *Adlumia fungosa*, Greene. R. H. F. Manske (Canad. J. Res., 1933, **8**, 210—216).—A general method for the separation of the alkaloids of fumaraceous plants is described. From *A. fungosa* are isolated fumaric acid, protopine, bicuculline, *adlumidine*, $C_{19}H_{15\text{-}17}O_6N$, m.p. 235° (OMe-free), and *adlumine*, $C_{21}H_{21}O_6N$, m.p. 180° [a $(OMe)_2$-compound]. The last-named is probably not identical with the alkaloid previously described under the same name, m.p. 188° (cf. A., 1900, ii, 746; 1903, i, 512), which may be the impure isomeride of bicuculline, m.p. 198°.

H. A. P.

***Kurchi* alkaloids. I. Bases from *Holarrhena anti-dysenterica*.** A. Bertho, G. von Schuckmann, and W. Schonberger (Ber., 1933, **66**, [*B*], 786—790).—The following bases are obtained from the crude alkaloids sol. in light petroleum after removal of conessine (I) as the oxalate. (A) *Conessidine*, $C_{21}H_{32}N_2$, m.p. 123°, $[\alpha]_D^{21}$ −52·2° in $CHCl_3$, a di-acid base containing 1NMe, which very closely resembles (I) and probably imparts the feeble pharmacological activity to conessine preps.; *hydriodide*, m.p. 259° (decomp.) after becoming discoloured at 200°; *perchlorate*, $C_{21}H_{32}N_2{,}2HClO_4{,}H_2O$, m.p. 243° (decomp.). (B) *Conkurchine*, $C_{20}H_{32}N_2$,

m.p. 153°, $[\alpha]_D^{21}$ −67·4° in 96% EtOH, a very sensitive base which does not contain NMe, gives an amorphous *methiodide*, m.p. 274° after becoming discoloured at 220°, *sulphate*, m.p. 342°, *oxalate*, decomp. 325°, and *Ac* derivative, m.p. 233°. (C) *Kurchenine*, $C_{21}H_{32}O_2N_2$, $[\alpha]_D^{21}$ −92·0° in 2*N*-HCl, a di-acid base which does not contain NMe or OMe, is insol. in Et_2O, sparingly sol. in MeOH or EtOH (*sulphate*, $C_{21}H_{32}O_2N_2,H_2SO_4,EtOH$, $[\alpha]_D$ −78·3° in H_2O). Reasons are advanced for considering many of the *Kurchi* alkaloids to be non-homogeneous. H. W.

Preparation and optical rotation of pure quinidine. C. L. Butler and L. H. Cretcher (J. Amer. Pharm. Assoc., 1933, **22**, 414—415).—Pure quinidine, prepared from quinine (C_5H_{11}·OH–KOH), had m.p. 170—171°, $[\alpha]_D$ +262·0° in abs. EtOH, +323·8° in HCl. E. H. S.

Strychnine and brucine. XXIV. Synthesis of dinitrostrycholamide. P. Hill and R. Robinson (J.C.S., 1933, 486—488).—3 : 5-Dinitro-2-hydroxybenzaldehyde, m.p. 62—63° (lit., 58—60°) [*phenylhydrazone*, m.p. 228° (decomp.); *semicarbazone*, prisms, decomp. 231°, needles, decomp. 239°], condenses with hippuric acid to give 2-*phenyl*-4-(3′ : 5′-*dinitro*-2′-*hydroxybenzylidene*)*oxazolone*, m.p. 302—303° (decomp.); 3 : 5-*dinitro*-2-*methoxybenzaldehyde*, m.p. 86—87° [methylation by CH_2N_2; *phenylhydrazone*, m.p. 214° (decomp.); *semicarbazone*, m.p. 205° (decomp.)], similarly forms the -2′-*methoxyoxazolone* (I), m.p. 185·5°, and in one experiment, a *substance*, m.p. about 215° (decomp.), has been obtained. (I) is hydrolysed by aq. NaOH to 3 : 5-*dinitro*-2-*hydroxy*-α-*benzamidocinnamic acid*, m.p. 218° (decomp.), and affords with MeOH–NH_3, 5 : 7-*dinitroindole*-2-*carboxylamide*, m.p. 263° (decomp.), identical with a specimen obtained from dinitrostrychol through the acid chloride. F. R. S.

Solanidine. A. Soltys (Ber., 1933, **66**, [*B*], 762—765).—Solanine is heated with 10% HCl at 100° under conditions such that most of the solanidine hydrochloride (I), m.p. 345° (decomp.), separates on cooling, whereas *solanthrene hydrochloride* remains dissolved. Purification of (I) from 80% EtOH and subsequent decomp. with NaOH and crystallisation of the base from Et_2O yields solanidine (II), $C_{27}H_{43}ON$, m.p. 170°, $[\alpha]_D^{15}$ −27·3° in $CHCl_3$, which does not contain NMe. The *Ac* derivative, m.p. 204°, and the methiodide (III), m.p. 280° (decomp.), of (II) are described. Treatment of (III) with Ag_2O and decomp. of the base at 130° gives MeOH and (II), whereas rapid heating to 280° affords iso*solanidine* $C_{27}H_{43}ON$, m.p. 169°. Although indifferent toward $KMnO_4$, (II) is converted by energetic hydrogenation (PtO_2–AcOH) into *tetrahydrosolanidine*, $C_{27}H_{47}ON_2$, m.p. 222°, $[\alpha]_D^{17}$ +28·8° in $CHCl_3$ [*hydrochloride*; *methiodide*, m.p. 280° (decomp.)]. (II) is therefore a doubly unsaturated, *tert.*-base with a *sec.*-OH. Solanthrene (IV), $C_{25}H_{39}N$, m.p. 170°, $[\alpha]_D^{15}$ −92·3° in $CHCl_3$, gives a *methiodide*, m.p. 260° (decomp.). Hydrogenation (PtO_2) of (IV) leads to *tetrahydrosolanthrene*, m.p. 165°, $[\alpha]_D^{17}$ +30·4° in $CHCl_3$ [*methiodide*, m.p. 285° (decomp.)]. (IV) is present as a glucoside in the initial material. H. W.

Alkaloid from *Ceanothus americanus*. A. Bertho and W. S. Liang (Arch. Pharm., 1933, **271**, 273—276).—The bark of this plant contains *ceanothine*, $C_{29}H_{36}O_4N_4$, dimorphic, m.p. 227—228° and 234° (contains 1NMe, but no OMe, group; *hydriodide*, m.p. 189—190°, decomp. 250°; *methiodide*, cryst.; *perchlorate* and *chloroaurate*, amorphous), and another *alkaloid*, m.p. 240°. R. S. C.

Aromatic tropane derivatives. I. Derivatives of 8 : 9-benz-$\Delta^{8:9}$-homogranatene. B. K. Blount (J.C.S., 1933, 553—555).—Tetrahydronaphthalene-1 : 2-diol (improved prep.) is oxidised by $Pb(OAc)_4$ to β-(o-*formylphenyl*)*propaldehyde* (*dioxime*, m.p. 116°), which condenses with Ca acetonedicarboxylate and NH_2Me to give, after acidification and heating, 8 : 9-*benz*-$\Delta^{8:9}$-*homogranaten*-3-*one*, m.p. 125° [*picrate*, m.p. 204° (decomp.); *hydrobromide*, m.p. 235° (decomp.)], reduced to the *ψ-alcohol* (+H_2O), m.p. 105—110° [*Bz* derivative, m.p. 98°, and its *hydrobromide*, m.p. 257°, and *hydrochloride*, m.p. 258° (decomp.)]. Similar condensation of homophthalaldehyde gives 2-methyl*iso*quinolinium hydroxide, identified as the picrate. F. R. S.

Colorimetric determination of alkaloids. R. Seifert (Diss., Halle, 1930; Bied. Zentr., 1933, **A**, 3, 282).—Methods are based on the pptn. of alkaloids by appropriate reagents and the colorimetric determination of a suitable element or radical in the washed ppt. Suggested reagents include picric, silico- and phospho-tungstic acid for strychnine, quinine, emetine, and cinchonine; Mayer's reagent for strychnine and emetine; $H_4Fe(CN)_6$ for strychnine. A. G. P.

Arsenical azo-derivatives. VI. S. Berlingozzi (Annali Chim. Appl., 1933, **23**, 168—173; cf. A., 1931, 105).—With 6 compounds obtained by coupling diazotised *p*-aminophenylarsinic acid with various derivatives of C_6H_6, C_9H_7N, etc., the toxicity towards rats, when injected intraperitoneally, depends mainly on the nature of the coupled grouping and not on the As content (cf. Arch. Sci. Biol., 1931, **16**, 4). The 2-phenylquinoline grouping is most interesting in this connexion. 3-*Amino*-4-(4′-*carboxy*-2′-*phenylquinoline*-3′-*azo*)*phenol*-2-*azophenylarsinic acid*, prepared from *m*-aminophenol-6-azo-*p*-phenylarsinic acid and 3-diazo-2-phenylquinoline-4-carboxylic acid, and the analogous 2′-p-*anisyl* compound similarly prepared from 3-diazo-2-*p*-anisylquinoline-4-carboxylic acid, do not melt at 250°. T. H. P.

3 : 4-Dimethoxy-2-anhydrohydroxymercuribenzoic acid. New synthesis of veratric acid. V. M. Rodionov and A. M. Fedorova (Arch. Pharm., 1933, **271**, 287—292).—Hemipinic acid and $Hg(OAc)_2$ give 3 : 4-*dimethoxy*-2-*anhydrohydroxymercuribenzoic acid*, $(MeO)_2C_6H_2<^{CO}_{Hg}>O$ (*Na* salt), in 90% yield and a *substance*, m.p. 118—120°. The former with hot, conc. HCl gives a 92% yield of veratric acid [sublimes in rhombic crystals (cf. lit.)]. R. S. C.

Organomagnesium compounds containing solubilising amino-groups. H. Gilman, S. A. Harris, and C. Liu (Proc. Iowa Acad. Sci., 1931, **38**, 167—168).—Compounds containing the ·MgX group attached to C in a mol. containing a basic group

(·NR_2 or substituted C_5H_5N, C_7N_7N) are formed from corresponding RX compounds less readily than when no basic group is present, but the presence of the basic group does not affect the general properties. CH. ABS.

Rearrangement reactions of organo-sodium and -lithium compounds. H. GILMAN and F. W. BREUER (Proc. Iowa Acad. Sci., 1931, **38**, 167).

Catalytic decomposition of organo-metallic compounds. G. A. RAZUVAIEV and M. M. KOTON (Ber., 1933, **66**, [*B*], 854—858; cf. A., 1932, 409).—The catalytic effect of metals on the decomp. of organo-mercury compounds is most strongly marked with $HgPh_2$, which undergoes slight decomp. at 200°, whereas $Hg(CH_2Ph)_2$ is unstable at its m.p. With the most active catalysts, decomp. is observed at room temp. For $HgPh_2$ between 200° and 25° the activity sequence is Pd>Pt>Ag>Au>Co>Cu>Fe>Ni, whereas for $Hg(CH_2Ph)_2$ between 75° and 25° it is Pd>Pt>Ag>Au>Cu>Ni>Fe>Co. The change is $HgR_2 \longrightarrow RR+Hg$ (I). In presence of compressed H_2 the reaction $HgR_2+H_2=2RH+Hg$ (II) also occurs, the ratio of (I) and (II) depending on the catalyst. For $HgPh_2$ and $Hg(CH_2Ph)_2$ the sequences of decreasing activity calc. on decomposed material are respectively: Pd>Pt>Ni>Ag>Au>Co>Cu>Fe and Pd>Pt>Ni>Au>Ag>Fe>Co>Cu. $PbPh_4$ and $SnPh_4$ behave analogously to $HgPh_2$. In presence of a large amount of Ni, $PbPh_4$ smoothly affords Ni and C_6H_6 (cf. Zartman *et al.*, A., 1932, 1050). H. W.

Racemic and active *cyclo*tetramethylenediselenidedicarboxylic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 15, 6 pp.).—*dl*-αα′-Di(selenocyano)adipic acid (from the *dl*-Br_2-acid and KSeCN) is converted by aq. H_2SO_4 into dl-*cyclotetramethylene*-1 : 2-*diselenide*-3 : 6-*dicarboxylic acid*, decomp. about 200° [*strychnine* salt ($+5H_2O$)], which is resolved by quinine into the (−)-form, decomp. about 200°, $[\alpha]_D$ −351° in dil. Na_2CO_3 [*quinine* salt ($+2H_2O$)], and then by strychnine into the (+)-*form*, $[\alpha]_D^{25}$ +351° in dil. Na_2CO_3, +178·5° in EtOH, −244° in 0·2*N*-HCl [*strychnine H* salt ($+2·5H_2O$)]. H. B.

Dilatometric investigation of the hydrolysis of proteins and their degradation products. I. Hydrolysis of dipeptides. P. RONA and H. FISCHGOLD (Biochem. Z., 1933, **261**, 66—75).—The change (I) in vol. which occurs during the hydrolysis of dil. (0·75%) solutions of dipeptides [glycylglycine (II), glycylalanine (III), alanylglycine (IV)], with dil. alkali (1·5*N*-NaOH) at 37° is about +9 c.c. per 0·001 mol., the reaction being unimol. When conc. HCl is used at 50° (I) is about −2·5 c.c. for (II) but cannot be determined for (III) and (IV) because the process is too slow. The difference in the type of ionisation in alkaline and acid solution is responsible for the different (I). The dilatometric method, which can also be used for kinetic determinations, gives here 10 times the accuracy of that obtained from determining N by Van Slyke's method. W. McC.

Relation between the chemical and colloidal structure of proteins. A. FODOR (Kolloid-Z., 1933, **63**, 203—214; cf. A., 1932, 529).—A general discussion of the structure of gelatin and casein, based on results obtained by the author's method of non-hydrolytic degradation by heating with anhyd. glycerol or *m*-$C_6H_4(OH)_2$, which are considered to cause the tautomeric change ·C(OH)·N·⟶·CO·NH·, thus breaking down the lateral linking between adjacent polypeptide mols. F. L. U.

Physico-chemical properties of proteins separated from serum by the acetone method. A. BOUTARIC (Protoplasma, 1933, **18**, 286—298).—The viscosity and optical properties of proteins and their influence on the flocculation of $Fe(OH)_3$ are discussed. Separation of proteins at low temp. by the $COMe_2$ method does not involve the disturbance of mol. structure. A. G. P.

Action of ultra-violet rays on aqueous solutions of gelatin. Modification of physico-chemical properties. Probable photolysis. P. PONTHUS (Compt. rend., 1933, **196**, 1248—1250).—On irradiation (total ultra-violet) of 0·25—0·75% aq. solutions of gelatin (⩾ 2 hr.) coagulation does not occur, n does not vary, electrical conductivity increases, and optical density (δ) and relative viscosity (η/η_0) decrease, whilst the ratio $\omega(=\eta/\eta_0-1)/\delta$ does not vary significantly. The results are explained by dehydration of gelatin particles, and the possibility of its photolysis is also suggested. A. C.

Adenylic acid and adenine nucleotide. J. K. PARNAS and R. KLIMEK (Z. physiol. Chem., 1933, **217**, 75—78).—The dissolution of $Cu(OH)_2$ by feebly alkaline solutions of adenylic and inosic acids and adenosine and its non-dissolution by adenine nucleotide and the guanylic acids is confirmed. Steudel's differing results (cf. this vol., 612) may be due to his having used too much NaOH. J. H. B.

Action of resorcinol on silk fibroin. I. R. O. HERZOG and J. WEINDLING. **II.** A. DOBRY-KURBATOV (Z. physiol. Chem., 1933, **216**, 248—250; 251—254).—I. Treatment of silk fibroin with resorcinol (I) at 120° for periods up to 6 hr. does not appreciably affect the N distribution on hydrolysis. The action of HCl at 0° slowly liberates more NH_2-N from the (I)-treated than from the untreated material.

II. Longer treatment with (I) at a higher temp. induces chemical combination, a greater proportion of the fibroin becoming sol. in *m*-cresol. The viscosity of the product decreases as the fusion time increases. J. H. B.

Physico-chemical studies on proteins. VII. Peptisation of gliadin by solutions of inorganic salts. W. SINCLAIR and R. A. GORTNER (Cereal Chem., 1933, **10**, 171—188).—Pure gliadin (I) prepared by Osborne's "70% EtOH method" and by Blish and Sandstedt's AcOH method (B., 1933, 894) was peptised with equi-ionic solutions of KI, KBr, and KCl. A lyotropic series was observed (Cl<Br<I). The non-peptisable residue from repeated extractions with *M*-KI, when purified by repeated pptn. from EtOH, could then be further peptised by KI solution. Similarly the "KI-sol." fraction, when re-worked, furnished a "KI-insol." residue. The of the fractions was practically unchanged. The treatment of (I) with these neutral salt solutions does not produce any "true hydrolysis," for no significant

change occurred in free NH_2-N, and in free CO_2H. The Hausmann N distribution vals. (NH_3-N, humin-N, basic N, and non-basic N) were practically the same as for untreated gliadin. The amount of (I) peptised by a particular salt solution depends both on the concn. of the solution and the amount of (I) present. (I) cannot be separated into chemically dissimilar fractions by differential dissolution in salt solutions and, therefore, from the viewpoint of org. chemistry, is probably a homogeneous protein, but the granules of the dry protein or the larger aggregates of the hydrated protein are not physically homogeneous. E. A. F.

Use of the orcinol reaction for determination of the kind and amount of carbohydrate in proteins. M. SØRENSEN and G. HAUGAARD (Biochem. Z., 1933, **260**, 247—277).—In the usual determination the step photometer replaces the colorimeter, and the effects on the course of the reaction of variation of temp., orcinol and H_2SO_4 concns., and time of warming with H_2SO_4 are determined. The form and position of the extinction–time curves enable glucose, mannose, galactose, fructose, sorbose, arabinose, xylose, and rhamnose to be differentiated. The reactions of raffinose, lactose, glycogen, and inulin with orcinol–H_2SO_4 are shown to be additive processes and the glucose contents of amygdalin and salicin are determined. Finally the kind and amount of carbohydrate in various proteins are determined. Ovalbumin before crystallisation often contains 1·7% of mannose, serum albumin after several crystallisations and horse-serum globulin after several pptns. contain 0·47 and 1·82%, respectively, of a carbohydrate containing mannose and galactose, purified caseinogen and lactalbumin contain 0·31 and 0·44%, respectively, of galactose but no lactose, and wheat gliadin 0·20% of mannose. P. W. C.

Union of biocolloids. XVII. Combination of proteins, polysaccharides, and nucleic acids. S. J. PRYZLECKI and M. D. GRYNBERG (Biochem. Z., 1933, **260**, 395—402).—In systems nucleic acid (I) +polysaccharide (II) no affinity exists at higher p_H and it seems improbable that union between glycogen and (I) occurs in the animal body. When a multivalent cation, protein, is present in addition to the negatively charged biocolloid (I+II) as anion, combination occurs, but only with small concns. of (I) and at a definite p_H. The existence of a four-component system at 7·3 is also detected using the system (I)+basic protein+neutral protein+(II). P. W. C.

Rontgenographic investigation of proteins. I. Behaviour of silk against acids and bases. C. TROGUS and K. HESS (Biochem. Z., 1933, **260**, 376—394).—A no. of *X*-ray fibre diagrams of various kinds of silk are given and show that the different types of silk are composed of at least two crystal forms. Silk fibres show considerable resemblance to cellulose fibres in their behaviour with reagents. P. W. C.

Semi-micro-determination of carbon and hydrogen according to the method of Orthner and Reichel. G. KOMPPA and W. ROHRMANN (Chem. Fabr., 1933, **6**, 201—202).—A form of apparatus is described. H. F. G.

Loading combustion tube in carbon and hydrogen determination on liquids. J. R. BAILEY (Ind. Eng. Chem. [Anal.], 1933, **5**, 171).—The apparatus allows the drops of liquid to fall on to the layer of CuO without impinging on the sides of the combustion tube, thus ensuring complete combustion. E. S. H.

Nickel tubes in organic combustions. F. E. RAY (Ind. Eng. Chem. [Anal.], 1933, **5**, 220).—Tubes of Ni are recommended. E. S. H.

Micro-analytical methods. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1933, **16**, 255—260).—The advantages of micro-analytical methods are discussed and semi-micro-methods are described for the determination of C, H, N, halogens, and OMe. T. McL.

Determination of nuclear halogens in organic compounds. Critical study and standardisation of the Stepanov method. W. A. COOK and K. H. COOK (Ind. Eng. Chem. [Anal.], 1933, **5**, 186—188).—Certain details of procedure are standardised. The method is not suitable for volatile substances. With cryst. substances, sparingly sol. in EtOH, the state of subdivision affects the result. E. S. H.

Detection of mercury in organic compounds. I. STONE (Ind. Eng. Chem. [Anal.], 1933, **5**, 220).—A glass rod, coated with CuI, is introduced into a test-tube containing a heated mixture of the org. compound and Na_2CO_3. In presence of Hg the CuI turns pink. 0·02 mg. of Hg can be detected. As and Sb do not interfere. The interference due to N can be overcome by placing a layer of $K_2S_2O_7$ over the alkaline mixture to absorb the NH_3 produced. Similarly, a layer of PbO obviates the interference due to S. E. S. H.

Identification and determination of methyl alcohol in the presence of ethyl alcohol. A. IONESCU-MATIU and C. POPESCO (Ann. Sci. Univ. Jassy, 1933, **17**, 205—215).—MeOH in alcoholic liquors can be identified by distillation with acid and alkali, and application of known tests to the distillate. Determination of small amounts can be effected only approx.. best by colorimetric examination of the oxidation products. R. S. C.

Formation of thiocyanates from cyanides [and analytical applications]. A. CASTIGLIONI (Gazzetta, 1933, **63**, 171—175).—KCN reacts at once with S in $COMe_2$, MeOH, EtOH, or amyl alcohol to form KSCN. This may be used to detect and determine free S, and to detect CN′, *e.g.*, that formed in a test for org. N. E. W. W.

Carbon tetrachloride : pyrolysis and analytical procedure. KOHN-ABREST (Ann. Chim. Analyt., 1933, [ii], **15**, 199—207).—CCl_4 passed with air through a quartz tube at 1000° decomposes (*a*) $CCl_4+0{\cdot}5O_2=COCl_2+2Cl_2$; (*b*) $CCl_4+2H_2O=CO_2+4HCl$. Absorption of the HCl in H_2O, Cl_2 in KI permits of the determination of the CCl_4. For toxicological investigation, air is aspirated over the organs under examination and the HCl produced by pyrolysis absorbed in $AgNO_3$. J. S. A.

Micro-determination of citric acid by Thunberg's methylene-blue method. A. C. KUYPER (Proc. Iowa Acad. Sci., 1931, **38**, 172).—Use of the

sp. property of citric acid to accelerate the decolorisation of methylene-blue (I) by an enzyme present in cucumber seed is trustworthy only when the enzyme extracts are prepared in the same way and used at the same age. Na, Ca, and hexose diphosphate do not interfere unless present in concns. > those in blood. $H_2C_2O_4$ interferes. The sensitivity is proportional to the amount of (I) present. CH. ABS.

Kogan's method for determining citric acid. E. EMILIANI (Annali Chim. Appl., 1933, **23**, 188—192).—With slight modification, Kogan's method (A., 1930, 743) gives satisfactory results (cf. Romani, A., 1932, 144). T. H. P.

Micro-determination of lactose by method of Hagedorn and Jensen. C. FROMAGEOT and M. MOULIN (Bull. Soc. chim., 1933, [iv], **53**, 266—267).—Vals. are given for the vol. of 0·005*N*-$K_3Fe(CN)_6$ reduced per mg. lactose from 0 to 0·509 mg. The vol. is proportional to the lactose present up to 0·4 mg. H. A. P.

Microanalytical detection and determination of fructose in presence of aldoses and sucrose. F. FISCHL (Chem.-Ztg., 1933, **57**, 393—394).—A solution of $CuSO_4$, Na K tartrate, Na_2CO_3, and Na_2HPO_4 is reduced by fructose but not by aldoses or sucrose; the resulting solution may be titrated iodometrically. F. R. S.

Colour reaction and micro-determination of *d*-fructose. K. YAMADA.—See this vol., 737.

Night-blue as an indicator for use in volumetric titrations with silicotungstic acid. H. L. FEINSTEIN and E. O. NORTH (J. Amer. Pharm. Assoc., 1933, **22**, 415—419).—1·5 mg. of dye per c.c. of 7—8 *N*-H_2SO_4 is used as external indicator. The method described is applicable to the analysis of other amines which form insol. ppts. with silicotungstic acid. E. H. S.

Colour tests for salicylic acid and its derivatives. A. ZAGORSKIKH (Khim. Farm. Prom., 1932, **10**, 377).—$(NH_4)_2MoO_4$ (1 g.) in H_2SO_4 (100 c.c.) gives with acetylsalicylic acid a blue colour changing to violet, and with salol and salicylic acid a violet colour changing to olive-green. CH. ABS.

Detection of saccharin and the composition of complexes with copper and pyridine. J. J. L. ZWIKKER (Pharm. Weekblad., 1933, **70**, 551—559).—Pptn. of saccharin (I) with $CuSO_4$–C_5H_5N gives three characteristic types of crystal depending on the concn. of (I). In dil. solution needles are formed of the *compound*, $[Cu(C_5H_5N)_2(H_2O)_2],2(C_7H_5O_3NS)$, converted into the *compound*, $[Cu\,2(C_7H_5O_3NS),C_5H_5N,H_2O]$, at 150°. More conc. solutions afford quadratic crystals and hexagonal prisms of *compound* (II), $(C_7H_5O_3NS)_6[Cu(C_7H_5O_3NS),(C_5H_5N)_2]_6,11H_2O$, converted into the *compound* $(C_7H_5O_3NS)_6[Cu(C_7H_5O_3NS),C_5H_5N]_6,4H_2O$, at 150°. The lattice structure of (II) is discussed. S. C.

Determination of small quantities of benzyl alcohol. J. CALLAWAY and S. REZNEK (J. Assoc. Off. Agric. Chem., 1933, **16**, 285—289).—Tables are given showing the sp. gr. and η of aq. solutions containing up to 3% of $CH_2Ph{\cdot}OH$ (I). The (I) is distilled with H_2O so that the distillate contains > 1·5% of alcohol and its sp. gr. and η are determined. If necessary, owing to the presence of other volatile substances, the (I) may be oxidised to BzOH by $KMnO_4$, extracted, and titrated. T. McL.

Micro-test for triarylcarbinols. A. A. MORTON and L. V. PEAKES, jun. (Ind. Eng. Chem. [Anal.], 1933, **5**, 185).—The carbinol is converted into the chloride and then into the free radical by treating with AcCl and dry, powdered Ag in a capillary. After centrifuging the Ag a coloured liquid layer is observed, due to the free radical. As O_2 diffuses slowly into the open capillary the liquid becomes decolorised. E. S. H.

Indirect enol titration. T. FJADER (Suomen Kem., 1933, **6**, 61—62).—The different behaviour of various bromoketones titrated by the Kurt Meyer method in presence of (*a*) HBr+β-$C_{10}H_7{\cdot}OH$ (I), (*b*) HBr, (*c*) (I), and (*d*) H_2O, HBr, + (I), indicates that the reaction is complex. Thus with bromomethylmenthone the $Na_2S_2O_3$ titre falls rapidly in (*a*) and much more slowly in (*c*), (*b*), and (*d*) (in this order). J. W. B.

Azo-derivatives of hydroxyquinoline in inorganic analysis. II, III. G. GUTZEIT and R. MONNIER (Helv. Chim. Acta, 1933, **16**, 478—485, 485—486; cf. this vol., 479).—II. 4′-Sulpho-*o*-tolyl-, *o*-carboxyphenyl-, and *p*-tolyl-azo-5:8-hydroxyquinoline give characteristic ppts. or colorations with $Hg^{\cdot\cdot}$, $Pd^{\cdot\cdot}$, and Mo (as $MoOCl_5''$), respectively. The reactions are sp. under conditions which are described. The corresponding Ph derivative is a sp. reagent for $Hg^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, and $Pd^{\cdot\cdot}$. Limits of sensitivity are given.

III. A table showing the reactions of sixteen azo-derivatives of 8-hydroxyquinoline is given. Substitution of different radicals in the quinoline nucleus weakens or enhances the reactions with certain ions, but does not lead to new reactions. F. L. U.

Quinoline and lignin. A. CASTIGLIONI (Atti R. Accad. Lincei, 1933, [vi], **17**, 469—473).—Lignin gives no coloration with *iso*quinoline, carbostyril, or acridine in acid solution, but, contrary to Grandmougin's statement (Z. Farbenind., 1906, **5**, 321), gives an intense wine-red colour with either 1% solution of quinoline in EtOH followed by conc. HCl or 10% aq. quinoline hydrochloride or sulphate solution. 4-Methylquinoline gives a faint colour and the reagent used by Ihl (B., 1891, 165) probably contained quinoline. T. H. P.

Analytical notes. II. L. ROSENTHALER (Pharm. Zentr., 1933, **74**, 288—290; cf. this vol., 41).—(1) A 10% "Pantosept" solution dissolves As stains immediately but Sb stains only after several hr. Differences between the dissolution velocities, when using NH_2Cl, are small. (2) Ac can be detected as amyl acetate instead of EtOAc by esterification with amyl alcohol and *p*-toluenesulphonic acid. Sensitivity of the test is reduced by the characteristic odour of amyl alcohol. (3) Use of $CaCO_3$ in place of alkali hydroxides and aq. NH_3 for neutralisation of acids is recommended. (4) The transient green colour given by 8-hydroxyquinoline, $CHCl_3$, and NaOH can be used to detect $CHCl_3$ and hydroxyquinolines, but is not given by chloroiodohydroxyquinoline ("Vio-

form "). (5) Piperazine gives with aq. benzoquinone (I) a brownish-violet colour, and with alcoholic (I) a wine-red colour. Both solutions later become turbid. (6) $CCl_3{\cdot}CO_2H$ solution, neutralised with $CaCO_3$, gives characteristic crystals with (*a*) solid Tl acetate, (*b*) $HgNO_3$, (*c*) solid $AgNO_3$, (*d*) $UO_2(OAc)_2$. (7) Cyanides heated with NaOH and colloidal S are converted into thiocyanates. (8) Descriptions with photographs are given of crystals deposited on treating (i) *p*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$ with (*a*) KOH, (*b*) *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$, (*c*) conc. HNO_3; (ii) caffeine, theobromine, and theophylline with (*a*) Zwikker's reagent (4 c.c. of 10% $CuSO_4$ solution, 1 c.c. of C_5H_5N, 5 c.c. of H_2O), (*b*) $CdSO_4$–C_5H_5N solution; (iii) saccharin with Tl acetate. (9) Colour reactions given by apiol are: (*a*) violet, with NH_2Cl in glacial AcOH, (*b*) dirty red on heating with conc. HBr, (*c*) from yellow to reddish-brown to dark brown with BzCl and $ZnCl_2$. (10) Aldehydes accelerate the reaction between CS_2 and alkali plumbites.

V. P. P.

Determination of labile sulphur in gelatin. N. V. KIRILENKO (J. Appl. Chem., Russia, 1932, **5**, 1119—1126).—Sheppard and Hudson's method is subject to an error of 14%; the colorimetric standard should be replaced by methylene-blue. CH. ABS.

Biochemistry.

Mechanism of the action of pyocyanine on respiration. K. G. STERN (Naturwiss., 1933, **21**, 350—351).—Addition of neutral 0·0005*M*-pyocyanine (I) to dil. aq. oxyhæmoglobin gives rise to absorption bands characteristic of methæmoglobin (II) which are shifted 20 mμ towards the blue by addition of NaF or of H_2PO_4' at p_H 6. With intact erythrocytes, formation of (II) occurs very slowly; hæmolysis with piperazine accelerates the reaction, the fall in O_2 consumption indicating a 50% conversion in 45 min. at 39°. F. O. H.

Specificity of hæmoglobins, including embryonic hæmoglobin. H. TROUGHT (Arch. Dis. Childhood, 1932, **7**, 259—262).—The rate of decomp. of hæmoglobin by 0·25*N*-NaOH depends on the source. CH. ABS.

Analysis. III. Detection of blood with 2 : 7-diaminofluorene hydrochloride. L. ROSENTHALER (Pharm. Zentr., 1933, **74**, 333—334).—Other oxidising agents and oxidases react with the reagent (cf. A., 1932, 242) to produce a blue colour (or other colour or ppt. in higher concns.). The presence of blood is confirmed if the blue colour is present in a $CHCl_3$ extract after acidification with AcOH. E. H. S.

Conductivity method for the determination of the cell-volume of blood. A. SLAWINSKI (Biochem. J., 1933, **27**, 356—360).—Formulæ are given whereby the cell-vol. of blood may be calc. from the ratio of the conductivities of blood after complete settling in two tubes, one horizontal and the other (I) vertical, together with a reading of the height of the settled cells in (I). The method is accurate to 0·1%. W. O. K.

Effect of ingestion of pure water and mineral diuretic water on blood-serum-protein. C. AUGUSTE (Ann. Med., 1933, **33**, 25—60).—Ingestion of H_2O or of a mineral diuretic causes a marked oscillation in the "coeff. of hydræmia" (ratio of increase in plasma vol. to the initial vol.). NUTR. ABS.

Determination of blood-urea-nitrogen by direct nesslerisation. W. F. TAYLOR and W. M. BLAIR (J. Lab. Clin. Med., 1932, **17**, 1256—1263).—The blood is allowed to react with a very conc. urease prep. which is pptd. with the proteins by Na_2WO_4 and H_2SO_4. The filtrate may be nesslerised directly. CH. ABS.

Cystine content of human serum-proteins. L. R. TRICHMAN and M. REINER (J. Biol. Chem., 1933, **100**, 775—778).—The total cystine content of human sera averaged 4·82%, 3·64% being in globulin and 6·07% in albumin. Variations such as have been observed by other workers in the cystine content of œdematous sera were not apparent. A. L.

Tyrosine and cystine content of serum-proteins. M. REINER and H. SOBOTKA (J. Biol. Chem., 1933, **100**, 779—781).—Results of determinations of the tyrosine (I) and cystine (II) factors for the serum-albumin and -globulin of various animals are in agreement with those made by Wu and Ling (A., 1929, 88) except in the case of the pig. The (I) and (II) contents of several fractions of typhoid-immunised horse serum are also determined, the immuno-active factor being richer than the others in (I). The (I) content of horse serum-proteins rises on acid hydrolysis. A. L.

Micro-photometric method for determination of free cholesterol and cholesterol esters in blood-plasma. E. OBERMER and R. MILTON (Biochem. J., 1933, **27**, 345—350).—Cholesterol digitonide derived from the EtOH–Et_2O extract of 1 c.c. of plasma (or its hydrolysate) is treated with *o*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ and $ZnCl_2$ in AcOH at 100° and the colour is measured. The accuracy is comparable with that of a macro-gravimetric method. R. K. C.

Effect of diet on the plasma-phosphatase of sheep. D. W. AUCHINACHIE and A. R. G. EMSLIE (Biochem. J., 1933, **27**, 351—355).—The plasma-phosphatase (I) of sheep, on a diet poor in Ca but rich in P, rose before any detectable fall in serum-Ca or deterioration of clinical condition. With a more adequate diet the rise in serum-Ca precedes the return to normal of (I). Cod-liver oil is more effective than Ca salts in preventing the rise in (I). W. O. K.

Phosphatases and glycolysis in blood. A. ROCHE and J. ROCHE (Bull. Soc. Chim. biol., 1933, **15**, 520—530).—In hæmolysates of red blood-corpuscles to which glucose monophosphate (I) and fructose mono- (II) and di-phosphate (III) have been

added, hydrolysis and glycolysis go on simultaneously. The liberated sugar in the case of (I) has the same reducing power as glucose, but with (II) and (III) a mixture of aldose and ketose is obtained. A. L.

Sugar content of the blood of ruminants. F. W. KRZYWANEK and H. BRÜGGEMANN (Biochem. Z., 1933, **261**, 170—175; cf. Pflüger's Archiv, 1929, **222**, 89).—In sheep, administration (oral or direct into stomach) of glucose has little effect on the sugar content of the blood. Probably most of the sugar is not resorbed as such, but fermented. W. McC.

Influence of proteins, amino-acids and their derivatives on the regulation of blood-sugar. II. E. G. SCHENCK (Arch. exp. Path. Pharm., 1933, **170**, 546—550).—Pure glycine administered orally to rabbits or to healthy and diabetic man has a hypoglycæmic action (cf. A., 1932, 1054; Paasch, A., 1928, 1151). W. O. K.

Blood-sugar regulation by reflexes from the sinus caroticus. P. THELEN (Z. ges. exp. Med., 1933, **86**, 231—243). NUTR. ABS.

Hormonal regulation of blood-sugar. F. HÖGLER and F. ZELL (Z. ges. exp. Med., 1933, **86**, 144—157).—Parathormone by itself or with ergotamine (sympathetic paralysis) or atropine (vagus paralysis) had no effect on blood-sugar (I) in rabbits. In some instances it weakened, in others it strengthened, insulin action. It increased the hyperglycæmic action of adrenaline and decreased or prevented that of $MgSO_4$. It had no effect on the rise of (I) following pyramidone or the ingestion of glucose or fructose. NUTR. ABS.

Lactic acid, sugar, and inorganic phosphorus of the blood of ruminants. W. M. ALLCROFT and R. STRAND (Biochem. J., 1933, **27**, 512—522).—Fasting for 7 days did not change the lactic acid (I) or the sugar content (II) of the blood of sheep; the initial increase of blood-P (inorg.) (III) was followed by a fall. Ingestion of a carbohydrate-rich meal did not change (I) and (II) appreciably; (III) after rising slightly tended to decrease slowly. Vigorous exercise produced corresponding increases in (I) and (II) proportional to length of period; (III) rose quickly, fell, and then rose again sharply to normal. Moderate exercise left (I) unchanged, (II) and (III) rising slightly. Nervous excitement caused a significant increase in (I) and (II) depending on the degree of excitation, that of (I) being greater and the increase in (III) being similar to that of (I). A. L.

Determination of calcium in blood-serum and cerebrospinal fluid. A. H. TINGEY (Biochem. J., 1933, **27**, 332—337).—Adsorbed org. matter and incomplete pptn. vitiate Ca determinations by $KMnO_4$ or acidimetric methods in non-deproteinised serum or cerebrospinal fluid. The method of Halverson and Bergeim (A., 1918, i, 50) as modified by Peters and Van Slyke ("Quantitative Clinical Chemistry," 1932, **1**, 767) including the Halverson and Bergeim washing with removal of the mother-liquors by suction, as modified by Van Slyke and Sendroy (A., 1929, 1476), is recommended and is successful with fatty and opaque sera. R. K. C.

Chemical action of sodium citrate as a cause of certain transfusion reactions. A. S. MINOT, K. DODD, and R. BRYAN (Amer. J. Dis. Children, 1933, **45**, 32—40).—Transfusions of blood containing 0·5% Na citrate into dogs following reduction of blood-Ca are followed by indications of acute lack of Ca; the symptoms are relieved by injection of Ca salts. CH. ABS.

Determination of chloride in blood. J. H. NORRIS and G. AMPT (Biochem. J., 1933, **27**, 321—325).—Fusion with NaOH is recommended for decomp. of org. matter in determination of Cl. The regular loss of Cl reported by others with HNO_3 decomp. was not found, but the Van Slyke method sometimes gives low vals. R. K. C.

Chlorine, total and residual nitrogen of the blood of the chick embryo. K. YAMADA (Japan. J. Med. Sci., Biochem., 1933, **2**, 81—83).—The Cl content of the blood rises during incubation; the reducing substances (as glucose) also increase. The total and residual N are less affected during the latter part of incubation, but a slight rise (7 mg. per 100 c.c.) occurs. P. G. M.

Alkaline reserve of the blood of fishes. FONTAINE and BOUCHER-FIRLY (Compt. rend., 1933, **196**, 1439—1441).—For sea fish, the alkaline reserve (I) (expressed by the no. of c.c. of CO_2 at 0° and 750 mm. liberated from 100 c.c. of plasma) of the blood of Teleosteans is always higher than for Selachians. Fresh-water Teleosteans have a much higher (I), whilst potamic fishes possess intermediate vals. H. B.

Mineral composition of circulating fluids in marine animals. K. BIALASZEWICZ (Arch. int. Physiol., 1933, **36**, 41—53).—The mineral elements in the circulating fluids of marine invertebrates (I) and fish differ considerably from one another and from sea-H_2O (II). The differences from (II) for (I) are most marked in the case of Mg and S. The greatest deficiency in Mg is shown in certain annelids and Crustacea, although Mg is always less conc. in (I) than in (II). The Mg : S ratio is const., showing that it is the $MgSO_4$ which varies in the body-fluids. The Ca : Cl ratio is also fairly const. and the actual vals. are close to those in (II). K was only a little more conc. in most of the (I) than in (II). In the serum of selachian and teleostean fish the K : Cl ratio is considerably > in sea-H_2O and the Mg very much lower. NUTR. ABS.

Comparative value of chlorobenzene and thymol when used with fluoride as preservatives of blood for chemical analysis. R. C. LEWIS and G. E. MILLS (Amer. J. Clin. Path., 1928, **3**, 17—28).—PhCl and KF are more efficacious than thymol and KF. CH. ABS.

Effect of tannin on hæmolysis, agglutination, and the action of toxins. A. KLOPSTOCK and E. NETER (Biochem. Z., 1933, **261**, 207—225).—Tannin (I), *in vitro* [(I) mixed with virus before adding to blood or added after mixing blood and virus] or injected with or before (even in another part of the body) cobra virus, rapidly and reversibly (reversal by dilution) inhibits the hæmolysis even when activation

by lecithin has preceded and hence acts as a certain prophylactic (for mice, at least). (I) also inhibits the action of ricin as well as those of saponin, Na oleate and Na glycocholate, and cobra virus–lecithin compound and prevents the agglutination of blood-corpuscles by anti-sera. The results support the view that the action of (I), although non-sp., resembles the second phase of action of anti-bodies and confirm the views of Sachs and Behrens (A., 1932, 1054). W. McC.

Purification of antitoxic sera in order to avoid serum shock. E. Savino (Rev. soc. argentina biol., 1932, **7**, 108).—Separation of the globulins with Na_2SO_4 is followed by dialysis and pptn. at the isoelectric point The prep. then contains only pseudo- and eu-globulins. Ch. Abs.

Serological studies on iodinated sera. I. Precipitins and precipitinogens. II. Anaphylaxis. J. Jacobs (J. Immunol., 1932, **23**, 361—374, 375—384).—I. When I is added to animal sera in the absence of acid or alkali, substances are formed which give ppts. with antisera prepared from iodinated sera. Di-iodotyrosine (I), but not KI, inhibits pptn. specifically in systems of iodinated sera (II).

II. (I), but not I′, inhibited anaphylaxis in animals sensitised to (II). Ch. Abs.

Quantitative study of the precipitin reaction with special reference to crystalline ovalbumin and its anti-body. J. T. Culbertson (J. Immunol., 1932, **23**, 439—453).—Cryst. ovalbumin affords a single type of anti-body. The amount of precipitable antibody in unit vol. of rabbit anti-cryst.-ovalbumin serum can be determined by finding the amount of antigen necessary to neutralise the precipitin of a small vol. of the antiserum. At the neutralisation point antigen and antibody combine in const. ratio with max. pptn. Corresponding quant. relations are not found in the titration of anti-sera to horse serum. Ch. Abs.

Antigenic property of gelatin-diazoarsanilic acid. S. B. Hooker, W. C. Boyd, O. E. Alley, and M. A. Derow (J. Immunol., 1933, **24**, 141—147).—Antigenicity may be conferred on gelatin (I) by coupling it with an unsaturated cyclic compound. Non-antigenicity of (I) is not necessarily due to its deficiency in aromatic NH_2-acids. Ch. Abs.

Hypothetical mechanism of anti-body production. S. Mudd (J. Immunol., 1932, **23**, 423—427).—Anti-bodies (I) are probably synthesised from less complex units, *e.g.*, peptides and NH_2-acids. Synthesis of (I) probably occurs at the antigen (II) surface. Specificity of (I) is attributed to sp. stereochemical correspondence with the (II). Dissociation of (I) and (II) is then governed by equilibrium conditions, the (II) being left free to incite further production of (I). Ch. Abs.

Quantitative aspect of the hypothetical incorporation of injected antigen in resulting anti-body. S. B. Hooker and W. C. Boyd (J. Immunol., 1932, **23**, 465—479).—Buchner's hypothesis requires the presence of 2·5—2500 times as much As in immune serum, prepared by injection of an arsenical diazo-protein, as is found chemically. Ch. Abs.

Union of serum-colloids. II. Binding of bile pigment, lipochrome, cholesterol, lecithin, and the anti-bodies of syphilis. W. M. Bendien and I. Snapper (Biochem. Z., 1933, **261**, 1—14; cf. this vol., 623).—Experiments with the membranes previously described show that bilirubin is not ultra-filterable. In sera from jaundiced patients it is very probably quantitatively combined with the albumin (I). The lipochrome of serum is neither combined with (I) nor distributed in combination over the whole globulin fraction (II), and the same holds for the cholesterol and lecithin, which are possibly partly combined with the euglobulin (III). In sera from syphilitics the anti-bodies are not united to (I) or (II), but may be to part of (III). W. McC.

Distribution of chlorine in the developing hen's egg. K. Yamada (Japan. J. Med. Sci., Biochem., 1933, **2**, 71—79).—The Cl content of the fresh egg (White Leghorn) is approx. 170 mg. per 100 g.; 3/5 of the total is in the white. During the first half of incubation Cl migrates into the yolk from the white, a process which runs parallel to the *k* of the white and regulates the osmotic pressure for the developing embryo. P. G. M.

Inorganic constituents of nerve tissue. K. Hayasi (Japan. J. Med. Sci., Biochem., 1933, **2**, 1—5).—The spinal cord of the whale is richer in inorg. P than any other nerve tissue examined and has a higher ash content, but only traces of S are present. The lingual nerve is the richest in Na and Cl, and the brain in K. All nerve tissue in the whale is richer in Na and Cl than that of land mammals. P. G. M.

Cation and chlorine content of rabbit's brain. M. Matsumoto (Japan. J. Med. Sci., Biochem., 1933, **2**, 11—20).—Grey matter contains Ca 7·7, Mg 14·6, K 351·7, Na 131·9, and Cl 181·9 mg. per 100 g.; the vals. for white are Ca 6·6, Mg 16·1, K 340·1, Na 121·7, and Cl 165·4. The osmotic pressure in nerve tissues is regulated in a different manner from that in other tissues. P. G. M.

Inorganic and phosphagen-phosphorus content of the brain. M. Matsumoto (Japan. J. Med. Sci., Biochem., 1933, **2**, 85—91).—Grey matter of the rabbit's brain contains 42—45 mg. of inorg. P and 3—5 mg. of phosphagen-P, white matter 25—30 mg. and 8—11 mg. per 100 g., respectively. Some hydrolysis of org. P compounds occurs in 4% $CCl_3{\cdot}CO_2H$ solution at room temp., but they are less labile than in muscle. Rat's brain contains 2—3 mg. of pyrophosphate per 100 g. P. G. M.

Muscle extractives. XXXIII. Extractives of crab's muscle (*Astacus fluviatilis*, L.). L. Broude. XXXIV. Oxalylmethylguanidine (creatone) as a constituent of muscle tissue. V. Gulevitsch (Z. physiol. Chem., 1933, **217**, 56—62, 63—67).—XXXIII. The total N of crab-muscle extract was much >, and the N of the Ag–$Ba(OH)_2$ ppt. of the Hg fraction much <, in pig's muscle. Carnosine, creatinine, oxalylmethylguanidine, and xanthine could not be detected, but *dl*-arginine and *dl*-lactic acid were isolated.

XXXIV. α-Oxalylmethylguanidine (+H_2O), m.p. 182·5°, was isolated from the filtrate after carnosine

pptn. with basic Hg sulphate. It is probably not an artefact, but may be the precursor of the $H_2C_2O_4$ found by Steudel (A., 1932, 1273) in ox-muscle. J. H. B.

Muscle extractives. T. Yazawa (Japan. J. Med. Sci., Biochem., 1933, **2**, 37—41).—The following were obtained from a H_2O extract of finback-whale muscle: lactic acid, xanthine (or adenine), hypoxanthine, histidine, creatine, and a substance (m.p. 259—261°; N 20·05%) similar to lysine. P. G. M.

Chemistry of muscle-adenosinetriphosphoric acid. Determination of muscle-adenosinetriphosphoric acid. D. Ferdmann (Z. physiol. Chem., 1933, **216**, 205—216).—Of the three P atoms of adenosinetriphosphoric acid, two are eliminated by hydrolysis for 7 min. with *N*-HCl at 100° and the third, remaining as adenylic acid, by ashing with conc. H_2SO_4. The pentose is estimated by Bial's method, hydrolysing with 4·5*N*-HCl for 5 min., which yields furfuraldehyde (I) giving the reaction with orcinol and $FeCl_3$, or accurately determined by the method of Simonokura (J. Biochem., Japan, 1931, **14**, 343), hydrolysing in this case with 6*N*-H_2SO_4. Longer hydrolysis with 20% HCl gives no (I); the pentose therefore differs from arabinose and xylose, which yield only (I) under these conditions. J. H. B.

Nitrogenous substances of the liver. T. Yazawa (Japan. J. Med. Sci., Biochem., 1933, **2**, 43—46).—Tyrosine, guanine, and xanthine, but not hypoxanthine, were isolated. Autolysis increased the (arginine+histidine)-N and the N not pptd. by phosphotungstic acid. Free sugar increased. P. G. M.

Nitrogenous extractives of ox testes. D. Trubizin (Z. physiol. Chem., 1933, **217**, 33—37).—Guanine, xanthine, adenine, hypoxanthine, but no carnosine were isolated from ox testes. The N distribution in the various ppts. was determined. J. H. B.

Composition of the lipins of normal and diseased organs. IV. Composition of the lipins of the corpus luteum, ovary, testis, and epididymis of cattle. B. Lustig and E. Mandler (Biochem. Z., 1933, **261**, 132—155; cf. A., 1932, 959).—The corpus luteum (I) is richer in combined lipins (II) than are the other sex organs (III), but in all the amount of (II) is very small. In both (I) and (III) the fatty acids which are free, combined in phosphatides, and combined in neutral fats are, in each case, different. The organs also differ greatly as regards the quant. composition (IV) of the lipins which they contain. In the epididymis (IV) depends on the content of semen. Details of the composition and physical and chemical consts. of the fatty acids, neutral fats, phosphatides, and phosphatides pptd. by $COMe_2$ are given. W. McC.

Composition of unsaturated fatty acids of animal tissues. H. G. Smith (Proc. Iowa Acad. Sci., 1931, **38**, 171—172).—The fatty acids of ox heart-muscle and liver contain Δ^{α}. Ch. Abs.

Cytological fixation with the lower fatty acids, their compounds and derivatives. C. Zirkle (Protoplasma, 1933, **18**, 90—111).—Use of a no. of fatty acids and their Cu and Ni salts in conjunction with CH_2O in the fixation of cellular structures is examined. A. G. P.

Cytolysis by fat solvents and the importance of calcium and lecithin in the physico-chemical behaviour of protoplasm. B. Hluchovsky and B. Sekla (Protoplasma, 1933, **18**, 130—140).—The antagonism of fat solvents with respect to their cytolytic action is discussed. In the structure of the protoplasm there is a Ca–lecithin equilibrium which is disturbed by the differential action on the components of the various solvents examined. A. G. P.

Insect wax. V. *Psylla* and *Schizoneura* wax. F. N. Schulz and M. Becker (Biochem. Z., 1933, **261**, 165—169).—*Psylla* wax, $C_{32}H_{64}O$, has m.p. 95—96°. *Schizoneura* wax, m.p. 47—49°, is probably a triglyceride containing 2 mols. of myristic and 1 mol. of palmitic acid or a mixture of triglycerides in which these acids, or other saturated fatty acids of mol. wt. of this order, are present in that ratio. The n_D of the wax is 1·4351, that of a 2 : 1 mixture of the acids named 1·4350. W. McC.

Intestinal worms. I. Chemical composition of *Taenia saginata*. I. A. Smorodincev, K. V. Bebeschin, and P. I. Pavlova (Biochem. Z., 1933, **261**, 176—178).—The average composition of the worms is: H_2O 87·8, org. matter 11·6, total N 0·64 (equiv. to 4% of protein), fat 1·36, ash 0·65%. Compared with that of earthworms the H_2O content is the same, the ash content much lower. The fat content exhibits very great variations, depending on the condition of the host. About 6·2% of the org. matter is probably glycogen, but chitin may also be present. W. McC.

Pigment of *Protoclepsis tesselata*. G. Gheorghiu (Bull. Soc. Chim. biol., 1933, **15**, 552—554).—The colouring matter is of the bile-pigment type. A. L.

Enzymes of *Hydrochelidon nigra*, L. A. Bernardi and M. A. Schwarz (Biochem. Z., 1933, **260**, 369—375).—The glycerol extracts of the blood, leg, breast, mucous membrane, and keratinoid layer of the gizzard of *H. nigra*, L., all contain amylase (cf. A., 1932, 1274) and an invertase which attains its max. action when the concns. of enzyme and sugar are approaching the equilibrium concns. The glycerol extracts of the keratinoid layer contain no protease, of the breast and gizzard musculature traces, and of the blood, leg, and mucous membrane of the gizzard considerable amounts. P. W. C.

Apatite structure of inorganic bone- and tooth-substance. M. A. Bredig (Z. physiol. Chem., 1933, **216**, 239—243).—Comparison of *X*-ray diagrams of synthetic preps., especially of carbonate-apatite with bone- and tooth-substance, indicates that the latter consists of hydroxyapatite. J. H. B.

Phosphorescence in human tissues. II. Phosphorescence of human concrements and pathological calcific tissues, and effect of calcination temperature on phosphorescence. S. Hoshijima (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 15—21; cf. this vol., 411).—The phosphorescence

spectra (I) of the tissues of various animals calcined at different temp. are examined. The ashes of calcified bronchial glands and muscular tissues give intense (I). The (I) of ashed human bones is identical with that of a mixture of calcite and hepatite. H. D.

Chinese silks. I. Glycine, alanine, and tyrosine contents of Chekiang silk. P. P. T. Sah, T. S. Ma, and S. Y. Ma (J. Chinese Chem. Soc., 1933, **1**, 17—22).—The amounts are glycine 18·8, alanine 16·5, and tyrosine 10·5%. A. A. L.

Sugar of amniotic fluid. Observations in chick embryos. K. Yamada (Japan. J. Med. Sci., Biochem., 1933, **2**, 47—69).—Fructose was identified. Creatine and creatinine are not present after 12 days' incubation, but lactic acid can be detected. A summary of the general physical and chemical properties is given. P. G. M.

Fructose in the amniotic fluid of chick embryos. K. Yamada (Japan. J. Med. Sci., Biochem., 1933, **2**, 107—113).—Using the cryogenin colour reaction (cf. following abstract) fructose was detected. P. G. M.

Colour reaction and micro-determination of *d*-fructose. K. Yamada (Japan. J. Med. Sci., Biochem., 1933, **2**, 93—105).—Cryogenin (I) (*m*-benzamidosemicarbazide) when heated at 100° for 3 min. with HCl and glucose (II) (>0·5%) gives a reddish-violet colour, whilst with fructose (III) a bluish-violet colour is produced (concn. >0·005%). For the determination of (III) 2 c.c. of solution are heated with 2 c.c. of 24% HCl [containing 2% of (I)] for 20 min. at 100°; the mixture is cooled rapidly, diluted to 25 c.c., and compared colorimetrically with a standard. A partial separation of (II) and (III) can be effected by treatment with an EtOH–Et_2O (2 : 1) mixture; the solubility of (II) is 46·6 and of (III) 286·0 mg. per 100 c.c. For detection of (III) in blood the proteins are first removed with $CCl_3{\cdot}CO_2H$. The method is more sensitive and sp. than the NHPh$_2$ test (0·002 mg. gives a positive reaction). Many other carbohydrates give different colours in 1% solution. P. G. M.

Lipase content of thoracic duct lymph. A. Kalló (Z. ges. exp. Med., 1933, **86**, 848—853).—The lymph usually contained much more lipase than the blood. Lymph-lipase, which contributes to the serum-lipase, is derived from pancreatic or hepatic lipase directly through the lymph vessels or by way of the bowel. Nutr. Abs.

Function of chloride secretion in the stomach. S. Kin (Keijo J. Med., 1933, **4**, 41—52).—Total chlorides, free HCl, and total acid have been determined in human gastric juice, fasting and after test meals. W. O. K.

Substances which stimulate secretion from the gastric juice of the dog. S. A. Komarow (Biochem. Z., 1933, **261**, 92—105).—From the gastric juice (I) of the dog, after removal of protein and inorg. matter, phosphotungstic acid ppts. nitrogenous bases (II) sol. as carbonates in EtOH, which stimulate secretion by the gastric glands. Some of (II) pass into the histidine–arginine fraction when $AgNO_3$ and $Ba(OH)_2$ are used for pptn. The extent of the stimulation is proportional to the amount of (I) from which the active material injected is obtained. W. McC.

Changes in alkali reserve and sugar content of bile as affected by different physiological agents. III. Effect of histamine, adrenaline, and insulin. W. M. Karatygin and A. I. Hefter (Z. ges. exp. Med., 1933, **86**, 697—708).—Histamine and insulin, both of which lead to an increase in the alkali reserve (I) of the blood, caused a rise in the (I) and a fall in the sugar content (II) of the bile: the vol. of bile secreted was increased. Adrenaline, which tends to cause a fall in blood-(I), caused a fall in (I) and a rise in (II) of the bile: the vol. was decreased. Nutr. Abs.

Excretion of nitrogen by the bile. H. Lucke and J. Frey (Z. ges. exp. Med., 1933, **86**, 1—11).—On ordinary diet only 0·1 g. N in 24 hr. (0·5—1% of total output) was excreted in the bile of dogs with bile fistulæ. When urea (50 g.) was given very little extra appeared in the bile. After the production of a nephritis ($HgCl_2$) the bile-N increased (usually 1—7% of total output). U nitrate nephritis often led to a greater % output of N in the bile because of the small amounts of urine excreted. Although the bile responds to excessive N retention, its output cannot significantly affect the amount retained. Nutr. Abs.

Proteins of the whey fraction in milk from normal and abnormal udders. F. S. Jones and R. B. Little (J. Dairy Sci., 1933, **16**, 101—109).—After removal of caseinogen the whey-proteins are pptd. by means of $CCl_3{\cdot}CO_2H$ and determined by the vol. of the ppt. after centrifuging. This vol. is correlated with the proportion of protein present as determined colorimetrically. Vals. for normal milk are fairly uniform, but increase considerably under abnormal conditions. The proteins found in milk during mastitis probably originate in the blood. Differences are established between the albumin : globulin ratios of normal and abnormal milks. A. G. P.

Acid milk in bovine mastitis. F. S. Jones and R. B. Little (J. Dairy Sci., 1933, **16**, 111—119).—Acidity in milk during mastitis is associated with high nos. of carbohydrate-decomposing streptococci and a poorly buffered condition in the altered milk. Lactic acid is always present under these conditions. A. G. P.

Acid changes in milk produced by certain bacteria. L. H. Lampitt and M. Bogod (Biochem. J., 1933, **27**, 361—369).—Milk was inoculated with various bacteria (100,000 per c.c.), including *E. coli* (I), *B. subtilis* (II), *A. aerogenes* (III), *B. alcaligenes fœcalis*, *S. lactis*, and a lipase-producing micrococcus (IV) of unknown species, and incubated at 30°. (I) and (III) show a general resemblance in the formation of total acidity, but (III) produces more lactic acid, whilst (I) destroys citric acid more completely. The citric acid loss with (II) is very small. The free fatty acid formation (chiefly higher fatty acids) is greatest in the case of (IV). (I) produces the largest amount of volatile acids. The destruction of

citric acid appears to be correlated with formation of volatile acids. W. O. K.

Source of volatile acidity produced in milk by citric acid-fermenting streptococci. M. B. Michaelian and B. W. Hammer (J. Dairy Sci., 1933, **16**, 157—164).—Volatile acids are produced from citric and not from lactic acid. Increased production of volatile acids following additions of lactic acid to milk cultures is due to the establishment of a more favourable p_H, and is also induced by appropriate additions of H_2SO_4, H_3PO_4, or tartaric acid. The amount of volatile acid thus produced is greatest in cultures yielding least titratable acidity and *vice versa*. A. G. P.

Excretion of fat through the skin. A. Perutz and B. Lustig (Biochem. Z., 1933, **261**, 128—131; cf. A., 1932, 958).—The increase (I) in the excretion of fat through the skin in rabbits receiving repeated subcutaneous injections of olive oil reaches 40%, the I val. (II) of the fat being doubled. When the injections cease (I) decreases, but (II) remains unchanged. If the mid-brain is destroyed similar changes occur, but (I) reaches 200% and the cholesterol content of the fat is greatly diminished. W. McC.

Identification of lactose in urine. R. Gootz and H. Tunger (Z. physiol. Chem., 1933, **217**, 28—32).—Lactose identification in presence of monoses is based on the determination of reducing power before and after enzymic hydrolysis. The urine must previously be boiled for 15 min. J. H. B.

Simultaneous determination of lactose and glucose in urine. I. S. Kleiner and H. Tauber (J. Biol. Chem., 1933, **100**, 749—754; cf. Tauber and Kleiner, this vol., 295).—The method consists in determining the total reducing power (I) and the monose content (II) of the filtrate obtained by treating the urine with $CuSO_4$ and $Ba(OH)_2$. For total reduction, Benedict's Cu reagent (A., 1931, 973) is used, and the Cu_2O formed is determined colorimetrically after addition of acid molybdate. The lactose val. is obtained by subtracting (II)+0·02% from (I), and multiplying by 2·2. A. L.

Colloid chemistry of Trommer's sugar test. F. Gebhardt, R. Kohler, and E. Korner (Kolloid-Z., 1933, **63**, 257—263).—Sedimentation and *X*-ray analysis of the reduction products of alkaline $Cu(OH)_2$ preps. show that a red product of relatively low dispersity is obtained with glucose solution, whilst reduction with glucose in presence of gelatin gives a yellow product of high dispersity. Both ppts. consist of Cu_2O. The product obtained with glucose-containing urine is generally yellow and contains a mixture of Cu and Cu_2O. E. S. H.

Is blood-protein amide-nitrogen a source of urinary ammonia? IV. Aeration set for use in the transfer and measurement of small quantities of ammonia. E. F. Williams, jun., and T. P. Nash, jun. (J. Biol. Chem., 1933, **100**, 737—741). A. L.

Form in which uric acid is excreted. M. Rangier (Compt. rend., 1933, **196**, 1441—1442).—The ureide previously described (A., 1925, i, 186) and almost the whole of the urochrome are adsorbed from urine by C. Subsequent elution with dil. aq. NH_3, evaporation to dryness, and extraction of the residue with H_2O (NH_4 H urate remains undissolved) gives glycine (I). Uric acid is thus excreted in the form of a complex with (I). H. B.

Hæmoglobin content of the blood of healthy and anæmic "salt-sick" cattle. W. M. Neal and R. B. Becker (J. Agric. Res., 1933, **46**, 557—563).—The following vals. are recorded: normal 10·94±1·54 to 11·06±1·40, anæmic cattle which subsequently recovered after administration of Fe and Cu, min. 3·02; anæmic calf shortly before death, 1·37 g. per 100 c.c. of blood. A. G. P.

Action of insulin on experimental beriberi and experimental avitaminosis-*B*. O. Kauffmann-Cosla and S. Oeriu (Arch. exp. Path. Pharm., 1933, **170**, 458—464).—The blood-sugar of pigeons on a diet deficient in vitamin-B_1 rises above normal, but falls when polyneuritic symptoms appear, and ultimately reaches 25—40% below normal. Administration of insulin (I) prevents the hyperglycæmia. The progressive rise of urea and other N compounds in the blood is not reduced by administration of (I). W. O. K.

Aluminium as a cause of cancer. O. Baumann (Chem.-Ztg., 1933, **57**, 424—425).—No ill-effects were observed on rats and mice fed with so-called harmless Al salts or with Al powder. The strong reducing powers of Al may produce changes in foodstuffs which account for the taste produced but are not necessarily harmful. Cut nasturtiums flourished in enamel, but died in Al, containers. J. G.

Aluminium as a cause of cancer. H. Zellner (Chem.-Ztg., 1933, **57**, 425).—A reply to Baumann (cf. preceding abstract). J. G.

Lipin content of malignant tumours. II. R. Bierich and A. Lang (Z. physiol. Chem., 1933, **216**, 217—223; cf. A., 1931, 1445).—Slow-growing Jensen sarcoma shows a large increase in cholesteryl ester (I) (up to 10 times the normal) and 100% increase in uncombined fatty acids (II). Flexner–Jobling carcinoma shows no increase in (I). The necrotic tissue of Jensen sarcoma of normal growth shows an increase in (I) and a decrease in (II). J. H. B.

Heavy metals in the cell. Copper and vitamin-*B*; copper and iron in tumours. S. G. Zondek and M. Bandmann (Deut. med. Woch., 1933, **59**, 91—94).—Cu had a similar distribution to that of vitamin-*B*. No Cu was found in Jansen's cryst. vitamin-B_1. The liver-Cu is at its max. in the human fœtus, and the blood-Cu rises considerably during pregnancy. The liver-Fe of the rat increased markedly to the end of the period of growth, when it became const. In the nervous system the grey matter contained most Fe, the white matter less, and the peripheral nerves practically none. Very little Cu or Fe was found in rat carcinoma or sarcoma. Similar findings were obtained with cellular human tumours. Nutr. Abs.

Immune reactions in diabetes. J. K. Moen and H. A. Reimann (Arch. Int. Med., 1933, **51**, 789—

795).—Severity of diabetes decreases the development of agglutinins for *B. typhosus*. H. G. R.

Reactions of respiratory exchanges of diabetics to ingestion of glucose and to insulin. F. Rathery, A. Plantefol, and L. Plantefol (Compt. rend., 1933, **196**, 1250—1252).—The effect of the ingestion of glucose (50 g.) on the R.Q. and metabolism of diabetics who (*a*) have had no insulin (I), (*b*) received (I) at least 12 hr. previously, and (*c*) received (I) with the glucose, varies markedly among individuals. An increase of R.Q. from 0·75 to 0·85—1·0 is, however, generally observed in group (*c*). A. C.

Consumption of blood-sugar by muscle in the non-diabetic and in the diabetic state. W. M. Yater, J. Markowitz, and R. F. Cahoon (Arch. Int. Med., 1933, **51**, 800—813).—Heart-muscle in a normal heart–lung perfusion consumes 4 mg. of glucose (I) per g. per hr. In the diabetic condition the val. is < 1 mg. The decline in blood-sugar following removal of the liver is the same in both the non-diabetic (II) and diabetic (III) state. It is suggested that in (III) the requirement of (I) of resting skeletal muscle is the same as in (II), but, in (III), contracting muscle is unable to utilise (I) for the purpose of obtaining extra energy. H. G. R.

Transient hyperglycæmia and glycosuria following discontinuation of insulin given non-diabetic patients. W. D. Paul, B. B. Clark, and R. B. Gibson (Proc. Soc. Exp. Biol. Med., 1932, **30**, 353—354).—Insulin (I) given in increasing doses up to 25 units thrice daily before meals to five non-diabetic subjects gave rise to no hypoglycæmic symptoms. On discontinuing (I) all patients showed hyperglycæmia, in one case up to 0·253% after sugar ingestion, four had temporary glycosuria, and three showed reduced sugar tolerance in response to a test dose. Nutr. Abs.

Mottled enamel and brown stain. G. Montelius, J. F. McIntosh, and Y. C. Ma (J. Dent. Res., 1933, **13**, 73—79).—Org. matter, Ca, P, and Fe in stained and mottled enamels gave vals. within the limits for normal unstained teeth. Nutr. Abs.

Late lactose-fermenting coliform bacilli in dysentery. F. F. Tang (Chinese Med. J., 1933, **97**, 161—167).—From eight cases of dysentery late lactose-fermenting bacilli classified under the genus *Escherichia* and one non-lactose-fermenting bacillus (*Aerobacter*) were isolated. H. D.

Behaviour of the adrenal lipins in anæmia caused by hæmorrhage and by hæmolytic poisons. S. Marino (Arch. Farm. sperim., 1933, **55**, 183—206).—During the early stages of anæmia caused by hæmorrhage, the free and combined cholesterol (I) of the adrenals (II) diminishes whilst the phosphatides (III), fatty acids (IV), and, sometimes, the lipin-P increase. Later, when the corpuscular blood-mass increases, all the lipin contents increase. With anæmia caused by hæmolytic poisons, during the period when small Heinz bodies or granules appear (12—18 hr. after the injection), the (I) and (IV) of the (II) increase, whilst (III) and (V) may rise or fall. During the period of hæmolysis (3—5 days after injection), (I) decreases, the (III) and (IV) increase, and (V) varies little. T. H. P.

Urea clearance in normal and in dehydrated infants. Renal function and intestinal intoxication. L. Schoenthal, D. Lurie, and M. Kelly (Amer. J. Dis. Children, 1933, **45**, 41—53).—The reduction in urea clearance in intestinal intoxication in infants is attributed to dehydration. Ch. Abs.

Cholesterol content of blood in Indians and its significance in jaundice. A. C. Ghose (Indian J. Med. Res., 1933, **20**, 883—888).—The average normal blood-cholesterol of healthy Indians is 146 mg. per 100 c.c. of whole blood and 140 mg. per 100 c.c. of blood-plasma, or 40 mg. per 100 c.c. < European and American standards. The vals. are the same on a vegetarian and on a mixed diet and show a temporary increase on feeding a rich fatty diet to a starving subject. Seasonal variations are small. Nutr. Abs.

Content of cholesterol, unsaponifiable fraction, and lipins in brain of lunatics. M. Polonovski and P. Lawrie (Compt. rend. Soc. Biol., 1933, **112**, 381—383).—Vals. for brains of psychotics were not appreciably different from the normal except perhaps for a small lowering in the H_2O content and an increase in the unsaponifiable substances of the white matter. Nutr. Abs.

Bromine in blood in manic depressive psychoses. C. L. Urechia and Retezeanu (Compt. rend. Soc. Biol., 1933, **112**, 411—412).—Blood-Br is diminished in melancholia or manic depressive psychoses. Nutr. Abs.

Bromine in blood in psychoses. H. Zondek and A. Bier (Klin. Woch., 1933, **12**, 55—56).—Although a fall in blood-Br is characteristic of 85—90% of cases of manic depressive insanity, a fall also occurs in cases of org. disease involving the brain. In cases of manic depressive psychosis, but not in org. brain diseases, the Br of the cerebrospinal fluid also falls. Nutr. Abs.

Mineral metabolism in renal disease. II. Excretion of minerals in the urine on K- and Na-rich diet. H. Glatzel (Z. ges. exp. Med., 1933, **86**, 103—129).—A normal subject showed on a Na-rich diet (I) an increase in Ca and Mg output due to the greater potential acidity of the diet, and a decrease in the urinary output of P, S, and org. acids attributed to the increase in Cl. On (I) the vol. of urine was greater and the molar concn. less. On both Na- and K-rich (II) diets the amount of anions excreted was < that of the cations, in contrast with the excess of anions found on ordinary diet. In nephritis the concn. of all the elements except Mg was decreased on (I) and (II). In health and in nephritis the state of the acid–base balance regulates the output of minerals. Nutr. Abs.

Effects of agave concentrate in the treatment of experimental nephritis induced in animals. I. Nephritis induced in rabbits by the use of tartrates. H. D. Jones, K. D. Crane, G. B. Johnston, and C. R. Henry. II. **Nephritis induced in dogs by the use of uranium nitrate.** H. D. Jones,

R. C. HUGHES, and G. B. JOHNSTON (J. Pharm. Exp. Ther., 1933, **48**, 1—24, 25—50).—I. Agave concentrate (fresh unfermented juice from *A. atrovirens*, Karw., conc. in vac. at 35—38°), administered orally to rabbits in which a kidney lesion is produced by an injection of tartrate, has a therapeutic effect on the nephritis shown by decreased mortality, improvement in the blood composition, and by the histological findings.

II. Similar favourable results were obtained in the case of dogs in which an acute nephritis was produced as the result of administration of $UO_2(NO_3)_2$.

W. O. K.

Experimental œdema in nephrectomised dogs. C. J. FARMER, F. S. BARRY, A. REED, and A. C. IVY (Arch. Int. Med., 1933, **51**, 704—713).—In the nephrectomised dog there is a marked decrease in total serum-protein and in the albumin fraction (I) with an increase in the globulin, on the day following the onset of œdema (II). The amount of (I) and the reversal of the serum-protein ratio have no direct relation to the development of (II). The effusion fluids of dogs treated with Ringer's solution have a protein content of 1·3—4·0%. H. G. R.

Relationship between plasma-protein content, plasma-specific gravity, and œdema in dogs maintained on a protein-inadequate diet and in dogs rendered œdematous by plasmapheresis. A. A. WEECH, C. E. SNELLING, and E. GOETTSCH (J. Clin. Invest., 1933, **12**, 193—216).—In dogs subjected to plasmapheresis each bleeding resulted in an immediate fall in plasma-protein concn. followed by a period of increase most marked in the first 24 hr., but continuing until the next bleeding. A diet producing a negative N balance led to gradual decrease of plasma-albumin which was not paralleled by decrease of total protein because the globulin tended to rise. Gradual retention of NaCl and H_2O is also indicated. With plasmapheresis œdema was present at plasma-albumin concns. < 1·0—1·5 g. per 100 c.c. and nutritional œdema at concns. < 1·5—2·0 g. per 100 c.c. The subcutaneous œdema fluid contained 0·10—0·35 g. of protein per 100 c.c. with a slightly higher average than the fluid in plasmapheresis cases. NUTR. ABS.

Effect of serum transfusion on the plasma-protein depletion associated with nutritional œdema in dogs. A. A. WEECH, E. GOETTSCH, and E. B. REEVES (J. Clin. Invest., 1933, **12**, 217—228).—The transfusion of normal dog serum to a dog with low plasma-albumin (I), due to low-protein diet, leads to an immediate rise in the concn. of (I) and a fall in globulin (II). When calc. as total circulating protein both (I) and (II) were increased. After the preliminary rise the concn. of (I) fell, whilst that of (II), after its initial fall, gradually increased; total protein and blood vol. gradually returned to the pre-transfusion vals. NUTR. ABS.

Hyperfunction of the thyroid in pregnancy. Effect of adrenaline on blood-iodine in pregnancy. W. SCHERINGER (Klin. Woch., 1933, **12**, 107—108).—During the second half of pregnancy intravenous injection of 0·005 mg. of adrenaline resulted in a marked fall in blood-I within 30 sec. After 30 min. the vals. reached, or even exceeded, the original level. NUTR. ABS.

Mechanism of the formation of phytobezoars (persimmon ball). S. IZUMI, K. ISIDA, and M. IWAMOTO (Japan. J. Med. Sci., Biochem., 1933, **2**, 21—35).—These may be composed either of fibrous matter (inio-bezoar) or of fruits (opo-bezoar), the latter being the commonest. The persimmon ball is formed from unripe fruit, the skins being cemented together by the sol. tannin, shibuol (I), which is coagulated by gastric acidity. On ripening, (I) becomes insol. and loses its astringent properties; (I)–protein complexes cannot be digested either by pepsin or trypsin. Bile salts are pptd. by sol. (I) in presence of NaCl. P. G. M.

Pathological excretion of oxyproteic acid. H. TSUTSUI (Japan. J. Med. Sci., Biochem., 1933, **2**, 185—187).—Oxyproteic acid constitutes normally about 3·4% of the total N of urine. The proportion is increased in kala-azar, diabetes, and carcinoma of the stomach, but lowered in acute yellow atrophy of the liver; it is not correlated with the neutral S content of the urine. P. G. M.

Urinary protein. S. KOZAWA, R. IWATSURU, and T. ADACHI (Biochem. Z., 1933, **260**, 313—325).—The isoelectric point of urinary protein is at p_H 4·4 and the protein on hydrolysis gives 80—82% of α-NH_2-acids, 1·04—1·29% of histidine, 0·86—1·12% of tryptophan, and 4·56—4·98% of tyrosine. These figures, together with the albumin : globulin ratio, are all closely related to the corresponding figures for serum-protein. P. W. C.

Relation between calcium–potassium equilibrium and antirheumatics. III. Influence of antirheumatics in rabbits with mustard-oil inflammation or experimental toothache. K. IN (Keijo J. Med., 1933, **4**, 56—72).—In rabbits blistering of the skin with mustard oil does not alter the K/Ca ratio (I) in the serum, but in animals so treated, administration of erycon (II), antipyrine (III), and Na salicylate (IV) but not cinnamon (V) decreases (I). In rabbits with experimental toothache (I) exceeds the normal val., and is reduced by (II)—(IV), but not by (V). The animals are soothed by injection of $CaCl_2$, but KCl has the opposite effect. W. O. K.

Treatment of endemic scurvy by the intravenous injection of citrus. T. J. DRY (Arch. Int. Med., 1933, **51**, 679—691).—Intravenous use of citrus juices is an efficient method of controlling scurvy. H. G. R.

Glycosuria in spirochætosis icterohæmorrhagica. M. KITAOKA (Japan. J. Med. Sci., viii, Int. Med. Ped. Psych., 1932, **2**, 239—266).—Glycosuria appears frequently after ingestion of food. CH. ABS.

Chemical composition of heart muscle. Water content, total nitrogen, total phosphorus, sterols, glycogen, and lipins (I) in normal and thyroidectomised animals; (II) in thyrotoxicosis; (III) after stimulation with adrenaline; (IV) in animals thyroidless or suffering from thyrotoxicosis. A. FIESCHI (Z. ges. exp. Med., 1933, **86**, 387—397, 398—407, 408—412, 413—419).—I.

Heart muscle of rabbits thyroidectomised 2—4 months previously showed a slight increase in H_2O content, a slight reduction of glycogen, a definite decrease in EtOH-sol. P, but a normal or slight increase in $COMe_2$-sol. P.

II. Intravenous injections of thyroxine or feeding with dried thyroid greatly reduced the heart-muscle-glycogen; total N and total P increased with slight increase in phosphatide, chiefly the $COMe_2$ fraction. Dried thyroid (thyreoidin) caused an increase in sterol content of heart muscle which was not found after thyroxine.

III. Intravenous injection of adrenaline (1 : 10,000) led to a marked increase in the H_2O content of heart muscle, but little change in the other constituents.

IV. Intravenous adrenaline produced in thyroidectomised rabbits a considerable increase in H_2O content and a reduction of EtOH-sol. P; in thyrotoxicosis (thyroid feeding or thyroxine injections) little change in H_2O content, increase in total P and phosphatide, and great diminution of glycogen. NUTR. ABS.

Excretion of iodine in experimental hyperthyroidism. B. O. BARNES (Amer. J. Physiol., 1933, **103**, 699—703).—When desiccated thyroid or thyroglobulin was fed to dogs, 50% of the I was eliminated through the urine and very little in the bile, but after thyroxine (I) intravenously, most of the injected I was excreted in the bile. It is concluded that free (I) is not liberated during the course of thyroid feeding. NUTR. ABS.

Growth, reproduction, and lactation in the absence of the parathyroid glands. F. L. KOZELKA, E. B. HART, and G. BOHSTEDT (J. Biol. Chem., 1933, **100**, 715—729).—In parathyroidectomised puppies fed on a complete diet including thyroxine and just sufficient vitamin-*D* to maintain the normal serum-Ca and inorg. P, Ca and P deposition in the soft tissues did not occur and calcification of the bones was normal. Mature dogs in similar circumstances were able to survive a complete reproductive cycle. It is believed that vitamin-*D* toxicity is due to increased blood-Ca, since the lactating animals were able to withstand up to 66,000 rat units per day (the amount necessary to maintain normal serum-Ca) without ill effect. A. L.

Effect of acids and other substances on the production of acute gastric ulcers. J. FRIEDENWALD, M. FELDMAN, and S. MORRISON (J. Exp. Med., 1933, **57**, 203—213). CH. ABS.

Tissue respiration and its relation to morphological changes, oxidase reaction, and hydrogen-ion concentration in tissues. H. NAKAMURA (Trans. Japan. Path. Soc., 1931, **21**, 282—295).—Respiration and oxidase reaction decreased in dying or starved liver and kidney tissue of rats, in tissues treated with HCl or $NaHCO_3$, or poisoned with U, $HgCl_2$, $K_2Cr_2O_7$, As, P, or cantharidin. CH. ABS.

Relation between degenerative changes and tissue respiration. Various toxins. M. NAKAMURA and K. SUZUKI. **Inorganic poisons and ligation of the excretory duct.** K. SUZUKI and M. NAKAMURA (Trans. Japan. Path. Soc., 1931, **21**, 298—302, 302—305).—Degenerative changes caused by bacterial toxins were accompanied by decreased tissue respiration (I) and oxidising granules. Those caused by inorg. poisons are generally so accompanied; in many cases the decrease in (I) is parallel with the decrease in oxidase content. The change in (I) is related to the appearance of fat. CH. ABS.

Iron as a cation in relation to reducing power of tissues. A. CANONICO and J. A. TAIANA (Compt. rend. Soc. Biol., 1933, **112**, 493—494).—The power of rat-liver tissue to reduce m-$C_6H_4(NO_2)_2$ was decreased by Fe^{II}. NUTR. ABS.

Carbohydrate metabolism and the function of the grey matter of the central nervous system E. G. HOLMES (Biochem. J., 1933, **27**, 523—536).—The central nervous system of frogs functions, as shown by the convulsive response of the animals to strychnine injections, after 20 min. perfusion with 0·04% $CH_2I{\cdot}CO_2H$ (I), the min. level of lactic acid having almost been reached by this time. Perfusion with 0·1% (I) for 1¼ hr. is necessary for complete destruction of the function. 0·5% Na lactate and 0·05% AcCHO partly prevent the effect of (I). The labile P of the central nervous system is likewise reduced by (I) more rapidly than the tissue function is affected. The activity of the grey matter is therefore not immediately dependent on phosphocreatine breakdown or lactic acid formation or oxidation. A. L.

Oxalic acid metabolism. R. JÜRGENS and G. SPEHR (Deut. Arch. klin. Med., 1933, **174**, 456—467).—The blood-serum-$H_2C_2O_4$ of the fasting dog was 5·4—19·3 mg. per 100 c.c., and in man, 5·2—9·7 mg.; in disease these vals. may be increased by 68%. Perorallv, $H_2C_2O_4$ (I) and its salts produced in dogs a sharp rise of blood-(I), with a return to normal in the 5th hr. after administration. Jaundice and blood-(I) ran parallel courses, suggesting a connexion between the liver and (I) metabolism. A daily intake of 2·74 g. of (I), derived from food, did not raise the normal fasting val. in the blood during 5 days. The blood-(I) increased in some cases of renal calculus, in diabetes (in which it varied with the blood-sugar), in uræmia, and in leucæmia. Glucose rapidly produced a considerable rise of blood-(I) which persisted after the fall of blood-sugar. There appeared to be some connexion between sugar tolerance and degree of oxalæmia. The results suggest a relationship between sugar and (I) metabolism. NUTR. ABS.

Metabolism of tissues. Role of glycolysis in the metabolism of embryonic cells. F. LIPMANN (Biochem. Z., 1933, **261**, 157—164).—Quant. measurements of the respiration (I) and glycolysis (II), under aerobic and anaerobic (III) conditions and at low O_2 pressures (IV), of growing embryonic (osteoblast fibroblast) cells (V) *in vitro* have been made. The metabolism of (V) varies considerably with their origin. Under (III), development of too great acidity being prevented, very slight growth is possible. At (IV) reduction of (I) by one third is accompanied by reduction of growth by one half with corresponding increase in (II) which provides the min. amount of

energy required for growth (VI), but is apparently not the sp. reaction of (VI). W. McC.

Anaerobic formation and disappearance of pyruvic acid in muscle. O. MEYERHOF and D. MCEACHERN (Biochem. Z., 1933, **260**, 417—445).—In minced muscle in PO_4''' solution with max. lactic acid (I) formation, $AcCO_2H$ (II) amounting to 2—4% of (I) is formed. This amount is increased at the expense of (I) in finely minced muscle and still further by addition of sulphite, when it amounts to 35% of (I). Formation of (II) is only transiently increased by addition of (I), but is strongly increased by addition of glycogen or hexose diphosphate. (II) added to muscle disappears to a slight extent, especially just after addition. In carbohydrate-free enzyme extracts, added (II) does not disappear, but the yield of (II) in presence of sulphite is increased several times. (II) arises therefore during the conversion of carbohydrate into (I) and not from (I). It is formed by the mutation of hexose diphosphate, the oxidised product being (II) and the reduced, α-glycerophosphoric acid. P. W. C.

Mechanism of deamination in heart and skeletal muscle. P. OSTERN and T. MANN (Biochem. Z., 1933, **260**, 326—353).—With heart-muscle pulp (I) of man, dog, hare, rabbit, pigeon, etc., deamination of adenosine (II) is considerably more rapid than of adenylic acid (III), the reverse being true only of frog's (I). Adenine nucleotide is deaminated by (I), but not by skeletal muscle pulp (IV). The reaction is slower than with (III) and is decreased or completely inhibited by PO_4'''. Presence of salts (Cl', PO_4''', SO_4'') accelerates deamination of (III) by (I). With (IV) formation of NH_3 from (II) is much < from (III) and from (III) is much greater with (IV) than with (I) of the same animal. The dependence of NH_3 formation on p_H is investigated. Adenosinetriphosphoric acid (V) is more slowly deaminised by (IV) than (III), the reaction being accelerated by alkali, Cl', PO_4''', SO_4'', and inhibited by F'. Mg salts inhibit deamination by (IV) both in the tissue pulp and of added (V) and (III). P. W. C.

Variation of volume of muscle in relation to the chemistry of contraction. I. Methods. II. Change of volume with various forms of contraction. O. MEYERHOF and W. MOHLE (Biochem. Z., 1933, **260**, 454—468; 469—489).—I. Apparatus for determination and photographic registration of the change in vol. of muscle on stimulation is described.

II. Of many such photographic registrations, a few characteristic curves and tables are given showing the change of vol. with the single muscle twitch, tetanus, isometric, isotonic, and auxotonic contraction, etc. P. W. C.

Theory of muscular contraction. P. FABRE (Compt. rend. Soc. Biol., 1931, **106**, 951—953; Chem. Zentr., 1933, i, 632).—$H^·$ and lactate ions diffuse with different velocities into the contractile element, forming an electric double layer and producing a change in surface tension. Relaxation takes place when the more slowly diffusing ion has neutralised the other. A. A. E.

Fat metabolism. II. P. E. VERKADE and J. VAN DER LEE (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 314—323; cf. this vol., 417).—When glyceryl trinonoate (A., 1932, 1018) is fed to man on a diet poor in carbohydrate, azelaic acid is excreted in the urine. Similarly, tridecoin, triundecoin (I), and trilaurin yield respectively sebacic, nonane-αι- and decane-ακ-dicarboxylic acids. With tristridecoin the corresponding diacid was not detectable. The conversion is most marked with (I). The significance of this ω-oxidation in fat metabolism and the therapeutic importance of (I) are discussed. F. O. H.

Combustion of fat in the lungs. L. BINET, E. AUBEL, and M. MARQUIS (Compt. rend. Soc. Biol., 1933, **112**, 540—542).—In lung perfusion experiments using citrated blood, the R.Q. after 1, 2, and 3 hr. was 0·95, 0·95, 1·00, whilst on perfusing with blood containing 0·5% $PrCO_2Na$ (I), it was 0·90, 0·73, and 0·64, respectively. In the first series, therefore, carbohydrate (II) only was burned, whilst in the second, (II) was burned in the first hr., both (II) and (I) in the second, and almost exclusively (I) in the third hr. NUTR. ABS.

Functions of the pancreas in fat resorption. M. NOTHMANN and H. WENDT (Klin. Woch., 1932, **11**, 2137—2139; Chem. Zentr., 1933, i, 627).—A discussion. The pancreas plays an important part in removal of fat from the stomach, but not in its resorption in the intestine after cleavage. A. A. E.

Effect of ultra-violet light on cholesterol metabolism. III. Methods. R. HUBERT (Arch. Gynakol., 1932, **151**, 681—685).—The colorimetric method for determination of cholesterol (I) (Autenrieth and Funk, modified by Pincussen) gives results averaging 11·9% > those by the gravimetric (Windaus) method. The same changes of (I) metabolism are, however, detected by both methods. NUTR. ABS.

Purine metabolism in man. F. CHROMETZKA (Z. ges. exp. Med., 1933, **86**, 483—528).—Feeding with uric acid (I) or its precursors led to an increase in the output of total creatinine. Even on meat-free diet small amounts of allantoin (II) were present in the urine (10—20 mg. in 24 hr.). In patients with disturbances of nucleoprotein metabolism (pituitary obesity) there was an increase in urinary (II). Feeding with (II) led to an increase in urinary urea; some of the urea must have been derived from the (II) by way of substances of the type of oxaluric acid. Evidence is given of an unknown nitrogenous end-product (III) (pptd. by $CuSO_4$) and of purine metabolism, probably an intermediate stage between (I) and (II). Feeding with nucleic acid, purine bases, or (I) leads to appearance in the urine of a labile form of (I) which readily undergoes hydrolysis, and it is suggested that this is the parent substance of (III). NUTR. ABS.

Production of kynurenic acid from tryptophan derivatives. C. P. BERG (Proc. Iowa Acad. Sci., 1931, **38**, 169).—Tryptophan Et ester hydrochloride, when administered orally or subcutaneously, gave rise to an output of kynurenic acid comparable with that afforded by an equiv. amount of free tryptophan;

the Ac derivative afforded a small, and the methylene and Bz derivatives an inappreciable, quantity. CH. ABS.

Labile role of sulphur in metabolism. H. E. C. WILSON (J. Physiol., 1933, **77**, 240—246).—Experimental evidence does not support the view that the labile nature of S in protein metabolism is due to preferential excretion of the S by the kidney, or that cystine is more easily attacked than other NH_2-acids. The hypothesis that a S compound, such as cystine, occupies a key position in the protein mol. and is the first to be eliminated in catabolism, or to be retained in anabolism, seems best to explain the peculiar metabolic behaviour of S. NUTR. ABS.

Digestibility of cheese. A. MOEN (Tidsskr. norske Landbruk, 1933, **40**, 3—5).—A fresh half-fat Gauda cheese contained 14·8% water-sol. and 92·0% digestible (HCl and pepsin) N; the ripe (6 months) cheese contained 52·0 and 99·3%, respectively. NUTR. ABS.

Relative digestibility by rats of the milk of five breeds of dairy cattle. W. B. NEVENS and D. D. SHAW (J. Agric. Res., 1933, **46**, 463—472).—With rats receiving milk only, no significant differences were observed in the digestibility of milks from different breeds of cattle. The % digestibilities of milk constituents were: fat 99, protein 91, total solids 92—93, sugars 100. A. G. P.

Nutritive value of the proteins of leguminous seeds. V. ZAGAMI and V. FAMIANI (Atti R. Accad. Lincei, 1933, [vi], **17**, 485—490; cf. this vol., 89).—Rat experiments show that the protein deficiency of grain may be supplied as well by the proteins of peas, beans, lentils, and the like as by caseinogen. T. H. P.

Digestive power of, and nitrogen retention by, four types of pigs. J. SCHMIDT, M. F. VON LAGNEAU, and C. ZIMMERMANN (Arch. Tierernähr. Tierzucht, 1933, **8**, 453—496).—The digestive power of pigs was not affected by age or type. N retention varied considerably among individual animals, but average vals. for 6—8 individuals of each of four types showed significant type differences. A. G. P.

Edible bird's-nests. A. HEIDUSCHKA and L. GRAEFE (Biochem. Z., 1933, **260**, 406—413).—The nest substance is a member of the group of salivary mucins of composition, C 49, H 6·9, N 9·8, S 0·9%, and is present chiefly as the sparingly sol. Ca and to a small extent as the Na salt. Traces of salivary enzymes are also present. On hydrolysis the substance yields 18% of carbohydrate (probably chitosamine) and the hydrolysate contains tyrosine 5·6, tryptophan 1·4, cystine 2·4, histidine 2·7, and arginine 2·7%. The heat of combustion of the swallow's nest is 4400 g.-cal. The nest substance is almost completely unattacked by pepsin and trypsin *in vitro*, and although intestinal bacteria attack it to a somewhat greater extent, the amount digested in the animal is very small. P. W. C.

Digestibility, metabolism, and energy exchange in hens as a basis for rational feeding. M. J. DIAKOW (Arch. Tierernähr. Tierzucht, 1932, **7**, 571—637).—Data are given showing respiratory and heat exchanges in hens receiving varied diets. Unbroken grain is most advantageous when used in such quantities that it is wholly utilised for heat maintenance. A. G. P.

Mineral metabolism in rabbits fed on a cabbage diet. S. RANGANATHAN (Indian J. Med. Res., 1932, **20**, 651—662).—The finding of Baumann *et al.*, that the hyperplastic goitres produced in rabbits on an exclusive cabbage diet are associated with Ca, Mg, and P retention, has not been confirmed in cases where the goitres so produced range between 150 and 170 mg. per kg. body.-wt. NUTR. ABS.

Mineral metabolism of farm animals. K. C. SEN (J. Indian Chem. Soc., 1933, Ray No., 143—159).—A summary. H. J. E.

Influence of the chief mineral nutrients on the structure and hygiene of the animal. U. DUERST (Ernähr. Pflanze, 1933, **29**, 141—145).—Effects of mineral salts on the digestive, metabolic, and reproductive changes in animals are discussed. Antagonism between $Ca^{\cdot\cdot}$ and $K^{\cdot}$ is considered. A. G. P.

Significance of calcium and phosphorus in the development and growth of pigs. J. H. W. T. REIMERS and D. B. SMUTS (Arch. Tierernähr. Tierzucht, 1932, **7**, 471—531).—Pigs developed rickets with a ration low in Ca and optimum in P (Ca : P = 1 : 4). The corrective action of cod-liver oil resulted from increased Ca and decreased P retention. Rations having excessive Ca and optimum P (Ca : P = 3·5 : 1) induced fits and blindness, high Ca and very low P contents in blood-serum, and decreased Ca and P retention. The Ca and P of the bones were unaltered. A ration having Ca : P = 1·8 : 1 produced no abnormal effects. The effects of excess-Ca rations were corrected by administration of Na_2HPO_4. Addition of CaO to a rachitic diet to produce Ca : P = 1·2 : 1 gave excellent results, which were not further improved by supplying cod-liver oil. Addition of Ca and P above certain limits to a ration having a normal Ca : P ratio increased the total ash content of bones without alteration of the % Ca and P. A. G. P.

Magnesium deficiency in animals. III. Chemical changes in the blood following magnesium deprivation. D. H. KRUSE, E. R. ORENT, and E. V. MCCOLLUM (J. Biol. Chem., 1933, **100**, 603—643; cf. A., 1932, 773).—In the blood of dogs fed on a diet containing 1·8 p.p.m. of Mg but adequate amounts of other constituents, serum-Mg decreases, this being followed by an increase in total cholesterol, particularly in the cholesteryl ester fraction, with a corresponding decrease in fatty acids, so that the total fat remains the same. Finally, before death, the non-protein-N rises. No change is observed in Na, K, Ca, inorg. P, lipin-P, bilirubin, CO_2 capacity, Cl', fibrinogen, albumin, globulin, glucose, creatine, or creatinine. A. L.

Salt economy in extreme dry heat. D. B. DILL, B. F. JONES, H. T. EDWARDS, and S. A. OBERG (J. Biol. Chem., 1933, **100**, 755—767).—The changes in urinary output of H_2O, Cl, Na, K, N, and inorg. P of individuals under conditions of extreme dry heat indicate that high concn. similar to that of serum is not maintained in profuse and continued perspir-

ation (I). The organism adapts itself, and the salt content of (I) decreases after the first few days, so that 10 litres of (I) may be excreted per day without the necessity of having a greater salt intake than 15 g. per day, except before acclimatisation. The (I) for the entire period of dry heat had the average composition Cl 14, Na 14, K 2 milli-equiv. per litre. A. L.

Resorption of water and of water from salt solutions in the intestine. W. Straub and E. Leo (Arch. exp. Path. Pharm., 1933, **170**, 534—545).—In the intestine of a guinea-pig the rate of resorption of H_2O (I) is decreased by the presence in it of salts, the effect being dependent on the osmotic pressure and not on the nature of the salt. When the concn. is isotonic with the tissue fluids (I) does not occur, whilst with hypertonic solutions secretion takes place into the intestine. (I) is more rapid from the large than from the small intestine and is increased by free CO_2. W. O. K.

Metabolism of alcohol. H. E. Himwich, L. H. Nahum, N. Rakieten, J. F. Fazikas, D. Du Bois, and E. F. Gildea (J. Amer. Med. Assoc., 1933, **100**, 651—654).—Ingestion of 10 c.c. of 19% EtOH (I) per kg. body-wt. by man and 50 c.c. by dogs was followed by a slight rise in blood-sugar, a marked rise in blood-lactic acid, and a decrease in blood-CO_2 and -p_H. (I) acts as a glycogenolytic agent on liver- and muscle-glycogen. The fall in p_H due to accumulation of lactic acid and lag in CO_2 excretion varied with the concn. of (I) in the blood. In patients suffering from the effects of excessive ingestion of alcohol the lactic acid of the arterial blood was increased. Intraperitoneal injection of 50 c.c. of 19% (I) per kg. of rat lowered the R.Q. of the cerebral cortex from 0·98 to < 0·9, indicating an oxidation of (I) and lactic acid. Nutr. Abs.

Determination of alcohol in blood. A. Heiduschka and E. Flotow (Pharm. Zentr., 1933, **74**, 329—333).—A modified Widmark method is recommended for forensic purposes. The blood-EtOH content is a more accurate measure of the EtOH consumed than is that of the urine. If the body-wt. and the time of consumption are known then the quantity of EtOH taken can be accurately calc. from the blood-EtOH. E. H. S.

Physiology of pyrimidines. VII. Metabolism of *iso*barbituric acid in man. J. S. Stekol and L. R. Cerecedo (J. Biol. Chem., 1933, **100**, 653—656).—*iso*Barbituric acid fed to man is partly broken down to urea and partly excreted as an ethereal sulphate at the expense of the inorg. SO_4 normally excreted. Neutral S remains unaffected. A. L.

Effect of soporifics on blood-sugar. J. Lerman (Z. ges. exp. Med., 1932, **85**, 536—546; Chem. Zentr., 1933, i, 255).—In dogs the barbituric acid group tends to lower the blood-sugar. Chloretone causes a rise followed by a fall; chloralformamide and dionine have no effect. A. A. E.

Hypnotic action of mixed ketones containing different types of aromatic nuclei. H. Gilman, L. W. Rowe, and J. B. Dickey.—See this vol., 720.

Alteration of the blood-[H$^+$] and mineral metabolism during narcosis. I. Calcium and phosphorus in blood during narcosis. J. Becka (Arch. exp. Path. Pharm., 1933, **170**, 377—383).—Of many hypnotics administered to rabbits, the greatest fall in the serum-Ca was effected by Mg salts, avertin, and hypnal (—4 mg. per 100 c.c.) whilst $CHCl_3$ caused the greatest increase (+3 mg.). Post-narcotic effects were < those during narcosis. The serum-inorg. P exhibited only slight changes except with $Mg_3(PO_4)_2$ (+5 mg.). The total P was increased by $Mg_3(PO_4)_2$ (+14 mg.), avertin (+12 mg.), chloralformamide (+10 mg.), and urethane (+7 mg.). The post-narcotic effects on total P were somewhat irregular and sometimes reversed. W. O. K.

Action of veratrine and urethane on tissue oxidations. F. Bernheim and M. L. C. Bernheim (J. Pharm. Exp. Ther., 1933, **48**, 73—78).—Veratrine (a mixture of cevadine and veratridine) (I) inhibits the O_2 uptake of mammalian muscle, kidney, and liver (ground or sliced tissue), being about 100—150 times as toxic as urethane (II), but has no effect on the R.Q. Its action is greater on broken than on intact cells. It has no effect on the oxidation of lactic and succinic acids by liver tissue, completely inhibits that of proline and xanthine, and accelerates that of tyramine. The O_2 uptake of yeast is accelerated by small and inhibited by large concns. of (I) or (II). W. O. K.

Test for the presence of novocaine in nervous tissue. M. Grodinsky, M. Beber, and C. P. Baker (Science, 1933, **77**, 450).—Novocaine in nervous tissue can be detected by diazotisation and the formation of an orange-red colour when β-$C_{10}H_7$·OH is added. L. S. T.

Antagonism of paraldehyde to strychnine. I. Simon (Arch. Farm. sperim., 1933, **55**, 214—218).—The antagonism of paraldehyde to strychnine (cf. Cervello, Arch. Sci. Med., 1883, **7**, 1) is confirmed. T. H. P.

Combination experiments on magnesium and calcium with morphine with regard to the influence on blood-sugar. K. Akimoto (Folia Pharmacol. Japon., 1933, **15**, No. 3, 185—192).—Rabbit's blood-sugar is increased by subcutaneous injection of $MgSO_4$ (0·2 g. per kg.) or $CaCl_2$ (0·01 g. per kg.); much smaller doses have no effect, but the hyperglycæmic action of morphine is greatly increased, whilst larger doses have no such action. Ch. Abs.

Pharmacological action of narcotine and its derivatives. M. Hayashi (Japan. J. Med. Sci., [iv], Pharmacol., 1932, **6**, 203—257). Ch. Abs.

Physiological action of norconessine. A. C. White (J. Pharm. Exp. Ther., 1933, **48**, 79 87).—The pharmacological action of norconessine (cf. Haworth, A., 1932, 406) is very similar to that of conessine. W. O. K.

Pharmacology of anabasine. H. B. Haag (J. Pharm. Exp. Ther., 1933, **48**, 95—104).—Anabasine (2-3′-pyridylpiperidine) resembles nicotine generally in its pharmacological actions, but it is somewhat less exciting and more depressing. W. O. K.

Effects of some quaternary ammonium and analogous compounds on the autonomic nervous system. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1933, **48**, 51—66).—The following compounds are approx. in order of decreasing muscarine-like action: $[NMe_3 \cdot CHPh \cdot CO \cdot NH_2]I$ (I), $[NMe_3 \cdot (CH_2)_2Ph]Br$ (II), $[NMe_3 \cdot CHPhMe]Br$ (III), $[NMe_3 \cdot CH_2 \cdot NO_2]Br$, $[NMeEt_2 \cdot CHPh \cdot CN]I$, $[NEt_3 \cdot (CH_2)_2Ph]I$ (IV), $[NEt_3 \cdot CHPh \cdot CN]Br$ (V), the last two compounds being inactive. (I), (II), and (III) have a nicotine stimulating action whilst (IV) and (V) have a paralysing nicotine action. W. O. K.

[Pharmacology of] ethers and thio-ethers of triethylammonium compounds. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1933, **48**, 105—125).—The compounds $[R \cdot CH_2 \cdot NEt_3]X$ (R= OMe, OEt, $CH_2 \cdot CH \cdot CH_2 \cdot O$, $OMe \cdot CH_2$, $OEt \cdot CH_2$, $OBu^{\alpha} \cdot CH_2$, $OPh \cdot CH_2$, SMe, SEt, SPr^{β}, SBu^{β}; X= Br or I) are all devoid of muscarine-like action or stimulating nicotine action, but exert a paralysing nicotine action. R=OPh was more active than the aliphatic ethers, of which $R=CH_2 \cdot CH \cdot CH_2 \cdot O$ and $R-OBu^{\alpha} \cdot CH_2$ were the most active. Of the thiols the most active was $R=SBu^{\beta}$, which had a powerful and brief curare-like action. W. O. K.

Depressor substance in extract of mistletoe. E. DRESSLER, H. KWIATKOWSKI, and E. SCHILF (Arch. exp. Path. Pharm., **170**, 428—431).—The depressor action of an acid EtOH mistletoe extract on cats is inhibited by atropine. Acetylation of the crude extract increases its activity. A leech prep. treated with eserine reacts only to the acetylated extract (cf. A., 1932, 966). The depressor principle in the crude extract is therefore probably choline. W. O. K.

Depressor action of stimulation of the chorda lingualis and influence of atropine. W. FELDBERG (Arch. exp. Path. Pharm., 1933, **170**, 560—570).—The lowering of blood-pressure which occurs on stimulation of the chorda fibres to the salivary gland or of the chorda lingualis fibres to the tongue in a cat injected with eserine takes place in 10—15 sec. after the beginning of stimulation and is inhibited by atropine. Acetylcholine, probably, is produced locally, enters the blood-stream, and thus produces the depressor action. W. O. K.

Substances regulating circulation and their significance in hypertonus. F. LANGE (Klin. Woch., 1933, **12**, 173—176).—A hypotensive substance (I) can be isolated from blood, urine, and all tissues, of which $5—7 \times 10^{-6}$ g. has a marked effect on the blood-pressure of the cat. In essential hypertension the blood contains less, the urine considerably more, of (I) than that of healthy subjects. When hypertension is due to chronic nephritis the blood contains more and the urine less (I) than that of normals. NUTR. ABS.

Substances regulating circulation. K. FELIX (Klin. Woch., 1933, **12**, 176—179).—The hypotensive substance (preceding abstract) is a (mono)Me methylenediguanidine compound. $5—7 \times 10^{-6}$ g. of the cryst. flavianate lowers the blood-pressure of a cat by 20—30 mm. NUTR. ABS.

Physiological action of cystinyl peptides and guanidine derivatives. H. J. HARWOOD (Iowa State Coll. J. Sci., 1932, **6**, 431—433).—Guanidine derivatives are classified as hyperglycæmic, hypoglycæmic, and inactive; in no case did the hypoglycæmic action approach that of insulin or synthalin, and it was usually accompanied by toxic effects. The prep. of dicarboxytyrosylcystine Et_2 ester, dicarbethoxy-cystinyltyrosine Et ester, -cystinyl chloride, -cystinyltyrosine, -cystinylhistidine Me ester, and -cystinylarginine is described. CH. ABS.

Influence of "anticoman" on carbohydrate metabolism. K. FROHLICH (Arch. Verdauungskrankh., 1932, **52**, 434—440; Chem. Zentr., 1933, i, 629).—In non-toxic doses "anticoman" has no effect on the blood-sugar of fasting dogs and rabbits, but the glucose tolerance of normal animals is increased during several hr. For diabetic dogs insulin can be partly substituted by "anticoman." A. A. E.

Interaction of histamine and nicotine on the intestine. F. BERNHEIM (J. Pharm. Exp. Ther., 1933, **48**, 67—72).—The action of histamine on the isolated guinea-pig intestine is quantitatively antagonised by nicotine. W. O. K.

Carbon dioxide changes in alveolar air and blood-plasma or -serum after subcutaneous histamine injection in man. L. MARTIN and M. MORGENSTERN (J. Lab. Clin. Med., 1932, **17**, 1228—1236).—The CO_2 contents of alveolar air and blood-plasma of individuals with normal gastric secretion are usually increased following injection of histamine, whilst those of individuals whose gastric juice contains no HCl may be increased or decreased. CH. ABS.

Perfusion of the stomach. I. Perfusion with histamine. Y. YOSHIDA. **II. Perfusion with *dl*- and *d*-alanine.** Y. MATSUOKA. **III. Ketonic substances in gastric juice and the fate of *l*-leucine in the stomach wall.** K. IKEBE (J. Biochem. Japan, 1933, **17**, 259—260, 261—266, 267—274, 275—283).—The significance of the constituents of gastric juice is discussed.

I. Perfusion of the isolated dog's stomach (I) with defibrinated blood containing histamine (II) leads to the appearance of (II) in the mucous membrane.

II. Lactic acid is formed in the stomach wall by oxidative deamination of *dl*- or *d*-alanine.

III. Intravenous injection of *l*-leucine (III) produces a higher content of ketonic substances in the gastric juice than does subcutaneous injection of (II). Perfusion of (I) with defibrinated blood containing (III) increases the levels in the blood of $COMe_2$, $CH_2Ac \cdot CO_2H$, and β-hydroxybutyric acid, whilst the NH_2-N level falls to approx. half of the initial val. (III) appears to be catabolised in the stomach wall. F. O. H.

Anaphylaxis in the rabbit. I. Factors concerned in the establishment of maximal hypersensitiveness in rabbits to egg-white and horse-serum. II. Effect of histamine, barium chloride, and adrenaline on unstriped muscle of the guinea-pig and rabbit. III. Sensitisation of rabbits with fowl corpuscles. IV. Simonds' explanation of the different pathologies of acute

anaphylactic shock in different animal species. V. Role of unstriped muscle in acute anaphylaxis in the rabbit. E. F. GROVE (J. Immunol., 1932, **23**, 101—123, 125—138, 139—145, 147—152).—II. Histamine, adrenaline, and $BaCl_2$ may produce a characteristically different effect on the same unstriated muscular tissue in the same animal. CH. ABS.

Action of hashish. H. MARZ and G. ECKHARDI (Arch. exp. Path. Pharm., 1933, **170**, 395—406).—The doses of crude cannabinol and of certain fractions and derivatives required to anæsthetise the rabbit's cornea have been determined. Hashish does not raise the body-temp. in dogs as in the case of men nor does it cause diuresis, whilst the pulse rate is lowered. The hæmoglobin content of the blood falls and other blood-constituents are also affected. W. O. K.

[Toxicity of] *Senecio riddelli*. F. S. BUKEY and R. W. CUNNINGHAM (J. Amer. Pharm. Assoc., 1933, **22**, 399—404).—Observations on horses are recorded. E. H. S.

Cattle poisoning by the feeding of rape cake. C. KUCERA (Int. landw. Rundsch., 1931, **37**, 915; Bied. Zentr., 1933, **A**, **3**, 261—262).—In samples of rape cake having a toxic action on cattle the mustard-oil content was low, but probably there was a deficiency of myrosin. Data are given showing the amounts of mustard oil developed by rations containing rape cake and various myrosin-containing feeding-stuffs. A. G. P.

Character of the dermatitis-producing factor in dietary egg-white as shown by certain chemical treatments. H. T. PARSONS and E. KELLY (J. Biol. Chem., 1933, **100**, 645—652).—The capacity of egg-white (I) to produce a pellagra-like condition in the rat is destroyed by peptic digestion or by mild treatment with aq. HCl. The toxicity persists after denaturation with conc. aq. EtOH. On saturation of the (I) with $(NH_4)_2SO_4$, the toxicity remains in the protein, but is absent from purified ovalbumin. (I) denatured by EtOH and dialysed is as active as before. A. L.

Toxic substances of *Amanita* species. H. A. RAAB and J. RENZ (Z. physiol. Chem., 1933, **216**, 224—228).—Several species of *Amanita*, including *phalloides*, contained no hæmolysin acting on ox-blood. The apparent destruction of the lysin of *A. excelsis* by heating is due to its adsorption on the pptd. protein. The sensitivity to HCl was confirmed. Only *A. phalloides* and *verna* contain the toxin. J. H. B.

Influence of theocin on the action of ephedrine and hypophysin. R. KOHN (Arch. exp. Path. Pharm., 1933, **170**, 432—442).—Theocin (I) does not inhibit the pressor action of ephedrine (II) or of hypophysin (III) to the same extent as that of adrenaline or sympatol. (I) has a paralysing effect on the intestine and uterus. The stimulating action of (III) and (II) on the intestine and uterus is decreased by (I), whilst the inhibiting action of (II) is reinforced by that of (I). W. O. K.

Amino-alcohols. IX. Biological assay of propadrin and ephedrine. T. S. GITHENS (J. Amer. Pharm. Assoc., 1933, **22**, 391—399).—Propadrin is of approx. the same activity as ephedrine and is equally stable in solution. E. H. S.

Comparison of two xanthine diuretics. Theophylline sodium acetate and theobromine sodium salicylate. A. R. BLISS, jun., and R. W. MORRISON (J. Amer. Pharm. Assoc., 1933, **22**, 404—410).—The two drugs are about equal in promptness of action (in rabbits) and both increase the vol. of urine. Uric acid and total solids are also increased. The theobromine compound is the safer of the two and produces no irritation. E. H. S.

Nature of phloridzin diabetes. I. Metabolism of individual organs after administration of phloridzin. E. S. LONDON and N. P. KOTSCHNEFF (Arch. exp. Path. Pharm., 1933, **170**, 384—394).—Phloridzin administered to dogs influences the metabolism of many organs, and the metabolism of fat, protein, and carbohydrate is disturbed. The NH_2- and polypeptide-N of the arterial blood is raised, the NH_2-N being given up by the muscle and retained by kidneys and liver. The fatty acid content of the arterial blood is also raised. Fatty acid is given up by the subcutaneous tissue, intestine, and kidney and is retained by the liver and lungs. Sugar is produced by the liver and taken up by the intestine, muscles, and kidneys. W. O. K.

Effect of intravenous injection of hypertonic glucose. E. VON GYORGY and L. VESZELSZKY (Arch. Kinderheilk., 1932, **98**, 70—74).—Intravenous injection of 4% glucose in amounts equiv. to 0·3—0·4 g. per kg. body-wt. produced in children no glycosuria (I). When 0·5—2·0 g. per kg. was given, (I) was present. In infants (I) was present when the dose exceeded 0·5 g. per kg. NUTR. ABS.

Calcium : magnesium ratio of blood-serum in oxalic acid poisoning. M. JACOBY and H. FRIEDEL (Biochem. Z., 1933, **260**, 451—453).—The serum-Mg content of dogs poisoned with $H_2C_2O_4$ increases, whilst the Ca content and the Ca : Mg ratio decrease. P. W. C.

Pharmacology of acetylsalicylic acid. I. SIMON (Arch. Farm. sperim., 1933, **55**, 151—182).—The min. lethal dose (intravenous) is for rabbits 0·7 g. per kg. of body-wt. The toxicity is greatly diminished by contact of the acid with NaCl in H_2O for a few hr. The acid has an intense hæmolytic action on human or rabbit blood both *in vivo* and *in vitro*. It has a toxic effect on the isolated heart of the frog, but only very large doses produce vaso-constriction. When 1 g. is ingested by a healthy man, 90% passes out in the urine, about one half of this being unchanged. It increases the elimination of uric acid with healthy individuals in purine equilibrium. T. H. P.

Microchemical colour reaction of *m*-dinitrobenzene for the forensic detection of benzene. F. KIRCHHOF (Chem.-Ztg., 1933, **57**, 425—426).—If Peltzer's reaction (B., 1931, 433; this vol., 532) is carried out by adding to a mixture of equal vols. of a solution of the NO_2-compound and 96% EtOH (instead of $COMe_2$) 1 drop of KOH in EtOH, a colour stable for 3—4 hr. is obtained. The reaction is also obtained with technical $PhNO_2$, presumably owing

to the presence of m-$C_6H_4(NO_2)_2$. The chemistry of the reaction is discussed. J. G.

Microchemical reaction of *m*-dinitrobenzene for the forensic detection of benzene. I. PELTZER (Chem.-Ztg., 1933, **57**, 426).—The modified reaction described by Kirchhof (preceding abstract) is not confirmed. A violet colour changing to carmine was obtained by the original method from $PhNO_2$, although it was weaker than that from m-$C_6H_4(NO_2)_2$. J. G.

Toxic action of cations on fibroblasts cultivated *in vitro*. J. VERNE and C. SANNIE (Compt. rend., 1933, **196**, 1246—1247).—Alkali, Ca, and Mg chlorides are not toxic to fibroblasts in Ringer solution containing plasma. NH_4, Sr, Ba, and Mn inhibit growth at concns. between N/120 and N/150. Fe, Pb, Al, U, Be, Y, Pr, La, Dy, and Th are toxic at N/200—1000; Ce, Tl, Ni, Co, Au, Pt, Cu, and Zn at N/1000—5000; Cd and Hg at N/10,000. Plasma-protein protects the fibroblasts from the toxic action of Cu, Pb, and Pt, and, to a smaller degree, from that of U, Cr, Fe, and Au, which are more toxic in the absence of plasma. There is no protective action with Tl, Cd, and Hg; Zn, Ni, and Co are more toxic in the presence than in the absence of plasma. A. C.

Iodine storage in [animal] organs. W. WEBER (Diss., Basle, 1930; Bied. Zentr., 1933, **A**, **3**, 258).—Administration of I, even in considerable quantities, does not increase the I content of the internal organs by > a few mg. per 100 g. Elimination of I is rapid and in some cases amounts in 1 day to 75% of the quantity ingested. A. G. P.

Metabolism of tissues growing in culture. V. Effect of radium on the metabolism of cultures of embryonic kidney tissue. B. E. HOLMES (Biochem. J., 1933, **27**, 391—396).—When kidney tissue in artificial culture is subjected to suitable degrees of irradiation by γ-rays from Ra, the oxidation of carbohydrate (glucose and galactose) is inhibited, although very small doses of radiation may produce a small acceleration. The utilisation of protein with the formation of NH_3 and urea does not appear to be affected by γ-rays. W. O. K.

Mercury poisoning. I. Influence of water and Ringer solution. M. KUSE (Folia Pharmacol. Japon., 1933, **15**, No. 3, 244—258).—Rabbits fed on oats are more resistant to Hg poisoning than those fed on bean jelly. Injection of Ringer solution soon after that of novasurol had a good effect. CH. ABS.

[Arsenical poisoning from] dangerous wall coverings. A. W. VERVLOET (Pharm. Weekblad, 1933, **70**, 578—584).—A case of As poisoning from wall panelling made from sugar-cane fibre is recorded. S. C.

Toxicity of osmium tetroxide. F. R. BRUNOT (J. Ind. Hvg., 1933, **15**, 136—143).—Rabbits exposed to an atm. containing OsO_4 vapour (0·25—1·0 g. in 190 litres) suffer bronchopneumonia, inflammation of the cornea, and ultimately death. Industrial protective measures are indicated. F. O. H.

Chemotherapy of organo-metalloid compounds. S. C. NIYOGY (J. Indian Chem. Soc., 1933, Ray No., 135—140).—Trypanocidal action is discussed. H. B.

Chemotherapy of paludism. Tests on the Java sparrow. E. FOURNEAU, J. TREFOUEL, D. BOVET, and G. BENOIT (Ann. Inst. Pasteur, 1933, **50**, 731—744).—A no. of derivatives of 8-aminoquinoline were tested for parasiticidal activity; the most effective were of the type 8-R-amino-6-methoxyquinoline (R=NEt_2·$[CH_2]_x$; x=4, 5, or 6). These compounds, in which the alkyl group is a straight chain, have a chemotherapeutic index of $\frac{1}{7}$ to $\frac{1}{150}$. Substitution of Me for OMe in the 6-position destroys the activity, whilst OEt is also much less effective. Activity is also reduced when the 8-NH_2 group of quinoline is substituted with a branched-chain alkyl group. All the products tested were much less toxic in the rabbit. P. G. M.

Determination of diffusion coefficients of substances of high mol. wt. Diffusion of catalase. K. ZEILE (Biochem. Z., 1933, **261**, 156; cf. this vol., 425).—Stern claims to have determined the mol. wt. of catalase by the diffusion method. W. McC.

Presence in cells of adipose tissues of a dehydrogenase acting on higher fatty acids. G. QUAGLIARIELLO (Atti R. Accad. Lincei, 1932, [vi], **16**, 552—554).—The adipose tissue of the dog contains a dehydrogenase which acts on higher fatty acids, causing either oxidation of existing double linkings or formation of new double linkings (cf. this vol., 413). T. H. P.

Dehydrogenase of the higher aliphatic acids in the liver. F. P. MAZZA and G. STOLFI (Atti R. Accad. Lincei, 1933, [vi], **17**, 476—480).—Confirmation is obtained of the presence in liver extracts of an enzyme capable of mobilising the H of higher fatty acids (cf. Quagliariello, this vol., 413), the point of attack being the ionised CO_2H of the acid. The enzyme is not found in muscle, kidneys, or pancreas, and differs from succino-dehydrogenase. A mechanism of its action is suggested. T. H. P.

Enzymic dehydrogenation of fat. N. BEREND (Biochem. Z., 1933, **260**, 490—498).—The detection, prep., determination, and properties of an enzyme from ox pancreas which on activation with bile is able to dehydrogenate tristearin, are described. P. W. C.

Glucose-dehydrogenase. Preparation and properties of the enzyme and its co-enzyme. D. C. HARRISON (Biochem. J., 1933, **27**, 382—386).—Dialysed aq. extracts of $COMe_2$-treated liver are mixed with an equal vol. of saturated $(NH_4)_2SO_4$ and the pptd. protein, which contains the enzyme (I), is separated from the mother-liquor in which the co-enzyme (II) remains. (II) is pptd. with protein on complete saturation with $(NH_4)_2SO_4$, the product taken up in H_2O, and the protein removed by heat-coagulation, a solution of (II) being obtained. (II) is not adenyl pyrophosphate. W. O. K.

Chemical nature of the active group in glucose-dehydrogenase. D. C. HARRISON (Proc. Roy. Soc., 1933, **B**, **113**, 150—160).—Xanthine-oxidase (Schardinger) (I) completely inhibits the oxidation of glucose by glucose-dehydrogenase (II). This is shown to be

due to oxidative destruction of (II). Since (I) acts on aldehyde and purine substrates, and the activity of (II) is reversibly inhibited by low concns. of $NaHSO_3$, the activity of (II) may be associated with an aldehyde group. A. C.

Effect of adenosinephosphoric acids on dehydrogenation processes by vegetable and animal enzymes. II. H. J. Deuticke (Pflüger's Archiv, 1932, **230**, 556—562; Chem. Zentr., 1933, i, 622).—Embden's heart nucleotide behaves like adenosinetriphosphoric acid towards methylene-blue in presence of dehydrogenases. A. A. E.

Co-enzyme of lactic acid oxidation. I. Banga and A. Szent-Gyorgyi (Z. physiol. Chem., 1933, **217**, 39—43).—The co-enzyme of lactic acid oxidation was further purified (cf. A., 1932, 1165) by pptn. with phosphotungstic acid followed by prep. of the picrate. It is a monoadenyl nucleotide monophosphate, not identical with muscle-adenylic acid or adenyl pyrophosphate, but possibly with Euler's co-zymase. J. H. B.

Oxidation of lactic and β-hydroxybutyric acids by heart-muscle. I. Banga, K. Laki, and A. Szent-Gyorgyi (Z. physiol. Chem., 1933, **217**, 43—51).—In presence of the dehydrogenase (I) of heart-muscle activated by co-enzyme (II), lactic acid (III) is reversibly oxidised to $AcCO_2H$ (IV). (I), (II), (III), and (IV) form a thermodynamically reversible oxidation system with E_0 −181 mv. β-Hydroxybutyric acid (V) is dehydrogenated to the β-keto-acid (VI). The dehydrogenation of (III) and (V) is activated by the same (II). Oxidation of (V) also forms a reversible system. Except (III), (V), and fructose diphosphate, no acid examined is oxidised by the enzyme. In each case of oxidation the enzyme requires its co-enzyme, but the hydrogenation of (IV) is unaffected by the co-enzyme. J. H. B.

Free energy of lactic acid oxidation. Scale for biological oxidation–reduction potentials. A. Szent-Gyorgyi (Z. physiol. Chem., 1933, **217**, 51—53).—The O_2 electrode is proposed as reference electrode for biological oxidation–reduction potentials. All biological potentials (EO_2) become negative and the sign may be neglected. In the system lactic acid–$AcCO_2H$–activated dehydrogenase EO_2=991 mv. and the change of free energy in the oxidation is 45·7 g.-cal. J. H. B.

Properties of glyoxalase and mechanism of antiglyoxalase action. J. O. Girsavicius (Biochem. Z., 1933, **260**, 278—312).—Complete inhibition of glyoxalase (I) occurs with such very small amounts of pancreatin that the direct action of the latter on BzCHO (II) can be neglected, and the non-enzymic conversion of (II) can thus be determined. A portion of (II) added to liver extract cannot be recovered, the amount being const. for one set of conditions. This loss decreases with increasing dilution of liver extract, but is independent of the concn. of (II). The loss is caused by substances present in both the $CCl_3{\cdot}CO_2H$ ppt. and filtrate, and is partly or wholly due to glutathione (III). Na H maleate buffer inhibits (I) more strongly than does PO_4''', whilst PrOH (optimum concn. 1·8%) activates. A concn. of (II) of 0·2% is optimal for (I) activity. The inhibition of (I) by pancreatin shows an induction period and is antagonised by addition of (III). (III) on incubating with pancreatin and liver extract loses its power to activate (I). P. W. C.

Glyoxalase activity of the red blood-cell. Function of glutathione. M. Jowett and J. H. Quastel (Biochem. J., 1933, **27**, 486—498).—Whilst the high glyoxalase (I) activity of human red blood-corpuscles disappears on lysis of the cells with H_2O, it is completely restored by the addition of glutathione (II) at a similar concn. to that present in the intact cell. The liberation of CO_2, and the change of the I titre of (II) when (II) is mixed with AcCHO (III), and a study of the reaction velocity of (I) in presence of (II), indicate that (II) and (III) combine reversibly. The (I) activity of red blood-cells lysed and intact under anaerobic is > that under aerobic conditions, the effect of O_2 being reversible. Glucose decreases the inhibition by O_2 only on the intact cell. These effects are believed to be due to interference with the equilibrium between oxidised and reduced (II). The (I) activity of red blood-cells is compared with the glycolytic activity of tissues under similar conditions. A. L.

Muscle-glyoxalase. J. Watanabe (J. Biochem. Japan, 1933, **17**, 307—313).—The incomplete transformation of AcCHO (I) into lactic acid (II) by muscle-glyoxalase preps. (A., 1928, 796) is due to creatine in the enzyme solution reacting with a part of (I) and inhibiting its conversion into (II). F. O. H.

Enzymic fission of polysaccharides. I. Specificity of cellulose- and hemicellulose-splitting enzymes. W. Grassmann, R. Stadler, and R. Bender (Annalen, 1933, **502**, 20—40).—The enzyme prep. (I) used (cf. A., 1932, 1062) is obtained from fungi and is purified by dialysis (cf. Karrer *et al.*, A., 1924, i, 471). (I) effects hydrolysis (max. at p_H 4·5) of cellulose, lichenin, and xylan; the crude (I) also hydrolyses hydropectin, mannan, inulin, and chitin. Max. hydrolysis of cellobiose occurs at p_H 4·5—5. The relationships between the amounts of (I) used and the substrate hydrolysed are investigated. Varying amounts of lichenase and xylanase are adsorbed from (I) by Al_2O_3, C, and kaolin. H. B.

Saccharification of starch. A. Tychowski (Przemysł Chem., 1933, **17**, 65—74).—The saccharification of dextrins by malt or barley diastase is due chiefly to α-diastase; the action of a mixture of purified α- and β-diastase is considerably < that of the unpurified malt extract, pointing to the presence of activators in the latter; such activators are also present in aq. extracts of yeast. The concn. of maltose in the reaction mixture does not affect the equilibrium point, the attainment of which depends solely on exhaustion of hydrolysable dextrins. R. T.

Takadiastase. II. Inactivation by heat and reactivation. E. Ohlsson and O. Edfeldt (Bull. Soc. Chim. biol., 1933, **15**, 470—481).—The enzyme is inactivated by heating in various buffer solutions. For max. reactivation, the inactivation must be

carried out rapidly. For a temp. of 90°, a p_H of 5·63—6·03 during deactivation gives max. reactivation at a fixed p_H, whilst for a fixed during inactivation the optimum for reactivation is 7·0. Reactivation occurs only between p_H 5·5 and 8·7.

A. L.

Specificity of α-glucosidase. R. Weidenhagen (Z. physiol. Chem., 1933, **216**, 255—259).—α-Glucosidase from takadiastase or from barley malt hydrolyses α-methylglucoside, α-phenylglucoside, and maltose, again indicating its identity with maltase.

J. H. B.

Action of amylase. E. M. Mystkowski and M. Landau (Biochem. Z., 1933, **261**, 116—127).—At other than the optimum (I) glycine (II) accelerates the action of amylase (III) on starch (IV), the effect being the greater the further the p_H is from (I). (II) does not increase the reaction velocity beyond that observed at (I), nor does it affect the degree of dispersion of (III). $CaCl_2$ counteracts the effect of (II) and also inhibits the degradation of (IV), colloidal factors being probably involved. The action of (II) is probably chemical.

W. McC.

Separation of the two malt-amylases by adsorption. O. Holmbergh (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 4, 6 pp.).—Max. adsorption of a dialysed amylase prep. (from kiln-malt) on starch occurs in 50% EtOH, α-amylase (I) being adsorbed in preference to β-amylase (II) (A., 1930, 955). Adsorption in 30% EtOH followed by washing of the complex with 50% EtOH yields a solution rich in (I), whilst the residual solution is rich in (II). Prolonged adsorption is attended by destruction of the enzymes. Pptn. of malt extract by 30—45% EtOH gives a ppt. rich in (I). Increase of acidity increases the adsorption of amylase, but destruction of the enzyme is accelerated.

F. O. H.

" Sisto-amylase," a natural inhibitor of amylase. T. Chrzaszcz and J. Janicki (Biochem. Z., 1933, **260**, 354—368).—During germination of buckwheat a substance (" sisto-amylase ") (I) is formed in the roots and leaves which paralyses the liquefying, dextrinifying, and saccharifying power of amylase. (I) is insol. in H_2O and EtOH, is fairly sensitive to rise in temp., and is protein-like in character, its action being rapid and due either to adsorption of, or formation of a complex compound with, amylase. (I) is not present in the seeds before germination.

P. W. C.

Reaction velocity-temperature constant of yeast-invertase in supercooled solutions. Z. I. Kertesz.—See this vol., 679.

Maltase. I. Blood-maltase. II. Origin of blood- and urine-maltase. III. Conditions for blood-maltase activity. IV. Maltase of human urine. T. Kokuryo (Japan. J. Med. Sci., Biochem., 1933, **2**, 115—130, 131—159, 161—174, 175—184).—I. Maltose is absent from the blood of the cat, guinea-pig, rabbit, and man; in the horse, sheep, and dog it is almost exclusively associated with the pseudoglobulin fraction, whilst in the pig it is conc. in the albumin and euglobulin fractions.

II. Maltase in the blood and urine has its origin in the pancreas and intestine. The diastase content is unaffected by starvation, but the maltase content is variable.

III. Substitution of 0·5% of NaF for PhMe as preservative increases the hydrolysis of a 2·5% solution of maltose by blood-maltase from 78·6 to 92·9% in 24 hr. A combination of 0·5% NaF and 0·9% NaCl is even more effective. The optimum p_H is 6·6.

IV. The urine-maltase in man has been investigated in health and disease. The occurrence is most frequent in an acid urine (p_H 4·0—4·9) and in cases of tuberculosis.

P. G. M.

Digestion and inactivation of maltase by trypsin and the specificity of maltase. H. Tauber and I. S. Kleiner (J. Gen. Physiol., 1933, **16**, 767—771).—Maltase (I) of saliva and of *B. coli* hydrolyses maltose but not α-methylglucoside or sucrose. (I) is rapidly inactivated by trypsin.

H. G. R.

Glucosulphatase. V. T. Soda and F. Egami (Bull. Chem. Soc. Japan, 1933, **8**, 148—160; cf. this vol., 534).—A modified prep. of a very active, solid glucosulphatase is described. The enzyme acts purely hydrolytically on glucose sulphate, is completely adsorbed by kaolin, but not by $BaSO_4$, $Al(OH)_3$ gel, or C. Its action is inhibited by glucose, galactose, $MgCO_3$, SO_4'', or PO_4''' (very greatly). It is not identical with pheno-sulphatase, which, however, is always present as an impurity.

R. S. C.

Proteolytic enzymes and the coagulation of caseinogen. S. Nishimura (J. Agric. Chem. Soc. Japan, 1932, **8**, 1323—1334).—Caseinogen (I) or milk is coagulated by takadiastase, papain, and pancreatin. When (I) is partly hydrolysed by protease of the tryptase type in presence of Ca, coagulation may occur. With pepsin, coagulation is accompanied by slight hydrolysis.

Ch. Abs.

Fractional enzymic degradation of ovalbumin. H. O. Calvery, E. Waldschmidt-Leitz, and A. Schaffner (Naturwiss., 1933, **21**, 316).—The successive action of pepsin, carboxy- (or amino-)poly- and di-peptidase on ovalbumin liberates 24% of the original total N as NH_2-groups at each stage. Pancreatic proteinase (I), carboxy- (or amino-)poly- and di-peptidase liberate 24, 36, and 12% in successive stages. Pepsin or (I) followed by protaminase (II) liberate 24 and 6%, respectively. Pepsin has no action after (I) and *vice versa*. It is concluded that peptic hydrolysis yields chiefly tripeptides, (I) yields also higher peptides, whilst (II) hydrolysis yields NH_2-groups corresponding with the α-NH_2-groups of arginine, histidine, and lysine.

R. K. C.

Effect of halogen salts on tryptic digestion. W. M. Clifford (Biochem. J., 1933, **27**, 326—331).—The digestion of fish protein by trypsin is depressed by addition of halides of Li, Na, K, and NH_4, in the order $F' > Cl' > I' > Br'$. The depressing action decreases as the concn. falls from 0·5*M* to 0·008*M*, but no accelerating action is observed. In conc. solutions NH_4 salts are the most depressant. NaF is less depressant than KF or NH_4F.

R. K. C.

Action of high pressures on pancreatic juice. J. Basset, M. Lisbonne, and M. A. Machebœuf (Compt. rend., 1933, **196**, 1540—1542).—After sub-

jection to pressures of 11,000—13,500 atm. for 30—40 min., pancreatic juice (I) is activated by kinase and Ca but not by acid; trypsinogen (II) and amylase (III) remain normal, whilst lipase is destroyed. (II) and (III) are partly destroyed at 15,500 atm./45 min. The trypsin content of activated (I) is reduced by 50% after 45 min. at 13,500 atm.; (III) is destroyed. H. B.

Enzymic degradation of diketopiperazine rings. T. ISHIYAMA.—See this vol., 723.

Tyrosinase from the skin of certain black rabbits. C. E. M. PUGH (Biochem. J., 1933, **27**, 476—479).—Mammalian tyrosinase (I) is shown to exist by the fact that tyrosinase extracts can be made from the skins of certain recessive black rabbits. Black Rex rabbits and black rabbits of unknown pedigree failed, however, to yield (I), although pyrocatechol-oxidase was present in all the skins examined. A. L.

Supposed oxidase activity of cobaltammines with particular reference to tyrosinase. C. E. M. PUGH (Biochem. J., 1933, **27**, 480—485).—Examination of a no. of cobaltammines has shown that they cannot imitate the action of tyrosinase. The colour change produced on tyrosine and *p*-cresol by $[3NH_3,CoCl_2,H_2O]Cl$ (I) does not require O_2; that, however, on pyrocatechol by (I), $[4NH_3,CoCl_2]Cl$, and $[3NH_3,Co(NO_3)_3]$ does. A. L.

Concentration of soya-bean urease. New method for the purification of enzymes. J. S. KIRK (J. Biol. Chem., 1933, **100**, 667—670).—Soya-bean urease (I) is completely pptd. from soya-bean extracts by adding excess of antiurease. By making such a pptn. fractionally, (I) has been purified 850 times. A. L.

Urea-splitting enzyme found in gastric juice. L. MARTIN (Bull. Johns Hopkins Hosp., 1933, **52**, 166—172).—Normal gastric juice contains a urease which is active between p_H 1·4 and 8·3 (optimum p_H 8·0). NUTR. ABS.

Thrombase. Preparation and properties. J. MELLANBY (Proc. Roy. Soc., 1933, B, **113**, 93—106).—Prothrombase (A., 1931, 111) undergoes spontaneous transformation into thrombase (I), the prep. and purification of which are described. (I) is a H_2O-sol., slowly dialysable (collodion) protein, destroyed by 0·01*N*-NaOH and 0·01*N*-HCl; 1 mg. coagulates 100 c.c. of oxalated plasma in 30 sec., and intravenous injection of 2 mg. into a 2-kg. rabbit rapidly causes intravascular coagulation and death. The time of coagulation of plasma varies inversely as the amount of (I), and directly as its dilution. When (I) converts fibrinogen into fibrin, the latter adsorbs (I) in proportion to its original concn. It is suggested that (I) is an essential factor in blood coagulation *in vivo*, and that it causes fission of fibrinogen into fibrin and serum-globulin. A. C.

Digestion in Selachians. H. BEAUVALET (Compt. rend., 1933, **196**, 1437—1439).—An extract of the anterior portion of the stomach of *Scyllium canicula* hydrolyses fibrin (I) in acid medium to albumoses and peptones, whilst the extract of the posterior portion hydrolyses (I), starch (II), and olive oil (III) in alkaline media. The pancreatic extract hydrolyses (II) and (III), whilst the liver extract and bile hydrolyse (I) (to peptones), (II), and (III). H. B.

Rate of oxygen utilisation by yeast as related to temperature. T. J. B. STIER (J. Gen. Physiol., 1933, **16**, 815—840).—The ratio of consumption of O_2 to temp. for *S. cerevisiæ* gave a reproducible "temp. characteristic" over a wide range. Plotted according to the Arrhenius equation, the const. μ has the following vals.: 35—30° 8290, 30—15° 12,440±290, 15—3° 19,530±154. The crit. temp. are at 29·0° and 15·7°. A close similarity exists between these vals. for u and those usually obtained for respiratory activities in other organisms. H. G. R.

Yeast growth in absence of oxygen. R. KOCH (Woch. Brau., 1933, **50**, 169—172).—Yeast grown under completely anaerobic conditions in a sealed drop culture containing also a culture of *B. putrificus* to remove O_2 develops initially at a rate slightly less than the aerobic control. After 1—3 days, however, the yeast decays and loses its power of propagation. Vigorous aeration of a fermenting wort produces a yeast of low fermentative power, and thus excessive aeration is as unsuitable as complete lack of O_2. R. H. H.

Fermentation of hexose monophosphate and glyceraldehyde-γ-phosphoric acid. C. V. SMYTHE and W. GERISCHER (Biochem. Z., 1933, **260**, 414—416).—For the same mol. concn. the initial velocity of hexose monophosphate fermentation using Lebedev's extract is at least as great as for glucose. At the corresponding concn. (same C content) the velocity of elimination of CO_2 from glyceraldehyde-γ-phosphoric acid is half that of glucose or hexose phosphate. When the concn. of triose ester is doubled, the total CO_2 formation is the same as for glucose or hexose phosphate, and the velocity of formation is the same. Glyceraldehyde itself is only very slowly fermented by the juice. P. W. C.

Zymophosphate and alcoholic fermentation. B. HVISTENDAHL (Angew. Chem., 1933, **46**, 335—337).—A discussion. The Harden–Young hexose diphosphate is probably a maltose tetraphosphate. W. O. K.

Decomposition of amino-acids by yeast. I—III. M. YAMADA (J. Agric. Chem. Soc. Japan, 1932, **8**, 428—432, 498—505, 506—508).—I. Leucine, glycine, alanine, and α-aminobutyric acid substituted for asparagine in Hayduck solution affect the production of fusel oil (I) by saké yeast (II). Valine and norvaline, but not asparagine, glutamic acid, and $(NH_4)_2SO_4$, produce traces of (I).

II. (I) from a solution containing glucose, *d*-alanine (0·4%), and Hayduck mineral solution fermented by (II) contained *iso*butyl and a little amyl alcohol. When *dl*-alanine was added the same result was obtained and *l*-alanine was recovered. Brewer's yeast afforded only amyl alcohol.

III. Replacement of the asparagine by *dl*-α-aminobutyric acid led with (II) to the formation principally of active amyl alcohol. The recovered NH_2-acid had $[\alpha]_D$ −1·14° (in 20% HCl solution). CH. ABS.

Role of iron in alcoholic fermentation. F. ZUCKERKANDL and L. MESSINER-KLEBERMASS (Biochem. Z., 1933, **261**, 55—63).—αα′-Phenanthroline (I), which forms very stable complex Fe^{II} compounds, reversibly inhibits fermentation by yeast, but does not combine with Fe which is already bound in a complex such as hæmin. αβ-Phenanthroline neither forms such complexes nor inhibits the fermentation. It follows that Fe is necessarily a constituent of holozymase and that it is probably Fe^{II} which is active, whilst Fe in hæmin complexes does not partake in the fermentation. F′ inhibits the fermentation probably by preventing the conversion of Fe^{III} into Fe^{II}. (I) resembles $CH_2I{\cdot}CO_2H$ (II) in the concn. at which it acts, but its activity increases with increasing p_H, whereas the activities of (II) and of F′ then decrease. Two complementary systems of fermentation involving Fe probably exist. One, which catalyses respiration, is sensitive to CN′; the other, which activates fermentation, is relatively insensitive to CN′.
W. McC.

Action of organic compounds on alcoholic fermentation. III. Compounds with condensed nuclei and their reduction products. E. MAMELI and A. MOSSINI (Giorn. Chim. Ind. Appl., 1933, **15**, 161—167; cf. A., 1932, 1288).—Compounds containing condensed nuclei with olefinic linkings in nuclei ($C_{10}H_8$, indene, acenaphthene, phenanthrene, cholesterol) determine or accelerate alcoholic fermentation, whereas the corresponding saturated compounds have little or no effect in this direction. An olefinic linking in such compounds appears to exert less influence on the fermentation when in the nucleus than when in a side-chain, and when the latter has this linking at its extremity the effect increases with the length of the side-chain. T. H. P.

Influence of organic dyes on cell and organ function. III. Fermentation by yeast cells and press juices in presence of organic dyes. F. AXMACHER (Arch. exp. Path. Pharm., 1933, **170**, 476—491).—Certain basic dyes inhibit the fermentation (I) of glucose and fructose by beer- and top yeasts, and have practically no effect on fermentation by cell-free zymase filtrate (II). Certain acid disazo-dyes are without action on (I) by yeast cells but inhibit that by (II). W. O. K.

Action of different kinds of light on glycolysis. E. KEESER (Arch. exp. Path. Pharm., 1933, **170**, 500—509).—Irradiation (red light) for 30 min. of 0·1% glucose solution (buffered with PO_4''') in presence of yeast cells accelerated the decrease in reducing power (I); white, green, or blue light had little effect. Similar results were obtained with fructose as well as in the glycolysis of glucose or fructose by guinea-pig serum. Irradiation (5 hr.) of ox-serum with visible light did not alter its (I) or its content in inorg. P (II), but ultra-violet irradiation increased (I) but did not change (II). Rabbits irradiated with visible light exhibited a reduction in the no. of white blood-corpuscles, but apart from a temporary eosinophilia no change in the differential count occurred.
W. O. K.

Effect of monochromatic light on yeast fermentation. R. MURAKAMI (J. Agric. Chem. Soc. Japan, 1932, **8**, 1237—1247).—In the fermentation of koji extract at 25—28°, EtOH production was max. in red light (> 6200 Å.); that of aldehydes was max. at 3960—5400 Å. Acetal was produced abundantly in white light. The production of volatile acids was max. in the dark, whilst that of non-volatile acids was max. at 3900—5800 Å. CH. ABS.

Relation of inorganic salts to growth and reproduction in *Amœba proteus*. D. M. PACE (Arch. Protistenk., 1933, **79**, 133—145).—A stimulatory effect on reproduction is shown by $FeCl_3$ in concns. $< 0{\cdot}0001N$ and by SO_4'', $< 0{\cdot}00007N$. Above these limits inhibition occurs. The stimulatory action of SiO_3'' was very marked. Increasing concns. of chlorides of Na, K, Ca, and Mg, or of Na_2SO_4 and Na_2SiO_3 have at first a stimulatory and at higher concns. an inhibitory effect. In still greater concns. a second optimum is reached. Similar effects are produced by solutions of mixed salts. The action of salts is ascribed to electrolytic effects rather than to sp. ionic properties. A. G. P.

Aspergillin, the spore pigment of *Aspergillus niger*. II. A. QUILICO and A. DI CAPUA (Atti R. Accad. Lincei, 1933, [vi], **17**, 177—182; cf. this vol., 536).—When extracted with 1—2% aq. NH_3 and pptd. with HCl, aspergillin forms shining black lumps with brown reflexion. EtOH or MeOH dissolves 12—14%, and the residue, containing 0·23—0·26% Fe, has C : H : O = 5 : 4 : 2 and behaves like certain oxypyrrole-blacks when heated (A., 1932, 1266). It contains an OH and forms *Me*, *Et*, and *Bz* derivatives.
T. H. P.

Occurrence of the growth-promotor *B* in urine. V. HARTELIUS (Biochem. Z., 1933, **261**, 76—88; cf. this vol., 189).—The substance *B* which promotes the growth of *A. niger* occurs in human urine (I) in amounts (II) proportional to the solid content. Age, sex, and pregnancy have no effect on (II). *B* is probably derived from food, since (II) increase after meals. (I) also contains a complementary substance (co-*B*), possibly a Zn compound, but in amount insufficient to enable *B* to produce its max. effect (III). (III) is produced by addition of filter-paper ash. *B*, which is insol. in Et_2O and resists destruction by heat or H_2O_2, is probably identical with similar substances previously described. W. McC.

Occurrence of the growth-promotor *B*. V. HARTELIUS (Biochem. Z., 1933, **261**, 89—91).—Foods (*e.g.*, cabbage, potatoes, apples, barley, milk) and also blood contain abundant quantities of *B*, but only small amounts of co-*B*. At least part of the *B* content of urine may therefore come from the food consumed. W. McC.

Biochemistry of filamentous fungi. I. Colouring matters of *Monascus purpureus*, Went. H. NISHIKAWA (J. Agric. Chem. Soc. Japan, 1932, **8**, 1007—1015).—The Et_2O extract afforded *monascorubin* (I), $C_{22}H_{24}O_5$, m.p. 136°, reduced (Pd–$BaSO_4$) to $C_{22}H_{26}O_5$, m.p. 95—96°. (I) with Br gave $C_{21}H_{23}O_3Br_3$, and with H_2O_2 or $KMnO_4$ gave *monascoflavin* (II), $C_{17}H_{22}O_4$, m.p. 145°. Reduction of (II) (Pd–$BaSO_4$) gives *dihydromonascoflavin*, m.p.

120°, phenolic. (II) affords $C_{17}H_{22}O_4Br_2$, m.p. 175—183°, and $C_{17}H_{21}O_4Ac$, amorphous. CH. ABS.

Biochemistry of micro-organisms. XXVII. Production of luteic acid from various sources of carbon by *Penicillium luteum*, Zukal. J. H. BIRKINSHAW and H. RAISTRICK (Biochem. J., 1933, 27, 370—375).—Luteic acid which is produced by *P. luteum* when grown on glucose (A., 1931, 1092) is also produced by this organism when grown on fructose, galactose, mannose, xylose, arabinose, and glycerol as the sole source of C. A similar product is also formed from succinic and from citric acids. W. O. K.

Biochemistry of micro-organisms. XXVIII. Helminthosporin and hydroxy*iso*helminthosporin, metabolic products of the plant pathogen *Helminthosporium gramineum*, Rabenhorst. J. H. V. CHARLES, H. RAISTRICK, R. ROBINSON, and A. R. TODD (Biochem. J., 1933, 27, 499—511).—The dried mycelium of *H. gramineum* responsible for the leaf-stripe disease of barley, when extracted with $CHCl_3$ gives 30% of a mixture of *helminthosporin*, $C_{15}H_{10}O_5$ (I), m.p. 225—226° [Ac_3 derivative (II), m.p. 223—224°], and *hydroxyisohelminthosporin*, $C_{15}H_{10}O_6$ (III), m.p. 238° (Ac_4 derivative, m.p. 234—235°), (I) being 2—3 times in excess of (III). (I) gives on distillation with Zn dust 2-methylanthracene. (II) with CrO_3 in AcOH yields *triacetylhelminthosporic acid*, $C_{21}H_{14}O_{10}$, m.p. 235—236° (*Et* ester, m.p. 205—206°), hydrolysed to *helminthosporic acid* (IV), $C_{15}H_8O_7$, m.p. 359—360° (*Et* ester, m.p. 194—195°). (IV) when heated with quinoline and $CuCr_2O_4$ gives 1 : 4 : 5-*trihydroxyanthraquinone*, m.p. 268—269° (*triacetate*, m.p. 224—225°), also prepared synthetically from 1 : 4 : 5-trichloroanthraquinone with $Ca(OH)_2$ and Cu-bronze. (I) with aq. HNO_3, *d* 1·42, gives a *substance*, m.p. 225—227° (decomp.), probably trinitrohelminthosporin, and also 2 : 4 : 6-trinitro-5-hydroxy-3-methylbenzoic acid. (I) is therefore 2-methyl-4 : 5 : 8-trihydroxyanthraquinone. (III) may be 1 : 8-dihydroxy-2-hydroxymethylanthraquinone. Colour reactions of (I) and (III) are described, and the optimum cultural conditions for the production of the pigments by the fungus are determined. A. L.

Carbon metabolism of *Fusarium oxysporum* on glucose. A. K. ANDERSON, E. L. EVERITT, and P. D. ADAMS (J. Agric. Res., 1933, 46, 473—482).—The principal products of the metabolism of glucose by *F. oxysporum* are CO_2 and EtOH, but this organism, unlike *F. lini*, utilises EtOH as a food source only to a very slight extent. A. G. P.

Comparative growth rates of different strains of *Rhizobium meliloti*. R. H. WALKER and D. A. ANDERSON (Proc. Iowa Acad. Sci., 1931, 38, 333—334).—Organisms which are less efficient in fixing N grow faster in presence of combined N or require it for growth; more efficient organisms grow faster in its absence, or may be inhibited by it. CH. ABS.

Production of gum by certain species of *Rhizobium*. D. A. ANDERSON (Iowa Agric. Exp. Sta. Res. Bull., 1933, No. 158, 27—56).—The amount of gum produced in *Rhizobium* cultures may be calc. from the alteration in viscosity of the medium. An equilibrium is indicated between the amount of gum formed and the quantity of sugar destroyed, irrespective of the size of the inoculum. Gum formation is a normal process in the metabolism of the organism, and increases with the exposed surface area of the cultures. Differences in the viscosity changes in cultures of different species of *Rhizobium* may be due in part to chemical differences in the gums produced. A. G. P.

Conditions governing the production of the plant-growth hormone by *Rhizopus* cultures. K. V. THIMANN and H. E. DOLK (Biol. Zentr., 1933, 53, 149—166).—Aeration of cultures increases the production of the hormone (I). Formation of (I) is either dependent on sp. peptones or is greatly inhibited by impurities in crude peptone. The production of coloured carotenoid substances proceeds approx. parallel with that of (I). Formation of (I) is associated with the formation of sporangia and (I) may be utilised, wholly or in part, by the germinating spores. A. G. P.

Conditions of culture and synthetic power of *Saprolegnia* sp. Carbon, nitrogen, and sulphur nutrition. M. VOLKONSKY (Ann. Inst. Pasteur, 1933, 50, 703—730).—A typical basic culture medium contains NaOAc 0·1, K_2HPO_4 0·1, $MgCl_2$ 0·01%, a trace of $FeCl_3$, and NaOH to p_H 7·0. Muscle peptone supplies complete org. nutriment. AcOH, OH·CHMe·CO_2H, and $AcCO_2H$ are poor sources of C; alanine, cysteine, and histidine are good sources. Glycine, sarcosine, and valine will not support development. In the presence of an unfavourable NH_2-acid a fermentable sugar is essential. Most of the NH_2-acids which are poor sources of C are good sources of N in the presence of glucose. Cysteine is the only source of S which is effective alone; H_2S and AcSH require the presence of glucose in addition. The synthetic power is greatly modified by the composition of the nutrient medium. P. G. M.

Fermentation of glucose by legume bacteria. A. I. VIRTANEN, M. NORDLUND, and E. HOLLO (Suomen Kem., 1933, B, 6, 62).—Fermentation is of the $PrCO_2H$ type. A. G. P.

Methane fermentation of carbohydrates. G. E. SYMONS [with A. M. BUSWELL] (J. Amer. Chem. Soc., 1933, 55, 2028—2036).—The CH_4 fermentation of 45 substances (carbohydrates, alcohols, aldehydes, ketones, acids) is studied. Fermentation is an anaerobic oxidation-reduction reaction involving H_2O and is catalysed by bacteria. CO_2 and H_2 appear to be the primary products and the reaction $CO_2+4H_2 \longrightarrow CH_4+2H_2O$ occurs to some extent; org. acids are probable intermediates. For compounds containing C, H, and O, the general reaction is $C_nH_aO_b+(n-a/4-b/2)H_2O \longrightarrow (n/2-a/8+b/4)CO_2+(n/2+a/8-b/4)CH_4$; an equation is formulated also for compounds containing C, H, O, N, S, and metal. Thermodynamic considerations indicate that if H_2O is the only source of O (other than that in the compound undergoing fermentation), then CH_4 and CO_2 are the expected end-products, since the greatest decrease in free energy occurs with their formation. Reaction

proceeds in the same manner at both 33—35° and 58—60°. H. B.

Hydrogen-producing organism from spoiled cream style maize. J. J. HARRIS (Zentr. Bakt. Par., 1933, 88, II, 54—57).—Swelled tins of maize contained CO_2 31·5, O_2 0·5, H_2 54·0%. A H_2-producing organism (probably *Es. pseudocoscorobal*) was isolated and examined. A. G. P.

Cellulose-decomposing bacteria requiring iron. R. BOJANOVSKY (Zentr. Bakt. Par., 1933, 88, II, 1—16).—Optimum growth of certain aerobic cellulose-decomposing bacteria isolated from soils occurred in media containing 0·0012—0·0026% Fe, supplied as Mohr's salt. On either side of this range development was retarded. A. G. P.

Activity of non-pathogenic bacteria utilising mineral matter in the thermal water of Aix-les-Bains and Aix-Burtscheid. I. A. SCHLOEMER.—See this vol., 691.

Kinetics of intracellular carbohydrate oxidation of *Sarcina lutea*. B. B. RUBENSTEIN (J. Cell. Comp. Physiol., 1932, 2, 27—40).—The O_2 consumption (I) of *S. lutea* in darkness is expressed by the equation for a unimol. reaction. The rate of (I) increases during irradiation at $< 30°$ and decreases at 35° with substrates of low concn. A. G. P.

Fermentative properties of the *Zymosarcina* group. J. SMIT (Ann. Inst. Pasteur, 1933, 50, 675—694).—This group can be regarded as allied to the bacilli of lactic fermentation and is frequently found in the stomach in cases of pyloric ulcer. In the presence of HCl the optimum p_H for growth is 0·9. $H_2C_2O_4$ will not allow growth below p_H 3·4, nor will AcOH below p_H 4·1. *Z. ventriculi* (I) is the only member of the group which contains catalase; none contains tyrosinase or will liquefy gelatin. From a glucose medium (I) produces CO_2 and EtOH, and *Z. maxima* yields CO_2 and BuOH with a trace of EtOH. All of the group are sensitive to antiseptics and to heating at 55°; they remain viable for long periods in the ground in some unknown form. P. G. M.

Oxygen-transporting enzyme of lactic acid bacilli. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1933, 260, 499—501).—The respiration of *B. Delbrücki* behaves both qualitatively (non-inhibition by HCN and CO, formation of H_2O_2, replaceability of O_2 by methylene-blue) and quantitatively in the same way as the oxidation *in vitro* of hexose monophosphate by the yellow oxidation enzyme. Irradiation of aerobic and anaerobic bacterial suspensions gives yellow and colourless solutions, respectively. The respiration of the bacillus is due to O_2 transference by the yellow oxidation enzyme. P. W. C.

Degradation of arginine to citrulline by *Bacillus pyocyaneus*. F. HORN (Z. physiol. Chem., 1933, 216, 244—247).—*B. pyocyaneus*, but not *B. coli*, converts arginine into citrulline. J. H. B.

Bacterial degradation of choline. K. POLLER (Z. physiol. Chem., 1933, 217, 79—82).—By the action of putrefactive organisms on choline NMe_3, EtOH, and probably neurine are formed. Neurine is not attacked. J. H. B.

Cultures and broth filtrates of *Staphylococci*. E. L. BURKY (J. Immunol., 1933, 24, 93—133).—Certain strains of *Staphylococcus* produce independently of hæmolysins in non-protein media, and not as the result of bacterial autolysis or the decomp. of protein constituents of the culture medium, a filterable substance lethal for rabbits $>$ 4 months old. Production of the lethal factor is associated with high initial acidity and high end alkalinity. Immunity in rabbits can be induced by intradermal injection of the toxic filtrates. CH. ABS.

Substance causing *Staphylococcus* food poisoning. E. O. JORDAN and W. BURROWS (Proc. Soc. Exp. Biol. Med., 1933, 30, 448—449).—The active principle is not volatile nor readily dialysable, and is best extracted by Et_2O or $CHCl_3$ from an acid aq. solution. It is not identical with the hæmolytic substance present in many *Staphylococcus* filtrates, and does not produce a skin reaction. NUTR. ABS.

Detection of *B. coli* in water. T. WATABIKI and S. HIMENO (Keijo J. Med., 1933, 4, 73—75).—The H_2O is incubated in a modified U-tube (with the longer limb closed) with neutral-red–lactose bouillon and *B. coli* are recognised by the production of acid, gas, and fluorescence. W. O. K.

Active immunisation of white mice by a non-polysaccharide and probably non-protein derivative of the pneumococcus. L. D. FELTON (J. Immunol., 1932, 23, 405—421).—White mice can be immunised with a fraction sol. in $Cu(OAc)_2$ in presence of saturated aq. NaCl and extractable from the dried Cu-free filtrate with EtOH. The antigen gives a negative Molisch reaction and is free from protein. No pptn. occurs with antipneumococcus horse serum. CH. ABS.

Relationship of the tuberculin proteins of different acid-fast bacilli to sensitisation as indicated by their reactivity in sensitised animals. F. B. SEIBERT and N. MORLEY (J. Immunol., 1933, 24, 149—156).—Tuberculin proteins from 3 different strains of human type tubercle bacilli induced skin-sensitivity approx. parallel to the virulence of the bacilli. On the basis of N content the 3 proteins possessed the same potency for tuberculous guinea-pigs. Proteins made by the same method from cultures of bovine, avian, and timothy bacilli produced skin reactions of decreasing severity in that order in guinea-pigs infected with the human strain. CH. ABS.

Are antiviruses specific? A. BESREDKA (J. Immunol., 1932, 23, 349—360).—Antiviruses are as strictly sp. as the bacteria from which they originate. CH. ABS.

Effect of meat-curing solutions on anaerobic bacteria. I. Sodium chloride. F. W. TANNER and F. L. EVANS (Zentr. Bakt. Par., 1933, 88, II, 44—54).—The tolerance towards NaCl of various strains of *Cl. botulinum* (I), *Cl. putrificum*, and *Cl. sporogenes* are recorded. Toxin production by (I) may occur in salt concns. much $>$ those permitting growth. A. G. P.

Antiseptic activity and chemical constitution of the xylenols and their monohalogen derivatives. G. LOCKEMANN and T. KUNZMANN.—See this vol., 707.

Grinder [for bacteria]. A. HOW (Ind. Eng. Chem. [Anal.], 1933, 5, 219).—The apparatus is designed to break up bacteria without causing degenerative protoplasmic changes. E. S. H.

Effect of liver extract on bile-pigment formation. M. S. KIM (J. Lab. Clin. Med., 1932, **17**, 1223—1227).—Oral administration of therapeutically active liver extracts does not affect the nutritional condition of, or output of bile-pigment from, dogs with biliary fistulas. CH. ABS.

Action of liver extracts on carbohydrate metabolism. K. ZIPF and H. DRINGENBERG (Arch. exp. Path. Pharm., 1933, **170**, 465—475).—Commercial anti-anæmic preps. exert no const. action on the fasting blood-sugar (rabbit), do not affect or only slightly diminish the hyperglycæmia following administration of glucose or fructose, do not alter the blood-sugar level of rabbits during insulin hypoglycæmia, and do not change the body-temp. W. O. K.

Effect of spleen extract on blood-sugar in man. N. FIESSINGER and S. GOTHIE (Compt. rend. Soc. Biol., 1933, **112**, 171—172).—Intravenous injection of a deproteinised, fat-free extract caused a 6—26% fall of blood-sugar in normal and diseased persons. Some cases, notably two splenomegalics, showed a small rise. NUTR. ABS.

Attempted peptic synthesis of insulin. A. M. FISHER and D. A. SCOTT (J. Gen. Physiol., 1933, **16**, 741—755).—A physiologically inactive plastein is obtained by the action of pepsin on the products of peptic hydrolysis of insulin (I). The physiological activity of (I) is not destroyed by repeated freezing and melting of aq. or EtOH solution, nor by incubation with pepsin at 37° and p_H 4. H. G. R.

Extraction of adrenal cortical hormone-like substance from urine. D. PERLA and J. MARMORSTON (Science, 1933, **77**, 432—433).—The substance obtained from urine by the method detailed increases the resistance of adrenalectomised rats to histamine poisoning, but proof that it is identical with the life-prolonging hormone is lacking. L. S. T.

Variations in blood-cholesterol on injection of adrenaline. E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1933, **107**, 1546—1547; Chem. Zentr., 1933, i, 626).—Injection of adrenaline increases the blood-cholesterol in normal, but not in splenectomised, persons. Blood-fat is unaltered. A. A. E.

Effect of the separated fractions of the posterior lobe of the pituitary on the fat content of the liver. A. C. WHITE (J. Pharm. Exp. Ther., 1933, **48**, 89—94).—Administration to rabbits of the oxytocic fraction of posterior pituitary lobe extract produced no apparent change in the liver, whereas a fraction containing predominantly pressor and some melanophore-active substance produced fatty infiltration accompanied by an increase in the Et_2O-extractable material. W. O. K.

Point of attack of pituitrin on antidiuresis and on sodium chloride excretion. Y. FUJIMOTO (Folia Pharmacol. Japon., 1933, **15**, No. 3, 19—26).—The point of attack is the kidney. CH. ABS.

Effect of anterior pituitary extract on blood-lipins. J. M. MUNOZ (Compt. rend. Soc. Biol., 1933, **112**, 502—504).—Repeated injection of anterior pituitary extract produced a marked increase of blood-fatty acid, -cholesterol, and -phospholipin in normal and thyroidectomised dogs. Removal of the pituitary caused a small decrease of these substances in the blood. NUTR. ABS.

Secretion of the thyreotropic hormone of the pituitary. G. KUSCHINSKY (Arch. exp. Path. Pharm., 1933, **170**, 510—533).—The secretion of thyreotropin (the hormone which stimulates secretion of the thyroid) by the anterior lobe of the pituitary is itself inhibited by the presence in the blood stream of high concns. of thyroxine. W. O. K.

Effect of thyroxine on tissue oxidation. G. MYHRMAN (Klin. Woch., 1932, **11**, 2139—2140; Chem. Zentr., 1933, i, 627).—The oxidation process in isolated tissue is not increased by thyroxine (I) in concns. of 10^{-4} to 10^{-14}, neither does injection of (I) into guinea-pigs affect tissue oxidation as determined by the methylene-blue method. A. A. E.

Oxygen consumption of animal tissues following administration of thyroxine. H. VON EULER and R. ENDERLEIN (Biochem. Z., 1933, **261**, 226—234; cf. this vol., 195).—In rats, repeated injection of thyroxine (I) results in a 25% increase in the O_2 consumption (II) of the liver, but the (II) of kidney and muscle seems to be scarcely, if at all, affected. The effect of (I) may also depend, to some extent, on concurrent action of vitamin-*A* or carotene. W. McC.

Preparation, properties, and occurrence of an antithyroid protective substance from blood and tissues. K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1933, **12**, 99—103).—The protective substance (I) is found in the saponifiable fraction of the Et_2O extract of blood and tissues. Fœtal blood contains > adult, human > that of animals. Extracts prepared were 1000 times as active as serum. Ingestion of (I) prevented the rise of basal metabolism and of ketones and loss of liver-glycogen following injection of thyroxine or the thyreotropic hormone of the pituitary, but has no effect on the diminution of liver-glycogen due to hunger. The potency of the serum of patients suffering from Graves' disease is diminished. NUTR. ABS.

Method of estimating the functional activity of the thyroid by means of urine or serum. I. Relations between the thyroid and the other endocrine organs. M. KOH (Keijo J. Med., 1933, 4, 1—24).—The mydriatic action of atropine sulphate (I) on the cat's eye is neutralised by previous incubation at 37° for 2 hr. with the serum or urine of normal rabbits. Thyroidectomy of the rabbit results in a decrease in the (I)-inactivating substance which is partly compensated for in about 2 weeks, whilst administration of thyroxine or implantation of thyroid tissue restores the (I)-inactivating power.

The (I)-inactivating substance exists in human serum and urine, and is increased in Basedow's disease and in pregnancy. Thymectomy, splenectomy, parathyroidectomy, or administration of adrenaline increases the (I)-inactivating substance in rabbit's serum and urine, whilst administration of suprarenal cortex, insulin, folliculin, prolan, or Indian ink, as well as starvation, has the opposite effect. The substance is stable at 80°, but destroyed at 100° and is associated with the serum-albumin. It is considered that the quantity of (I)-inhibiting substance in the serum and urine is a measure of thyroid activity. W. O. K.

Hormones and growth-promoting substances. H. VON EULER, H. HELLSTROM, L. PULKKI, and D. BURSTROM (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 5, 5 pp.).—Apples were extracted with 95% EtOH, the extract was conc. and extracted with Et_2O, and the extract (absorption max. at 284—285 mμ) was washed with dil. alkali, acid, and H_2O and finally dried when it had max. at 265, 274, and 282 mμ. Parallel experiments were made with the leaves and floral parts of begonia (I), alder, hawthorn, and elder. Application of the purification method of Butenandt for œstrin (II) to the extracts of stamens or pistils of (I) gave solutions showing absorption spectra not characterised by any max. and also sensitive to acid or alkali. Comparison of the absorption data with those for (II) (max. at 278 and 289 mμ for EtOH solutions and at 280 mμ for aq. solutions) indicates that some of these plant products resemble (II) in structure and act as precursors for the hormone in the animal body. F. O. H.

Œstrogenic substance from plant material. B. SKARZYŃSKI (Nature, 1933, **131**, 766).—The female flowers of the willow yield a semi-cryst. substance (I) having a strength of 35,000 mouse units of the follicular hormone. Extraction of (I) with 60% EtOH gave crystals identical with trihydroxy-œstrin (from female urine) in respect of mixed m.p., absorption spectra, m.p. of Ac derivatives, but not of biological activity, which was 1000 mouse units per mg. of plant material and 4000 units per mg. of (I). L. S. T.

Sensitivity to light of sexual hormone and chlorophyll. G. KOGEL (Strahlenther., 1932, **45**, 587—589; Chem. Zentr., 1933, i, 625).—Both sexual hormones are sensitive to light; the effect is attributed to reversible reduction of the keto-group by activated H. The photo-sensitivity of chlorophyll *a* and *b* is also attributed to the keto-group. A. A. E.

Effect of sex hormones on creatine metabolism. F. BUHLER (Z. ges. exp. Med., 1933, **86**, 638—649).—About 70% of intravenously injected creatine (I) was excreted unchanged. When testicular (proviron) or ovarian (progynon) hormone was injected on the same day as (I), practically none of the injected (I) appeared in the urine; in children the hormones had no effect on creatinuria, indicating that they act through the corresponding sexual glands, proviron only on testes, since it had no action on the creatinuria of females, and similarly progynon only on the ovaries. A method of determining (I) and creatinine by the step photometer is described. NUTR. ABS.

Effect of prolan on the magnesium balance and on the magnesium content of organs. L. CANNAVÓ and R. INDOVINA (Biochem. Z., 1933, **261**, 45—46; cf. A., 1932, 1068).—Previous findings are confirmed. In rabbits administration of prolan (I) has very little effect on the excretion of Mg, which seems rather to be retained in the blood-plasma. The Mg content of the organs of rabbits receiving (I) and of controls has been determined. W. McC.

Effects observed in mice under continued treatment with œstrin. H. BURROWS, E. C. DODDS, and N. M. KENNAWAY (Nature, 1933, **131**, 801—802).—Male mice treated with superficial applications or subcutaneous injections of œstrin develop hernia. Female mice are kept in œstrus by superficial applications. L. S. T.

New hydrogenation products of the follicular hormone. W. SCHOELLER, E. SCHWENK, and F. HILDEBRANDT (Naturwiss., 1933, **21**, 286).—A vitreous mixture of octahydro-derivatives, $C_{18}H_{30}O_2$, has been obtained which yields cryst. fractions on distillation. The mixture and part of the fractions promote comb-growth (1 capon unit=8—10 mg.). This supports Butenandt's hypothesis that the male hormone is derived from the female hormone by hydrogenation of the aromatic ring. R. K. C.

Vitamin-*A*, thyroxine, and œstrin. H. VON EULER and E. KLUSSMANN (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 1, 6 pp.).—The corpus luteum (I) of cows contains only traces of xanthophyll (II), whilst β-carotene (III) but not vitamin-*A* (IV) is detectable. A growth of 6·5 g. per week is induced in rats by feeding with 0·17 g. of (I) per day. Cow's placenta appears to contain (III), whereas human placenta contains (II). The nerve tissue of rabbits fed with large doses of carotene is free from carotenoids (V). The follicle probably plays some part in the conversion of (V) into (IV) during maturation of the ovum. The antagonism of carotene and (IV) towards thyroxine (A., 1932, 782) is confirmed. Vitamin-*E* concentrates do not promote growth in young rats. F. O. H.

Substances interfering with the antimony trichloride test for vitamin-*A*. R. E. CORBET, H. H. GEISINGER, and H. N. HOLMES (J. Biol. Chem., 1933, **100**, 657—666).—The effect on the $SbCl_3$ colour test (I) for vitamin-*A* (II) of boiling cod-liver oil in $CHCl_3$ solution with certain org. compounds, and the interference produced on (I) by mixing various substances with (II) concentrate, are studied, the max. amounts of the substances investigated which cause no interference being given. Among the most active substances are PhCHO, $CH_2Ph{\cdot}OH$, *cyclo*hexene, benzoquinone, oleic acid, lecithin, C_5H_5N, indole, and terpenes. The extent of the interference depends on the configuration of the mol. and increases with the degree of unsaturation. A. L.

Chinese citrus fruits. I. Vitamin-*A* and -*B* in the peel of Fu Chü (Chinese tangerine). P. P. T. SAH (J. Chinese Chem. Soc., 1933, **1**, 23—28).—Tangerine oil is rich in vitamin-*A*, and the peel also

contains vitamin-*B*. Analyses for moisture, ash, essential oil, and non-volatile oil are recorded. A. A. L.

Vitamins-B_1 and -B_2. B. C. GUHA (J. Indian Chem. Soc., 1933, Ray No., 185—188).—A survey. H. B.

Adsorption of vitamin-B_1 by plant tissue. I. C. D. MILLER and M. G. ABEL (J. Biol. Chem., 1933, **100**, 731—735).—*Brassica chinensis* lost approx. 50% of its original vitamin-B_1 content (I) and the p_H of the leaf extract changed from 6·3 to 4·91 after 3 days' pickling in aq. NaCl. After pickling for the same time, however, in a paste of salt and rice bran, the (I) increased to 4 times the original val., and the p_H became 4·74. A. L.

Glycolytic enzyme in liver of animals with vitamin-*B* deficiency. Effect of iodine in avitaminosis-*B*. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1932, **8**, 756—764).—The livers of white rats fed on synthetic diets without vitamin-*B* (I) contained 10% less glyoxalase than those of normal rats, but the same quantity as those of starved rats. Liver-glycolase is also low in avitaminosis-*B* and starvation. NaI (hypodermic) or thyroxine (oral) checks the antineuritic symptoms produced by a diet free from (I). CH. ABS.

Influence of diet and vitamins on blood-glycolysis. II. Glycolysis and the distribution of free and combined cholesterol. III. Glycolysis in rabbits fed on polished rice. J. CHIWAKI (J. Biochem. Japan, 1933, **17**, 171—213, 215—251).—II. The feeding of cholesterol to rabbits produces a decrease in blood-glycolysis (I) together with increases in the free (II) and combined cholesterol (III), that of (II) being most marked in the plasma and that of (III) in the corpuscles. The amount of vitamin-*B* in the diet does not influence the effect. The decrease in (I) appears to be related to the amount of (III) in the corpuscles. When normal erythrocytes are suspended in serum from cholesterol-fed rabbits, (I) decreases and the corpuscular content of (III) simultaneously increases.

III. Neither (I) nor the blood-sugar level (IV) is appreciably changed by extreme starvation of rabbits. The survival period of starvation averages 18 days, during which period the body-wt. decreases by approx. 37%. Feeding with polished rice produces a marked decrease in (I) of both serum and corpuscles and in (IV). The low (I) is increased by administration of vitamin-*B* concentrate, but not by that of insulin, lecithin, or PO_4''' buffer. F. O. H.

Vitamin-*C*. P. KARRER, H. VON EULER, and H. HELLSTROM (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 6, 6 pp.).—Aq. 1·00, 1·62, 2·00, and 4·00% vitamin-*C* (I) have $[\alpha]_{578}^{20}$ +32·8°, +27·2°, +23·7°, and +18·5°, respectively (cf. A., 1932, 548). Heating at 60—80° has no effect on $[\alpha]$. The Na salt of (I) has $[\alpha]$ +102·2°. Strongly acidic or alkaline solutions of (I) show decreases in $[\alpha]$. The absorption max. for solutions in EtOH is at 245 mμ, in dil. HCl at 245 mμ, and in 0·0002—0·01*N*-NaOH at 263—301 mμ. Vals. for galactose and fructose are 264—275 and 265—295 mμ, respectively. On oxidation of (I) the loss in reducing power is not proportional to the diminution in absorption coeff. Parallel data for methylnornarcotine (A., 1932, 310) are given. Addition of (I), its Na salt, or the $COMe_2$ derivative to hæmin in C_5H_5N and in presence of O_2 produces absorption spectra characteristic of hæmochromogen and finally of green hæmin (A., 1930, 1199). F. O. H.

Vitamin-*C* and sugar derivatives. H. VON EULER and E. KLUSSMANN (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 7, 6 pp.).—Relatively to the adrenal gland (I), the liver is poor in vitamin-*C* (II), whilst the thymus has a comparatively high content. Intraperitoneal injection of (II) into guinea-pigs increases the content of (II) in (I) by approx. 30%, whilst administration of adrenaline considerably lowers it. When tested by the 2 : 6-dichlorophenol-indophenol reagent, normal human urine has an appreciable reduction val. (III) which is not increased by fever. Suspensions of dried or living yeast have a high (III) due to cell constituents. Glucose, on fermentation with yeast, produces derivatives with high (III). F. O. H.

Vitamin-*C* and related substances. H. VON EULER and M. MALM (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 9, 5 pp.).—Heating simple sugars with 0·2*N*-alkali produces a substance (I) which in reducing properties and absorption spectrum resembles vitamin-*C* (II). (I) in PO_4''' buffer decolorises methylene-blue (III), a min. velocity occurring at p_H 7, whilst addition of KCN inhibits the reaction. The decolorisation of (III) by (II) is accelerated by presence of Cu. Suspensions of adrenal gland and of liver also decolorise (III). The mechanism of the reduction and the probable constitution of (I) and (II) are discussed. F. O. H.

Vitamin-*C* and ascorbic acid. V. DEMOLE (Z. physiol. Chem., 1933, **217**, 83—88).—Various preps. of ascorbic acid (I) cured scurvy in guinea-pigs in daily doses of 1 mg. The activity of dehydroascorbic acid was slightly less, but the regenerated (I) was fully active. Methylnornarcotine, dihydroxyphenylalanine, dihydroresorcinol, and alloxantin were inactive. J. H. B.

Oxygen uptake by organs containing vitamin-*C* and by gluco-reductone. H. VON EULER, K. MYRBACK, and H. LARSSON (Z. physiol. Chem., 1933, **217**, 1—22).—The velocity of O_2 uptake by ascorbic acid (I) increases rapidly above p_H 9. Cu, Ni, and Mn catalyse the oxidation. The O_2 uptake is activated by constituents of Ringer's solution (NaCl, $CaCl_2$), also slightly by KCN. The velocity of methylene-blue reduction by (I) shows a min. at 5—6 which is a combined function of the p_H effects of (I) and methylene-blue. The O_2 uptake of gluco-reductone (enol tartronaldehyde) formed by the action of alkali on sugars is of the same order as that of (I). The O_2 uptake of the medulla of the adrenals far exceeds that of the cortex. J. H. B.

Oxidation–reduction potential of ascorbic acid. K. LAKI (Z. physiol. Chem., 1933, **217**, 54—55).—Ascorbic acid (I) does not form a thermodynamically reversible system, *i.e.*, the oxidised form does not show a definite oxidation potential. The potential of 0·2% solution of (I) falls 53 mv. per p_H unit increase. J. H. B.

Vitamin formation in plants. S. VON HAUSEN (Suomen Kem., 1933, **B**, 6, 62).—The carotene (I) and vitamin-*C* (II) contents of plants are largely dependent on the nature of the N source, high vals. for both in sand-cultured peas being associated with N supplied as KNO_3, glutamic or aspartic acid. The proportions of N, P, and K in the nutrient which produce max. plant growth are also optimal for the formation of (I) and (II). With increasing divergence of N, P, and K concns. from the optimum, there was a corresponding decline in (I) and (II) in the plants. Changes in the latter were observed where differences in nutrient ratios were too small to produce differences in plant yields. Excessive N supplies did not affect the formation of (I) and (II), but concns. of P and K above the optimum led to reduced production of these. A. G. P.

Determination of vitamin-*D* by the preventive method. The preventive dose established as curative. P. SCHULTZER (Biochem. J., 1933, **27**, 376—381).—The development of rickets in rats on a rachitic diet, examined radiographically, is inhibited by the addition of sufficient quantities of irradiated ergosterol or of cod-liver oil. The dose of the latter required to prevent completely any signs of rickets is practically the same as the curative dose. W. O. K.

Toxicity of preparations of irradiated ergosterol. M. SCHIEBLICH (Deut. tierarztl. Woch., 1931, **39**, 750; Bied. Zentr., 1933, **A**, **3**, 254—255).—Administration of excessive amounts of irradiated ergosterol causes hypercalcæmia in dogs and hyperphosphatæmia in Herbivoræ. Heating to 200° destroys the antirachitic properties of the prep. without affecting its toxicity. The toxic action is ascribed directly to vitamin-*D* rather than to secondary substances present. A. G. P.

Photo-electric measurement of the penetration of light of various wave-lengths into the sea and the physiological bearing of the results. W. R. G. ATKINS and H. H. POOLE (Phil. Trans., 1933, **B**, 222, 129—164).—The antirachitic portion of the spectrum is reduced to 0·001% of the sub-surface val. at 2·9—5·5 m., and appears inadequate to account for the vitamin-*D* content of zooplankton. J. S. A.

Diet and reproduction. IV. Bipartite nature of vitamin-*E*. G. GRIJNS and E. DINGEMANSE (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 242—248; cf. A., 1929, 359).—Wheat germ is extracted with 40% EtOH in presence of $Ca(OH)_2$ and kieselguhr. The extract contains an Et_2O-sol. fraction which is dissolved in petrol and extracted with 90% EtOH. On evaporating the petrol an oil is obtained which cures sterility in male (but not female) rats on a diet free from vitamin-*E* (I). With (I) concentrates from wheat germ, fractionation with org. solvents yields two fractions, one extractable with 90% EtOH and responsible for fertility in female rats, and the other non-extractable with 90% EtOH and responsible for fertility in male rats. F. O. H.

Carotenoids, vitamin-*E*, and sex hormones. H. VON EULER, B. ZONDEK, and E. KLUSSMANN (Arkiv Kemi, Min., Geol., 1933, **11 B**, No. 2, 5 pp.).—The livers of human fœtuses of 2—7 months contain no carotene (I), but are rich in vitamin-*A* (II). The placenta probably converts (I) into (II). (I) is also found in ox pituitary gland, the anterior lobe containing $2{\cdot}2 \times 10^{-6}$ g. per 278 g. and the posterior lobe $0{\cdot}3 \times 10^{-6}$ g. per 52 g. Wheat oil, xanthophyll, and (I) neither influence the dicœstrous condition of spayed rats nor modify the action of œstrin in such animals. F. O. H.

Root respiration of young coffee plants. E. HERNDLHOFER (Z. Pflanz. Düng., 1933, **29 A**, 290—298).—Respiration increases with light intensity. In darkness respiration is small and tends to maintain a const. rate throughout the day. A. G. P.

Photosynthesis in maize. W. E. LOOMIS and K. H. BURNETT (Proc. Iowa Acad. Sci., 1931, **38**, 150).—The upper leaves of maize are more efficient than the lower; removal of leaves tends to reduce the yield of grain and total dry matter. Removal of the ear produces a stiff stalk and much anthocyanin. The rate of photosynthesis in maize is affected by grain production and therefore depends on soil fertility and genetic factors. CH. ABS.

Carbon dioxide assimilation of leaves of *Oryza sativa*, L. R. H. DASTUR and J. J. CHINOY (Indian J. Agric. Sci., 1932, **2**, 431—454).—Photosynthetic activity rises rapidly soon after transplantation, remains fairly const. in August, is depressed in September, rises again in October, and thereafter falls rapidly. CH. ABS.

Relations between various physiological phenomena in plants and the occurrence of colouring matter in different vegetative organs. IV. Presence of anthocyanin and assimilation in cultivated plants. H. KOSAKA (J. Dept. Agric. Kyushu, 1933, **3**, 251—267).—In plants in which anthocyanins occur in leaves or skins assimilation is stimulated by the presence of the pigment or chromogen. A. G. P.

Organic matter and the life of the green plant. N. A. CLARK (Proc. Iowa Acad. Sci., 1931, **38**, 168—169).—*Lemna major* grows and reproduces in absence of org. matter. Stimulation of reproduction by org. matter does not occur in absence of micro-organisms. CH. ABS.

Mechanism of the action of growth substance of plants. K. V. THIMANN and J. BONNER (Proc. Roy. Soc., 1933, **B**, **113**, 126—149).—The growth produced in decapitated *Avena* coleoptiles is linearly related to the added growth promoter (I). The calc. relation between the amount of (I) entering the cells and the cell-wall material produced shows that (I) is not stoicheiometrically concerned in the formation of cellulose or cell wall, and that (I) does not influence growth by effecting permeability changes in the cell wall. The growth-promoting effect is indirect and one in which the mol. of (I) reproduces its action several times. A. C.

Ash constituents of the apple during the growing season. E. F. HOPKINS and J. H. GOURLEY (Ohio Agric. Exp. Sta. Bull., 1933, No. 519, 30 pp.).—Physiological breakdown of apples is not closely related to either the N or ash content of the fruit.

Deficiency of mineral nutrient in soil is likely to show itself in foliage, top, and root growth and in the character of the fruit. Breakdown is largely affected by seasonal conditions. A. G. P.

Progressive changes in the cuticle of apples during growth and storage. K. S. MARKLEY and and C. E. SANDO (J. Agric. Res., 1933, **46**, 403—412; cf. B., 1931, 775).—A new method for determining cutin is described. The % of cutin in the cuticle at maturity and at the end of storage was > in the earlier stages of growth. Variations in the ratio cutin : total Et_2O extract are considerable, but the average val. for a no. of samples was approx. 56 : 44. The proportions of ursolic acid, oily fraction, and total Et_2O extract in the cuticle are to some extent characteristic of the locality in which the fruit is grown. A. G. P.

Electrical resistance of pear tissue as an index of maturity. J. C. MOORE (Oregon Agric. Exp. Sta. Bull., 1932, No. 300, 18 pp.).—Changes in resistance of pear tissue with advancing maturity are generally similar to those of the customary pressure test and may be utilised in assessing the state of maturity. A. G. P.

Formation of betaine and alkaloids in plants. II. Stachydrine and trigonelline. G. KLEIN and H. LINSER (Planta [Z. wiss. Biol.], 1933, **19**, 366—388; cf. A., 1932, 975).—Variations in the trigonelline (I) content throughout the growth of several plants are recorded. Formation of (I) was not increased by injection of tyrosine, arginine, asparagine, aspartic acid, NH_4NO_3, alanine, leucine, or citrulline. Increases produced by ornithine and proline were confirmed. The action of proline was markedly accentuated by the simultaneous injection of $(CH_2)_6N_4$ as a source of CH_2O. Formation of (I) was also increased by injection of substances intermediate in its formation from NH_2-acids. A. G. P.

Variations in nitrogen content of lilac during forcing. R. QUETEL (Compt. rend., 1933, **196**, 1243—1245).—Exposure of lilac plants to an atm. containing Et_2O during a forcing process lowers the protein-N content (P) of the branches from about 0·95 to 0·75%. The content of sol. N (S) shows no marked variation from about 0·13%. In the buds P remains approx. const., whilst S increases from 0·28 to 1·66%, the ratio P/S at the commencement of flowering being much < in normal plants. A. C.

Assimilation of atmospheric nitrogen by the root fungus of *Coralliorrhiza innata*, R. Br., and of the ephiphytes *Cattleya Bowringiana*, Veit, and *Laelia anceps*, Ldl. H. WOLFE (Jahrb. wiss. Bot., 1933, **77**, 657—684).—The organisms from *Coralliorrhiza* utilise tannin and glucose and those from *Cattleya* and *Laelia*, tannin, glucose, mannose, and arabinose. The presence of N compounds did not influence the fixation of free N. A. G. P.

Relationship between nitrogen assimilation and hydrogen-ion concentration of some fungi. K. RIPPEL (Diss., München, 1930; Bied. Zentr., 1933, **A**, **3**, 223—224).—Interrelationships between [H·], isoelectric point, and N assimilation are established. The organism plays a passive role and possesses no "selective" power in assimilation. NH_2-acids are not preferentially assimilated. A. G. P.

Changes in fibre in a peat bog. E. V. RAKOVSKI and V. A. VUISOTSKAYA (Khim. Tverd. Topl., 1931, **2**, No. 11—12, 80—92).—Vals. for a freshly-cut pine tree (air-dry) and a tree submerged in a peat bog for 1500—2000 years were : ash 0·65—0·68, 0·26—0·77; Et_2O extract 4·57—6·08, 10·19—12·57; EtOH–C_6H_6 extract 0·16—0·05, 0·1; pentosans 6·82—9·78, 5·79—8·45; hemicellulose 15·69—18·41, 11·08—16·31; cellulose 28·25—32·08, 27·73—34·93; lignin 29·05—29·84, 29·12—32·33; OMe (Willstatter) 11·29—13·77, 11·98—12·37; humic substances 0, 19·5%. The solubilities of the fibre and the properties of the resins, composition of extracts, etc. are recorded. CH. ABS.

Role of organic acids in plant metabolism. I. T. A. BENNET-CLARK (New Phytologist, 1933, **32**, 37—71).—Common org. acids present in various species of plants are discussed and methods of analysis noted. Three groups of plants are distinguished, (*a*) plants containing malic acid (I) and having the crassulacean type of acid metabolism [(I) formed from carbohydrate in darkness and reconverted into it in light], (*b*) (I) plants in which $H_2C_2O_4$ gradually replaces (I) with increasing age, (*c*) $H_2C_2O_4$ plants which may be represented as special cases of (*b*) in which the change (I)$\longrightarrow H_2C_2O_4$ is accelerated. Acid production by moulds is not strictly comparable with that by higher plants. A. G. P.

Micro-gas analysis and its application particularly for biological purposes. H. SCHWARZ and F. RAPPAPORT (Mikrochem., 1933, **13**, 235—273).—A summary.

Electrical resistance thermometers as applied to human calorimetry. G. F. SODERSTROM.—See this vol., 689.

Biochemical gravimetric methods. III. Weighing of heat-dried filters and precipitates on the torsion balance. L. JENDRASSIK and A. BOKRETAS (Biochem. Z., 1933, **261**, 106—109).—To prevent absorption of H_2O when using the torsion balance, the material is weighed in the oven or a drying agent ($CaCl_2$) is introduced into the weighing chamber on the balance. W. McC.

Nephelometric determination of cholesterol. W. KRONER (Biochem. Z., 1933, **260**, 403—405).—Details concerning the prep. of MeOH for successfully carrying out the nephelometric determination of cholesterol by the method of Mühlbock, Kaufmann, and Wolff (A., 1932, 666) are given. P. W. C.

Determination of cystine in biological material. F. T. G. PRUNTY (Biochem. J., 1933, **27**, 387—390).—The cystine is reduced with Zn dust in acid solution to cysteine, which is then determined colorimetrically by means of Sullivan's Na β-naphthoquinonesulphonate reagent. The results agree well with those obtained by the method of Folin and Marenzi (A., 1929, 1093). W. O. K.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1933.

General, Physical, and Inorganic Chemistry.

Intensity of spectral lines in the glow discharge of "mottled" hydrogen. A. GUNTHER-SCHULZE and H. BETZ (Z. Physik, 1933, **83**, 152—163).—A study of the relative intensity of H and Hg lines in highly dried H_2 containing traces of Hg. A. B. D. C.

Intensity ratio of Balmer to Paschen lines. II. L. S. ORNSTEIN and H. C. BURGER (Z. Physik, 1933, **83**, 177—178).—Earlier results were confirmed (cf. A., 1930, 1073); different sources may give different vals. A. B. D. C.

Spectroscopic search for H^3 in concentrated H^2. G. N. LEWIS and F. H. SPEDDING (Physical Rev., 1933, [ii], **43**, 964—966).—The proportion of H^3 in ordinary H_2, if present at all, must be < 1 in 6×10^6. The relative fine structure resolution of H^1 and H^2 is shown. N. M. B.

Theory of hyperfine structure. E. FERMI and E. SEGRE (Z. Physik, 1933, **82**, 729—749).—Experimentally observed hyperfine structure of Li, Na, Cu, Ga, Rb, Cd, In, Cs, Ba, Au, Hg, Tl, Pb, and Bi is shown to agree in general with the hypothesis of magnetic coupling of nuclear and electron spin, although lesser perturbations due to other phenomena may have to be included. A. B. D. C.

Anomalous dispersion of lithium vapour. A. N. FILIPPOV (J. Exp. Theor. Phys., Russia, 1932, **2**, 24—41).—Vals. for the first three doublets agree with those calc. by wave-mechanics. CH. ABS.

Long-wave arc spectra of alkalis and alkaline earths. W. F. MEGGERS (Bur. Stand. J. Res., 1933, **10**, 669—684).—Using plates sensitised with meso- and xeno-cyanine the arc spectra of alkali metals have been photographed in the region 8500—11,800 Å. and of the alkaline-earth metals in the range 6500—11,300 Å. Almost all lines are accounted for as combinations of identified spectral terms. A new system of band heads observed with Ca is attributed to CaO. J. W. S.

Excitation of band systems. I. L. S. ORNSTEIN and G. O. LANGSTROTH (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 384—390).—As a preliminary to formulating a theory of excitation for band systems on assumptions similar to those of the Frank–Condon emission theory the relative intensities of the bands $0 \longrightarrow 2$ (λ 3805), $1 \longrightarrow 3$ (λ 3755), and $2 \longrightarrow 4$ (λ 3710) of the second positive group of N were determined at electron voltages of range 14—25 volts. N. M. B.

Absorption of oxygen in the ultra-violet. L. HERMAN (Compt. rend., 1933, **196**, 1877—1880).—The triplets in the O_2 spectrum between λ 2750 and 2400 Å. consist of numerous lines made up of several superposed spectra, one of which is clearly a family of vibration–rotation bands, best observed at 5—25 atm. pressure. It includes P and R branches. The initial moment of inertia is $0{\cdot}9 \times 10^{-40}$ g.-cm.^{2} (cf. this vol., 5). C. A. S.

Intensity variations in some fluorescence series of sodium. W. G. BROWN (Z. Physik, 1933, **82**, 768—775).—The intensities of Na_2 fluorescence series were observed for excitation by the Cd lines at 4800 and 5086 Å., and the results are discussed theoretically. A. B. D. C.

Unplaced terms in the alkaline-earth spectra. H. C. BRINKMAN (Z. Physik, 1933, **83**, 259—265).—Russell and Saunders' x terms in the spectra of Ca, Sr, and Ba are classified. A. B. D. C.

Zeeman effect in the arc spectrum of nickel. H. H. MARVIN and A. E. BARAGAR (Physical Rev., 1933, [ii], **43**, 973—979).—Data for Zeeman patterns for 113 lines in the region λ 5500—3000 are tabulated, and g factors for 61 terms are calc. Applicability of the q-sum rule is discussed. N. M. B.

Stark effect in the krypton spectrum. N. RYDE (Z. Physik, 1933, **83**, 354—370). A. B. D. C.

Isotope displacement. H. SCHULER and H. WESTMEYER (Z. Physik, 1933, **82**, 685—689).—The hyperfine structure of Cd II is investigated. A. B. D. C.

Heat of dissociation of the cadmium molecule from thermo-optical measurements. H. KUHN and S. ARRHENIUS (Z. Physik, 1933, **82**, 716—722).—The heat of dissociation of Cd_2 is $2{\cdot}0 \pm 0{\cdot}5$ volts. A. B. D. C.

Magnetic quenching of tellurium fluorescence. R. SMOLUCHOWSKI (Nature, 1933, **131**, 914).—The magnetic quenching of fluorescence has been established in the case of Te. L. S. T.

Quenching of fluorescence and transfer of energy in iodine vapour. M. A. ELYASHEVICH (J. Exp. Theor. Phys., Russia, 1932, **2**, 59—73).—The fluorescence spectrum of I excited by 5461 Å. in presence of H_2 shows the transitions $v'-26 \longrightarrow 25$, 24, 27, 28. The collision radius is 6 times $>$ the gas-kinetic val., and in presence of N_2 is 7 times greater. With N_2, change of rotational energy is shown by a continuous background. CH. ABS.

Spectrum of barium hydride. A. SCHAAFSMA (Arch. Néerland., 1933, [iii*a*], **14**, 1—52).—An extension of previous work (cf. A., 1932, 104, 315). Complete wave-lengths, intensities, wave-nos., and classifications of the red and green bands are tabulated. N. M. B.

Spark spectrum of barium. E. RASMUSSEN (Z. Physik, 1933, **83**, 404—411). A. B. D. C.

Anomalies in hyperfine structure. S. GOUDSMIT and R. F. BACHER (Physical Rev., 1933, [ii], **43**, 894—899).—Deviations from the interval rule in the hyperfine structure of two of the energy states in Hg, and the forbidden line Hg I λ 2967·5 and its hyperfine structure, are explained by perturbations. The hyperfine structure of the $3s\,4f$ levels in ionised Al is corr. N. M. B.

Excitation function of the mercury resonance line 2537. L. S. ORNSTEIN, H. LINDEMAN, and J. OLDEMAN (Z. Physik, 1933, **83**, 171—176).—The intensity of the line was obtained for each of three sources: (*a*) direct excitation, (*b*) excitation of higher levels, and (*c*) ionisation. A. B. D. C.

Physical analysis of Wolf–Rayet spectra. (MISS) C. H. PAYNE (Proc. Nat. Acad. Sci., 1933, **19**, 492—494).—Recent work on the analysis of the spectra of stripped lighter atoms provides the identification of the lines of the Wolf–Rayet stars. Atoms indicated are H, He, C, N, O, Al, Si, P, and S. The probable min. temp. is 100,000°. N. M. B.

Hyperfine structures. H. SCHULER and H. WESTMEYER (Z. Physik, 1933, **83**, 270—274).—Hyperfine lines observed by several authors are discussed; ghosts appear with Lummer plates giving erroneous results. A. B. D. C.

Hyperfine structures. B. VENKATESACHAR (Z. Physik, 1933, **83**, 275—276; cf. preceding abstract). A. B. D. C.

Hyperfine structure and the polarisation of resonance radiation. II. Magnetic depolarisation and the determination of mean lives. A. C. G. MITCHELL (Physical Rev., 1933, [ii], **43**, 887—893; cf. A., 1932, 891).—Mathematical. N. M. B.

Absorption measurements and other optical investigations of radiating substances by the intermittent light method. F. G. HOUTERMANS (Z. Physik, 1933, **83**, 19—27).—A photo-cell connected to a valve relay that responds only to a given frequency may be used for absorption measurements of emitting systems; the source for the absorption measurements emits with the given frequency, whilst the steady emission of an excited system produces no effect. A. B. D. C.

Emission of light by a mixture of gases and vapours in the positive column of a luminous discharge. W. UYTERHOEVEN, J. BRUYNES, and C. VERBURG (Compt. rend., 1933, **196**, 1653—1655).—The compound effect produced by the passage of d.c. through a tube of varying diam. containing several gases or vapours, *e.g.*, Ne and Hg, and enclosing the whole in a ground-glass globe, is obtainable directly by passing a.c. of 50 ~ through a tube of const. diam. containing a rare gas, Na, and Hg. C. A. S.

Spectrum of the night sky. J. DUFAY (J. Phys. Radium, 1933, [vii], **4**, 221—235).—Data are given for the region 3900—6315 Å. In the blue and violet a bright band and line spectrum was observed in Sept. and Oct., becoming prominent in Nov., and differing from the polar aurora by the feeble intensity of the N bands, and the presence of bands and lines of unknown origin. Lines 5893 and 6315 Å., and new weak lines in the green were observed. N. M. B.

Measurements of intensity of Compton modified radiation by means of filters. E. O. WOLLAN (Physical Rev., 1933, [ii], **43**, 955—963).—A new method of measuring the intensity ratio of modified to unmodified scattering by gases or solids, using a triple balanced filter, is described. Data for O_2, N_2, and A and for several solid elements and compounds are given. N. M. B.

Structure of *K* spectrum of very light atoms. A. HAUTOT (Compt. rend., 1933, **196**, 1727—1729).—Wolfe's modification of Langer's scheme (cf. this vol., 332) for calculating the satellites in the *K* spectrum of K applies satisfactorily to C, N, O, and F, but not to B and Be (cf. this vol., 201, 440). C. A. S.

Influence of lattice type and temperature on the fine structure of *X*-ray absorption edges. II. J. VELDKAMP (Z. Physik, 1933, **82**, 776—748).—Ni–Fe alloys gave fine structures identical with that of Ni. Ca gave a structure analogous to Ni and Cu. The Ni fine structure showed no discontinuity at the Curie point. These observations agree with Kronig's theory. A. B. D. C.

***X*-Ray emission spectra and chemical binding. II. Investigation of the $K\alpha_1\alpha_2$ doublet of chlorine.** O. LUNDQUIST (Z. Physik, 1933, **83**, 85—91).—The doublet separation remained unchanged in all compounds, but although chlorides gave no displacement of the doublet, chlorates gave a shift of 2·19 and perchlorates one of 2·93 X towards shorter wave-lengths. A. B. D. C.

Probabilities of *K*-electron ionisation of silver by cathode rays. D. L. WEBSTER, W. W. HANSEN, and F. B. DUVENECK (Physical Rev., 1933, [ii], **43**, 839—858).—Ratios of probabilities of *K* ionisation at various voltages are found as ratios of corr. *K* line intensities. N. M. B.

Excitation of characteristic *X*-rays by canal-ray collision. C. GERTHSEN (Physikal. Z., 1933, **34**, 478—482).—Experiments are described indicating the excitation of the *K* radiation of Al and Mg, and the *L* radiation of Se by protons of energy 30—150 kv. A. J. M.

Ionisation of air and hydrogen in high-frequency discharge. T. V. IONESCU and (MME.) I. MIHUL (Compt. rend., 1933, **196**, 1873—1875; cf. this vol., 548).—Appearances are described in a tube 1 m. × 4 cm., with external electrodes connected with an oscillator and subjected to a magnetic field parallel to the tube. Ionisation is plotted against strength of magnetic field for pressures of H_2 and of air of

0·001, 0·1, and 0·2 mm. Hg. The phenomena are explained by variation with pressure of the no. and arrangement of electrons associated with mols., their period of vibration, and resonance. C. A. S.

Dissociation of excited diatomic molecules by external perturbations. C. ZEUER (Proc. Roy. Soc., 1933, **A**, **140**, 660—668).—Mathematical. Electric fields of 20,000 volts cm.$^{-1}$ have a marked dissociating effect on excited states which are crossed by appropriate repulsive states. All types of transitions are readily induced by collisions. L. L. B.

Ionisation of inert gases by X-rays. W. WILHELMY (Z. Physik, 1933, **83**, 341—350).—The mean energy per ion pair produced is 27 electron volts for Ne and 24·6 for A; the vals. are independent of the ionising wave-length. A. B. D. C.

Possible common cause of sub-electronic discharges and electrophotophoresis. K. SITTE (Physikal. Z., 1933, **34**, 473—478).—It is suggested that elementary discharges involving small particles may be satisfactorily explained if it is assumed that the particles are surrounded by a space-charge cloud of electrons, gaseous ions, or perhaps ions of the material itself, which increases their mobility, and leads to false vals. for their charge. The hypothesis provides an explanation of electrophotophoresis and the effects associated with it. A. J. M.

Electron-nebula ratio. J. D. M. SMITH (Chem. and Ind., 1933, 364—365). D. R. D.

Theory of the electron microscope. W. GLASER (Z. Physik, 1933, **83**, 104—122). A. B. D. C.

Images obtained in the electron microscope of foils transmitting the electrons. B. VON BORRIES and E. RUSKA (Z. Physik, 1933, **83**, 187—193).—Images obtained include absorption, velocity loss, and diffusion of the electrons while passing through the foil. A. B. D. C.

Gas concentration of electron beams. O. SCHERZER (Z. Physik, 1933, **82**, 697—708).—Theoretical. A. B. D. C.

Electron release in cathode spots of an arc discharge. F. LUDI (Z. Physik, 1933, **82**, 815—832).—Current theories fail to explain the release of electrons from cathode spots, and an attempt is made to explain it by collisions of the second kind of multiply-charged positive ions. A. B. D. C.

Elastic electron scattering in neon. A. L. HUGHES and J. H. MCMILLEN (Physical Rev., 1933, [ii], **43**, 875—882).—The angle distribution of electrons of energies 10—800 volts scattered by Ne atoms was measured for the range 7—150°. The elastic cross section calc. from the scattering coeffs. for the voltage range is compared with direct absorption measurements. Formulæ for the scattering curves are discovered. N. M. B.

Fine structure of electron diffraction beams from a gold crystal and from a silver film on a gold crystal. H. E. FARNSWORTH (Physical Rev., 1933, [ii], **43**, 900—906; cf. A., 1932, 789).—Differences in the positions, structure, and relative intensities of the corresponding beams from Ag and Au crystals were found. Results for a thin Ag film on a Au crystal are, in general, similar to those for a single Ag crystal. Since no beams characteristic of a surface gas lattice on the Au were observed, the gas layer must be non-cryst. N. M. B.

Application of electron diffraction to detection of impurities in canal rays. H. RAETHER (Physikal. Z., 1933, **34**, 492—493).—The presence of C in canal rays in an experiment was proved by this method. A. J. M.

Secondary emission of electrons from metals. P. L. COPELAND (Proc. Iowa Acad. Sci., 1931, **38**, 215). CH. ABS.

Collision of slow electrons with atoms. III. Excitation and ionisation of helium by electrons of moderate velocity. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1933, **A**, **140**, 613—636).—The range of validity of Born's method of approximation has been determined by extending the calculations to higher velocities of impact (up to 400 volts) (cf. A., 1931, 403). Ionising collisions are also considered. The comparison of calc. and observed results is discussed, and Born's approximation is found to be valid for electrons with energies $>$ 200 volts. L. L. B.

Electron polarisation. R. WHIDDINGTON (Nature, 1933, **131**, 908).—Magnetic spectra of 300-volt electrons making inelastic impacts in He are reproduced. They suggest that inelastically scattered electrons from He are polarised. L. S. T.

Polarisation of the light emitted from the particles in movement and at rest in the canal rays of hydrogen. W. A. LUB (Arch. Neerland., 1933, [iii*a*], **14**, 118—164).—The polarisation measured previously is due principally to the particles in movement, but the light emitted by stationary particles is also polarised. The polarisation decreases with increase in velocity of the positive rays. Besides the indirect influence exercised by the accelerating potential on the ratio between the intensities of the radiation from the particles in movement and from those at rest, the ratio between light polarised parallel and that polarised perpendicular is also changed. J. W. S.

Recoil atoms in gaseous media: electronic affinity. L. GOLDSTEIN (Compt. rend., 1933, **196**, 1792—1793).—The conclusion that the electron affinity of the gaseous medium influences the yield of activation at a cathode (cf. A., 1931, 889) is confirmed by determining the yields for a mixture of He and O_2 containing 0·1% O_2 at pressures of 51—253 mm. Hg and of mixtures of Ne and O_2 at 440 mm., the partial pressure of O_2 varying from 0 to 0·5. The variations are attributed to the probability of an ionised recoil atom capturing one or more electrons, and so becoming neutralised, being less the greater is the electronic affinity of the gaseous medium. C. A. S.

At. wt. of tellurium. Analysis of tellurium tetrabromide. O. HÖNIGSCHMID, R. SACHTLEBEN, and K. WINTERSBERGER (Z. anorg. Chem., 1933, **212**, 242—256).—From the ratios $TeBr_4$: 4Ag : 4AgBr the val. Te=127·61 (Ag=107·880), with a mean deviation of 0·01, has been found. F. L. U.

At. wt. of ytterbium. Analysis of ytterbium trichloride. O. HONIGSCHMID and H. STRIEBEL (Z. anorg. Chem., 1933, **212**, 385—392).—Determination of the ratio $YbCl_3 : 3Ag : 3AgCl$ gives Yb=173·04 (Ag=107·880, Cl=35·457). Anhyd. $YbCl_3$ has *d* 3·781. F. L. U.

Isotopic constitution and at. wt. of lead from different sources. F. W. ASTON (Proc. Roy. Soc., 1933, **A**, **140**, 535—543; cf. A., 1932, 554).—Ordinary Pb and seven specimens of radiogenic Pb have been analysed with the mass-spectrograph by means of their volatile Mo compounds, and the abundance of their isotopes has been estimated by means of photometry. Corrections have been made for the presence of small quantities of hydride. No isotopes other than 206, 207, and 208 were found. The abnormally low val. reported for Pb from Great Bear Lake has not been supported. L. L. B.

Radioactivity of samarium. G. VON HEVESY, M. PAHL, and R. HOSEMANN (Z. Physik, 1933, **83**, 43—54).—α-Rays of short range were detected. A. B. D. C.

Mesothorium II; element 87. G. GUÉBEN (Ann. Soc. Sci. Bruxelles, 1933, **B**, **53**, 115—118; cf. A., 1932, 707).—Ms II gives an α-particle of range 3·03 cm. at 15°, and forms an isotope of element 87. H. J. E.

α-Radiation of radiothorium and its derivatives. S. ROSENBLUM and (MLLE.) C. CHAMIÉ (Compt. rend., 1933, **196**, 1663—1664; cf. A., 1932, 555).—By working with a prep. free from Po it is shown that the weak ray α_x 1·594(2) probably belongs to Po. Redetermination of the rays of Rd-Th, Tn, Th-*X*, and Th-*A* gave results in close agreement with recent determinations (cf. this vol., 443). C. A. S.

Determination of the stopping power of gases for α-particles of various speeds by the scintillation method. W. MUND and P. C. CAPRON (Bull. Soc. chim. Belg., 1933, **42**, 163—171).—The stopping powers of H_2, NH_3, and H_2S for α-particles of ranges (in air) of from 0 to 4·54 cm. vary from 0·206 to 0·265, 0·767 to 0·963, and 1·093 to 1·117, respectively, according to speed. H. F. G.

Ionisation produced by α-particles passing through the thin walls of a small sphere. P. C. CAPRON and G. ROGMANS (Bull. Soc. chim. Belg., 1933, **42**, 172—175).—A method of calculation is given, based on Bragg's data, which obviates errors introduced by the use of Geiger's law. H. F. G.

Nuclear diffusion of γ-rays. R. STAHEL and H. KETELAAR (Compt. rend., 1933, **196**, 1664—1666).—γ-Radiation from Ra fell on thick and thin screens of Pb, Fe, Sn, and Al and the radiation diffused in directions of 80—135° was measured. This consists in varying proportions of radiation due to the Compton effect (*a*), and radiation of nuclear origin (*b*). Thick and thin screens give respectively a max. of diffused radiation rich in hard components, and radiation approx. unaltered in composition. A thick screen of Pb gives 65% of (*b*). Fe and Sn yield smaller proportions of (*b*); Al gives only (*a*). With thin screens Pb gives the components of (*b*); results with Al agree with the Klein–Nishina formula. Deductions as to the coeff. of photo-electric absorption agree with other results (cf. A., 1931, 1346; 1932, 671, 791). C. A. S.

Absorption effects of γ-rays. G. GUEBEN and L. HERMANS (Compt. rend., 1933, **196**, 1789—1791).—γ-Rays from Ra after passing through 5 cm. Pb were passed through varying thickness of Pb, Al, or Pb and Al together, and the absorption was measured. Comparing electronically equiv. thicknesses, the additional metal, if $\geq$ 0·1 cm. thick, caused an increase in ionisation (for Al < for Pb), followed, with increasing thicknesses, by a more rapid decrease than in the absence of such addition, but always tending to the same limit. The behaviour resembles that of cosmic radiation (cf. A., 1932, 5). C. A. S.

Excitation of positive electrons by γ-rays from thorium-*C*″. L. MEITNER and K. PHILIPP (Naturwiss., 1933, **21**, 468).—Positive electrons were produced by the interaction of hard γ-rays on the at. nucleus of Pb. A. J. M.

Secondary effects in ionisation by hard γ-rays. E. J. WORKMAN (Physical Rev., 1933, [ii], **43**, 859—870).—The dependence of the ionisation produced in a counting chamber by γ-rays on the at. nature and thickness of the chamber walls, and on the nature, amount, and distribution of matter in the neighbourhood of the chamber was investigated with regard to the secondary β-particles (the effective ionising agencies), and the effects of nuclear scattering of the β-particles. N. M. B.

Positive electrons of transmutation. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1933, **196**, 1885—1887; cf. this vol., 658).—When α-particles from Po fall on Al, positive electrons are emitted, equally backwards or forwards, but none when such particles fall on Ag, Li, or paraffin. Such positive electrons have as a rule an energy $< 1{\cdot}6\times10^6$ ev., but a few have $2—3\times10^6$ ev. The energy of the negative electrons from Al and other radiators is usually $< 0{\cdot}7\times10^6$ ev., and such electrons are probably to be ascribed to the γ-radiation of Po. The emission of positive electrons may be due to the emission under the action of the α-particles of a neutron and positive electron separately. C. A. S.

Proton emission from aluminium excited by α-rays from radium-*C* and thorium-*C*. O. HAXEL (Z. Physik, 1933, **83**, 323—337). A. B. D. C.

Neutron, proton, and positron. N. THON (Nature, 1933, **131**, 878).—If the neutron (I) is a proton (II)+electron, then H atoms should show a strong tendency to change spontaneously into (I) and the no. of (I) in the universe ought to be much > is generally assumed. (II) should be regarded as (I)+positron (III), and (I) as an elementary material corpuscle without electric charges. (II) could then dissociate into (I)+(III). The small no. of (I) and (III) in the universe would then be explained by the fact that the dissociation of (II) requires a large quantity of energy and is not spontaneous. L. S. T.

Ionisation of gases by neutrons. T. W. BONNER (Physical Rev., 1933, [ii], **43**, 871—874).—The ionis-

ation currents produced in H_2, He, N_2, CH_4, C_2H_2, and A by the neutrons from Be were measured for the gas pressure range 5—80 atm., and the relative diameters of at. nuclei were calc. therefrom. Pressure–ionisation curves for neutrons differ from those for γ-rays. N. M. B.

Scattering of neutrons by protons. E. WIGNER (Z. Physik, 1933, **83**, 253—258).—Theoretical. A. B. D. C.

Investigation of cosmic rays in the Wilson chamber. P. KUNZE (Z. Physik, 1933, **83**, 1—18).—Paths due to cosmic rays and their bursts under a magnetic field in Wilson chambers are discussed in relation to curvature, ionisation, and distribution in space. Observed multiple paths may be due to secondary electrons from solid walls, to nuclear explosions, or to double collisions. A. B. D. C.

Secondary effects of cosmic rays. E. FUNFER (Z. Physik, 1933, **83**, 92—103).—Range and absorption coeffs. were determined for secondary radiation excited by cosmic rays in Pb, Fe, and Al. A. B. D. C.

Analysis of absorption curve of cosmic rays. E. LENZ (Z. Physik, 1933, **83**, 194—213).—A method for obtaining the components of cosmic rays from absorption curves is developed. Five components are deduced from known data. A. B. D. C.

Absorption of cosmic rays. B. GROSS (Z. Physik, 1933, **83**, 214—221).—A method is given for deducing radiation incident in one direction from that incident in all directions. A. B. D. C.

Statistical averages for perturbed systems. R. SERBER (Physical Rev., 1933, [ii], **43**, 1011—1021).—Mathematical. N. M. B.

Atomic distances for closest packing. B. N. SEN (Z. anorg. Chem., 1933, **212**, 410—414).—Interat. distances calc. for 11 elements by the formula $D=P/Vd^{K/n}$ (P=parachor, V=ionisation potential, d=at. diameter, n—valency, $K=1{\cdot}58$) agree with observations. F. L. U.

Spectrum of the OH molecule: a new (2,2) band; satellite series in λ 3122; Λ-type doubling and electronic spin doubling. D. H. DAWSON and H. L. JOHNSTON (Physical Rev., 1933, [ii], **43**, 980—991; cf. this vol., 445).—Approx. 400 lines of the (0,0) and (1′,0″) bands were observed; data are given for 120 new lines, all but 18 being assigned. A new (2,2) band with its principal head at λ 3185 is assigned. The R and satellite branches of the λ 3122 band, the R branches of the λ 2875 band, and extensions of the λλ 3064, 2811, and 2875 bands are given. Λ and spin doublets are obtained. N. M. B.

Excitation potential of the λ 2883 and 2895 bands of carbon dioxide. A. S. ROY and O. S. DUFFENDACK (Proc. Nat. Acad. Sci., 1933, **19**, 497—503).—Excitation of the CO_2 emission spectrum in presence of excess of O_2 and a trace of CO or C shows that the λ 2883 and 2895 bands are due to the CO_2^+ ion, with excitation potential approx. 18·7 volts, and that the rest of the spectrum is due to the neutral mol. N. M. B.

Hydrogen isotope effect in the OH bands. H. L. JOHNSTON and D. H. DAWSON (Naturwiss., 1933, **21**, 495—496).—Using a sample of H_2O d 1·035, photographs of the emission bands of the isotope mol. $O^{16}H^2$ were obtained. The observed isotopic displacements of the principal edges of the bands are compared with the calc. vals. A. J. M.

Ultra-violet absorption spectrum of ozone and structure of the ozone molecule. V. KONDRATÉEV and A. JAKOVLEVA (J. Exp. Theor. Phys., Russia, 1932, **2**, 50—58).—75 bands (29,000—33,000 cm.$^{-1}$) are represented by $\nu=29404+335{\cdot}5(v_1'+1/2)-7{\cdot}5(v_1'+1/2)^2+59(v_2'+1/2)-433(v_1''+1/2)$. The term 433 cm.$^{-1}$ is due to transverse vibrations of the O_3 mol. and is linear in form. In the region 33,000—42,000 cm.$^{-1}$ a set of diffuse bands with separation 300 cm.$^{-1}$ was found. CH. ABS.

Ultra-violet absorption of benzene derivatives. II. K. L. WOLF and O. STRASSER (Z. physikal. Chem., 1933, **B**, **21**, 389—409; cf. A., 1931, 996).—The absorption curves of di- and tri-substituted derivatives in various solvents have been obtained. For solutions in heptane the influence of each substituent in the solute mol. on the position of the absorption bands is smaller than in the mono-substituted compound. This mutual interaction of two substituents is the greater the smaller is the distance between them and the stronger their polarity. The influence of OH on Me in the p-position is about the same as that of Me on Me in the o-position. A third substituent group weakens the interaction of the other two, particularly if it is between two groups in the m-position to each other. Dipole moments of nitriles and carbylamines and Raman frequencies of PhCN have been determined. R. C.

Effect of auxochromes. M. HORIO (Mem. Coll. Eng. Kyoto, 1933, **7**, 177—248).—Analysis of the absorption spectra of CHPh:CH_2, CPh·CH, and PhEt shows the frequency of vibration to be little influenced by the introduction of the substituent, but the strongest series of bands is displaced towards the red, the effect being in the order, ·CH:CH_2, ·C:CH, Et. The spectra of the vapours of PhOH and PhOMe are similar. Comparison of these spectra and that of NH_2Ph with those of o-, m-, and p-$C_6H_4Me{\cdot}NH_2$ and o- and p-$OMe{\cdot}C_6H_4{\cdot}NH_2$ shows that the effect of two substituents is not the simple sum of their individual actions. H. W.

Characteristic oscillations of ozone in the range 9—20 μ. G. HETTNER, R. POHLMAN, and H. J. SCHUMACHER (Naturwiss., 1933, **21**, 467).—In addition to the previously known band at 9·7 μ two absorption max. were noted at 13·9 and 14·6 μ, the former corresponding roughly with that predicted by Benedict at 13·2 μ. There was, however, no trace of the Gerhard band at 18·9 μ. The new band appears to be double with absorption min. at 14·2 μ. A. J. M.

Infra-red absorption bands of acetylene. G. B. B. M. SUTHERLAND (Physical Rev., 1933, [ii], **43**, 883—886).—A new arrangement of the complete infra-red spectrum of C_2H_2 is given, in accord with the selection rules. N. M. B.

Investigations in the infra-red region of the spectrum. VIII. Application of the grating spectrometer to certain bands in the spectra of triatomic molecules (sulphur dioxide and carbon disulphide). C. R. BAILEY and A. B. D. CASSIE (Proc. Roy. Soc., 1933, **A**, **140**, 605—612; cf. A., 1932, 444, 1075).—Reinvestigation of the SO_2 bands at 4·01 and 4·37 μ, using a grating spectrometer, shows that the mol. is triangular, with a vertical angle of 120°. Exploration of the CS_2 band at 4·61 μ confirms the previously determined separation for the *P* and *R* branches. L. L. B.

Infra-red absorption of benzene in the liquid, solid, and vapour states. C. E. LEBERKNIGHT (Physical Rev., 1933, [ii], **43**, 967—972).—The 2·19, 2·46, and 3·25 μ bands were investigated with high resolving power. Solid absorption was approx. the same as that of the liquid, with slight shift to longer wave-lengths. The 3·25 and 2·46 μ bands shifted 13 Å., and the 2·19 μ band 20 Å. approx. Differences from the liquid were shown by vapour. The 3·25 μ region had two strong bands, each showing evidence of three components. Interpretation of the three components as the envelopes of the vibration rotation bands gave the val. 14×10^{-39} g.-cm.^{2} for the moment of inertia of the C_6H_6 mol. The 2·46 μ region showed a doublet for the vapour, and a single strong band for the liquid. N. M. B.

Dependence of Raman radiation from quartz on the frequency of the exciting radiation. L. S. ORNSTEIN, J. J. WENT, and A. H. W. ATEN, jun. (Z. Physik, 1933, **82**, 750—753).—The ν^4 law appears to hold. A. B. D. C.

Raman effect of aqueous nitrate solutions. P. GRASSMANN (Z. Physik, 1933, **82**, 765—766).—The 1048 cm.$^{-1}$ line was observed under high dispersion and showed no fine structure. A. B. D. C.

Application of the Raman effect to the investigation of molecular constitution in organic chemistry. I. Aliphatic diketones and resorcinol. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 69—79).—The Raman spectrum of Ac_2 suggests that there is an equilibrium COMe·COMe $\rightleftharpoons$ CMe:CMe (cf. J C S, 1906, **89**, 497). Liquid CH_2Ac_2 and $(\cdot CH_2Ac)_2$ are equilibrium mixtures of keto and enol forms. Evidence is advanced for the existence of the diketo-form (Δ^5-*cyclo*hexene-1 : 3-dione) in a solution of *m*-$C_6H_4(OH)_2$ in MeOH. D. R. D.

Width of the 992 cm.$^{-1}$ benzene Raman line. P. GRASSMANN (Z. Physik, 1933, **82**, 767).—Under high dispersion this line shows no fine structure, and has a half width of 3·6 cm.$^{-1}$ A. B. D. C.

Structure of the principal Raman line of benzene. L. BLOCH and E. BLOCH (Compt. rend., 1933, **196**, 1787—1788).—The Raman line 992 cm.$^{-1}$ of C_6H_6 is accompanied by four satellites, for which $\Delta\nu$ is +13·7, +8·4, −6·8, and −13·8, with perhaps a fifth with $\Delta\nu$ +3·1 (cf. A., 1932, 109). C. A. S.

Effect of dissolved metallic perchlorates on the Raman frequencies of alcohols. J. GOUBEAU (Naturwiss., 1933, **21**, 468).—$LiClO_4$ dissolved in MeOH or EtOH causes decrease in the lowest, and increase in the higher, frequencies. The band at 1050 cm.$^{-1}$ of higher alcohols is lowered by addition of perchlorates. If the oscillating masses in the pure alcohol and solution are the same, and there is no difference in the coupling of atoms and mols., addition of perchlorate to MeOH must cause a weakening of the C–O linking by about 2%, and a strengthening of the C–H linking by about 1%. In EtOH similar effects take place, and the C–C linking is not appreciably altered. The frequency of the dissolved perchlorate depends on concn. A. J. M.

Photo-electric measurement of penetration of light of various wave-lengths into the sea, and the physiological bearing of the results. W. R. G. ATKINS and H. H. POOLE.—See this vol., 757.

Emission of radiation in chemical reactions. R. AUDUBERT and VAN DOORMAAL (Compt. rend., 1933, **196**, 1883—1885).—Using a modified Geiger–Müller counter with photo-cathodes of CuI. Cu_2O, CuO, Cu, or Al in air or N_2 at 0·1—27 mm. Hg and 900 volts, the comparative nos. of photons emitted in 20-min. periods in the dark and in presence of the reaction in the following reactions are respectively: oxidation of hyposulphite, 40, 70; of pyrogallol, 20, 60 (cf. A., 1932, 966); of EtOH by CrO_3, 6, 80; of Ta (anodic), 20, 150; of Si (anodic), 25, 75; decomp. of H_2O by Hg+Mg 6, 30. Emission of photons was also observed during the anodic oxidation of Al and Mg; of H_2O by Hg+Na or K, and slow oxidation of P. The emission may be due to the return to normal of some of the activated mols. C. A. S.

Correlation of fluorescence spectra with chemical structure of some naphthalene derivatives. A. J. ALLEN, (MISS) R. FRANKLIN, and (MISS) E. MCDONALD (J. Franklin Inst., 1933, **215**, 705—722).—Investigation of fluorescence spectra of $C_{10}H_8$ and 10 of its sulphonic acids and salts, $C_{10}H_7\cdot OH$ and 10 of its compounds, and $C_{10}H_7\cdot NH_2$ and 10 of its acids and salts shows a definite relation between their chemical constitution and fluorescence and absorption. The substances vary in intensity and region in which they fluoresce; change of a radical from an α to a β position results in a shift in wave-length of the max. intensity. The quality of fluorescence is approx. independent of the source of excitation, concn., and the presence of traces of impurities. N. M. B.

Photo-effect in cuprite crystals. ANNA JOFFE and A. JOFFÉ (Z. Physik, 1933, **82**, 754—758).—Photo-e.m.f. and inner photo-effect were investigated for cuprite crystals and gave results in disagreement with theory. Illumination at one electrode gave great asymmetry of current, and above 1000 volts per cm. illumination with white or red light gave a current diminution of 30%. A. B. D. C.

Electronic conductivity of the copper oxides. M. LE BLANC, H. SACHSE, and H. SCHOPEL (Ann. Physik, 1933, [v], **17**, 334—344; cf. A., 1931, 785; 1932, 8).—The conductivity of Cu_2O depends to a great extent on its purity. Vals. are given for the sp. conductivity of Cu_2O and CuO in various states of division; for both it is greatly increased through

absorption of O_2. Both oxides are to be regarded as typical semi-conductors with positive temp. coeffs. A. J. M.

Optical absorption at photo-electric dual selective surface layers. W. KLUGE (Physikal. Z., 1933, **34**, 465—472).—Determinations with a simple photo-electric cell arranged for measuring the absorption of layers with a dual selective action are described and discussed. A. J. M.

Theory of electronic semi-conductors, and their possible properties. R. H. FOWLER (Proc. Roy. Soc., 1933, **A, 140**, 505—522).

Influence of moisture on the breakdown strength of insulators. E. HIPPAUF (Z. Physik, 1933, **82**, 803—814). A. B. D. C.

Susceptibility and electrical conductivity of Cu–Mn alloys. S. VALENTINER and G. BECKER (Z. Physik, 1933, **82**, 833).—Correction of earlier paper (this vol., 449). A. B. D. C.

Electrical structure of crystals of Rochelle salt with admixture of sodium rubidium tartrates and sodium thallium tartrates. M. A. EREMEEV, P. P. KOBEKO, B. V. KURCHATOV, and I. V. KURCHATOV (J. Exp. Theor. Phys., Russia, 1932, **2**, 102—107).—Equimol. concns. of $NaXC_4H_4O_6,4H_2O$ (X=Rb or Tl) lower the dielectric const. of Na K tartrate to the same extent (*e.g.*, 10,000 to 50 by 5% at 0°) at all temp. CH. ABS.

Dielectric constant of liquid iodine. A. JAGIELSKI (Bull. Acad. Polonaise, 1932, **A**, 327—335).—Vals. from 11·08 at 118·1° to 12·98 at 167·7°, with a mean error of 2%, have been obtained. F. L. U.

Dielectric polarisation of liquid phosphorus. S. DOBINSKI (Z. Physik, 1933, **83**, 129—138).—Dielectric const. and density were determined between 40° and 80°. The dielectric const. shows a discontinuity at 48·6°, indicating a transition point between two phases. P has zero dipole moment in these phases. A. B. D. C.

Electric dipole moments of nickel carbonyl, di-iodoacetylene, diethyl sulphide, diethylsulphone, and decalin. L. E. SUTTON, R. G. A. NEW, and J. B. BENTLEY (J.C.S., 1933, 652—658; cf. A., 1932, 1077).—The moments found were (0·3), (0·3), 1·61, 4·41, and $0·0\times10^{-18}$ e.s.u., respectively. $Ni(CO)_4$ and C_2I_2 have a symmetrical structure, which is discussed. Vals. for Et_2S and Et_2SO_2 support Sutton's rule, connecting moments of groups with their orienting power in the C_6H_6 ring (A., 1931, 1354). The zero moment of $C_{10}H_{18}$ supports the generalisation that all strainless cyclic paraffins are non-polar. H. J. E.

Orientations of molecules of permanent moment in an alternating field: application to dispersion of the dielectric constant and the Kerr effect. Y. ROCARD (J. Phys. Radium, 1933, [vii], **4**, 247—250).—Mathematical. A distribution function is obtained, and from it are deduced a theory of dispersion in the Hertzian region and a theory of the Kerr effect in alternating fields. N. M. B.

Dispersion of gases and vapours and its representation by the dispersion theory. IV. Dispersion of mercury between 2800 and 1890 Å. and the life period of the Hg $7p1p_1$ state. G. WOLFSOHN (Z. Physik, 1933, **83**, 234—246).—This life period is given as $1·30\times10^{-9}$ (cf. A., 1930, 1239). A. B. D. C.

Refraction and dispersion of crystals. VI. Width of absorption band and dispersion of potassium chloride. VII. Representation of course of dispersion in visible and ultra-violet. P. WULFF (Z. physikal. Chem., 1933, **B, 21**, 353—367, 368—381; cf. A., 1931, 455).—VI. The effect of damping on the vals. of $\phi-(n^2-1)/(n^2+2)$ for KCl in the ultra-violet is small, but a simplified dispersion formula neglecting damping represents the course of the dispersion in the far ultra-violet only with an error of at least 1% of ϕ. Owing to damping, the frequency of the absorption max. is about 1% > if the absorption band were of infinitesimal width.

VII. A graphical method of extrapolating dispersion data to give characteristic frequencies and probabilities of transition for a two-term dispersion formula and a numerical method of checking the extrapolation are described. Mol. refraction vals. derived in this way for KCl deviate by at most 0·25% from the observed vals. R. C.

Refractive index. I, II. A. M. TAYLOR and A. M. GLOVER (J. Opt. Soc. Amer., 1933, **23**, 206—211, 211—215).—I. Four methods for measuring the refractive index of strongly absorbing liquids are described; (*a*) and (*b*) depend on determination of the crit. angle of reflexion of monochromatic light at a glass–liquid interface; (*c*) white light is reflected at angles near the crit. angle and allowed to enter a spectrograph; peaks in the microdensitometer records of the resulting spectrograms correspond with max. of the refractive index; (*d*) the transmitted light is examined visually in a spectroscope.

II. Application to saturated aq. $KMnO_4$ gave a dispersion curve with a strong anomaly around 5473 Å., the band being attributed to the fundamental frequency of an electronic transition in the Mn atom, and a series of minor anomalies corresponding with the banded structure of the absorption spectrum. N. M. B.

Thermal variation of abnormal magnetic birefringence. R. LUCAS (Compt. rend., 1933, **196**, 1657—1659; cf. this vol., 448).—Mathematical support on the lines of that for similar variation in ordinary rotatory power (cf. A., 1928, 461) is given to the view that such variation is due to the presence of two or more isomerides of the substance concerned. C. A. S.

Paramagnetism and magnetic birefringence of gaseous or liquid oxygen. L. GOLDSTEIN and Y. ROCARD (Compt. rend., 1933, **196**, 1722—1724).—The paramagnetism and magnetic birefringence of liquid and gaseous O_2 and their variations with temp. are satisfactorily explained by Kramers' theory regarding the multiplicity of the normal $^3\Sigma$-state of the O_2 mol. (cf. A., 1929, 623). C. A. S.

Circular magnetic dichroism of aqueous solutions of cobalt sulphate and nitrate. M. SCHERER and R. CORDONNIER (Compt. rend., 1933, **196**, 1724—1727; cf. this vol., 10).—With aq. $CoSO_4$ of d^{19} 1·117

and d^{16} 1·27, and aq. $Co(NO_3)_2$ of d^{19} 1·158 dichroism curves similar to that of $CoCl_2$ were obtained, showing the dichroism to depend solely on the [Co$^{\cdot\cdot}$]. Both salts exhibit negative rotation for small and large λ in the visible spectrum, that for small λ being the stronger, with two points of inflexion in the magnetic rotation dispersion curve, indicating more complex structure of the bands of these salts than of the chloride (cf. A., 1930, 668). C. A. S.

Depolarisation, optical anisotropy, and the Kerr effect. R. Serber (Physical Rev., 1933, [ii], 43, 1003—1010).—Mathematical. N. M. B.

Intermediate states of aggregation. H. Zocher and M. Jacobowitz (Kolloid-Beih., 1933, **37**, 427—464).—The substances which were obtained by Perrin (A., 1930, 687) in a lamellar form of the thickness of a wave-length of light can be obtained in the smectic state under different conditions of temp. and concn. A no. of compounds, mainly K or Na salts of org. acids, which have been obtained in this state are listed, and their optical properties are described. E. S. H.

Vibrational structure of electron transitions in polyatomic molecules. G. Herzberg and E. Teller (Z. physikal. Chem., 1933, **B**, **21**, 410—446).—Selection rules for the vibrational quantum nos. in electron transitions of polyat. mols. are derived. From the Franck–Condon principle it follows as a first approximation that in absorption starting from the vibrationless ground state those bands are strong in which only totally symmetrical vibrations are excited. Assuming the probability of electron transition to be independent of the position of the nucleus, the selection rule for the faintly appearing transitions in which quantum nos. of vibrations not totally symmetrical change, is: the transformation properties of the vibrational proper functions of the initial and final states must be the same. The symmetry properties of polyat. mols. are, however, often modified by nuclear displacements, in which case electron transitions forbidden for the original mol. symmetry may occur. The application of the above rules to various mols. with $\leqslant 3$ atoms is discussed. R. C.

New chemical theory: electrovalency, ionisation, free radicals. A. Gosselin (J. Chim. phys., 1933, **30**, 356—366).—Further examples are given of the application of the author's theory (A., 1929, 1130). D. R. D.

Planar forms of large carbon rings. H. D. K. Drew (Chem. and Ind., 1933, 538—540).—Large polymethylene rings may exist in planar configurations of two kinds, both involving re-entrant angles: (i) with internal and external re-entrant angles equal, (ii) a form of min. strain with internal and external angles distorted in opposite senses. The strain is especially small in rings of the form C_{5n}. J. S. A.

Determination of the angles between covalencies from measurements of electric dipole moments. G. C. Hampson and L. E. Sutton (Proc. Roy. Soc., 1933, **A**, **140**, 562—579).—Methods of determining angles between covalencies from measurements of electric dipole moments are discussed, and extensions to more complex mols. are described. Methods of minimising the effects of the more important errors are indicated. L. L. B.

Form and vibrational frequencies of the nitrogen dioxide molecule. C. R. Bailey and A. B. D. Cassie (Nature, 1933, **131**, 910—911).—A reply to criticism (this vol., 557). L. S. T.

Form and vibrational frequencies of the nitrogen dioxide molecule. R. Schaffert (Nature, 1933, **131**, 911; cf. preceding abstract).—Infra-red absorption bands were obtained at 15·6, 13·3*, 7·85*, 7·28, 6·14, 5·7*, 3·89*, and 3·3 μ at room temp. The bands marked * decreased in intensity with a rise in temp. and disappeared at 150°, and hence are attributed to N_2O_4. The remainder persisted and decreased in intensity with a fall in temp. and are ascribed to NO_2. The results support the view (this vol., 557) that the NO_2 mol. is not linear. The fundamental frequencies of the NO_2 mol. are probably 641, 1373, and 1628 cm.$^{-1}$ L. S. T.

Diamagnetism of water at different temperatures. B. Cabrera and H. Fahlenbrach (Z. Physik, 1933, **82**, 759—764).—The temp. variation of the susceptibility of H_2O is independent of previous treatment, and between 0° and 100° the temp. coeff. is $1·15\times10^{-7}$ (cf. Wills and Boeker, this vol., 212). A. B. D. C.

Demagnetisation of iron and nickel by high-frequency alternating fields. S. Procopiu and N. Florescu (J. Phys. Radium, 1933, [vii], **4**, 251—261).—Curves and data are given for wires of various dimensions and a range of frequencies and field intensities. The demagnetisation decreases with rise of frequency and fall of intensity. Ni shows spontaneous remagnetisation due to a weak or zero magnetic viscosity. N. M. B.

Principal magnetic susceptibilities of some paramagnetic crystals at low temperatures. L. C. Jackson (Proc. Roy. Soc., 1933, **A**, **140**, 695—713).—The principal susceptibilities of several crystals containing the ions Mn^{2+} and Fe^{3+}, as examples of s-moment ions, and of $CoSO_4,7H_2O$ (I) as an example of a Co salt, have been measured over the temp. range 70—300° abs. with accuracy of 0·5—1·0%. The principal susceptibilities of $K_3Fe(CN)_6$ are also recorded. The crystals containing ions with s-moment only present are found to be magnetically isotropic, in agreement with recent theory. The $1/\chi$–T curves for (I) are straight, but not parallel, lines over the range of temp. employed. L. L. B.

Magnetic dipole fields in unstrained cubic crystals. L. W. McKeehan (Physical Rev., 1933, [ii], 43, 912—923).—Mathematical. N. M. B.

Magnetic dipole fields in dislocated cubic crystals. L. W. McKeehan (Physical Rev., 1933, [ii], 43, 924—930).—Mathematical. N. M. B.

Magnetic susceptibilities of some common gases. G. G. Havens (Physical Rev., 1933, [ii], **43**, 992—1000).—The Faraday test-body method previously used (cf. A., 1932, 985) gave for the mol. susceptibilities $\times10^6$, on the basis of 3335 for O_2 at 20°, vals. at room temp., H_2 —4·0051, He —1·906,

Ne −7·651, A −19·23, CO_2 −20·88, N_2 −11·938, and at liquid air temp., H_2 −3·98, He −1·91, Ne −7·64, A −19·8, O_2 11,830. The 40% change over the temp. range found by Bitter (cf. A., 1931, 155) is not supported. The susceptibility of O_2 followed Curie's law to within 2%. N. M. B.

Magnetic moment of the nitrogen nucleus. R. F. BACHER (Physical Rev., 1933, [ii], **43**, 1001—1002).—Absence of hyperfine structure in three of the lines of N I and deductions from the measured line widths indicate an unusually low magnetic moment for the N nucleus. It is concluded that the neutron has a magnetic moment opposite in direction to its mechanical moment and about one proton magneton in magnitude. N. M. B.

Magnetic dipole energy in homogeneously strained cubic crystals. L. W. MCKEEHAN (Physical Rev., 1933, [ii], **43**, 1022—1024).—Mathematical. N. M. B.

Magnetic dipole energy in hexagonal crystals. L. W. MCKEEHAN (Physical Rev., 1933, [ii], **43**, 1025—1029).—Mathematical. N. M. B.

Investigations of Heusler alloys. S. VALENTINER and G. BECKER (Z. Physik, 1933, **83**, 371—403).—Magnetic behaviour of these alloys shows the presence of $MnAlCu_2$ crystals. A. B. D. C.

Susceptibility of salts of the iron group by a modified Quincke's method. H. BRETERNITZ (Physikal. Z., 1933, **34**, 507—516).—A modification of Quincke's method was used to determine the effect of field strength (100—600 gauss) and concn. on the susceptibilities of solutions of $FeCl_3$, $FeSO_4$, $Fe_2(SO_4)_3$, and $MnSO_4$. Within the range susceptibility was independent of field strength; magnetisation at first increases and then rapidly decreases with decreasing concn. A. J. M.

Magnetochemical study of the constitution of peroxylaminesulphonic acid. R. W. ASMUSSEN (Z. anorg. Chem., 1933, **212**, 317—320).—Measurement of the susceptibility of the K salt supports the view that in the solid state it is represented by $N_2O_2(SO_3K)_4$ and when dissolved by $NO(SO_3K)_2$. The magnetic properties of these two forms resemble those of N_2O_4 and NO_2 F. L. U.

Should the vitreous state be called a fourth state of matter? H. SALMANG (Naturwiss., 1933, **21**, 391—392). A. J. M.

Atomic radius of carbon in diamond. V. POSEJPAL (Compt. rend., 1933, **196**, 1655—1657; cf. this vol., 213).—Equally good agreement is obtained by using n_B and n_0 as bases of calculation. The cause of difference between these results and those obtained by means of Martens' dispersion formula is discussed. C. A. S.

Thermal expansion according to the lattice theory. A. PAPAPETRU (Physikal. Z., 1933, **34**, 487—490).—Mathematical. A. J. M.

Calculation of corrections for *X*-ray spectrometers. H. SEEMANN (Z. Physik, 1933, **82**, 835).—Polemical against Siegbahn (this vol., 340). A. B. D. C.

Application of concentrating screens to *X*-ray spectroscopy. G. KUPFERLE (Z. Physik, 1933, **83**, 79—84). A. B. D. C.

Debye–Scherrer rontgenograms of greatest accuracy. A. I. KRASNIKOV (J. Exp. Theor. Phys., Russia, 1932, **2**, 74—77).—Precisely cylindrical samples and a long diaphragm were used. CH. ABS.

Reflexion of cathode rays at a single-crystal face. S. KIKUCHI and S. NAKAGAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 80—91).—A photographic apparatus is described and data obtained with ZnS are discussed. D. R. D.

Effect of temperature on the intensity of *X*-rays scattered by powdered sodium fluoride. J. J. SHONKA (Physical Rev., 1933, [ii], **43**, 947—954).—The ratio of the integrated intensities of a no. of regularly reflected lines varies with the angle as predicted by the Debye–Waller formula. The characteristic temp. of NaF is 442° abs. Assumption of zero-point energy leads to correct structure factors for the atoms at rest. N. M. B.

***X*-Ray investigations of the thermal expansion of solids. I.** G. SHINODA (Mem. Coll. Sci. Kyoto, 1933, **16**, 193—201).—In the temp. range 23—194°, expansion coeffs. ($\times 10^6$) were: Al, α 22·9; Sn, $\alpha_{\parallel}$ 45·8, $\alpha_{\perp}$ 25·7; In, $\alpha_{\parallel}$ 45·0, $\alpha_{\perp}$ 11·7; Zn, $\alpha_{\parallel}$ 64·5, $\alpha_{\perp}$ 10·8; Tl, $\alpha_{\parallel}$ 72, $\alpha_{\perp}$ 9. Lattice consts. were: Sn, a 5·824 Å., c/a 0·5415; In, a 4·581 Å., c/a 1·077. H. J. E.

Recrystallisation phenomena in synthetic metallic bodies. F. SAUERWALD (Naturwiss., 1933, **21**, 467).—Trzebiatowski's results (this vol., 450) contradict the earlier ones of the author, but more recent work on decrease in hardness with increasing glowing temp. after compression, and alteration of the Debye diagram on compression (B., 1932, 428), shows good agreement. A. J. M.

Zone-like structure of electrolytically prepared nickel layers. W. G. BURGERS and W. ELENBAAS (Naturwiss., 1933, **21**, 465).—The structures of electrolytic Ni layers are discussed. It has been shown that many factors influence the formation of a certain thread structure. A. J. M.

Phenomena occurring in the melting of metals. W. L. WEBSTER (Proc. Roy. Soc., 1933, **A**, **140**, 653—660).—The relation between the degree of superheating above the m.p. and the degree of subsequent under-cooling below the m.p., together with the influence of time on this relation, have been investigated for Cd, Bi, Sn, and Pb. In Bi, Pb, and Sn there is evidence that persisting nuclei remain when the solid is melted. In the case of Sn they are easily destroyed by superheating and are not re-formed until a definite degree of supercooling follows. In Bi and Pb the nuclei are only slowly destroyed on superheating, and for each stage of destruction there is a characteristic degree of supercooling at which what remains of the nuclei recovers the power to act as a centre of crystallisation. Cd showed no under-cooling, even after superheating 165°; presumably no nuclei are required for crystallisation. L. L. B.

Electro-crystallisation of metals. III. Structure of electrolytic deposits of silver from its

fused salts. K. M. GORBUNOVA (Bull. Acad. Sci. U.R.S.S., 1933, 255—266).—Ag deposits, obtained by electrolysis of fused $AgNO_3$–KNO_3–$NaNO_3$ mixtures at various concns., temp., c.d., adhere badly to the cathode and are readily removed by rubbing. Except when high c.d. (0·5—1 amp. per sq. cm.) are used, the initial layers from AgCl–KCl–NaCl mixtures hold firmly on the cathode; the microstructure shows Ag atoms dispersed through a network of crystals of the cathode. The results obtained, together with the low temp. of recrystallisation of Ag, indicate the impossibility of obtaining finely-cryst. deposits of Ag from its fused salts; the electro-crystallisation of Ag depends mainly on the temp. (cf. Kistiakovski, A., 1930, 1381; this vol., 468). T. H. P.

Structure of liquid mercury. O. KRATKY (Physikal. Z., 1933, **34**, 482—487).—The assumption that there is a fundamental lattice with hexagonal close packing gives calc. vals. in agreement with the Debye–Menke curve (A., 1930, 1350). A. J. M.

Arrangement of the micro-crystals in the graphite flakes segregated from solidifying pig iron. S. SHIMADZU (Mem. Coll. Sci. Kyoto, 1933, **16**, 215—218).—The [1120] axis is a fibrous axis, parallel to the flat flake surface. H. J. E.

Crystal structure and orientation in thin films. G. I. FINCH and A. G. QUARRELL (Nature, 1933, **131**, 877).—Abnormal crystal structures shown by thin films of Al on Pt, ZnO on Zn, and MgO on Mg are described. L. S. T.

Detection of sodium chloride lattice in cæsium chloride. G. WAGNER and L. LIPPERT (Z. physikal. Chem., 1933, **B**, **21**, 471).—The body-centred lattice of CsCl changes into the face-centred NaCl lattice above 450±5°, the lattice const. of the new lattice being 7·10 Å. R. C.

Structure of the molecule of 12-phosphotungstic acid. J. F. KEGGIN (Nature, 1933, **131**, 908—909).—*X*-Ray analysis shows that the P atom is at the centre of a regular tetrahedral group of 4 O and each W atom is approx. at the centre of a distorted octahedral group of 6 O. The complex acid anion is a co-ordinated structure consisting of a central PO_4 group surrounded by a shell of 12 WO_6 groups linked together by shared O atoms and arranged in four groups. Details of the structure of the $PW_{12}O_{40}$ anion are given. In the partly dehydrated acid containing 6 or 7 H_2O per mol. of acid, these acidic anions are packed together with body-centred cubic symmetry: edge of the unit cube 12·14±0·005 Å. The H_2O packs in the interstices between the anions. The formula of 12-phosphotungstic acid given by the above structure is $H_3PW_{12}O_{40}$, best written as $H_3P(W_3O_{10})_4,nH_2O$. Other 12-heteropoly acids have this type of structure. L. S. T.

Crystal structure of vitamin- and of adenine hydrochloride. J. D. BERNAL and D. CROWFOOT (Nature, 1933, **131**, 911—912).—Crystals of vitamin-B_1 hydrochloride from various sources are substantially identical in form and *X*-ray pattern. A slight difference in optical properties may point to a variable amount of impurity in solid solution. The crystals are monoclinic with *a* 12·62, *b* 20·53, *c* 6·96 Å., β 66° 5′: space-group probably C_{2h}^5—$P2_{1a}$: mol. wt. 358, assuming 4 asymmetric mols. per cell and *d* 1·43. The mols. must be flat, approx. 8×10 Å., suggesting conjugated ring structure. S and Cl do not lie at the ends of the mol. Crystallographic investigations confirm the close resemblance between vitamin-B_4 prepared by Peters, and adenine hydrochloride (this vol., 541, 646). The crystals are monoclinic with *a* 8·71± 0·015, *b* 4·80±0·005, *c* 20·00±0·05 Å., β 62° 0′: space-group probably C_{2h}^5—$P2/c$. There are 4 mols. of the hydrochloride and $2H_2O$ per cell. The results suggest that the substance showing B_4 activity can exist only as an impurity in the substance prepared by Peters. Optical properties are recorded. L. S. T.

Protons in the conductivity of metals. III. The photographic plate as indicator. A. COEHN and K. SPERLING (Z. Physik, 1933, **83**, 291—312).—Motion of H_2 in Pd can be followed by the action of a surface layer of H_2O_2 on a photographic plate. Images due to Al, Fe, Ni, Pb, Cr, Ta, and Pt were also investigated. A. B. D. C.

Magnetic permeability of iron wires in the wave-length range 46—1000 m. K. KREIELSHEIMER (Ann. Physik, 1933, [v], **17**, 293—333).—A Wheatstone bridge method was used. There is an increase of permeability with wave-length, and dependence on field strength. No anomaly was found in the neighbourhood of 100 m. A. J. M.

Magnetic properties of thin nickel films. H. E. MALMSTROM (Proc. Iowa Acad. Sci., 1931, **38**, 214). CH. ABS.

Molecular rotation in solid ammonium chloride. A. HETTICH and S. B. HENDRICKS (Naturwiss., 1933, **21**, 467).—The anomalous form of the heat capacity–temp. curve for NH_4Cl and other NH_4 salts can be explained as a quantum jump of an unknown nature, or as a consequence of the commencement of rotation of the NH_4 ion. For certain NH_4 salts the latter could be investigated by noting any change in cryst. symmetry, and the development of piezo-electricity. For NH_4Cl piezo-electricity was developed at −30·59°, the temp. at which the salt possesses its max. heat capacity. A. J. M.

Propagation of large Barkhausen discontinuities. IV. Regions of reversed magnetisation. L. TONKS and K. J. SIXTUS (Physical Rev., 1933, [ii], **43**, 931—940; cf. this vol., 216). N. M. B.

Elastic constants of single aluminium crystals. E. GOENS (Ann. Physik, 1933, [v], **17**, 233—242).—Elastic consts. of single Al crystals were obtained by dynamic methods. Compared with other cubic metallic crystals the elastic anisotropy is negligible. A. J. M.

Stretching experiments on copper–nickel crystals. E. OSSWALD (Z. Physik, 1933, **83**, 55—78). A. B. D. C.

Problem of crystal strength. A. SMEKAL (Z. Physik, 1933, **83**, 313—316).—Distinguishing tenacity and plasticity shows that tenacity of pure rock-salt crystals decreases, whilst plasticity increases, with increasing distortion of the crystal due to impurities. A. B. D. C.

Influence of foreign substances on the low-temperature tensile strength of synthetic rock-salt crystals. W. BURGSMULLER (Z. Physik, 1933, **83**, 317—320).—The breaking strength of rock-salt crystals for tension normal to the cubic plane increases at room temp. with increasing quantity of $SrCl_2$ as impurity, but diminishes between −190° and −252°. A. B. D. C.

Measurements with liquid helium. XXI. Breaking strength of rock-salt at 4·2° abs. K. STEINER and W. BURGSMULLER (Z. Physik, 1933, **83**. 321—322).—The strength of rock-salt at 0° abs. is little different from that at liquid air temp. A. B. D. C.

Effect of admixtures on the polymorphism of iron. V. N. SVECHNIKOV (Domez, 1932, No. 8, 6—15).—Saturation curves of the γ-phase of Fe in the systems Fe–Al, Fe–V, Fe–Mo, Fe–Cr, Fe–Ni, etc. are analysed mathematically. CH. ABS.

Polish on metals. R. C. FRENCH (Proc. Roy. Soc., 1933, **A**, **140**, 637—652; cf. A., 1932, 219).—An investigation of the structures of polished surfaces of Cu, Ag, Au, and Cr by means of electron diffraction photographs shows that highly-polished surfaces are almost amorphous, in agreement with the Beilby theory. The polishing is thought to reduce the size of the crystals, and finally to displace the atoms from their arrangement in the crystal lattice to a new spacing corresponding with the separation of the atoms by a common distance determined by the size of the atoms. Reasons are given against the view that the polishing is only a levelling of the cryst. surface. Single crystals of Cu and Cr have also been studied. L. L. B.

Superconductivity of aluminium. W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 381—383).—Data for Al and Ga wires are given. Al becomes superconductive at 1·14° abs. N. M. B.

Possible explanation of superconductivity. J. FRENKEL (Physical Rev., 1933, [ii], **43**, 907—912).—It is proposed to take into account the electromagnetic (inductive) forces, mutually exerted by the electrons moving in an organised way, as stabilising the motion against the perturbations due to the thermal agitation of the crystal lattice. N. M. B.

Electrical conductivity of crystallised antimony trisulphide. G. S:SON FREY (Arkiv Kemi, Min., Geol., 1932, **11A**, No. 4, 1—22).—Pure synthetic Sb_2S_3 can be prepared in the form of rod-like crystals, of which the crystallographic axis is oriented in the long direction of the rods. The electrical conductivity of this form is very low, and exhibits the anomalies previously noticed for native stibnite, which therefore cannot be attributed to impurities in the mineral. The sudden increase in conductivity shown after prolonged passage of the current is due to electrolysis of the sulphide, fine threads of metallic Sb being formed which gradually extend from the cathode to the anode. The decomp. cannot be detected by analytical means, but the production of the fine connecting bridge of Sb has been proved by electrical methods. H. F. H.

Theory of thermo-electric e.m.f. between a semi-conductor and metal according to Fermi statistics. G. MÖNCH (Z. Physik, 1933, **83**, 247—252). A. B. D. C.

Determination of the optical constants from light-absorption measurements with thin metal films. C. F. VEENEMANS (Arch. Neerland., 1933, [iii*a*], **14**, 84—117).—It is possible to determine the optical consts. of a metal from absorption measurements with two or more thin films of known thickness. The method is applicable also in the infra-red region. Sb has been investigated in detail over the range 6500—15,000 Å. The optical properties are independent of film thickness, but at −180° and at a wave-length about 1 μ show a measurable variation with temp., this variation increasing with increasing wave-length. J. W. S.

Reflecting power and double reflexion of niccolite. W. FABER (Z. Krist., 1933, **85**, 223—231; cf. A., 1931, 587; this vol., 451). C. A. S.

International comparison of temperature scales between 660° and 1063°. W. F. ROESER, F. H. SCHOFIELD, and H. A. MOSER (Ann. Physik, 1933, [v], **17**, 243—250).—A comparison of the temp. scales in use at the National Physical Laboratory (N.P.L.), the National Bureau of Standards (N.B.S.), and the Physikalisch-Technische Reichsanstalt (R) has been made. The difference between the scale of the N.P.L. and the N.B.S. amounts to a max. of 0·7° at 850°, this difference being due to a difference of 0·42° in the m.p. of Ag, taken as a fixed point. The max. difference between the R and the N.P.L. scales was 0·4° at 850°, due to a difference of 0·27° in the m.p. of Ag. These differences can be reduced to 0·1° by interchange of Ag test-pieces. Six different thermo-elements in the three laboratories agree to this degree of accuracy, on the average. Individual elements differ rather more from each other. A. J. M.

Attainment of low temperatures by adiabatic demagnetisation. W. J. DE HAAS, E. C. WIERSMA, and H. A. KRAMERS (Naturwiss., 1933, **21**, 467).—Determination of the susceptibility of CeF_3 at the temp. of liquid He boiling under reduced pressure shows that by adiabatic demagnetisation of this substance a temp. of 0·27° abs. could be produced. A. J. M.

Melting curve of neon to 200 kg. per sq. cm. W. H. KEESOM and J. H. C. LISMAN (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 378—380).—The curve and data are given from the triple point to 198·4 kg. per sq. cm. and 27·42° abs. N. M. B.

Conditions affecting the freezing temperature of silver. W. F. ROESER and A. I. DAHL (Bur. Stand. J. Res., 1933, **10**, 661—668).—The f.p. of Ag containing 0·068% Cu is 0·5° < that of Ag containing 0·008% impurities. The f.p. of Ag in a graphite crucible exposed to the atm. is within 0·05° of that of the same Ag in a vac. The f.p. of Ag saturated with air at 760 mm. is 11·2° <, and that of Ag saturated with O_2 at 760 mm. 22·6° <, that of the same Ag protected from O_2. J. W. S.

Relationships between constitution and mol. depression of the m.p. of organic compounds. II. J. PIRSCH (Ber., 1933, **66**, [*B*], 815—817; cf. this vol., 172).—The mol. m.-p. depressions of camphorquinone and pinene dichloride (I) approximate closely to the calc. vals. (*loc. cit.*). (I) and pinene dibromide give an unbroken series of mixed crystals showing additivity of mol. m.-p. depression.

Volatility of slightly volatile acids. P. JAULMES (J. Chim. phys., 1933, **30**, 274—287).—The coeff. of distillation K and volatility const. X (cf. this vol., 16) of solutions of HCO_2H, AcOH, $EtCO_2H$, BzOH, lactic and salicylic acids were determined under various conditions. For a pure solute K is a const., except at the beginning and end of a distillation. The significance of the results is discussed. H. F. G.

Thermodynamic properties of real gases as explicit functions of the pressure and temperature. T. C. HUANG and K. C. SU (Sci. Rep. Nat. Tsing Hua Univ., 1933, **2**, 37—48).—Theoretical. H. J. E.

Nature of critical state in the transition liquid–gas. WO. OSTWALD (Kolloid-Z., 1933, **64**, 50—62).—The transition liquid–gas is homogeneous above the crit. temp. and pressure, but " disperse " in the crit. region. The disperse effect is due to the stages liquid foam cloud gas. The foam and cloud stages are immiscible. E. S. H.

Compressibilities of certain gases at low pressures and various temperatures. W. CAWOOD and H. S. PATTERSON (J.C.S., 1933, 619—624; cf. A., 1932, 980).—The compressibilities of C_2H_4, SO_2, CO_2, N_2O, and Me_2O between 1 and 3 m. pressure and at 0° and 21—50° were measured. In this range the pv–p isothermals are almost linear, and were extrapolated to $p=0$. The expression p_cA_c/T_c was not const. (A_c=compressibility coeff., T_c—crit. temp., p_c—crit. pressure). Mol. wts. were calc. H. J. E.

Viscosities of acetaldehyde and paraldehyde. W. H. HATCHER and C. T. MASON (Canad. J. Res., 1933, **8**, 402—403).—The abs. viscosities of MeCHO and paraldehyde at 15° are 0·02456 and 0·1359, respectively. The vals. for the binary mixtures are always < those calc. additively, the max. deviation being 47% for the 1 : 1 mixture. H. F. G.

Viscosity of homogeneous liquids. R. O. HERZOG and H. KUDAR (Z. Physik, 1933, **83**, 28—42).—Viscosity depends on the stereochemical structure and at. distances in mols. Formulæ are developed to include these factors, and are applied to tetrachlorides, Cl_2, I, SO_2, CS_2, C_6H_6, C_5H_5N, and paraffin hydrocarbons. A. B. D. C.

Viscosity of liquids, their b.p. and critical temperatures. B. PRASAD (J. Indian Chem. Soc., 1933, **10**, 135—136).—For a no. of hydrocarbons and halogen derivatives β/T_B and β/T_C are const. [T_B and T_C=b.p. and crit. temp. abs., and β is const. in the formula $\log \eta=\alpha+\beta/T$ (abs.)]. F. L. U.

Viscosity of liquids and dependence of viscosity constants on constitutional factors. B. PRASAD (J. Indian Chem. Soc., 1933, **10**, 143—152; cf. preceding abstract).—There is agreement between the recorded viscosities at different temp. of 25 non-associated liquids and those calc. by the formula $\log \eta=\alpha+\beta/T$. Vals. of β show some regularity for homologous compounds differing by C_2H_4 (not by CH_2), and for Cl- and Br-derivatives. No relation between the α and constitution is observable. F. L. U.

Self-diffusion of hydrogen. P. HARTECK and H. W. SCHMIDT (Z. physikal. Chem., 1933, **B**, **21**, 447—458).—From observations on the diffusion of para-H_2 into normal H_2 the self-diffusion coeff. has been found to have the vals. $0{\cdot}00816\pm0{\cdot}0002$, $0{\cdot}172\pm0{\cdot}008$, and $1{\cdot}28_5\pm0{\cdot}002_5$ at 20·4°, 85°, and 273° abs., respectively. The difference in viscosity between the two forms of H_2 even at 20·4° abs./1·5 mm. is < 0·1%, so that the gas-kinetic properties of the two forms can be regarded as identical. R. C.

Molecular viscosities. J. TAUSZ and A. RABL (Erdöl u. Teer, 1932, **8**, 396—398; Chem. Zentr., 1932, ii, 2439).—Viscosities of PhMe solutions of various substances have been determined. The theoretical significance of the data is discussed. A. A. E.

Electrochemistry of ethereal solutions. XI. Viscosity of the system sulphuric acid–ethyl ether. L. SABININA (J. Gen. Chem. Russ., 1933, **3**, 87—90).—Measurements of viscosity and of its temp. coeff. indicate the formation of a compound, Et_2O,H_2SO_4. R. T.

Vapours of reciprocal salt-pair NaCl–KI and of binary mixtures $PbCl_2$–$PbBr_2$, $PbCl_2$–PbI_2, PbI_2–CuI, and $CdCl_2$–$CdBr_2$. B. GREINER and K. JELLINEK (Z. physikal. Chem., 1933, **165**, 97—120).—For the reciprocal salt-pair at 1180° the at. fractions of Na and K are almost equal in the liquid and vapour phases, independent of the proportions in which the anions are mixed, but the at. fractions of the anions are not the same in the liquid and vapour phase, the at. fraction of I being always greater in the vapour than in the liquid. The partial pressures and activities in the vapours of the mixtures NaCl–KCl, NaI–KI, NaCl–NaI, and KCl–KI show these to be approx. ideal solutions. At. fractions in the vapours given off by $PbCl_2$–$PbBr_2$, $PbCl_2$–PbI_2, PbI_2–CuI, and $CdCl_2$–$CdBr_2$ have been determined, but activities and partial pressures could not be ascertained, since compound formation apparently occurs in the vapours. R. C.

Heats of vaporisation of binary mixtures. V. FISCHER (Ann. Physik, 1933, [v], **17**, 209—220).—The various heats of vaporisation of binary mixtures are defined, and expressions given from which they may be calc. Dana's observations for O_2–N_2 mixtures can be used for calculating the heat of mixing of these elements in the liquid state. A. J. M.

System methyl alcohol–*iso*butyl alcohol–water. E. JÄNECKE (Z. physikal. Chem., 1933, **164**, 401—416; cf. A., 1931, 793).—The binodal curves for the ternary system at 0—120° and the composition of the vapour given off by binary and ternary mixtures at the b.p./1 atm. have been determined. d and n diagrams for the complete range of ternary mixtures at 15° and 17·5°, respectively, are shown. R. C.

Structure of alloys. W. L. Bragg (Nature, 1933, **131**, 749—753).—A lecture. L. S. T.

Equilibrium diagrams of binary alloys of alkali metals: Na–K alloys. E. Rinck (Compt. rend., 1933, **197**, 49—51).—An apparatus is described which enables the alloys to be prepared by distilling into the same receptacle the required amounts of the constituents in vac. or in an atm. of A. Results for Na–K alloys confirm those previously obtained (cf. A., 1912, ii, 348). C. A. S.

System copper–beryllium. H. Borchers (Metallwirt., 1932, **11**, 317—321, 329—330; Chem. Zentr., 1933, i, 296).—Thermal, resistometric, dilatometric, and microscopical tests are described, and the Cu–Be diagram is modified. A. A. E.

Equilibrium diagram of the antimony–manganese system. T. Murakami and A. Hatta (Sci. Rep. Tohoku, 1933, **22**, 88—103).—Thermal, electrical resistance, and microscopical observations have been utilised. There are three intermetallic phases, η (MnSb), ε (Mn_3Sb_2), and δ (Mn_2Sb). The η phase forms a eutectic (9·5% Mn) at 570°. MnSb melts at 809°. Mn_3Sb_2 is formed by a peritectic reaction at 872°, and forms a series of solid solutions in the range 32—41% Mn. Mn_2Sb forms solid solutions in the range 45—50% Mn at high temp. and 47—48% at low temp. The β phase (Mn) forms a eutectic with the δ phase at 922° (55% Mn). γ-Mn changes to β-Mn at 1202°. A. J. M.

Structure of iron–nickel alloys. W. Broniewski and J. Smolinski (Compt. rend., 1933, **196**, 1793—1796).—The alloys prepared from electrolytic Fe and Ni were mostly homogeneous, but those containing 28—32% Ni showed two phases. Curves relating composition to conductivity, temp. coeff. of resistance, thermoelectric power, and dilatation and their variations with temp., hardness, sp. magnetisation, and energy loss for a hysteresis cycle are given. Those for hardness and hysteresis are strikingly similar, and hysteresis for alloys containing 33—90% Ni is much < that for either Fe or Ni. Most variations are explicable in terms of the lowering of the transformation point of Fe caused by Ni, but there is considerable evidence for the existence of $FeNi_2$, and the alloys probably consist of a series of solid solutions; those with 0—28% Ni are represented by $FeNi_2$ in Fe; 28—32% by mixtures of two solid solutions; 32—67% by Fe in $FeNi_2$; and 67·8—100% by $FeNi_2$ in Ni. C. A. S.

Electrochemical investigation of brass. A. Ölander (Z. physikal. Chem., 1933, **164**, 428—438).—Measurements of the e.m.f. of the cell Zn|(Li,Rb,Zn)Cl|$(Zn,Cu)_{solid}$ for 46 alloys at 333—626° confirm Bauer and Hansen's equilibrium diagram for brass (B., 1927, 939). The β phase apparently has an ordered structure both above and below the β-brass transformation. The γ phase has the ordered structure Cu_5Zn_8. In the η phase the activity coeff. of the Zn is unity. The latent heat of fusion of Zn is 28·4 g.-cal. per g. R. C.

Gallium alloys. W. Kroll (Metallwirt., 1932, **11**, 435—437; Chem. Zentr., 1932, ii, 3781).—Alloys of Ga with Fe, Ni, and Cu do not exhibit ageing. Ga dissolves (4·6%) in Mg. Binary and other low-m.p. alloys of Ga with Cd, Bi, Pb, Sn, and Zn show a min. m.p. (−15°) at 12% Sn. Ga increases the corrodibility of Al. A. A. E.

Diffusion of thorium in tungsten. G. R. Fonda, A. H. Young, and A. Walker (Physics, 1933, **4**, 1—6).—Variations in grain length of thoriated W wires cause changes in thermionic emission characteristics, but the heat of diffusion is unaffected. The intergranular diffusion is immeasurably rapid. Ch. Abs.

Binary mixed crystals of magnesium. E. Schmid and H. Seliger (Metallwirt., 1932, **11**, 409—411, 421—424; Chem. Zentr., 1933, i, 495).—Changes in the lattice consts. of Mg on formation of mixed crystals with Al and Zn have been measured, and the dependence of the solubility of these metals in Mg on the temp. has been ascertained. Mechanical properties are considered. A. A. E.

Rontgenographic determination of the solubility of cadmium in zinc. W. Boas (Metallwirt., 1932, **11**, 603—604; Chem. Zentr., 1933, i, 3).—At 20° Zn has a 2·6584, c 4·9353 Å.; Cd has a 2·6622, c 4·9456 Å. Experiments on single crystals show that about 0·80% Cd passes into solution; at room temp. slow separation occurs. A. A. E.

Nature of solid solution of aluminium in silver. C. S. Barrett (Met. and Alloys, 1933, **4**, 63—64, 74).—The lattice parameter of Ag is reduced by 0·0012 A. and the d by 0·069% for every 1 at.-% Al in solid solution, indicating that the solid solution is of the simple substitutional type. A. R. P.

***X*-Ray examination of the solubility of aluminium in copper.** I. Obinata and G. Wassermann (Naturwiss., 1933, **21**, 382—385).—The solubility limits previously recorded (B., 1922, 818) have been confirmed. Below 650° the solubility is independent of the temp. In the Al–Cu mixed crystal system no relation between lattice consts. and size of nucleus or separation of crystals was found. A. J. M.

Reciprocal solubility of fused lead or bismuth and fused zinc. K. Hass and K. Jellinek (Z. anorg. Chem., 1933, **212**, 356—361).—Solubility data and curves are given. The crit. solution temp. (by extrapolation) is 945° for Pb–Zn and 820° for Bi–Zn. F. L. U.

Vapour pressures and activities of binary alloys. E. Burmeister and K. Jellinek (Z. physikal. Chem., 1933, **165**, 121—132).—The activities of Cd in Cd–Sn alloys at 540°, of Zn over Sn–Zn alloys at 684°, and of Cd and Zn in Zn–Cd alloys at 682° indicated by v.-p. measurements made by an improved dynamic method agree substantially with Taylor's vals. (A., 1924, ii, 89). R. C.

Ternary system silver–copper–nickel. W. Guertler and A. Bergmann (Z. Metallk., 1933, **25**, 53—57).—In the Ni–Ag system the miscibility gap at the m.p. of Ni extends from 4 to 98·5% Ag; its extent is gradually reduced with addition of Cu until it finally disappears at 42·5% Cu. A space model of the ternary diagram is given and characteristic microstructures of the ternary alloys are illustrated. The solid solubility of Ag in Ni appears to fall with fall of temp. A. R. P.

Ternary alloys of copper, silicon, and magnesium. A. PORTEVIN and M. BONNOT (Compt. rend., 1933, **196**, 1603—1605).—The existence of the compound Mg_2Cu_3Si, m.p. 927°, three eutectics: (*a*) very near Mg_2Cu, 565°, (*b*) containing 16% Mg_2Si and 84% Mg_2Cu_3Si, 857°; and (*c*) 32·5% Cu+0·4Si+67·1Mg, 479°; and a ternary peritectic, 508°, has been demonstrated. C. A. S.

Carbides in carbon-containing alloys of tungsten and molybdenum with chromium, manganese, iron, cobalt, and nickel. V. ADELSKOLD, A. SUNDELIN, and A. WESTGREN (Z. anorg. Chem., 1933, **212**, 401—409).—*X*-Ray analysis reveals the existence of the *compounds* Co_3W_3C and Ni_3W_3C in alloys containing the respective elements. The stability of such double carbides decreases in the order Fe, Co, Ni. Analogous compounds cannot be detected in the systems Co–Mo–C and Ni–Mo–C. Fe_3Mo_3C at a high temp. gives rise to Mo_2C, whereas $(Fe,Co,Ni)_3W_3C$ give WC. In Cr–W–C alloys a phase $(Cr,W)_4C$, with the same structure as Cr_4C, has been detected. F. L. U.

Magnetic properties of iron–cobalt–tungsten alloys. B. A. ROGERS (Met. and Alloys, 1933, **4**, 69—73).—From the changes which occur in the physical and magnetic properties of W–Co–Fe alloys with 10—30% W on ageing it is possible to classify these alloys into five groups: (*a*) alloys with 0—20% Co and 10—30% W behave similarly to binary Fe–W alloys with the same W content; (*b*) alloys with 40—20% Co and 10—30% W suffer a peculiar fall in coercive force at a relatively low temp. when the hardness is at a max. and the *d* at a min., and on further heating a very rapid rise occurs in the electrical conductivity within a narrow temp. range; (*c*) alloys with 60—40% Co and 30—10% W are relatively non-magnetic in the quenched state, but become equal to Co magnet steels on heat treatment, although there is a tendency towards instability in the magnetic state; (*d*) alloys with about 20% W and 60% Co are inert to all heat treatment; (*e*) alloys with 90—70% Co and 10—30% W are difficult to obtain homogeneous, but all show a large increase in hardness on ageing, and this is associated with rise in coercive force and electrical conductivity. A. R. P.

Calorimetric method for determining rates of interdiffusion of reacting liquids. F. BARRY and A. K. SMITH (J. Amer. Chem. Soc., 1933, **55**, 2215—2230).—Apparatus and technique for determining the heat generated over long periods in an unstirred liquid which develops a vertical inhomogeneity of temp. (due to thermal stratification) are described. The rise of temp., *T*, due to interdiffusion of equimol. solutions of aq. HCl and aq. NaOH after the small initial turbulence has subsided, is given by $T=0{\cdot}05Ct^{0{\cdot}584}$, where *C* is normality and *t* (min.) is the time elapsed after the liquids were brought into contact. The rate of interdiffusion, *R* g.-equiv. per min. per sq. cm., at a plane horizontal interface at 20—25° after *t* min. is given by $R=k10^{-6}t^{-0{\cdot}416}$, where *k* is 2·64, 5·27, and 10·25, respectively, for 0·125, 0·25, and 0·5*N*-HCl and -NaOH. J. G. A. G.

Rate of evaporation of liquid in a stream of air. M. CENTNERSZWER, (MLLE.) C. WEKEROVNA, and (MLLE.) Z. MAJEVSKA (Bull. Acad. Polonaise, 1932, **A**, 369—382).—The rate of evaporation (*V*) of H_2O, C_6H_6, and PhMe in an air stream of varying velocity (*A*) has been measured. When the surface of the liquid is maintained at a const. temp., $V \propto A$ up to the highest velocities used; otherwise a limiting *V* is reached due to the cooling effect. The process is purely physical, and is determined by diffusion from a saturated layer in contact with the liquid. No chemical equilibrium such as liquidogenic gasogenic mols. is involved. F. L. U.

Rectification. W. H. KEESOM (Chem. Weekblad, 1933, **30**, 339—343, 354—359, 370—373, 382—385).—The theory of rectification is discussed in reference to the development of enthalpy–entropy–composition surfaces. The N_2–O_2 system is considered in some detail. Various methods of graphical representation are described, and the energy losses in the fractionating column (particularly losses arising from irreversible processes) and the influence of low temp. on the losses are discussed. A graphical method of determining the reversible work of separation is given. H. F. G.

Ternary azeotropic mixtures. I. Application of differential ebullioscope to study of ternary azeotropic mixtures. W. SWIENTOSŁAWSKI (Rocz. Chem., 1933, **13**, 227—235).—The use of a differential ebullioscope with a rectifying column for the study of the phenomena of homo- and heteroazeotropy in ternary liquid mixtures is described. R. T.

Free energy of normal aliphatic alcohols in aqueous solution. I. Partial vapour pressures of aqueous solutions of methyl, *n*-propyl, and *n*-butyl alcohols. II. Solubilities of normal aliphatic alcohols in water. III. Theory of binary solutions, and its application to aqueous-alcoholic solutions. J. A. V. BUTLER, D. W. THOMSON, and W. H. MACLENNAN (J.C.S., 1933, 674—679, 679—680, 681—686).—I. Partial v.p. of mixtures of H_2O with MeOH, Pr^{n}OH, and Bu^{n}OH have been determined. Activity coeffs. are calc.

II. The mutual solubility of Bu^{n}OH and H_2O, and solubility of *n*-alcohols from C_5 to C_8 in H_2O, have been measured.

III. The calc. free energy of transfer of the alcohols from the pure liquids to dil. aq. solution increases by about 800 g.-cal. for each additional CH_2 after EtOH. That of H_2O from its liquid to dil. solution in the respective alcohols increases by decreasing amounts with rise of mol. wt. A modified form of Langmuir's theory of solutions accounts for the main differences between the alcohols and for the variation of the activity coeffs. of lower alcohols with concn. Deviations which occur in solutions with much H_2O are attributed either to association of the latter or to its orientation around the alcohol mols. F. L. U.

Increase in the volatility of volatile acids in aqueous solution by the action of electrolytes having one ion in common. P. JAULMES (J. Chim. phys., 1933, **30**, 347—355).—Quant. data obtained with aq. HCO_2H and HCO_2Na, H_2SO_4, or tartaric

acid (I), with aq. AcOH and H_2SO_4 or (I), and with aq. $EtCO_2H$ and (I) agree well with theory. D. R. D.

Solubility of single crystals of gold–silver [alloy]. E. SCHIEDT (Z. anorg. Chem., 1933, **212**, 415—419).—The solubility of single crystals of Au–Ag (35—45% Au) in 33 and in 65% HNO_3 at 25° is the same as that of a multicryst. specimen. The rate of dissolution is not appreciably affected by the orientation of the crystal. F. L. U.

Solubility of silver chloride in water at 0°. C. R. JOHNSON and G. A. HULETT (J. Amer. Chem. Soc., 1933, **55**, 2258—2262).—The solutions in equilibrium with three samples of pure AgCl (differently prepared) contain different amounts of Cl′, which indicate the existence of adsorption equilibria. Pure AgCl cannot be obtained by washing with H_2O. Conductivity data show that the effect is not due to the action of light or impurities. J. G. A. G.

Solubility of silver chloride in nitric acid at 0°. C. R. JOHNSON and G. W. LOW, jun. (J. Amer. Chem. Soc., 1933, **55**, 2262—2265).—The nephelometrically and potentiometrically determined solubilities of AgCl in 0·001—15·2*M*-HNO_3 are concordant and independent of particle size. J. G. A. G.

Solubility of silver oxide in water, in alkali, and in alkaline salt solutions [at 25°]. Amphoteric character of silver hydroxide. H. L. JOHNSTON, F. CUTA, and A. B. GARRETT (J. Amer. Chem. Soc., 1933, **55**, 2311—2325).—The potentiometric determination of traces of Ag is described. The solubility of Ag_2O in pure H_2O is $2{\cdot}22\times10^{-4}$ g.-equiv. per 1000 g.; it decreases rapidly with the addition of KOH, NaOH, or $Ba(OH)_2$ to a min. of $6\times10^{-6}N$ in 0·015*N*-alkali, and then increases linearly. Inert salts increase the solubility in H_2O, but are without effect on the alkaline solutions. The equilibrium const. for the reaction $Ag_2O+2OH'=2AgO'+H_2O$ is $3{\cdot}8\times10^{-8}$ and the standard free energy change is 10,120 g.-cal. The dissociation const. of argentic acid is $7{\cdot}9\times10^{-13}$. The anomalous conductivity of aq. Ag_2O is discussed. J. G. A. G.

Solubility of certain substituted benzoic acids in typical salt solutions at 25°. J. N. PEARCE and J. W. NEWSOME (Proc. Iowa Acad. Sci., 1931, **38**, 163—164).—The solubilities of *o*- and *m*-nitro- and of *o*-, *m*-, and *p*-hydroxy-benzoic acids in NaCl, $BaCl_2$, K_2SO_4, and $MgSO_4$ solutions at 25° have been determined. Whilst $BaCl_2$ and NaCl show the general tendency to increase the activity coeffs. of the acids, the reverse holds for the two sulphates owing to the formation of HSO_4'. The greater decrease in the activity coeffs. in presence of K_2SO_4 is attributed to the greater hydration of $Mg^{\cdot\cdot}$. CH. ABS.

Influence of electrolytes on the solubility of the nitroanilines. P. PUTZEYS and J. BROSTEAUX (Ann. Soc. Sci. Bruxelles, 1933, B, **53**, 118—126).—The solubility in H_2O and solutions of NaCl, Na_2SO_4, $(NH_4)_2SO_4$, and $MgCl_2$ at 25° has been measured. For NaCl and $(NH_4)_2SO_4$ solutions the activity coeff. of the nitroaniline is the same at the same ionic strength. H. J. E.

Partition coefficient of iodine between water and ethylene dibromide and nitrobenzene. G. HERRERO (Anal. Fís. Quím., 1933, **31**, 5—10).—For $C_2H_4Br_2$ at 20° the coeff. increases from 650 to 696 when the aq. concn. rises from 0·03 to 0·183 g. per litre. For $PhNO_2$ the coeff. (196) is independent of the concn. These results support the Hantzsch–Landau rule, that the coeff. varies with concn. when one solution is violet and the other brown, and is independent of concn. when both solutions are brown. H. F. G.

Absorption of hydrogen by palladium-black under high pressures. V. V. IPATIEV, jun., and V. G. TRONEV (J. Gen. Chem. Russ., 1933, **3**, 78—86).—The absorption–pressure isotherms for H_2 in Pd, at 25°, 100°, 150°, 200°, and 300°, and 0—27 atm., tend to become flatter with increasing temp.; at the same time the region of abrupt rise in absorptive power becomes displaced in the direction of greater pressure. R. T.

Nature of the sorption of water by charcoal. J. W. MCBAIN, J. L. PORTER, and R. F. SESSIONS (J. Amer. Chem. Soc., 1933, **55**, 2294—2304).—Highly compressed sugar C, activated at 1000° and rigorously evacuated, expands during the adsorption of C_6H_6, C_7H_{16}, and H_2O at 0—60°. Substantial adsorption of the org. vapours occurs at low pressures, but with H_2O this takes place only at higher pressures. The observations are interpreted in terms of Langmuir's adsorption theory. The sp. heat of the adsorbed H_2O is approx. 1. The theories of capillary condensation and high compression are not applicable, and it is inferred that the H_2O is adsorbed or persorbed reversibly as a two-dimensional liquid film permeating the accessible structure of the C. H_2 is evolved after long contact between H_2O and the very active exceptionally evacuated C. J. G. A. G.

Adsorption of sulphurous acid by platinum, ferric oxide, and chromic oxide. I. B. NEUMANN and E. GOEBEL (Z. Elektrochem., 1933, **39**, 352—362).—The heat of adsorption of SO_2 by Cr_2O_3 at 100° is 34,500 g.-cal. per mol. The adsorption of SO_2 by Pt has been measured at temp. between 20° and 400°. The results are in fair agreement with the Freundlich isotherm. The heat of adsorption is greater for the first small amounts taken up and falls steadily as adsorption continues. Extrapolation leads to the val. 7000 g.-cal. per mol. at 0°. E. S. H.

Adsorption of electrolytes by activated charcoal. J. MUKHERJEE, S. ROYCHOUDHURY, and M. MAJUMDAR (J. Indian Chem. Soc., 1933, Ray No., 209—223; cf. A., 1931, 1226).—The adsorption of HCl, H_2SO_4, NaOH, $Ba(OH)_2$, BzOH, NaOBz, and picric acid from aq. solution by negatively-charged and neutral C has been studied conductimetrically and by the use of indicators. Alkali is less adsorbed by the neutral than by the charged C. HCl is equally adsorbed in both cases. H. J. E.

Adsorption from solutions of electrolytes by ash-free adsorbent charcoal. E. J. MILLER and S. L. BANDEMER (Mich. Agric. Exp. Sta. Rep., June 1932, 22).—Adsorbed acids can be quantitatively removed from C by electrodialysis, leaving the C able to adsorb NaOH or KOH. CH. ABS.

Adsorption of silver and mercury salts by sugar charcoal. M. WARLET (Bull. Soc. chim. Belg., 1933, **42**, 127—140).—The consts. in the Freundlich equation $A=kT^{1/n}$ have been determined for the adsorption of Ag (from $AgNO_3$ solution) and Hg (from $HgCl_2$ solution) on C. The equilibrium established between solvent and C carrying adsorbed salt is discussed in relation to the separate adsorption of the salt and the metal. Desorption experiments show that the ratio of the total quantity of metal adsorbed to the quantity which re-enters solution when the C is treated with H_2O is approx. 0·5 for Ag and 0·79 for Hg. H. F. G.

Relation of adsorption to the degree of dispersion of the adsorbent. G. ROSSI and G. SCANDELLARI (Gazzetta, 1933, **63**, 261—266).—Measurements of the adsorption of night-blue from aq. solution by $BaSO_4$ (*a*) suspended directly in the solution and (*b*) produced by pptn. in the solution show that the adsorption is dependent on the degree of dispersion of the $BaSO_4$. O. J. W.

Active oxides. LXV. Elucidation of thermal decomposition of zinc carbonate and zinc oxalate by sorption measurements with dye solutions and methyl alcohol vapour. A. MELLER and G. F. HUTTIG (Z. physikal. Chem., 1933, **B**, **21**, 382—388).—The sorptive power for dyes in aq. solution of $ZnCO_3$ partly converted into ZnO by being heated in a vac. increases as CO_2 is lost until the composition is about $ZnO,0{\cdot}9CO_2$, beyond which there is no further change. This agrees with the theory that shortly after decomp. has started the $ZnCO_3$ crystals have become coated with a film of ZnO, from which further transformation nto ZnO progresses inwards (A., 1932, 1211; this vol., 233). In partly decomposed ZnC_2O_4 the pores are apparently wider than in $ZnCO_3$–ZnO, methylene-blue being able to penetrate through them. The sorption of MeOH vapour at 20° shows that in both systems the pore vol. is greater the further the decomp. has progressed, and for a given degree of decomp. is greater in the system ZnC_2O_4–ZnO. When the decomp. is on the point of completion the pore space diminishes again. R. C.

Japanese acid clay. XI. Sorption of gases by Japanese acid clay. K. KAMAMOTO and Y. OOTSUBO (J. Soc. Chem. Ind. Japan, 1933, **36**, 150—151B; cf. B., 1932, 228).—The sorptive power of the clay is < that of active C, but > that of SiO_2 gel. It is increased by activation or acid treatment. The mechanism of the adsorption is the same. J. S. A.

Absorption of the arsenite ion by soils. S. M. DRATSCHEV (Z. Pflanz. Düng., 1933, **30**, **A**, 156—167).—Soils having high absorption capacity for bases also absorb AsO_3''' readily from 0·001—0·01*N* solutions, but there is no obvious relation between the two effects. The absorption of AsO_3 increases with time (20 days) without reaching an end-point. The energy charge and the capacity for absorption of AsO_3''' by soils are considerably increased by addition of Fe_2O_3 or $CaCO_3$ but not by $CaSO_4$ or $CuSO_4$. The absorption process follows the normal equation $x=K(a-x)^{1/n}$. A. G. P.

Binding of iodine by caseinogen. I. S. YAITSCHNIKOV (J. Gen. Chem. Russ., 1933, **3**, 1—4).—Absorption of I vapour by caseinogen proceeds continuously during 4·5 years of observation, without attainment of equilibrium. The final product contained 53% I. R. T.

Reversal of Traube's rule in adsorption. B. ILJIN (Kolloid-Z., 1933, **64**, 99—101).—A reply to criticism (cf. A., 1932, 689). E. S. H.

Measurements of the surface tension of solutions of sodium and potassium salts by the ring method. II. A. LOTTERMOSER and E. SCHLADITZ (Kolloid-Z., 1933, **64**, 44—49; cf. this vol., 672).—Using surface tension measurements as an indicator for the titration of fatty acids with NaOH, the equivalence point falls on the descending branch of the curve for dil. solutions, at the surface tension min. for solutions of medium concn., and on the rising branch for conc. solutions. The observations indicate how the surface tension of soap solutions of different concn. is influenced by excess of fatty acid or NaOH. In a mixture of fatty acids those of lower mol. wt. are neutralised first. The min. observed by du Noüy at extreme dilutions were not found. In presence of a trace of soap, surface tension measurements can be used as indicator in the titration of alkalis with acids. E. S. H.

Surface tension studies with *n*-butyl acetate. E. R. WASHBURN and C. H. SHILDNECK (J. Amer. Chem. Soc., 1933, **55**, 2354—2357; cf. A., 1928, 472).—Data for 20—35° show that the Eotvos const. is 2·26 and the parachor 294·3, indicating that the ester is a "normal" liquid. The surface tension of aq. solutions at 25° increases on exposure to air, suggesting that the surface loses ester mols. more rapidly by evaporation than can be replaced by liquid diffusion. Experiments indicate that the surface layer is many mols. thick. J. G. A. G.

Contact angle measurements. II. O. HERSTAD (Kolloid-Z., 1933, **64**, 6—12; cf. A., 1931, 816).—The contact angles of many volatile org. liquids in the form of drops on a glass plate have been determined by the method previously described. In all cases the contact angle varies with time, sometimes very considerably, throwing doubt on the validity of the accepted laws of capillary behaviour. The use of a "contact angle characteristic" is suggested in place of a const. contact angle. The results are influenced by the thermal history of the glass plate. E. S. H.

Capillary action as a function of temperature and pressure. F. W. CONSTANT (J. Elisha Mitchell Sci. Soc., 1932, **48**, 28—29).—As the air pressure above a capillary column of H_2O is reduced the column is unaffected until the pressure is about 30 mm.; below this the observed fall suggests that the capillary rise would be zero in a perfect vac. Liquids, like Hg in glass, having an inverted meniscus do not show the effect of reduced pressure. CH. ABS.

Capillary systems. XV (1). Cohesion and adhesion in ideal and real sphere packing. E. MANEGOLD and C. STUBER (Kolloid-Z., 1933, **64**, 12—21; cf. this vol., 458).—Mathematical. E. S. H.

Interfacial tension of mercury in contact with organic liquids. F. E. Bartell, L. O. Case, and H. Brown (J. Amer. Chem. Soc., 1933, **55**, 2419—2426).—The drop-wt. and capillary-rise methods afford concordant vals. for the interfacial tension of 12 pure org. liquids against Hg at 25°. Some of the vals. are > those previously recorded and data for halogen compounds indicate that the attraction of halogen radicals towards Hg is not so strong as believed hitherto. In the absence of solubility effects, the vals. for the members of an homologous series against a given liquid will decrease progressively if the surface tension vals. increase progressively. J. G. A. G.

Interfacial tension of mineral oil against various aqueous solutions at 40°. W. G. Eversole and D. S. Dedrick (Proc. Iowa Acad. Sci., 1931, **38**, 163).—An apparatus employing the drop-wt. method is used. The interfacial tension (I) diminishes as the C chain increases in length. For NaOAc and $EtCO_2Na$ (I) decreases hyperbolically up to saturation, but for HCO_2Na (I) is min. at about 2·5 molal. Ch. Abs.

Influence of surface energy in disperse systems. C. P. Yap (Phil. Mag., 1933, [vii], **16**, 80—96).—The effect of surface energy in disperse systems is discussed in connexion with the phase rule. An additional degree of freedom must be assumed in such systems, thus making $P+F=C+3$. Equations are given connecting solubility and heat of dissolution with particle size. Regarding supercooling as a case of delayed pptn. and supersaturation, the effect of particle size is discussed, and an equation is derived similar to that of Jones and Partington. The stability of disperse states is discussed. A disperse state acts as if it were under negative pressure, to counteract the positive pressure due to surface forces. The effect of surface energy considerations in metallurgical problems, such as the pptn. of Fe_3C in steel, and solubility of one metal in another, is discussed. A. J. M.

Mathematics of effervescence. O. Stuhlman, jun. (J. Elisha Mitchell Sci. Soc., 1932, **48**, 19—20).—The formation and properties of gas bubbles in H_2O and C_6H_6 are discussed. Ch. Abs.

Phase boundary potentials of adsorbed films on metals. I. Oxygen on gold. H. K. Whalley and E. K. Rideal. **II. Iodine on platinum.** L. Jacobs and H. K. Whalley. **III. Examination of the interaction of copper and iodine vapour by the method of surface potentials.** H. K. Whalley and E. K. Rideal (Proc. Roy. Soc., 1933, A, **140**, 484—489, 489—496, 497—504).—I. Methods of measuring changes of metal–gas p.d. are reviewed, and a new method is described. If a film of O_2 is present on the surface, the surface potential of Au is changed by 1·46 volts, a val. comparable with the alteration in the thermionic work function caused by an O_2 layer on the metal.

II. The rate of evaporation of I from a Pt surface, on which an O_2 film is present, is unimol. in character, and the latent heat of evaporation is shown to be dependent on the phase boundary potential, which can be altered by O_2.

III. The rate of evaporation of monolayers of I from Cu_2I_2 follows a unimol. law, but the phase boundary potential between Cu and I is changed by the presence of a layer of Cu_2I_2. The magnitude of this potential is controlled by both the thickness and the cryst. state of the Cu_2I_2 layer. L. L. B.

Adhesion tension. Pressure of displacement method. F. E. Bartell and H. J. Osterhof (J. Physical Chem., 1933, **37**, 543—552; cf. A., 1932, 690).—The pressure needed to prevent wetting of compressed powders by liquids has been measured. Vals. of adhesion tension and work of adhesion are given for a no. of liquids in relation to C and SiO_2. When the liquids are arranged in the order of the adhesion tension, the C series is the reverse of the SiO_2 series. H. J. E.

Formation of unimolecular films of substances not containing a polar group. J. J. de Haas (Chem. Weekblad, 1933, **30**, 347).—A mixture of paraffin (average mol. wt. 313) and palmitic acid gives a unimol. film on H_2O even when 66% of paraffin is present; the area covered per g. is very little < that for the pure acid. H. F. G.

Behaviour of dyes in two dimensions. S. Veil (J. Chim. phys., 1933, **30**, 266—273).—Such phenomena as diffusion, cataphoresis, and electrolytic pptn. may with advantage be studied in two-dimensional films. Experiments with a no. of dyes are described. Methylene-blue diffuses without discontinuity through a gelatin film. Rhythmic pptn. occurs when a drop of $K_2Cr_2O_7$ solution is applied to a film of gelatin impregnated with a dye. H. F. G.

Heat of wetting of metallised carbon. M. S. Belenki, W. P. Jouse, and L. J. Kovaleva (Z. anorg. Chem., 1933, **212**, 362—368).—Heats of wetting by C_6H_6 of specimens of activated C metallised with 0·002—1·6% of Ag, Au, or Pt have been measured at room temp. C dried at 100—105° (after metallisation) exhibited heats of wetting which decreased rapidly with increasing % of metal, whereas that dried at 250—270° showed the opposite effect, an approx. const. val. being attained in each case. The results are discussed. F. L. U.

Evaporation from salt solutions and from oil-covered water surfaces. C. Rohwer (J. Agric. Res., 1933, **46**, 715—729).—Surface oil films reduce evaporation of H_2O in proportion to their thickness, but the relatively rapid dissipation of oil by wind, rain, etc. renders this method uneconomical for the conservation of large areas of H_2O. Meteorological factors controlling evaporation from free H_2O surfaces do not operate on oil-covered H_2O. Temp. of oil-covered H_2O is higher than that of a free H_2O surface. Evaporation from 2, 5, 10, and 20% solutions of NaCl averages 0·97, 0·98, 0·93, and 0·87 of that from H_2O, and is subject to the usual meteorological conditions. Evaporation from Na_2SO_4 solutions agrees closely with that from H_2O under similar conditions. A. G. P.

Anomalous velocity distribution in oil layers. II. H. Umstatter (Kolloid-Beih., 1933, **37**, 421—426; cf. A., 1931, 554).—A mathematical treatment of the deviations from the normal, linear velocity

distribution under conditions of poor thermal conductivity. E. S. H.

Quantitative study of a simple system of periodic precipitation. R. FRICKE [with J. LUKE and K. MEYRING] (Kolloid-Z., 1933, **64**, 62—65).—The simplest case of periodic structure formation, by salting out a salt solution [$Ba(NO_3)_2$] by a conc. acid (HNO_3) in a capillary (cf. A., 1930, 158), has been followed by quant. analysis. The existence of considerable supersaturation is established, and the phenomenon is found to be in accordance with normal diffusion and pptn. processes. E. S. H.

Diffusion of hydrogen through palladium. Influence of pressure, temperature, and purity of metal. V. LOMBARD and C. EICHNER (Compt. rend., 1933, **196**, 1998—1999; cf. A., 1932, 906).—The rate of diffusion of H_2 at pressure P into a space where the pressure of H_2 is p varies as P^m—p^n. The sp. diffusion (c.c. per hr. per sq. cm. per mm. thickness) for temp. 350—850°$=20{\cdot}73\times T^{0{\cdot}5}\times e^{2022/T}$. The purity of the Pd has considerable effect. C. A. S.

Diffusion of gases at high temperatures through porous materials. P. BREMOND (Compt. rend., 1933, **196**, 1651—1653; cf. this vol., 668).—Experiments with unglazed porcelain and air, CO_2, H_2, SO_2, and coal gas between 17° and 700° show that the diffusion effects are not in accordance with the requirements of Graham's law. C. A. S.

Diffusion of helium through quartz: relation to temperature. E. F. BURTON, E. O. BRAATEN, and J. O. WILHELM (Canad. J. Res., 1933, **8**, 463—466).—For fused quartz the rate is nearly proportional to the pressure at const. temp. The rate has been measured at const. pressure between −185° and 110°. The rate increases rapidly at about −30°. The permeability of single quartz cryst. plates is independent of the direction in which the plate is cut, but is about half the val. for fused quartz. R. P. B.

Compounds of the inert gases. H. KADING and N. RIEHL (Naturwiss., 1933, **21**, 479).—Results of experiments on the absorption of Ra-Em by Br solution before and after subjecting the mixture to a continued electric discharge might be interpreted as indicating the formation of compounds, but this is erroneous, since the discharge causes absorption of emanation by the glass. A. J. M.

Influence of parchment membrane on the transport numbers of cations in solutions of sodium and barium chlorides. J. BABOROVSKY and O. VIKTORIN (Coll. Czech. Chem. Comm., 1933, **5**, 211—217).—The cation transport nos., n_{Na}, n_{Ba}, have been deduced from the e.m.f. of concn. cells with and without parchment membranes. The membrane causes an increase in n_{Na}, which becomes more pronounced as the concn. ratio in the cell diminishes. This effect is probably due to adsorption of Cl' by the membrane. With dil. aq. $BaCl_2$, is similarly higher in presence of the membrane, but in conc. solutions the reverse is the case, suggesting that Cl' adsorption is predominant in dil., and Ba'' adsorption in conc., solution. D. R. D.

Dependence of the electrokinetic potential on the current density. N. SCHONFELDT (Wiss. Veroff. Siemens-Konz., 1933, **12**, No. 1, 39—43; cf. A., 1932, 1208).—Electro-osmotic measurements on several org. and inorg. diaphragms show that the assumption of a flow strength in the boundary layer in combination with the effect of change of concn. in the double layer provides a satisfactory qual. explanation of the shape of the c.d.-electrokinetic potential curves. A. R. P.

Absorption and osmosis. II. F. A. H. SCHREINEMAKERS and C. L. DE VRIES (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 406—414).—An investigation of the system $H_2O+Na_2CO_3$ with a membrane of pig's bladder is described. N. M. B.

Membrane equilibria and "harmonies." J. STRAUB (Kolloid-Z., 1933, **64**, 72—83).—Experiments formerly described (A., 1931, 163) are reviewed in the light of the general theory of Schreinemakers (A., 1924, ii, 389, 601). E. S. H.

Osmotic equilibrium of Congo-red at various membranes. G. SCHMID (Z. Elektrochem., 1933, **39**, 384—398, 453—464).—Apparatus and technique for measuring the osmotic pressure and membrane potential of Congo-red (I) at membranes of collodion (of graded permeability), parchment, and pig's bladder are described. The results for osmotic pressure, membrane potential, and distribution of KOH are independent of the membrane. The van 't Hoff factor is about 1·19 and the membrane potential 0·037 volt. The activity coeff. of $K^{\cdot}$ in the 0·01*N*-K salt of (I) is 0·5. The K salt behaves in accordance with Kohlrausch's conductivity law at high dilutions. Conductivity and osmotic data show that (I) in dil. solution is an almost completely dissociated, strong electrolyte, which forms highly-charged, complex anions. E. S. H.

Structure and permeability of collodion membranes. K. HRYNAKOWSKI and W. NOWATKE (Rocz. Chem., 1933, **13**, 256—263).—Collodion membranes formed on Hg surfaces are more homogeneous than those formed on glass surfaces. The permeability is increased by diluting the solution with $COMe_2$. The membranes are traversed by capillary canals of various diameters, and running in all directions. Contrary to Manegold's findings (A., 1930, 154) the dialysis coeff. δ does not diminish with time, but remains const. during 150 min. for a no. of solutions. The vals. of δ are directly proportional to the mol. wt. and diameter of the substances examined. R. T.

Endosmosis through a spherical, expansible, semipermeable membrane. A. SKAPSKI (Bull. Acad. Polonaise, 1932, A, 347—351).—Taking into account the elastic resistance of a membrane as a factor retarding endosmotic flow, a formula for the rate of flow is derived and compared with observations on the osmotic regulation in snails. The agreement is good. F. L. U.

Physical properties of aqueous salt solutions. J. N. PEARCE and M. A. HOOPER (Proc. Iowa Acad. Sci., 1931, **38**, 164).—Dielectric consts. of alkali halide and nitrate solutions, calc. from Huckel's

relation involving n, decrease with increase in concn.; all approach the same small val. at saturation. The activities calc. from Huckel's equation for conc. solutions of strong electrolytes agree qualitatively with experimental vals. CH. ABS.

Dielectric constant of liquids. X. Aqueous solutions of aminobenzoic acids. G. DEVOTO (Gazzetta, 1933, **63**, 247—250).—Measurements of the dielectric const. indicate that in aq. solution *m*-$NH_2 \cdot C_6H_4 \cdot CO_2H$ exists mainly in the amphoteric polar form $NH_3^+ \cdot C_6H_4 \cdot CO_2^-$, whereas the *o*- and *p*-acids have a non-polar structure. O. J. W.

Optical methods for the study of solutions of electrolytes. A. I. BRODSKI (Uspekhi Khim., 1932, **1**, 712—743).—A discussion. CH. ABS.

Cryoscopic determination of hydration of ions of ammonium chloride. F. BOURION and E. ROUYER (Compt. rend., 1933, **197**, 52—54; cf. this vol., 673).—The hydration of the ions in *M*- and 0·5*M*-NH_4Cl is represented by $NH_4Cl,6{\cdot}2H_2O$ and $NH_4Cl,7{\cdot}5H_2O$, respectively. C. A. S.

Theory of Brownian motion and the operational method. J. METADIER (Compt. rend., 1933, **197**, 29—31).—Mathematical. C. A. S.

Colloid correlation principle. S. C. BLACKTIN (Chem. and Ind., 1933, 544—545; cf. this vol., 123).—The mode of growth of colloidal aggregates in smokes and of the degradation of dust particles is related to their gravitational distribution in the atm. J. S. A.

Elastic properties of foams. B. DERJAGUIN (Kolloid-Z., 1933, **64**, 1—6).—A theoretical investigation of foams and emulsions of similar type, with reference to the vol. elasticity of the interior of each cell and the interfacial tension of the bounding walls, gives the following results. A foam has the properties of a solid elastic substance, independently of the elasticity of the bounding walls. The difference between the mean inner pressure and the outer pressure is 2/3 the free sp. interfacial energy. The equation of state of a foam containing gas is given by $(p+a/v^{\frac{1}{3}})(v-b)=RT$, where a is a function of T, which is proportional to surface tension. The elasticity modulus=0·4× the difference between the inner and outer pressures and is proportional to the dispersity. Poisson's coeff. is approx. 0·5. E. S. H.

Investigation of systems with coarse particles and its value for a knowledge of colloidal systems. H. FREUNDLICH (J. Indian Chem. Soc., 1933, Ray No., 93—97).—A discussion. H. J. E.

Preparation of sulphur sols. A. JANEK (Kolloid-Z., 1933, **64**, 31—32).—Dil. H_2SO_4 is added to two solutions containing respectively (*a*) Na_2SO_3, (*b*) Na_2S+a little Na_2SO_3. The two solutions are then mixed, left for 1 hr., filtered, and the ppt. is washed and peptised with distilled H_2O. Definite concns. of the reagents must be used. E. S. H.

Action of potassium cyanide solutions on colloidal gold. F. P. WORLEY and E. D. ROBINS (Trans. Faraday Soc., 1933, **29**, 764—770).—The main reaction is $4Au+8KCN+2H_2O+O_2=4KAu(CN)_2+4KOH$, occurring in the stages: $4KCN+4H_2O=4KOH+4HCN$, $2Au+2HCN+O_2=2AuCN+H_2O_2$, $2Au+2HCN+H_2O_2=2AuCN+2H_2O$, $4KCN+4AuCN=4KAu(CN)_2$. This reaction is probably preceded by the dissolution of the hydrated Au_2O_3 normally present as a mol. layer coating the Au particles. D. R. D.

Influence of temperature on certain properties of zirconium oxide sols. F. J. ROBINSON and G. H. AYRES (J. Amer. Chem. Soc., 1933, **55**, 2288—2294).—Rise of temp. decreases the viscosity (at 25°), the flocculation val., and the p_H val., and increases the intensity of scattered light. J. G. A. G.

Effect of optical constants on the Mie absorption curve for coloured colloidal systems. I. Silver–water system. A. KREBS (Physikal. Z., 1933, **34**, 490—491).—The fact that the optical consts. of substances vary with the state of division of the substance necessitates the use of new consts. in Mie's absorption formula. These have been determined for Ag by Murmann (this vol., 332), and are used to calculate the refractive index of Ag in small particles, and the absorption of colloidal Ag solutions is calc. from Mie's formula. A. J. M.

Mechanism of coagulation of colloids. S. G. CHAUDHURY and S. ROYCHOUDHURY (J. Indian Chem. Soc., 1933, Ray No., 201—207).—Various mechanisms are discussed. H. J. E.

Coagulation of colloids. The wall effect. S. S. JOSHI and V. L. NARAYAN (J. Indian Chem. Soc., 1933, Ray No., 41—52).—The coagulation by KCl and $BaCl_2$ of MnO_2, Sb_2S_3, and $Fe(OH)_3$ sols is accelerated and the autocatalytic effects are diminished by adding glass beads. When the walls of the containing vessel and the beads are coated with paraffin wax coagulation is retarded. H. J. E.

Inorganic jellies. S. PRAKASH (J. Indian Chem. Soc., 1933, Ray No., 99—106; cf. A., 1929, 1008, 1235).—A summary. H. J. E.

Behaviour of colloids towards electrolytes and non-electrolytes with progress of dialysis. B. N. DESAI (J. Indian Chem. Soc., 1933, Ray No., 37—40).—Colloids dialysed for different periods show apparent inconsistencies, due to varying amounts of the peptising electrolytes present. H. J. E.

Physico-chemical analysis and problems of flocculation. I. Flocculation of grape-juice colloids. S. I. INOZEMTZEV (J. Gen. Chem. Russ., 1933, **3**, 115—120).—The colloid content (I) of grape juice (II) can be roughly deduced from the stability of emulsions formed by shaking (II) with C_6H_6, PhMe, or Et_2O, the best results being obtained with C_6H_6. The observations indicated that (I) varies greatly with different samples of (II), as well as for the same sample during maturation. (I) is greatly diminished by boiling (II). The system (II)–EtOH–Et_2O exhibits every stage from complete clarity to complete flocculation. R. T.

Electrical adsorption and stability of colloids. A. GANGULI (Kolloid-Z., 1933, **64**, 65—72).—Mainly theoretical. The charge of a colloid particle depends mainly on chemical adsorbability, which is determined by the nature of the adsorbing surface, the

adsorption potential, mobility, and valency of the ions. Ion antagonism and reversal of charge are explained in terms of preferential adsorption of ions. Decrease of the charge on dilution is attributed to displacement of the adsorption equilibrium of the peptising ion. Causes of the anomalous behaviour of diluted sols towards electrolytes are suggested. The sensitising influence of non-electrolytes is due mainly to repression of ion adsorption and to changes in the dielectric const. E. S. H.

Influence of adsorbed ions on the dissolution of colloidal aluminium hydroxide in hydrochloric acid. H. V. TARTAR, C. C. BRYAN, and H. SHINN (J. Amer. Chem. Soc., 1933, **55**, 2266—2272; cf. A., 1932, 693).—The dissolution of aged colloidal $Al(OH)_3$ in 0·2*N*-HCl is catalysed by sulphates, arsenates, and phosphates in increasing order. Within limits, the wt. of $Al(OH)_3$ dissolved, X, in 24 hr. is given by $X=K \log a+C$, where a is mol. concn. of electrolyte affording bi- or ter-valent anions and K and C are sp. consts. The catalysis is attributed to a decrease in the electrical potential at the solid–liquid interface by the adsorption of anions of high valency. J. G. A. G.

Effect of ions in lyotropic series on the swelling of organic matter. Spreading of the ions on non-ionised organic substances. VI. Effect of aromatic compounds containing a hydrophilic group on the swelling of starch. VII. Effect of normal aliphatic and alicyclic compounds containing a hydrophilic group on the swelling of starch. J. R. KATZ, F. J. F. MUSCHTER, jun., and A. WEIDINGER (Biochem. Z., 1933, **261**, 15—21, 47—54; cf. this vol., 462).—VI. The swelling produced by salts (I) (Na, K) of aromatic sulphonic acids is parallel to that of sulphites and sulphates and is similar to that produced by PhOH, NH_2Ph, NaOBz, Ph arsinate, and Na phenylselenonate. Sulphinates are less active than the corresponding sulphonates. When an alkyl side-chain (II) is present, the action increases with the length of (II), and the same holds for the salts $Ph{\cdot}[CH_2]_n{\cdot}CO_2Na$. $C_{10}H_7{\cdot}SO_3Na$ is more active than $PhSO_3Na$, the 2-compound being more active than the 1-. Amongst these and other (I) it is the length of the C chain and not the mol. wt. which is the determining factor. Decreasing solubility in H_2O is frequently accompanied by increasing swelling power.

VII. Amongst the *n*-fatty acids (C_1—C_9, C_{12}, C_{18}), *n*-alkyl-sulphonic, -sulphuric, and -arsinic acids, non-ionising org. compounds (aliphatic alcohols, *n*-carbamates, *n*-amides), and probably also amongst salts of alicyclic carboxylic and sulphonic acids and alicyclic ketones the swelling power increases with increasing length of C chain. The action of the alicyclic compounds is weaker than that of the corresponding aliphatic compounds. W. McC.

Lyotropic series in swelling and its extension to organic and non-ionising substances. VIII. Influence of nitro-compounds on the swelling of potato starch. J. R. KATZ, A. WEIDINGER, and F. J. F. MUSCHTER, jun. (Biochem. Z., 1933, **261**, 433—435).—The influence of $NO_2{\cdot}CH_2{\cdot}CO_2Na$, $NO_2{\cdot}[CH_2]_3{\cdot}OH$, nitrocarbamide, *o*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2Na$, and *m*-$NO_2{\cdot}C_6H_4{\cdot}SO_3Na$ on the temp. of paste formation has been compared with that of NaOAc, PrOH, carbamide, NaOBz, and $PhSO_3Na$. The NO_2 group increases the swelling action. In the aromatic compounds, the *p*- has a greater influence than *o*-. P. W. C.

Migration studies with colloids. I. Effect of electrolytes and of colloids of opposite sign on the stability of colloidal systems. II. Mechanism of the mutual coagulation process. F. HAZEL and D. M. MCQUEEN (J. Physical Chem., 1933, **37**, 553—570, 571—582; cf. A., 1931, 1232).—I. The effect of $Fe(CN)_6''''$, CrO_4'', PO_4''', SO_4'', and Cl' on the cataphoresis of positive sols (I) of As_2S_3, Fe_2O_3, Cr_2O_3, and Al_2O_3, and of Th'''', Al''', Cr'', Fe''', Ba'', and K' on that of negative sols (II) of Fe_2O_3, SnO_2, MnO_2, and As_2S_3 has been studied ultramicroscopically. Migration velocities for mixtures of (I) and (II) are correlated with their mutual coagulation. All the particles in the mixed sols migrate in the same direction with the same velocity.

II. The effect of KH_2PO_4, $BaCl_2$, $AlCl_3$, $FeCl_3$, and K_2SO_4 on the migration velocities of mixed (I) and (II) (Al_2O_3–MnO_2, Al_2O_3–As_2S_3, Fe_2O_3–MnO_2, As_2S_3–Fe_2O_3) has been measured. A mechanism of mutual coagulation is advanced. H. J. E.

Physical unreality of the terms used in cataphoresis and the fictitious ζ-potential. J. W. MCBAIN (J. Indian Chem. Soc., 1933, Ray No., 67—72).—Theoretical. H. J. E.

Cataphoresis. III. Comparison of results of measurements by the transport and moving boundary methods, and theory of the latter method. D. C. HENRY and J. BRITTAIN (Trans. Faraday Soc., 1933, **29**, 798—815).—Using Ag sols, an accuracy of 3% can be obtained by either method. The usual method for calculating results from moving boundary data is erroneous, but correct results are obtained by an application of the Kohlrausch–Weber theory of ionic displacements. D. R. D.

Electrophoretic behaviour of lecithin and certain fats. C. W. PRICE and W. C. M. LEWIS (Trans. Faraday Soc., 1933, **29**, 775—787).—Electrometric measurement of the p_H of aq. choline chloride gives $p_{Eb}=5{\cdot}06$, indicating that the isoelectric p_H of lecithin should be approx. 5·2. Electrophoretic experiments, however, confirm the accepted val., 2·7. The discrepancy is attributed to adsorption of OH' by the fatty portions of the particles. The electrophoretic mobilities of aq. dispersions of tristearin, αα′-dipalmitin, and β-azelao-αα′-distearin have been determined. In the first two cases the mobility is a linear function of $1/[H^{\cdot}]^{1/3}$, the gradient being the same for both. D. R. D.

Time changes in resin sols (ageing phenomena). N. PESKOV and E. PREIS (Kolloid-Z., 1933, **64**, 36—44).—A nephelometric study of the ageing of gamboge sols has shown that the process is accelerated by heat, and by adding definite quantities of EtOH or other liquids which can serve as a solvent for the disperse phase. The process appears to be due to the growth of large particles at the expense of the smaller, rather than to aggregation of the particles. E. S. H.

Viscosimetric effect in formation of starch paste. II. W. SECK (Kolloid-Z., 1933, **64**, 86—91; cf. this vol., 674).—Very dil. pastes follow the Hagen–Poiseuille law (I). Less dil. pastes show structure viscosity (II) at low velocities of flow and follow the Ostwald–de Waele law, but after heating they behave in accordance with (I). Conc. pastes exhibit (II) even after long heating. The decrease of viscosity on heating is due entirely to the loss of (II), the "pure" viscosity remaining unaltered. The relation between relative viscosity, η, and concn., c, is given by $\log \eta = A+Kc$. K is const. throughout, but the val. of the "const." A changes suddenly when c reaches 0·15—0·2M. This is the region in which a strong increase of (II) is observed. E. S. H.

Lyophilic colloids. XVIII. Concentrated sols and the structure of the micelle. H. G. B. DE JONG, H. R. KRUYT, and J. LENS (Kolloid-Beih., 1933, **37**, 395—420; cf. this vol., 23).—The electroviscous effect in gum arabic sols decreases rapidly with increasing concn. of the sol; the curves obtained vary in a similar way to the viscosity–p_H curves for gelatin sols of different concn. These effects cannot be ascribed to the influence of parasitic electrolytes or to an equivalence between the added electrolyte and the colloid, but it is probable that the potential of the particles is already lowered by the increase of concn. This view is supported by measurements of electro-osmosis through gelatin gels and of the electrical conductivity of gelatin and gum arabic sols. The stability, as determined by the EtOH no., falls with increasing concn. A conception of the colloid particle in vol. equilibrium is put forward, according to which the particle is subject to expansion factors (capillary-electric charge and solvation tendency) and contraction factors (cohesion forces). The effect of such vol. influences on the electroviscous effect is discussed. E. S. H.

Viscosity curves of sols of lyophile colloids, and other curves. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1933, **3**. 13—16).—The viscosity of flax mucilage sols is given by $\mu=(A-1)C+e^{bC}$, where A and b are consts., and C is the % concn. of colloid. The μ–[$MgSO_4$] curve exhibits a min.; this phenomenon is ascribed to neutralisation of the charge of colloidal particles, followed by dehydration and supercharging. R. T.

Depression of the specific viscosity of cellulose nitrate. G. S. BARSUKOV (J. Appl. Chem. Russ., 1933, **6**, 99—102).—On the addition of NH_3–EtOH the sp. viscosity (I) of cellulose nitrate in EtOH rises to an extent which is proportional to the NH_3 content during the first 5 hr.; subsequently it falls continuously. The N content and (I) fall continuously with duration of immersion in boiling xylene or aq. NH_3. R. T.

Viscosity of cuprammonium cellulose solutions. III. M. NEGISHI and T. NAKASHIMA (J. Soc. Chem. Ind. Japan, 1933, **36**, 275—276B).—The influence of time on the viscosity of the solutions has been examined. The const. (K) which measures the rate of fall of the viscosity with time is found to diminish with increasing Cu concn. At 0° the viscosity is independent of the Cu content. With increase in the NH_3 concn. the relative viscosity diminishes, but K is independent of the NH_3 and cellulose content. V. E. Y.

Influence of a magnetic field on the viscosity of colloids. A. GARCIA BANÚS and M. MASRIERA (Anal. Fís. Quím., 1933, **31**, 236—241).—Magnetic fields of 3000—10,000 gauss have no appreciable influence on the viscosity of colloidal solutions of V_2O_5, $Fe(OH)_3$, aniline-blue, or rubber; any variation due to the field is $< 1\%$. H. F. G.

Gelation of silicic acid. M. PRASAD (J. Indian Chem. Soc., 1933, Rây No., 119—123).—A review. H. J. E.

Electrical conductivity of silicic acid gel mixtures during gelation. C. B. HURD and H. J. SWANKER (J. Amer. Chem. Soc., 1933, **55**, 2607).—Increase in the electrical resistance of a mixture of Na_3SiO_3 and AcOH during the setting of the gel would support the cellular theory. No change of resistance was observed. J. G. A. G.

Influence of lyotropic substances on the mutarotation and gelatinisation of gelatin–water mixtures. III. Substances which retard gelatinisation without influencing mutarotation. J. R. KATZ and J. F. WIENHOVEN (Rec. trav. chim., 1933, **52**, 487—492).—Many substances lower the rate of gelatinisation without influencing the mutarotation (after 48 hr.). It is probable that the nuclei of the new phase are surrounded by an envelope of the capillary-active substance which reduces the rate of coalescence but does not alter the equilibrium condition. H. F. G.

Effect of lyotropic substances on the mutarotation and gelation of gelatin–water mixtures. J. R. KATZ and J. F. WIENHOVEN (Collegium, 1933, 287—289).—The mutarotation of a 3% gelatin solution caused by Na salts of aliphatic acids is diminished by the introduction of another CO_2H group. A similar effect is observed with aromatic acids and is greatest when substitution takes place in the *o*-position. The mutarotation is increased by a second or third SO_3H group in $PhSO_3H$. D. W.

Effect of lyotropic substances on the shrinkage temperature of collagen. J. R. KATZ and A. WEIDINGER (Collegium, 1933, 290—292).—The shrinkage temp. of collagen is appreciably lowered by substances containing one hydrophilic group; when two such groups are present it is sometimes slightly lowered and in other cases increased. D. W.

Mechanism of the swelling of gels. K. KRISHNAMURTI (J. Indian Chem. Soc., 1933, Rây No., 193—199; cf. A., 1929, 260, 264).—During the swelling of gelatin in H_2O the light-scattering power of the gel first increases and then diminishes. A mechanism for the swelling process is suggested. H. J. E.

Diffusion of tannin solutions in gelatin gels. S. V. SOLOTAREVA and N. E. PESKOV (J. Appl. Chem. Russ., 1933, **6**, 131—138, and Kolloid-Z., 1933, **64**, 32—35).—Only those parts of tannin

sols (I) which are in mol. dispersion and possess no tanning activity diffuse into gelatin gels (II). The membrane forming at the surface of contact of (I) with (II) is more turbid and less compact at $p_H > 4$ than at lower p_H. It is inferred that only those processes taking place on the surface of hides are of importance in the process of tanning. R. T.

Morphology of chemical reactions in gels. VI. Significance of "autoform" and of "form" catalysis in colloidal media for the interpretation of certain biological phenomena. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1933, **3**, 137—143).—The close resemblance between the morphology of periodic reactions taking place in gels and certain figures encountered in living cells is discussed. R. T.

Dissociation constants of monobasic acids. D. J. G. IVES (J.C.S., 1933, 731—737).—An equation based on Ostwald's dilution law, Onsager's equation, and the Debye–Hückel equation has been devised whereby vals. of Λ_0 and dissociation consts. may be calc. from conductivity data obtained over the range of concn. in which the Debye–Hückel theory is applicable. Precise comparative measurements have been made with AcOH, BzOH, and vinylacetic acid, and accurate dissociation consts. have been determined by this means without reference to mobility data and independently of the abs. accuracy of conductivity measurements. F. L. U.

Ionisation constants of *p*-nitrophenylacetic and phenylmalonic acids. S. BASTERFIELD and J. W. TOMECKO (Canad. J. Res., 1933, **3**, 447—449).—From conductivity measurements at 25° $K = 1{\cdot}04 \times 10^{-4}$ and $2{\cdot}77 \times 10^{-3}$, respectively. The mobilities of the anions are 64·14 and 62·32. R. P. B.

Olefinic acids. VIII. Dissociation constants. D. J. G. IVES, R. P. LINSTEAD, and H. L. RILEY (J.C.S., 1933, 561—568; cf. A., 1932, 251).—Dissociation consts. of 14 olefinic acids have been determined. The results afford evidence of the polarisability of the olefinic double linking. Alkyl substitution on the ethylenic C atom further from the CO_2H group lowers the dissociation const., the val. of which is determined, not by the nature of the substituent, but by its distance from the CO_2H group. Conductivities of the Na salts have been measured and the mobilities calc. F. L. U.

Dissociation constant of propionic acid at 0—60°. H. S. HARNED and R. W. EHLERS (J. Amer. Chem. Soc., 1933, **55**, 2379—2383).—From the e.m.f. of the cell $H_2|EtCO_2H(m_1),EtCO_2Na(m_2),NaCl(m_3)|AgCl|Ag$, the dissociation const. of $EtCO_2H$ is $\log K = -1274{\cdot}95/T - 1{\cdot}31574 \log T - 0{\cdot}012843T + 6{\cdot}48708$ between 0° and 60°. The heat of ionisation and the difference in sp. heats of the ions and undissociated mol. have been evaluated. J. G. A. G.

***iso*Carbamides and *iso*ureides. III. Ionisation constants of *iso*carbamides.** S. BASTERFIELD and J. W. TOMECKO (Canad. J. Res., 1933, **8**, 458—462; cf. A., 1930, 329).—The recorded vals. of $K \times 10^4$ for the substituted *iso*carbamides are: Me 0·60, Et 1·08, $CH_2Ph{\cdot}CH_2$ 0·62, Pr$^\alpha$ 1·43, allyl 0·50, Bu$^\alpha$ 1·40, Bu$^\beta$ 2·00, *iso*amyl 1·30, *cyclo*hexyl 1·56. R. S. C.

Dissociation of acids in salt solutions. VI. Dissociation of some monohalogeno-fatty acids in sodium chloride and potassium chloride solutions. E. LARSSON (Z. physikal. Chem., 1933, **165**, 53—64; cf. A., 1932, 572).—For ionic concns. up to about N all the acids investigated and the corresponding unsubstituted acids have about the same val. for $-\log \phi$ in presence of a given concn. of a given salt; the same is true of $-\log \psi$. At higher ionic concns. the constitution of the acid makes itself felt, and the more so the higher is the ionic concn. Substitution of Cl, Br, or I in AcOH or $EtCO_2H$ increases $-\log \phi$ and $-\log \psi$ somewhat more in presence of KCl than in presence of NaCl. β substitution in $EtCO_2H$ has a smaller effect than α substitution. R. C.

Ionisation constant of water and the dissociation of water in potassium chloride solutions from e.m.f. of cells without liquid junction. H. S. HARNED and W. J. HAMER (J. Amer. Chem. Soc., 1933, **55**, 2194—2206).—E.m.f. data for the cells $H_2|0{\cdot}01M\text{-HCl},0{\cdot}01—3{\cdot}5M\text{-KCl}|AgCl|Ag$ and $H_2|0{\cdot}01M\text{-KOH},0{\cdot}01—3{\cdot}5M\text{-KCl}|AgCl|Ag$ between 0° and 60° lead to $\log K = -4787{\cdot}3/T - 7{\cdot}1321 \log T - 0{\cdot}010365T + 22{\cdot}801$. The heat of ionisation is given by $\Delta H = 21{,}926 - 14{\cdot}812T - 0{\cdot}04746T^2$. The activity coeff. and partial mol. heat content of $0{\cdot}01M$-HCl in aq. KCl have been evaluated. The ionic activity coeff. product of H_2O in aq. KCl decreases with rise of temp. and has min. at ionic strength, μ, 0·5 approx. at all temp. K is a max. at $\mu = 0{\cdot}7$ approx. J. G. A. G.

Dissociation of water in lithium chloride solutions. H. S. HARNED and H. R. COPSON (J. Amer. Chem. Soc., 1933, **55**, 2206—2215; cf. A., 1926, 245).—From the e.m.f. of the cells $H_2|0{\cdot}01M\text{-LiOH},LiCl(m)|AgCl|Ag$, and $H_2|0{\cdot}01M\text{-HCl},LiCl(m)|AgCl|Ag$ between 15° and 35°, where $m = 0{\cdot}01—5M$, the standard potential of the $Ag|AgCl|Cl'$ electrode and K for H_2O have been calc. (cf. preceding abstract). The activity coeff. and partial mol. heat content of HCl, and the ionic activity coeff. and dissociation of H_2O in aq. LiCl have also been determined. J. G. A. G.

Relative strength of benzoic and salicylic acids in alcohol–water solutions [at 25°]. J. O. HALFORD (J. Amer. Chem. Soc., 1933, **55**, 2272—2278).—The relative strength varies with the concn. of alcohol (0—94 wt.-%) by as much as 0·5 log unit. The vals. obtained with the Sb electrode accord with those derived from the solubilities of the acids and their Ag salts. J. G. A. G.

Constitution of aqueous solutions of the hydrogen soap, cetylsulphonic acid. J. W. MCBAIN and R. C. WILLIAMS (J. Amer. Chem. Soc., 1933, **55**, 2250—2257).—The prep. of pure cetylsulphonic acid, m.p. 53—54°, is described. The electrical conductivity, lowering of v.p., and H_2 electrode potential of 0·0001—0·7N solutions have been determined at 90°. The conductivity has a min. val. in 0·1N solution, and at all concns. is > that of palmitate and stearate soaps. The acid seems to be only partly

dissociated even at dilutions where colloid is absent. The large differences in dissociation obtained by the different methods are discussed. J. G. A. G.

Activity ratio of zwitterions and uncharged molecules in ampholyte solutions. Dissociation constants of amino-acid esters. J. T. EDSALL and M. H. BLANCHARD (J. Amer. Chem. Soc., 1933, **55**, 2337—2353).—The consts. for eight NH_2-acid esters and of ε-aminohexoic acid (I) have been determined by electrometric titration of the hydrochlorides in aq. solution. Data are also given for 10—90% aq.-EtOH solutions. In aq. solution the vals. of the ratio, K_z, of "zwitterions" ($^+H_3N{\cdot}R{\cdot}CO_2'$) to uncharged mols. ($NH_2{\cdot}R{\cdot}CO_2H$) range from 4×10^4 for glycylglycine to nearly 10^6 for (I). Isoelectric lysine and arginine exist chiefly as very polar zwitterions, with positive and negative charges at opposite ends of the long C chain, whilst dicarboxylic NH_2-acids exist partly in this form but chiefly as less polar zwitterions similar to those of simple NH_2-acids. K_z decreases with rise of temp., and the heat of the reaction $NH_2{\cdot}R{\cdot}CO_2H \longrightarrow {}^+H_3N{\cdot}R{\cdot}CO_2'$ is 11,000 g.-cal. K_z diminishes with decrease of dielectric const., although zwitterions still predominate in 90% EtOH. The relative solubility in 90% EtOH as compared with H_2O increases with length of C chain or the introduction of a Ph nucleus. J. G. A. G.

Thermodynamics of aqueous hydrochloric acid solutions from e.m.f. measurements. H. S. HARNED and R. W. EHLERS (J. Amer. Chem. Soc., 1933, **55**, 2179—2193).—From the e.m.f. of the cell $H_2|0{\cdot}004—4{\cdot}1M$-HCl|AgCl|Ag, the standard potential of the Ag–AgCl electrode has been evaluated for the range 0—60° (cf. A., 1932, 695). From an equation which reproduces the activity coeff. of 0—4M-HCl in H_2O at 0—60°, relative partial mol. heat contents of the acid in good agreement with calorimetric data have been derived. Calc. relative partial mol. sp. heats accord with existing calorimetric data. J. G. A. G.

Activity of each component in aqueous solutions of sulphuric acid and acetic acid. F. H. MACDOUGALL and D. R. BLUMER (J. Amer. Chem. Soc., 1933, **55**, 2236—2249).—The activity coeffs. of H_2SO_4 in aq. AcOH have been derived from the e.m.f. of the cell $H_2|0{\cdot}05—3{\cdot}3M$-$H_2SO_4$,0—4·5$M$-AcOH|$Hg_2SO_4$|Hg at 25°. The partial v.p. of AcOH calc. from the activity coeff. of H_2SO_4 and the observed partial v.p. of H_2O accords with the observed vals. The equilibrium between single and double mols. of AcOH is discussed. J. G. A. G.

Preparation of acetate and phosphate buffer solutions of known p_H and ionic strength. A. A. GREEN (J. Amer. Chem. Soc., 1933, **55**, 2331—2336).—The p_H of K_2HPO_4–KH_2PO_4 buffers at concn. up to 2M have been determined by the H_2 and the glass electrode. The data agree with vals. calc. from Cohn's equation (A., 1927, 206). Data for OAc' and phosphate buffers record the mol. fractions corresponding with definite mol. concn. and p_H vals. between 3·8 and 7·7. J. G. A. G.

Effect of different sugars on the reaction of borate solutions. P. THOMAS and C. KALMAN (Compt. rend., 1933, **196**, 1672—1673).—Equiv. amounts of neutral solutions of glucose, galactose, mannose, and arabinose develop the same acidity when added to $Na_2B_4O_7$ solution. Xylose and fructose exert the greatest acidifying effect, p_H 4 being reached. Rhamnose is the least effective. The effect falls to zero when the initial acidity of the borate solution is increased to p_H 3. A. C.

Absorption of carbon dioxide in sodium carbonate–hydrogen carbonate solutions. C. R. HARTE, jun., E. M. BAKER, and H. H. PURCELL (Ind. Eng. Chem., 1933, **25**, 528—531).—The ratios of $NaHCO_3$ to Na_2CO_3 in N and 2N solutions in equilibrium with air containing various amounts of CO_2 were determined. From these and previously published data the equation $X^2C^{1\cdot29}/SP(1-x)(185-t)=10$, in which X is the fraction of Na in the form of $NaHCO_3$, C the normality of total Na, S the solubility of CO_2 in H_2O (g.-mol. per litre) at 1 atm., and P is the partial pressure of CO_2, is deduced for 0·5—2N solutions at t=20—70°. A. G.

Connexion between complex formation, solvation, and formation of electroconductive systems. II. Ebullioscopic study of the systems dimethylpyrone–group V element halide–benzene. V. S. FINKELSCHTEIN and P. V. KURNOSOVA (J. Gen. Chem. Russ., 1933, **3**, 121—133).—B.-p. determinations indicate association or complex ion formation between $AsCl_3$, $AsBr_3$, $SbCl_3$, or $SbBr_3$ and dimethylpyrone in C_6H_6 solution. In the case of $SbCl_3$ the complex is probably of the type $[Sb(SbCl_3)_4(C_7H_8O_2)_4]Cl_3$. R. T.

Demonstration of solvation phenomena by an optical method. W. WEYL and E. KREIDL (Naturwiss., 1933, **21**, 478).—If a substance has an absorption spectrum with fine structure, this usually becomes levelled in solution due to solvation. Quinizarin in non-polar C_6H_{14} shows two sharp max., but in other solvents (*e.g.*, C_6H_6, Et_2O) these are levelled, whilst in some (*e.g.*, EtOH) they disappear altogether. $PhNO_2$ is especially active in this way owing to its dipole moment and the easy deformation of its electron orbits. The effect of introduction of substituents into the dye mol. can be studied in a similar way. Groups which are specially active increase the chemical affinity of the colour centres, and by increased solvation produce deformation of electron orbits, and thus affect the absorption spectrum. A. J. M.

Application of the Debye theory to solutions of copper sulphate. (MLLE.) M. QUINTIN (J. Chim. phys., 1933, **30**, 319—336).—A more detailed account of work already noted (this vol., 468). Similar results are obtained by replacing the $Hg|Hg_2SO_4$ electrode by $Pb|PbSO_4$.

Comparison of desiccating agents. I. E. MOLES and C. ROQUERO (Anal. Fís. Quím., 1933, **31**, 11—25).—According to the % of H_2O removed from a current of saturated air under standardised conditions, SiO_2 gel, $Mg(ClO_4)_2$, and freshly ignited BaO are practically as efficient as P_2O_5 until the composition approximates to $2SiO_2,H_2O$ (or somewhat beyond), $Mg(ClO)_4,4{\cdot}5H_2O$, and $Ba(OH)_2$, respectively. B_2O_3 is rather less efficient. H. F. G.

Binary systems: nitrates of metals of group II and water. III. $Ca(NO_3)_2$–H_2O, $Sr(NO_3)_2$–H_2O, and $Ba(NO_3)_2$–H_2O. A. SIEVERTS and W. PETZOLD (Z. anorg. Chem., 1933, **212**, 233—241; cf. this vol., 676).—Temp.-composition data and eutectic and transition points are given. The principal data for these systems and those previously studied (Be, Mg, Zn, Cd nitrates) are summarised. F. L. U.

Nitrogen fluorides: partial diagram of the system NH_3–HF. O. RUFF and L. STAUB (Z. anorg. Chem., 1933, **212**, 399—400; cf. A., 1931, 809).—The f.-p. diagram reveals the existence of the *compounds* $NH_3,4HF$ and $NH_3,6HF$. The m.p. of $NH_3,2HF$ is $124{\cdot}6\pm0{\cdot}3°$. The various compounds (including probably $NH_3,3HF$) are associated with a series of eutectics. F. L. U.

Solid–liquid equilibria in system nitrobenzene–*m*-dinitrobenzene. D. L. HAMMICK and T. K. HANSON (J.C.S., 1933, 669—670; cf. A., 1932, 228).—A reply to the criticism of Lehmstedt (*ibid.*, 939). Temp. of equilibria have been redetermined and the previous results confirmed. F. L. U.

Aromatic bisnitroso-compounds of the type $R'N_2O_2R''$. D. L. HAMMICK, W. A. M. EDWARDS, W. S. ILLINGWORTH, and F. R. SNELL (J.C.S., 1933, 671—674).—F.-p. curves of binary mixtures reveal the existence of equimol. *compounds* of 4-nitroso-*m*-xylene with nitrosomesitylene and of o-NO·C_6H_4·NO_2 with nitrosomesitylene. Cryoscopic measurements in C_6H_6 show the presence of unsymmetrical bisnitroso-mols. in mixtures of nitrosomesitylene with o-C_6H_3Me·NO, o-OMe·C_6H_4·NO, or CH_2Ph·NO. F. L. U.

System anthracene–phenanthrene. G. BRADLEY and J. K. MARSH (J.C.S., 1933, 650—652).—Liquidus and solidus curves have been determined. A continuous series of mixed crystals is formed. The m.p. of pure phenanthrene is (by a slight extrapolation) 97·3°. F. L. U.

Higher aliphatic compounds. IV. Systems with ethyl margarate and heptadecyl alcohol. P. C. CAREY and J. C. SMITH (J.C.S., 1933, 635—637; cf. this vol., 590).—In the systems Et margarate–Et palmitate and Et margarate–Et stearate the transparent forms of the esters give unbroken series of solid solutions, whilst the opaque forms give systems of type III. The system heptadecanol–octadecanol gives evidence of separation into two series of solid solutions. Both heptadecanol and its acetate are trimorphous. F. L. U.

Amphoteric nature of organic oxygen compounds. N. A. PUSHIN and R. ZIVADINOVIC (Bull. Soc. Chim. Yougoslav., 1933, **4**, 23—30).—The fusion diagrams of the systems NH_2Ph–piperonal and β-$C_{10}H_7$·NH_2–camphor do not give evidence of compound formation; p-C_6H_4Me·NH_2 forms a *compound* with 1 mol. of o-$C_6H_4(CO)_2O$, m.p. 195°, and with 2 mols. of coumarin, m.p. 42°. R. T.

Thermal study of some mixtures having an analgesic action. L. NOBILI (Boll. chim. farm., 1933, **72**, 361—367).—M.-p. curves are given for the following binary systems: NHAcPh–pyramidone; antipyrine–"esalgine"; diethylbarbituric acid–pyramidone, and acetylsalicylic acid–pyramidone. O. J. W.

Phase diagram for ternary mixtures. V. FISCHER (Ann. Physik, 1933, [v], **17**, 421—424).—A diagram is described from which the equilibrium concns. of liquid and vapour can be obtained for any temp. W. R. A.

F.p. of the system MgF_2–BaF_2–CaF_2. G. FUSEYA, M. MORI, and H. IMAMURA (J. Soc. Chem. Ind. Japan, 1933, **36**, 175—176B).—The data for MgF_2–BaF_2 afford no evidence of the compound MgF_2,BaF_2 (cf. Grube, A., 1928, 376), but there is a eutectic at 912° and 30—35% MgF_2. MgF_2–CaF_2 has a eutectic at 970° and 52% MgF_2. CaF_2–BaF_2 shows solid solutions with a min. m.p. 1277° and 50% BaF_2. The ternary eutectic lies at 817°, 40% MgF_2, 18% CaF_2, and 42% BaF_2. J. S. A.

System sodium iodate, sodium carbonate, water. H. W. FOOTE and J. E. VANCE (Amer. J. Sci., 1933, [v], **25**, 499—502).—No double salts are formed between 0° and 50°. C. W. G.

Equilibrium of the system Na_2SiF_6–NaCl–H_2O. V. J. ANOSOV and S. K. TSCHIRKOV (J. Appl. Chem. Russ., 1933, **6**, 224—227).—The solubility of Na_2SiF_6 in H_2O at 15° is 0·65%, in 12·7% NaCl 0·013% and in 31·6% NaCl 0·007%. R. T.

Solubility isotherms and ice field of the ternary system Na_2CO_3–NaCl–H_2O. S. Z. MAKAROV (J. Gen. Chem. Russ., 1933, **3**, 234—248).—Phase diagrams are given for temp. from −21·4° to 60°. R. T.

System magnesium chloride–lime–water. C. R. BURY and E. R. H. DAVIES (J.C.S., 1933, 701—705; cf. A., 1932, 913).—The 3-component systems CaO–MgO–H_2O and $CaCl_2$–$MgCl_2$–H_2O and the 4-component system CaO–$MgCl_2$–H_2O have been studied. It is found, with reference to the deleterious influence of CaO on Mg oxychloride cement, that addition of CaO causes progressive decrease in the amount of $3MgO,MgCl_2,11H_2O$ (which appears to act as binding material), and a steady increase in the amount of solution phase, *i.e.*, the cement becomes more porous and hygroscopic. A further process, regarded as a form of syneresis, occurs after the setting of the cement. F. L. U.

F.p. of mixtures of water, ethyl alcohol, and ethyl ether. A. LALANDE (Compt. rend., 1933, **196**, 1666—1668; cf. this vol., 345).—The ternary eutectic is 55·5 wt.-% EtOH, 39·5 Et_2O, 5·0 H_2O, −127°±0·5. No compound is indicated. C. A. S.

Equilibrium in the system sodium phthalate, phthalic acid, and water. S. B. SMITH and W. A. STURM (J. Amer. Chem. Soc., 1933, **55**, 2414—2419).—The data at 0°, 25°, 35°, and 50° show the existence of the double salt $2NaHC_8H_4O_4,H_2O$. When used as a volumetric standard it should be crystallised at temp. < 50° in the presence of a slight excess of alkali. J. G. A. G.

Formation of oxynitrates of lead in molten salts. D. FREEMAN, K. LAYBOURN, and W. M. MADGIN (J.C.S., 1933, 648—650; cf. A., 1932, 707,

1205).—When PbO_2 is dissolved in a melt of $Pb(NO_3)_2$ and KNO_3, extraction with ice-cold H_2O leaves a yellow *compound* $PbO_2,Pb(NO_3)_2$. A ternary diagram for the system Pb_3O_4–$Pb(NO_3)_2$–KNO_3 is given. F. L. U.

Iron ions of iron equilibrium under pressure of hydrogen. K. MURATA (J. Soc. Chem. Ind. Japan, 1933, **36**, 160—161B).—The partial pressure of H_2 corresponding with $3Fe+8H_2O \rightleftharpoons Fe^{++}+2Fe^{+++}+8OH'+4H_2$ is calc. as 566 atm. J. S. A.

Reduction equilibrium between metal oxide and hydrogen. I. Measurement of $CoO+H_2 \rightleftharpoons Co+H_2O$ by a new method. Z. SHIBATA and I. MORI (Z. anorg. Chem., 1933, **212**, 305—316).—Pressures of H_2 have been measured with greatly increased accuracy by means of a differential manometer. The equilibrium const. K for the above reaction, measured at a series of temp. between 422° and 921°, is given by $\log K=494{\cdot}19/T+1{\cdot}0869$. With the aid of these and other data various thermodynamic quantities, including water-gas equilibria between 500° and 1000°, are calc. F. L. U.

Metal displacement equilibria of lead with cadmium or silver in their molten chlorides, bromides, and iodides. D. HEWSKYJ and K. JELLINEK (Z. Elektrochem., 1933, **39**, 444—453).—Displacement was effected by direct action and also by electrolysis of the molten salt, using the molten metal as cathode. Equilibrium data are recorded for (*a*) $Cd+PbCl_2 \rightleftharpoons CdCl_2+Pb$, with and without dilution of the metal phase with Bi, at 600°, (*b*) $Cd+PbBr_2 \rightleftharpoons CdBr_2+Pb$ at 600°, (*c*) $Cd+PbI_2 \rightleftharpoons CdI_2+Pb$ at 500°, (*d*) $Pb+2AgX \rightleftharpoons PbX_2+Ag_2$ at 800° (X=halogen). All the components behave as ideal solutions. In (*a*), (*b*), and (*c*) the equilibrium is independent of the nature of the halogen atom, but in (*d*) Pb ppts. much less Ag from AgI melts than from AgCl. Ag is diat. in molten Pb. Analytical procedures are suggested for determining small amounts of Cd in Pb, and for Bi containing small quantities of Pb and Cd. E. S. H.

Halogen displacement equilibria in fused chlorides and bromides of silver, potassium, and lead: $Cl_2+M^{II}Br_2 \rightleftharpoons M^{II}Cl_2+Br_2$. K. JELLINEK and H. WEBERBAUER (Z. anorg. Chem., 1933, **212**, 337—355).—Equilibria in the reaction between Cl_2 and fused AgBr have been measured at 594° and 804°, between Cl_2 and KBr at 804° and 905°, and between Cl_2 and $PbBr_2$ at 594°. The anions in the first two reactions are mainly Cl_2'' and Br_2'', and in the third Cl_4'''' and Br_4''''. F. L. U.

Precipitation of hydroxides. IX. Action of ammonia on solutions of mercuric chloride. H. T. S. BRITTON and B. M. WILSON (J.C.S., 1933, 601—607; cf. this vol., 242).—The reaction between $HgCl_2$ and aq. NH_3 has been studied analytically, potentiometrically, and conductometrically. In dil. solution the composition of the ppt. is $3HgO,HgCl_2,2NH_3$, whilst in more conc. solution it approximates to $HgO,HgCl_2,2NH_3$. In presence of NH_3 the val. of the product $[Hg^{\cdot\cdot}][OH']^2$ is 0·001 of that in its absence. The constitution of the various ppts. is discussed. F. L. U.

Thermal dissociation of chemically pure gypsum in presence of oxides of iron, aluminium, and chromium. I. E. ADADUROV, A. GALAMEEVA, and D. V. GERNET (J. Appl. Chem., Russia, 1932, **5**, 897—901).—The heat of reaction is 6000—9000 g.-cal. at 900—1000° and 35,000—48,000 g.-cal. at 1000—1200°. SiO_2, Fe_2O_3, and Cr_2O_3 greatly increase the yield of SO_2+SO_3 even at $< 900°$. The heat of activation at 1000—1200° is: $CaSO_4$, −99,000; $CaSO_4+SiO_2$, −27,000; $CaSO_4+5\%Al_2O_3$, −48,000; $CaSO_4+3\%Fe_2O_3$, −32,000; $CaSO_4+3\%Cr_2O_3$, −40,000 g.-cal. Mixed catalysts are not additive in their action. CH. ABS.

***X*-Ray investigation of the mercuric sulphates.** M. PAIÓ (Ann. Chim., 1933, [x], **19**, 427—497).—The system HgO–SO_3–H_2O forms solid phases $3HgO,SO_3$ (I), $3HgO,2SO_3,2H_2O$, $HgSO_4,H_2O$, and $HgSO_4$. The system HgO–SO_3–H_2S–H_2O forms at 0° $HgSO_4,2HgS$ (II), $HgSO_4,HgS$ (α) (III), and two phases characterised only by their *X*-ray spectrograms. At 25° the solid phases are (II), (III), and $HgSO_4,HgS$ (β) (IV); at 50°, (II) and (III), and at 100° $3HgO,2SO_3,3HgS$, $3HgO,2SO_3,2HgS$, together with (II), (III), and (IV). (II) is formed with aq. $HgSO_4$ and CS_2. Gaseous or aq. halogen acids liberate H_2SO_4 from the Hg^{II} sulphates. Conc. H_2SO_4 at 300° does not react with $HgCl_2$ or $HgBr_2$. With HgI_2 it forms $HgSO_4,HgI_2$ (V), m.p. 332° (decomp.). The m.-p. curves of $HgSO_4$–$HgBr_2$ and of $HgSO_4$–$HgCl_2$ were examined. Oleum (20% SO_3) decomposes HgI_2 forming successively (V) and HgSO.. Saturated aq $HgSO_4$ and HgI_2 form $3HgO,2SO_3,HgI_2$ (VI). Aq. $HgSO_4$ reacts with I to form (VI) and $Hg(IO_3)_2$. The following reactions occur on grinding the solids: $HgSO_4+2HgO \longrightarrow$ (I); $3HgO,2SO_3,2H_2O+3HgO \longrightarrow$ (I)$+2H_2O$; $HgSO_4+HgS \longrightarrow$ (IV); $HgSO_4+HgI_2 \longrightarrow$ (V); $3HgO,2SO_3,2H_2O+HgI_2 \longrightarrow 2HgO,2SO_3,HgI_2+2H_2O$. *X*-Ray spectral data and chemical and physical properties of these compounds are recorded. H. J. E.

Law of displacement of chemical equilibrium. H. LE CHATELIER (Compt. rend., 1933, **196**, 1557—1560).—The variant of the author's principle (cf. A., 1885, 117), as given later (cf. Ann. Mines, 1888, **13**, 200), is not correct and conflicts with deductions by Montagne's method (cf. this vol., 464). C. A. S.

Law of displacement of chemical equilibrium. H. LE CHATELIER (Compt. rend., 1933, **196**, 1753—1757; cf. preceding abstract).—The Le Chatelier principle is derived by a reversible cyclic process. C. A. S.

Displacement of equilibrium by variation of mass. R. ETIENNE (Compt. rend., 1933, **196**, 1887—1889; cf. preceding abstract).—An alternative mathematical proof of Le Chatelier's principle. C. A. S.

Internal effect accompanying thermodynamic transformations. III. V. NJEGOVAN (Arh. Hemiju, 1933, **7**, 65—67).—Mathematical. R. T.

Free energy of reactions involving the fused chlorides and bromides of lead, zinc, and silver. E. J. SALSTROM (J. Amer. Chem. Soc., 1933, **55**, 2426—2428).—The e.m.f. of the cell $Ag(s)|AgCl(l)|$

$Cl_2(g)$ in the range 470—600° is given by $E=1{\cdot}0461-0{\cdot}000292t$ and that of the cell $Zn(l)|ZnBr_2(l)|Br_2(g)$ in the range 401—504° by $E=1{\cdot}6112-0{\cdot}000682t$. From existing data for similar cells involving Zn, Pb, Ag, Cl, and Br, the free energy, entropy, and heat of reaction of a series of reactions have been calc. J. G. A. G.

Entropies of polyatomic molecules. D. M. Yost and C. Blair (J. Amer. Chem. Soc., 1933, **55**, 2610—2611).—Entropies of polyat. mols. calc. from spectroscopic data may be in error by several e.u. owing to incomplete knowledge of the necessary energy levels. J. G. A. G.

Thermodynamic data for metallic sulphates. I. F. Ishikawa. II. F. Ishikawa and T. Murooka (Sci. Rep. Tohoku, 1933, **22**, 131—137, 138—155).—I. The free energy of formation and the entropy of Hg_2SO_4, $PbSO_4$, Tl_2SO_4, Ag_2SO_4, and the heat content change of $PbSO_4$ and Tl_2SO_4 have been derived from existing data.

II. Thermodynamic data for $CuSO_4$, $ZnSO_4$, and $CdSO_4$ are derived from e.m.f. data and the v.p. of the hydrates and their saturated solutions. A. J. M.

Heat of combustion of glycogen. N. Brookens (Biochem. Z., 1933, **260**, 446—450).—Vals. recorded are: 0·9 g. anhyd. glycogen 3787·7 g.-cal.; 1·0 g. $C_6H_{10}O_5,H_2O$ 3768·5 g.-cal.; 1·0 g. dissolved glycogen hydrate 3761·3 g.-cal. P. W. C.

Heats of dilution of potassium chlorate and perchlorate at high dilution at 15° and 25°. M. Andauer and E. Lange (Z. physikal. Chem., 1933, **165**, 89—96).—At a given concn. the integral heat of dilution, V_m, is more negative for $KClO_4$ than for $KClO_3$ and more negative for $KClO_3$ than for $NaClO_3$. It is probable that at very high dilutions the form of the V_m–concn. curve of salts and acids is materially influenced by displacement of the equilibrium $H^{\cdot}+OH' \rightleftharpoons H_2O$. R. C.

Electrical conductivities of aqueous solutions of sodium and potassium hydroxides at 25° and the validity of the "water correction." G. H. Jeffery and A. I. Vogel (Phil. Mag., 1933, [vii], **16**, 64—65).—Agreement between the results of Jeffery and Vogel (this vol., 353), and of Gowerecka and Hlasko (A., 1932, 1092) shows that the "H_2O correction" applied by the former is valid, and that the only impurity which need be taken into account when dealing with solutions in equilibrium H_2O (A., 1931, 801) is H_2CO_3. A. J. M.

Role of the solvent in electrolytic dissociation. J. A. V. Butler and L. C. Connell (Nature, 1933, **131**, 800; cf. this vol., 569).—For LiCl in H_2O–EtOH, $\Lambda_0.\eta$ is const. in solvents containing up to approx. 20 mol.-% EtOH. As the proportion of EtOH is further increased, $\Lambda_0.\eta$ decreases continuously to its val. in pure EtOH. This supports the view that the ions remain solvated almost entirely by H_2O up to 20 mols.-% EtOH and that EtOH mols. enter the solvation sheath to an increasing extent when the proportion of EtOH increases further. L. S. T.

Limiting conductivities of salts in non-aqueous solvents. C. W. Davies (J.C.S., 1933, 645—648).—A method of obtaining the val. of Λ_0 by a linear extrapolation is described. It assumes ionic association and the applicability of the Debye–Hückel–Onsager equations to the free ions in dil. solution. Examples are given. F. L. U.

Effect of acetaldehyde on conductivities of electrolytes in ethyl alcohol. D. N. Clark, O. Gatty, O. L. Hughes, and H. Hartley (J.C.S., 1933, 658—660).—The effect of MeCHO on the conductivities of KI and $AgClO_4$ in EtOH has been measured. The amount of MeCHO likely to be present in "conductivity" EtOH would not have an appreciable effect on the conductivity of electrolytes in that solvent. F. L. U.

Conductivity of hydrogen chloride in anhydrous ether. T. Mounajed (Compt. rend., 1933, **197**, 44—45).—The equiv. conductivity first decreases from 0·00588 mho for 0·02*N* to a min. of 0·00053 for 1·1*N*, and then rises rapidly to 0·0629 for 5·5*N* and 0·4123 for 6·8*N*, possibly due to formation of complex combinations of $H^{\cdot}$ or Cl' with HCl. On keeping, the conductivity slowly increases, *e.g.*, to 0·0853 for 0·02*N*, and 0·5947 for 5·5*N* due to formation of EtCl and H_2O (cf. A., 1890, 97). C. A. S.

Conductivity measurements in aniline. P. Walden and L. F. Audrieth (Z. physikal. Chem., 1933, **165**, 11—25).—Data for solutions of alkylammonium salts, org. picrates, and Ag picrate at 25° and dilutions up to 250,000 litres agree with Kohlrausch's square-root formula, but the limiting slope of the conductivity curve is quite different from the val. calc. by the Debye–Hückel–Onsager equation. This divergency probably arises because the latter equation takes no account of the sp. chemical character of the solute. NH_2Ph is a strongly differentiating solvent. Tetra-alkylammonium salts deviate from the rule that the product of Λ_∞ and viscosity is const., independent of the solvent. Strong binary salts obey the mass law over a dilution range of 5000—150,000 litres. R. C.

Conductivity measurements in acetophenone. P. Walden and E. J. Birr (Z. physikal. Chem., 1933, **165**, 26—31).—Data for NEt_4 and NH_2Et_2 picrates and chlorides at 25° at dilutions up to 100,000 litres show that Kohlrausch's square-root formula is valid for these solutes at dilutions above 3000 litres, and that the NH_2Et_2 salts obey the mass law over a wide range of dilutions. NEt_4 picrate deviates from the rule that the product of limiting conductivity by viscosity is const. COPhMe is a differentiating solvent. The differentiating power of a ketone towards alkylammonium salts increases with the mol. wt. of the ketone. R. C.

Conductivity measurements in *cyclo*hexanone. P. Walden and E. J. Birr (Z. physikal. Chem., 1933, **165**, 32—38).—Data for solutions of NEt_4 and NH_2Et_2 salts at 25° at dilutions up to 50,000 litres agree with Kohlrausch's square-root formula. *cyclo*-Hexanone is a differentiating solvent; weak and moderately strong salts obey the dilution law. For NEt_4 picrate the product of limiting conductivity and viscosity has the val. 0·645 instead of 0·563 deduced by Walden's rule. R. C.

System $AlBr_3$–$SbBr_3$ in benzene solution. V. A. PLOTNIKOV and I. A. SCHEKA (J. Gen. Chem. Russ., 1933, **3**, 214—221).—Conductivity measurements suggest the formation of a *compound*, $Al_2Br_6,SbBr_3,nC_6H_6$. On electrolysis Sb deposits on the cathode; the decomp. potential is 1·2 volts. R. T.

Electrochemistry of the system $AlBr_3$–CuBr in toluene solution. V. A. PLOTNIKOV and Z. A. JANKELEVITSCH (J. Gen. Chem. Russ., 1933, **3**, 208—213).—Conductivity measurements indicate the formation of a *compound*, $Al_2Br_6,CuBr,n$PhMe. On electrolysis Cu is deposited on the cathode, and, using a Cu anode, $Cu^{\cdot}$ is transported to the cathode. The decomp. potential is 1·4 volts. R. T.

Electrochemistry of the systems AgBr–$AlBr_3$ and CuBr–$AlBr_3$ in ethylene dibromide. V. A. PLOTNIKOV and V. A. KIKETZ (J. Gen. Chem. Russ., 1933, **3**, 52—58).—The conductivity of the systems AgBr or CuBr–$AlBr_3$–$C_2H_4Br_2$ is of the order of 0·001 mho. The sp. conductivity, κ, rises with concn. of AgBr or CuBr when $[AlBr_3]/[C_2H_4Br_2]$ is const.; the val. of κ increases in the order CuBr<KBr<AgBr. Where [MBr]/[$AlBr_3$] is const., κ diminishes with dilution. Cryoscopic measurements indicate the formation of compounds of the type Al_2Br_6,nMBr. Cu or Ag is deposited on the cathode during electrolysis in accordance with Faraday's law; the decomp. potential is 0·76 volt for AgBr and 1·0 volt for CuBr. R. T.

Differences between coefficients of conductivity of strong electrolytes in the same solvent. M. HŁASKO (Bull. Acad. Polonaise, 1932 **A**, 336—346; cf. A., 1932, 575).—Conductivities of HX and of MX (X=F, Cl, Br, OH; M=Li, Na, K, Rb, Cs, NH_4) dissolved in MeCN, MeOH, EtOH, Pr$^{\alpha}$OH, Bu$^{\alpha}$OH, C_5H_5N, and NH_2Ph have been measured at different dilutions (v). The conductivity coeffs. at a given v diminish in the order: HI, HBr, HCl; KOH, NaOH, LiOH; MI⟶MF; CsX⟶LiX. The differences, which are small in H_2O, increase rapidly as the dielectric const. of the solvent decreases, and are attributed to the presence of undissociated mols. F. L. U.

Electrolytic solutions. IV. Conductance minimum and the formation of triple ions due to the action of Coulomb forces. R. M. FUOSS and C. A. KRAUS (J. Amer. Chem. Soc., 1933, **55**, 2387—2399; cf. this vol., 230, 464).—The hypothesis that a triple ion, formed from a neutral mol. and a simple ion by the action of electrostatic forces, is stable in solvents of sufficiently low dielectric const. accounts in a large measure for the appearance of min. in conductance curves and affords a theoretical basis for the observed shift of the min. towards higher concn. and eventual disappearance with increasing dielectric const. Dissociation consts. of the triple ions computed theoretically accord with vals. from conductance data (*loc. cit.*). J. G. A. G.

Electron paths in solutions during electrolysis using a sparking cathode. P. FISCHER and KATZNELSON (J. Gen. Chem. Russ., 1933, **3**, 5—6).—The blue striæ observed by Pisarshevski and Rozenberg (A., 1923, ii, 729) in KI–starch solutions during electrolysis with the cathode not immersed in the solution, and ascribed by them to the action of electrons discharged from the cathode, are in reality due to O_3. R. T.

Experimental detection of transport heats in electrolytic Peltier heats. E. LANGE and T. HESSE (Z. Elektrochem., 1933, **39**, 374—384).—A method of measuring Peltier heats by means of the Ag|AgCl electrode is described. The significance of heats of transport is discussed. The vals. are probably about 100—300 g.-cal. per mol. They depend little on concn. or activity, but are related to transport no. E. S. H.

Electrocapillary maximum for a mercury electrode. S. R. CRAXFORD (Phil. Mag., 1933, [vii], **16**, 66—79).—The drop-wt. method has been used for determining the electrocapillary curves for solutions containing Hg^I salt. The potential of dropping Hg differs from that of a stationary Hg electrode. There is no max. in the surface tension–potential curve in the neighbourhood of 0·5 volt. The theory of electrocapillarity is discussed. A. J. M.

Liquid junction of dilute electrolytes. III. M. PLANCK (Sitz. preuss. Akad. Wiss., Phys.-math. Klasse, 1933, **8**, 3—9; cf. A., 1931, 569).—Theoretical. H. J. E.

Reduction potential of organic compounds. XIII. Azobenzene. M. SHIKATA and I. TACHI. **XIV. Dinitrophenols.** M. SHIKATA and N. HOZAKI. **XV. Nitroanilines.** M. SHIKATA and E. TAGUCHI (J. Agric. Chem. Soc. Japan, 1932, **8**, 954—961, 1121—1128, 1225—1236).—XIII. There is a reversible azo–hydrazo-system in the range p_H 1·2—5·0. The reduction potential measured with the Pt cathode (150—200 mv.) is more negative than that obtained with the Hg cathode.

XIV. In the reduction of the first NO_2 group of $OH{\cdot}C_6H_3(NO_2)_2$ the order of potentials is 2:5-> 2:6->2:4-, and in that of the second, 2:6-> 2:4->2:5-. Solubilities in H_2O at 25° are: 2:4-, 0·0865; 2:6-, 0·2853; 2:5-, 0·1123 g. per litre.

XV. *m*- is more easily reduced than *o*- or *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. Ionised $NO_2{\cdot}C_6H_4{\cdot}NH_2$ is more, and undissociated is less, easily reduced than C_6H_6. CH. ABS.

Reduction potentials of cysteine, glutathione, and glycylcysteine. D. E. GREEN (Biochem. J., 1933, 678—689).—A mixture of cryst. cysteine and cystine yields vals. which differ from those obtained when a solution of cystine is subjected to electrolytic reduction with a Hg electrode. A Hg–cysteine complex is rapidly formed in presence of O_2, and this determines the reversibility of the system. The colorimetric (reduction) data obtained with glutathione do not agree with potentiometric data, although the latter depend only on the concn. of the reduced component. E_0 for glutathione is +0·062, for glycylcysteine +0·025. The anomalies of thiol potentials are discussed. P. G. M.

Limiting currents in the anodic polarisation of metals in aqueous solutions. II. E. MÜLLER and K. SCHWABE (Z. Elektrochem., 1933, **39**, 414—423; cf. A., 1932, 814).—A reply to W. J. Müller

(this vol., 30) and a general criticism of the latter's theory of passivity. E. S. H.

Mechanism of hydrogen overvoltage and the electrolytic oxidation of hydrogen. L. P. HAMMETT (Trans. Faraday Soc., 1933, **29**, 770—775).—Current–potential curves for the reaction $2H^+ + 2e \rightleftharpoons H_2$ are deduced theoretically on the assumption that the stages $H^+ + e \rightleftharpoons H$ and $2H \rightleftharpoons H_2$ are of comparable importance in determining the velocity. For large polarisations the first step becomes dominant, for small polarisations the second. D. R. D.

Effect of the internal resistance of the galvanic cell on the measurement of its e.m.f. by the capillary electrometer, and a method of correction. I. Effect of internal resistance. T. ISHINO (J. Soc. Chem. Ind. Japan, 1933, **36**, 161—162B).—The position of balance is affected by the internal resistance of the cell. J. S. A.

Physical meaning of Peukert's formula for lead accumulators. R. TOMII (J. Soc. Chem. Ind. Japan, 1933, **36**, 162—164B).—Mathematical. A relation between discharge current and the thickness of the active layer is deduced. J. S. A.

Liesegang rings produced by electrolysis. E. BANDERET (Compt. rend., 1933, **196**, 1785).—Liesegang rings are formed around the anode when a current is passed between Ag electrodes through gelatin impregnated with $K_2Cr_2O_7$, the distance between rings varying approx. inversely as the voltage (2—40 volts). With agar the rings do not form or are very indistinct, but with Pb electrodes and agar containing KI periodic deposits of PbI_2 are produced.

Transformation of ortho- into para-hydrogen in the solid state. E. CREMER and M. POLANYI (Z. physikal. Chem., 1933, B, **21**, 459—468).—The rate of change in the solid state at 4—14° and in the liquid state at 14—20° abs. has been measured. The reaction velocity is in each phase independent of the temp., but is greater in the solid than in the liquid state. Since it follows the bimol. law, reaction must occur by interaction between two ortho mols.; it is not effected by exchange of atoms, but solely by forces which operate when the two mols. approach closely. In the solid state the velocity coeff. falls towards the end of the transformation because there then remain ortho mols. which are unable to react owing to their being entirely surrounded by para mols. R. C.

Calculation of the ignition limits [of explosive gas mixtures] from rate of propagation of the flame. K. BUNTE and G. JAHN.—See B., 1933, 531.

Variation of temperature of spontaneous inflammation of hydrogen–air mixtures with velocity of heating. M. PRETTRE (Compt. rend., 1933, **196**, 1891—1893; cf. A., 1928, 271).—A 55 : 45 H_2–air mixture has a higher inflammation temp. when more slowly heated. It does not inflame if introduced at the rate of 1·5 litres per hr. into a vessel at 800°, at 654° if introduced at 4 litres per hr., at 550° if at 7 litres, and at 480° when introduced suddenly into a vacuous vessel. Results of other investigators are discussed (cf. A., 1926, 689; this vol., 30). C. A. S.

Technical aspects of gaseous explosions. H. K. SEN (J. Indian Chem. Soc., 1933, Ray No., 225—233).—Temp. have been recalc. for the flames of H_2, C, CO, a hydrocarbon (C 84, H 14, S 2%), and producer gas in air or O_2. H. J. E.

Flame movements in gaseous mixtures. I. Movement of explosion waves in gases contained in tubes of non-uniform diameter. C. CAMPBELL and C. WHITWORTH. **II. Pressure conditions ahead of flames.** C. CAMPBELL and A. KING (Mem. Manchester Phil. Soc., 1931—1932, **76**, 45—49, 49—52).—I. The effect of increased tube diameter in damping the detonation wave depends on the nature and composition of the explosive mixture. Examples are given. The observations were made with a tube in which an effective increase in diameter was obtained by sealing on at right angles another tube of the same bore.

II. An increase of pressure has been observed 75 cm. ahead of the flame in a mixture of CO and O_2 burning in a cylindrical tube. No such increase could be detected in advance of the detonation wave in a similar mixture or in $2H_2+O_2$. F. L. U.

Influence of temperature on the velocity of oxidation of nitric oxide to peroxide. A. BERTHOUD (J. Chim. phys., 1933, **30**, 337—346).—A thermodynamic treatment. D. R. D.

Slow combustion of gaseous saturated cyclic hydrocarbons having side-chains. I. LEWIN (Bull. Soc. chim. Belg., 1933, **42**, 141—152).—Time–pressure curves are given for the course of the reaction between O_2 and 15 hydrocarbons at 200° and 780—1110 mm. initial pressure. In all cases the pressure at first remains const. for a considerable time, falls and passes through a min., and then rises steadily; ultimately it tends to become const. again. 1 : 1-Dimethyl*cyclo*hexane is exceptional in that the min. is absent. The min. probably corresponds with the formation of peroxides which initiate the reaction chains. The rates of oxidation are discussed in their relation to the structure of the hydrocarbons. For homologous *cyclo*-pentane and -hexane derivatives, the apparent induction period becomes shorter as the length of the side-chain increases, and therefore cannot be attributed to the presence of impurities. H. F. G.

Hydrolysis of hydrogen cyanide by acids. II. V. K. KRIEBLE and A. L. PEIKER (J. Amer. Chem. Soc., 1933, **55**, 2326—2331).—The rate of hydrolysis of HCN at 45° and 65° is independent of [HCN], but increases rapidly with increasing concn. of HCl and HBr; these velocities are increased several fold by adding the Na and K salts of the acids, thus indicating that the principal catalyst is the undissociated acid mol. The ratio of the velocities at two acid concns. is independent of the temp. H_2SO_4 is a weaker catalyst than HCl and HBr. J. G. A. G.

Reaction velocities of chloro- and bromo-2 : 4-dinitrobenzene with aliphatic amines. J. J. BLANKSMA and H. H. SCHREINEMACHERS (Rec. trav.

chim., 1933, **52**, 428—436).—The rates of the bimol. reaction of chloro- and bromo-2 : 4-dinitrobenzene with various primary and *sec.*-amines in EtOH (100%) solution at 25° have been determined. *iso*Amines react more slowly than *n*-amines, and *sec.* much more slowly than primary (NHMe$_2$ is exceptional). NH_3 reacts very slowly, and, in the case of the Cl-derivative, the rate is reduced somewhat by addition of H_2O (25%) to the solvent. The reaction velocity is apparently not related to the dissociation consts. of the amines in aq. solution and differs but little for the chloro- and bromo-compounds. 2 : 4-Dinitrodimethylaniline and -diethylaniline are both dimorphous, the respective m.p. being 87° and 74°, and 80° and 69°. 2 : 4-*Dinitroisobutylaniline* has m.p. 56°, and 2 : 4-*dinitroisohexylaniline*, m.p. 63°.

H. F. G.

Velocity of inversion of sucrose. IV. (1) Relation between velocity of inversion and hydrogen-ion concentration. (2) Effect of neutral salts on velocity of inversion and hydrogen-ion concentration. N. Taketomi and T. Horikoshi (J. Soc. Chem. Ind. Japan, 1933, **36**, 187—189B).—With HCl, the velocity of inversion (I) increases more rapidly than [H$^+$]. KCl and NaCl have no effect on [H$^+$] but increase (I); K_2SO_4 and Na_2SO_4 decrease [H$^+$] and lower (I).

J. S. A.

Velocity of reaction of halogen-substituted benzene derivatives with sodium methoxide. E. A. Kriuger and M. S. Bednova (J. Gen. Chem. Russ., 1933, **3**, 67—77).—The reactivity of halogen in the reaction RX+NaOMe ⟶ ROMe+NaX increases in the order Cl<Br<I. The presence of certain substituents in the C_6H_6 ring enhances reactivity of halogen in the order: *p*-NO_2>*o*-NO_2>*m*-NO_2>Cl, Br, whilst Me, OH, OMe, and NH_2 reduce reactivity. Halogeno-naphthalenes and -anthracenes are considerably more reactive than are the corresponding C_6H_6 derivatives.

R. T.

Theoretical investigations on the combustion of carbon. I. General equation of the velocity of combustion. Y. Fukuda (J. Soc. Chem. Ind. Japan, 1933, **36**, 246—248B).—Theoretical.

J. S. A.

Theory of the rate of dissolution of solid into liquid. S. Miyamoto (Trans. Faraday Soc., 1933, **29**, 789—794).—The equations $dc/dt=KS(c_\infty-c)$, for the rate of simple dissolution of a solid in a liquid, and $dc/dt=-KSc$ for that of a metal or metallic oxide in an acid, are deduced from kinetic considerations without assuming the existence of a diffusion layer. Expressions are deduced for the val. of the velocity coeff. K and the solubility c_∞, and the influence of particle size, curvature of surface, difference between different faces of a crystal, etc. are satisfactorily explained.

D. R. D.

Theory of the rate of sublimation. S. Miyamoto (Trans. Faraday Soc., 1933, **29**, 794—797).—Expressions for the rate of sublimation and v.p. of a solid are deduced from kinetic considerations (cf. preceding abstract).

D. R. D.

Kinetics of the precipitation of small amounts of mercury by iron and copper. V. Majer (Z. Elektrochem., 1933, **39**, 439—444).—The pptn. of Hg from very dil. aq. $HgCl_2$ (10^{-5} to 10^{-7} mol. per litre) by Fe (in presence of Cu$^{\cdot\cdot}$) is a first-order reaction. The rate is controlled by diffusion processes. Under similar conditions the reaction with Cu appears to be a balanced reaction, which does not agree with the thermodynamic equilibrium.

E. S. H.

Rate of reaction between silica and sodium carbonate at different temperatures, and the process of vitrification. J. T. Howarth, W. Maskill, and W. E. S. Turner (J. Soc. Glass Tech., 1933, **17**, 25—49).—The reaction between Na_2CO_3 and SiO_2 (1 : 1 to 1 : 4 mixtures) is unimol. and commences at 390°. For the 1 : 3 mixture reaction is complete in 35 hr. at 650° and 14 min. at 820°. Traces of CO_2 remain in the product even at 1200°. Incipient sintering occurs at 700—750°, according to the composition of the mixture. The reaction takes place on the surface of the SiO_2 grains and the reaction products penetrate, slowly at low temp., to the interior; in nearly all cases in which the reaction temp. is < 820° the kernel of each grain contains all the uncombined SiO_2 and the surface layer relatively alkaline compounds, even if all the Na_2CO_3 has disappeared. Determination of sol. SiO_2, therefore, does not indicate the extent of reaction in such systems.

H. F. G.

Influence of temperature on the rate of dissolution of pure thallium in nitric acid. M. Centnerszwer and S. Levi (Bull. Acad. Polonaise, 1932, **A**, 362—368; cf. A., 1931, 1243).—The rate of dissolution of pure Tl in HNO_3 (0·5—2N) increases 2·06 times in the interval 25—35°. The process of which the rate is measured is therefore chemical. HNO_2 exercises no appreciable catalytic influence.

F. L. U.

Corrosion of lead. A. H. Loveless, T. A. S. Davie, and W. Wright.—See B., 1933, 590.

Theory of passivity. XVIII. Fluctuation phenomena in anodic passivity. W. J. Muller (Monatsh., 1933, **62**, 220—231; cf. this vol., 30).—In some cases (*e.g.*, for Fe in N-H_2SO_4) the graphical relation between $t-C$ and $-1/(i_0+i)+(2\cdot3/i_0)\log(i_0-i)/i$ ($=A$; cf. A., 1928, 247) is not linear, but consists of several intersecting straight lines. This is due to changes in thickness of the film formed on the passive metal, which normally remains const. The evaluation of the consts. C and A in this case is described.

H. J. E.

Kinetics of coagulation of ceric hydroxide sol. M. V. Nabar and M. Prasad (J. Indian Chem. Soc., 1933, **10**, 153—159).—The course of coagulation of CeO_2 sols by NaCl and $MgCl_2$ has been followed by means of a thermopile. The S-shape of the curves, which is most marked with a high concn. of electrolyte, vanishes when the sol is sufficiently diluted, or is dialysed for a long time. The results are discussed.

F. L. U.

Ageing of oxide hydrates. A. Lottermoser and E. Lottermoser (Kolloid-Beih., 1933, **38**, 1—39).—The ageing of hydrated oxides of Al, Cr^{III}, Fe^{III}, Ni^{II}, and Co^{II}, prepared by adding 0·2N-NH_3 to 0·1N solutions of the respective chlorides, has been studied by sedimentation experiments and X-ray

diagrams, thus giving an indication of (*a*) the rate of growth of the secondary particles and (*b*) the rate of orientation of the structural units of the secondary particles. With $Al(OH)_3$ (*a*) and (*b*) are approx. equal. With $Cr(OH)_3$ (*a*) is fairly great above 40°, but at lower temp. there is an induction period, after which ageing occurs suddenly; (*b*) is very low, as the *X*-ray diagrams show amorphous rings. (*a*) is high for $Fe(OH)_3$ and increases with rising temp., but (*b*) is very low. $Co(OH)_2$ resembles $Fe(OH)_3$ with regard to (*a*) and $Al(OH)_3$ with respect to (*b*). The highest (*b*) is observed in $Ni(OH)_2$. E. S. H.

Detonation of explosives by ionic and electronic collision. H. KALLMANN and W. SCHRÄNKLER (Naturwiss., 1933, 21, 379—382).—$C_6H_2Me(NO_2)_3$, Hg fulminate, and cellulose nitrate were bombarded in vac. with electrons and ions of various kinds, and the current and potential necessary to produce detonation were determined. With particles of very small mass (*e.g.*, electrons) there was no explosion. Ions of H, A, and Hg caused explosion with the greater ease the greater was the mass. Excitation of nuclear oscillations appears to be necessary to bring about explosion, and this will be more easily accomplished by ions than by electrons. A. J. M.

Rate of reaction of cellulose fibres with cuprammonium. I. SAKURADA and Y. SHINODA (J. Soc. Chem. Ind. Japan, 1933, **36**, 304—306B).—The rate of reaction of cellulose fibres with a cuprammonium hydroxide solution containing NaOH to prevent dissolution is represented by the equation $kt^m=\tan^{-1}\{a/(b-a)\}^{\frac{1}{2}}-\tan^{-1}\{(a-x)/(b-a)\}^{\frac{1}{2}}$, where m is a const. and a and b are the mg.-mols. per 100 c.c. of cellulose and Cu, respectively. A. G.

Kinetics of cellulose reactions. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1933, **36**, 299—303B).—Reaction of a liquid with a constituent of a gel is represented by $x=kt^m$, where t is the time and m a const. This applies to a cylindrical filament whether the reaction within it is homogeneous, takes place only on the micelle surfaces, or also throughout the micelles. If the concn. of the reactant in the liquid phase (initially a) falls significantly, the equation becomes $kz^m=\tan^{-1}\{a/(b-a)\}^{\frac{1}{2}}-\tan^{-1}\{(a-x)/(b-a)\}^{\frac{1}{2}}$, where b is the amount of active OH groups per unit vol. A. G.

Halogenation reactions. I. Regularities of relative rates of reaction in liquid media. E. A. FLOOD and L. HORVITZ (J. Amer. Chem. Soc., 1933, **55**, 2534—2539).—The velocity of the reaction, $R_3MX+X'_2 \longrightarrow R_2MXX'+RX'$, where R=Et or Ph, M=Si, Ge, Sn, or Pb, and X=halogen or OH, and X′=Br or I, increases successively as X=I, Br, Cl, F, or OH, this order being unaltered by change of solvent or temp., or by the presence of H_2O. R. S. C.

Pulsating character of reactions between proteins and alkali. G. ETTISCH and G. V. SCHULZ (Z. physikal. Chem., 1933, **164**, 417—427).—Viscosity measurements show that the reaction between casein and NaOH in aq. solution takes the form of pulsations separated by periods during which there is apparently no reaction. From e.m.f. measurements it appears that all the protein mols. react simultaneously and the reaction follows a parallel course with each. R. C.

Para-hydrogen conversion at paramagnetic surfaces. H. S. TAYLOR and H. DIAMOND (J. Amer. Chem. Soc., 1933, **55**, 2613—2614).—Van der Waals adsorption of H_2 by paramagnetic substances at liquid air temp. is accompanied by very rapid ortho $\longrightarrow$ para conversion. Adsorption by substances with low paramagnetism is accompanied by low conversion. J. G. A. G.

Temperature coefficient of the recombination of hydrogen atoms. A. L. ROBINSON and I. AMDUR (J. Amer. Chem. Soc., 1933, **55**, 2615—2616; cf. this vol., 582).—The temp. coeff. between —79° and 99° indicates an apparent energy of activation of 900 g.-cal. This is further evidence for the existence of a wall reaction (cf. A., 1931, 1239). J. G. A. G.

Are traces of water really necessary for the occurrence of many chemical reactions? M. BODENSTEIN (Z. physikal. Chem., 1933, **B**, **21**, 469—470).—The interpretation of the effect of drying on chemical change previously suggested (this vol., 575) is supported by Coehn and Spitta's observations on the photochemical decomp. of CO_2 (A., 1930, 1383). R. C.

Complex formation and catalysis; highly active intermediate phases. R. KUHN and A. WASSERMANN (Annalen, 1933, **503**, 203—232).—Under certain conditions Fe^{III} is reduced by H_2O_2 and in the stationary state of catalysis a univalent valency variation $Fe^{II} \rightleftharpoons Fe^{III}$ is postulated. The assumed Fe^{II} can be quantitatively enchained by complex formation with 2 : 2′-dipyridyl (I) or phenanthroline (II). The rate of formation of the complex is governed by that of the process $Fe^{III} \xrightarrow{\ominus} Fe^{II}$ and by the ratio of the velocities with which the intermediate Fe^{II} enters into the complex or is oxidised to Fe^{III}. Since the complexes possess catalytic activity, reaction does not cease when all the Fe^{II} has entered into complex union. Excess of (I) enhances the activity of $[Fe(dip)_3]^{++}$, whereas excess of (II) restricts the effect of $[Fe(phen)_3]^{++}$. Change is accelerated by light and the reaction has an unusually high temp. coeff. Addition of $FeSO_4$ to a mixture of (I) and H_2O_2 causes immediate evolution of O_2 about 100 times as rapid as that induced by $FeSO_4$ alone and 20 times as quick as by preformed $[Fe(dip)_3]$ salt. Similar observations are made when $FeSO_4$ is replaced by $Fe_2(SO_4)_3$ or when (I) and $Fe_2(SO_4)_3$ are treated with H_2O_2. Admixture of $[Fe(dip)_3]SO_4$ with $Fe_2(SO_4)_3$ or (I) does not cause corresponding activation. HCN and Na_2SO_4 restrict the "catalytic impulse." A similar effect is not induced by $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, or $Mn^{\cdot\cdot}$; (I) can be replaced by (II) but not by 4 : 4′-dipyridyl, C_5H_5N, or 2-hydroxyquinoline. Activation is not accompanied by a corresponding increase in peroxidase or oxidase action (substrate $AcCO_2H$, fructose, or octatrienoic acid). The effects are attributed to highly active intermediate phases; it is not necessary to consider these due to intermediate compounds, but rather as due to intermediate reactions. H. W.

Influence of graphite on the decomposition of hydrogen peroxide by iron. R. KUHN and A. WASSERMANN (Annalen, 1933, **503**, 232—248; cf. A., 1928, 1044).—When H_2O_2 is shaken with graphite (I) slight evolution of O_2 is observed, which becomes vigorous after addition of a Fe salt, although in absence of (II) the added Fe is nearly inactive. The rate of reaction depends greatly on the concn. of H_2O_2. The change is of the first order and independent of the rate of shaking with H_2O_2 concn. $< 0{\cdot}5N$, whereas with 0·84—5·0N-H_2O_2 an action of zero order takes place. Catalysis appears to occur at the boundary of (I) and solution and not to be due to the dissolution of material from (I). The mechanism of the reaction is discussed. Restriction of the catalytic action of the graphite adsorbate by PO_4, CN, and OAc indicates the existence of Fe^{III} compounds at the surface. Contrary to the behaviour in homogeneous solution, the activity of Fe adsorbed by (I) is unusually markedly restricted by substances which form Fe^{III} complexes (2 : 2′-dipyridyl; phenanthroline), indicating that Fe^{II} compounds exist at the surface. H. W.

Kinetics and impediment of the hydrogen peroxide–hydrogen sulphide reaction catalysed by iron. A. WASSERMANN (Annalen, 1933, **503**, 249—268; cf. A., 1932, 704).—The rate of reaction between H_2O_2 and H_2S in presence of Fe salts is investigated by measurement of the rate of dissolution of the gas. 1·5—2·0 mols. of H_2O_2 are required per mol. of H_2S and 0·6—0·8 mol. of S and 0·2—0·4 mol. of H_2SO_4 are formed. Reaction proceeds relatively slowly at p_H 0, its rate increases until $p_H=2$, and then remains const. until $p_H=4{\cdot}1$. The rate of H_2S consumption increases with increasing initial concn. of H_2S, but depends less on that of the H_2O_2 or catalyst; under optimum conditions, the dissolution of H_2S is the slowest process. The temp. coeff. of the change diminishes with rise of temp. The peroxidative action of Fe in this case is at least 10^4 times the catalytic or the oxidative effect. In the H_2S–H_2O_2 reaction hæmin is less active than Fe salts, whilst the Fe^{II} 2 : 2′-dipyridyl and phenanthroline complexes and $Fe_3(PO_4)_2$ have little activity. At p_H 4, HCN, $AcCO_2H$, fructose, $CH_2Ph{\cdot}OH$, or solid S has no marked restrictive action. Pyrogallol, p benzoquinone, and quinol are restrictive. H. W.

Neutral salt effect in ionic reactions. A. PARTS (Z. physikal. Chem., 1933, **164**, 439—441).—Polemical (cf. von Kiss, A., 1932, 818). R. C.

Simultaneous reduction of vanadic acid and oxygen by iodide. Induced catalysis of oxygen reactions. W. C. BRAY and J. B. RAMSEY (J. Amer. Chem. Soc., 1933, **55**, 2279—2288; cf. A., 1927, 640).—By a suitable choice of concns., the induction factor, (O_2 reduced)/(HVO_3 reduced, g.-equiv. per litre), for the reaction induced between dissolved O_2 and I′ during the reduction of HVO_3 by I′ in H_2SO_4 solution is increased from 0·01 to 12. A survey of the literature indicates that in induced O_2 reactions of this type the results are highly sp. with respect to the reducing and the oxidising agents, and the induction factor increases without limit as conditions become more favourable to the induced reaction. The results support the theory that O_2 reactions, in general, are chain reactions. J. G. A. G.

Glutaconic acids. XXIII. Catalytic effect of acids on the rate of racemisation of *l-trans*-αγ-dimethylglutaconic acid. J. S. FITZGERALD and J. PACKER (J.C.S., 1933, 595—600).—The rate of racemisation of *l-trans*-αγ-dimethylglutaconic acid by HCl and H_2SO_4 shows a min. at 0·1—0·2M-acid. The curve correlating rate of racemisation and p_H may be fitted by a catalytic catenary of the form $k=k'+k_{OH'}[OH']+k_{H'}[H_3O^+]$. From the p_H at the min., $k_{OH'}/k_{H'}$ is approx. 10^{11}, in agreement with accepted theories of tautomeric change. J. S. A.

Anti-oxygenic properties of alkaloids. C. ACHARD, A. BOUTARIC, and J. BOUCHARD (Compt. rend., 1933, **196**, 1757—1759).—Using an aq. or EtOH solution of uranine containing 1 g. of acid fluorescein per litre and solutions of alkaloids which do not appreciably diminish the p_H, addition of 0·5—10 g. of 18 alkaloids (or their salts) per litre in all cases reduces the fluorescence, showing a behaviour similar to that of anti-oxygenic substances, in agreement with the similarity in the effect of both on the velocity of decolorisation of methylene-blue by milk or liver-tissue (cf. A., 1927, 609; Bul. Acad. Med., 1932, **107**, 1054). C. A. S.

Catalysts for the production of hydrogen by the water-gas reaction. XIV. Thermal sensitivity of ferric oxide. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1933, **36**, 306—308B).—The activity of pure Fe_2O_3 fell much more rapidly than that of a sample containing traces of Si, Cu, Al, Cr, Mn, Ni, Ca, S and P. A. G.

Catalysts for the production of hydrogen by the water-gas reaction. XI—XIII. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1933, **36**, 282—286B).—XI. Activity, represented by % CO oxidised, of (1) Al_2O_3 is 2% at 500°, 6% at 600°, 25% at 800°, (2) Cr_2O_3 is 8% at 400°, 85% at 600°, 74% at 800°, (3) Fe_2O_3 is 85% at 400°, 88% at 500°, 86% at 600°, the theoretical val. being 96, 93, 87, and 76% at 400°, 500°, 600°, 800°, respectively. Optimum temp. are Fe_2O_3, 450°; Cr_2O_3, 550°; Al_2O_3, 1000°. No diminution in activity of Cr_2O_3 and Al_2O_3 occurred at 800—1000°, as occurs with Fe_2O_3 at 800°.

XII. The liberation of C by the reaction $2CO \rightleftharpoons C+CO_2$ and formation of Fe_3C_4 on the surface of the Fe_2O_3 catalyst, which were suggested as causing irregular variations in the activity–time relation at 410°, have no effect at 560°.

XIII. Fe_2O_3 is activated by Cr_2O_3, the optimum amount being 7 mol.-%. A catalyst containing 87% Cr_2O_3 first exhibited catalytic action at the same temp. as Fe_2O_3 alone, *i.e.*, at 450—500°. V. P. P.

Iron catalyst for hydrogenation of carbon monoxide at ordinary pressure. DECARRIERE and J. ANTHEAUME (Compt. rend., 1933, **196**, 1889—1891; cf. B., 1929, 840; 1931, 231).—Catalysts containing 4Fe+1Cu+0·02K_2CO_3 (formula wts.) and less or none of Cu and/or K_2CO_3 were prepared by suspending kieselguhr in aq. $Fe(NO_3)_3$ and $Cu(NO_3)_2$, pptg. with slight excess of K_2CO_3, washing, adding the desired amount of K_2CO_3, drying at 110°, and

reducing by H_2 at 250°. $CO+1{\cdot}75H_2$ is passed over the catalyst at 250°. Reduction of the amount of Cu from 1 to 0·1 (at. wts.) and absence of K_2CO_3 increased the yield, which was further greatly increased by electrolytically washing the catalyst. K_2CO_3 is unfavourable, and it is probable that Cu acts solely by reducing the temp. of reduction of Fe_2O_3 from 300° (necessary for pure Fe_2O_3) to 250°. C. A. S.

Catalytic reaction of reduced nickel on the methane–water reaction. H. FUJIMOTO (J. Soc. Chem. Ind. Japan, 1933, **36**, 147—148B).—The reactions $CH_4+H_2O=CO+3H_2$ and $CH_4+2H_2O=CO_2+4H_2$ in presence of a Ni catalyst commence at 400°. The velocity reaches a max. at 600° and a min. at 800°. The decrease is attributed to the action of the CO on the catalyst. Using Ni+10% Al the velocity rises normally with temp. The reaction $CH_4=C+2H_2$ commences at 700° with a Ni catalyst, but below 400° with Ni+10% Al. J. S. A.

Reaction regions. XXV. Systems of two gases and one solid, and of two solids and one gas. W. P. JORISSEN, A. A. VAN DER DUSSEN, W. P. M. MATLA, and J. H. DE LIEFDE (Rec. trav. chim., 1933, **52**, 403—412).—The quenching action of finely-divided powders on the explosion of CH_4 (10%)–air mixtures is most effective with KCl, NaCl, $NaHCO_3$, $KNaCO_3$, NaF, K Sb tartrate, K pyrosulphate, $Ba(NO_3)_2$, $HgCl_2$, As_2O_3. KCl and NaCl are more effective than stone dust in preventing or arresting gas explosions in coal mines. The explosion limits of mixtures of dextrin, air, and an inert powder such as Fe_2O_3, slate or stone dust, or fuller's earth have been determined as a function of the concn. of inert material. In all cases the limiting dextrin concn. at first falls and then rises to a relatively high val. as the % inert dust is increased. Stone dust should prove effective in extinguishing a dextrin fire. Dextrin dust in air is not likely to ignite if the O_2 concn. is reduced to $\geq$15·5% by addition of N_2; addition of CO_2 should be even more effective. H. F. G.

Action of alkali halides on the auto-ignition temperature of carbon monoxide–air mixtures. M. PRETTRE.—See B., 1933, 532.

Auto-ignition temperatures of hydrogen–air mixtures in presence of alkali halides. M. PRETTRE. —See B., 1933, 532.

Catalytic oxidation of ammonia on platinum gauze. I. E. ADADUROV (J. Chem. Ind. Russ., 1933, No. 2, 37—41).—The reaction of oxidation of NH_3 to NO and H_2O is one of the first order, as is shown by its const. velocity under different conditions of pressure and concn. of NH_3. The process consists of the following series of reactions, of which probably the first conditions the velocity of the whole process: $NH_3 \rightleftharpoons N+H+H_2$; $H+O_2 \longrightarrow OH+O$; $OH+H_2 \longrightarrow H_2O+H$; $O+N \longrightarrow NO$. The greater vol. of the products of the reaction than of the initial mixture is ascribed to the side-reaction $2NH_3 \longrightarrow N_2+3H_2$. R. T.

Thermal decomposition of phosphine by tungsten and molybdenum. H. W. MELVILLE and H. L. ROXBURGH (J.C.S., 1933, 586—595).—The decomp. of PH_3 at a pressure of 0·01—300 mm. by a W filament at 400—600° is practically unimol. and little affected by the pressure. With Mo, the reaction is unimol. at low pressure, but of zero order at higher pressure. The products of the reaction are red P and H_2. The presence of H_2 has no inhibiting effect, in contrast to the NH_3 decomp. The heat of adsorption of PH_3 is calc. from the temp. coeff. at high and low pressures. J. S. A.

Good and poor catalysts for production of sulphuric acid. I. E. ADADUROV (J. Appl. Chem. Russ., 1933, **6**, 193—205).—The SO_3 content–temp. curve derived theoretically from a thermodynamic consideration of the reaction $2SO_3 \rightleftharpoons 2SO_2+O_2$ practically coincides with that representing % SO_3 synthesis from SO_2 and O_2 in presence of Pt, at 400—900°; other catalysts have higher activation temp., at which, however, they are not less efficient than is Pt. The activity of mixed oxide catalysts is not the mean of that of their constituents, but may be less or greater, according to the relative proportions of the constituent oxides. R. T.

Oxidation of arsenious sulphide by atmospheric oxygen in alkaline media, under pressure, and at high temperatures. G. A. RAZUVAIEV, V. S. MALINOVSKI, and E. P. LOPATINA (J. Appl. Chem. Russ., 1933, **6**, 206—219).—The process of dissolution of As_2S_3 in aq. NaOH is extremely complex, consisting of a no. of successive reactions, and represented summarily at 100—110° by $2As_2S_3+8NaOH+5O_2 \longrightarrow 4NaAsO_2+2Na_2S_2O_3+2S+4H_2O$, and at 150—300° by $As_2S_3+10NaOH+7O_2 \longrightarrow 2Na_2HAsO_4+3Na_2SO_4+4H_2O$, with Na_2HAsS_3 in both cases as an intermediate product. Oxidation proceeds very slowly in acid or neutral solutions. $CuSO_4$ catalyses the reaction to an extent increasing with rise of temp. R. T.

Relations between catalyst structure and chemical change. I, II. J. ECKELL (Z. Elektrochem., 1933, **39**, 423—432, 433—439).—I. A general discussion.

II. The relation between the catalytic activity of Ni foil and the degree of cold work to which it is subjected has been followed by catalysis of the hydrogenation of C_2H_4. Cold-rolled foil (reduced from 3 mm. to 0·1 mm.) is active, but becomes inactive after recrystallisation by heating in vac. for 5 hr. at 900°. Polishing the surface increases the catalytic activity about 600—1000 times. A p.d. is observed between cold-rolled or polished Ni and annealed Ni when immersed in aq. $NiSO_4$. *X*-Ray examination indicates deformation of the lattice on cold-working. The structural change is considered to account for the change in activity and other properties. E. S. H.

Use of catalysts for the high-pressure hydrogenation of phenols and hydrocarbons. H. TROPSCH and O. WEINSTEIN.—See B., 1933, 581.

Catalytic reduction of aromatic nitro-compounds. S. J. GREEN.—See B., 1933, 539.

Kinetics of the acetylation of cellulose. III. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1933, **36**,

280—282B).—The acetylation of cellulose in the presence of catalysts and diluents follows the equation which has been established for non-catalytic acetylation (B., 1932, 498). V. E. Y.

Hydrogenation of acetylene derivatives. XIX. Dependence of direction and course of hydrogenation on the chemical nature of the catalyst. J. S. SALKIND, M. N. VISCHNJAKOV, and L. N. MOREV.—See this vol., 805.

Fractionation of isotopes by electrolysis. J. KENDALL (J. Amer. Chem. Soc., 1933, **55**, 2612—2613).—Electrolysis of an acid solution of $Hg_2(NO_3)_2$, using a low voltage and low c.d., afforded Hg with d only 0·999981 of that of ordinary Hg. J. G. A. G.

Electrolytic oxidation or reduction with alternating current. N. KAMEYAMA and K. TAKAHASHI (J. Soc. Chem. Ind. Japan, 1933, **36**, 174—175B).—Using 50-cycle a.c. the following reactions occurred. Cu, Ni, and Pb electrodes dissolved in H_2SO_4 and NaOH. NaCl yielded Cl_2 and NaOCl. KI yielded I and KIO_3. Oxidation occurred with $FeSO_4$, $FeCl_2$, $SnCl_2$, $K_4Fe(CN)_6$, K_2SO_3, $Na_2C_2O_4$, and $Na_2S_2O_3$, whilst $FeCl_3$, $Fe_2(SO_4)_3$, $HgCl_2$, H_2CrO_4, $KMnO_4$, and $K_3Fe(CN)_6$ were reduced. Aliphatic compounds, using Pt electrodes and H_2SO_4 as electrolyte, were usually oxidised. EtOH gave MeCHO, AcOH, and CH_4; $Pr^{\beta}OH$ gave $COMe_2$; MeCHO gave AcOH; CH_2O gave CO_2; $COMe_2$ yielded C_3H_8. J. S. A.

Deposition of copper and silver from iodide solutions. M. SCHLOTTER, J. KORPIUN, and W. BURMEISTER.—See B., 1933, 552.

Action of the silent discharge on ethylene. W. SZUKIEWICZ (Rocz. Chem., 1933, **13**, 245—255).—Up to 95% of C_2H_4 subjected to the silent discharge is converted into C_2H_2, erythrene, diacetylene, C_4H_{10}, C_6H_{14}, and other products, according to the following reactions: $2C_2H_4 \longrightarrow (CH_2{\cdot}CH{\cdot})_2$ (or $CHMe{\cdot}CH{:}CH_2$) $\longrightarrow C_4H_{10}$; $3C_2H_4 \longrightarrow C_6H_{12} \longrightarrow C_6H_{14}$; $C_2H_4 \longrightarrow C_2H_2+H_2$. The yield of products of higher mol. wt. increases with the density of charge. The reaction of production of C_2H_2 is reversible, 18% of C_2H_2 being present in the equilibrium mixture under the mildest conditions of discharge studied. R. T.

Photosynthesis of hydrogen chloride. III. Mixtures containing oxygen. R. G. W. NORRISH and M. RITCHIE (Proc. Roy. Soc., 1933, **A**, **140**, 713—740).—The kinetics of the photochemical combination of H_2 and Cl_2 in the presence of large or small quantities of O_2 have been studied by means of a new technique (this vol., 576). The results of Chapman and his co-workers, and especially of M. C. C. Chapman (A., 1924, ii, 668), are confirmed. The HCl produced by the reaction has a powerful inhibiting effect, in accord with a similar effect observed by Christiansen in the thermal union of H_2 and Cl_2 (A., 1929, 654). H_2 also has an inhibiting effect, and the quantum efficiency (γ) passes through a max. as the pressure of H_2 increases. The effect of H_2 is about 0·25 of that of HCl. The effect of variation of O_2 on γ can be expressed by $\gamma_{HCl}=k/([O_2]+k')$, when all other factors, including the intensity of absorbed light (I_{abs}), are const. The progressive addition of small amounts of O_2 to H_2–Cl_2 mixtures initially containing no O_2 involves the consideration of a change in reaction mechanism, one notable feature being the progressive change from $I^2_{abs.}$ to as a factor determining the rate of reaction. By an extension of the Nernst scheme of reactions already adopted for O_2-free mixtures (this vol., 576) to include ternary and binary reactions of H atoms with O_2 mols., an expression is derived from which γ may be calc. over a wide range with a high degree of accuracy. The calc. vals. vary from 10^5 to 20. This formula reduces to the empirical formula of M. C. C. Chapman for mixtures containing O_2. L. L. B.

Temperature coefficient of the photochemical oxidation of HI. N. VITA (Gazzetta, 1933, **63**, 211—223).—In the photochemical oxidation of HI in aerated aq. solutions with practically pure monochromatic light in the range 365—579 mμ, the temp. coeff. is in general high (1·3—2·0) and does not vary regularly with the frequency of the radiation. The temp. coeff. is considerably lower when the monochromatic light is mixed with band radiation. With a mixture of two monochromatic lights the temp. coeff. lies between the vals. obtained with the two separate wave-lengths. O. J. W.

Yield of photochemical reactions using complex light compared with that using the component lights. N. VITA (Gazzetta, 1933, **63**, 223—227).—Measurements have been made of the I liberated in the photochemical oxidation of aerated aq. HI solutions using (*a*) monochromatic light of 546 mμ and (*b*) light containing approx. equal intensities of 546 and 579 mμ. The yield with light (*b*) is much < that to be expected if an additive law held. The ratio of the yields $a : b$ decreases with rise of temp. O. J. W.

Importance of density of illumination in photochemical reactions. N. VITA (Gazzetta, 1933, **63**, 227—234).—In the oxidation of HI solutions (cf. preceding abstracts) the yield of I with continuous light is equal to that with intermittent light below a certain threshold val. of the light density, which is dependent on the conditions and in particular on the temp. O. J. W.

Photochemical properties of chromyl chloride. KANTZER (Compt. rend., 1933, **196**, 1882—1883).—Decomp. of CrO_2Cl_2 vapour by light is produced only by light of $\lambda < 4200$ Å.; at λ 3500—4200 Å., $CrO_2Cl_2 = CrO_2+Cl_2$. C. A. S.

Theory of the ideal colour sensitivity of photographic emulsions. J. E. DE LANGHE (Z. wiss. Phot., 1933, **32**, 76—82).—Mathematical. The Goldberg equation is extended to give formulæ expressing ideal colour sensitivity relations, allowing for the spectral sensitivity range of the eye. J. L.

Nature of the latent image for physical development. IV. H. ARENS (Z. wiss. Phot., 1933, **32**, 65—75; cf. A., 1932, 1098; 1931, 806).—The relative velocity of grain growth (A) is defined as the amount of Ag developed in unit time on unit surface of a Ag particle, and the abs. velocity of grain growth (B) as the Ag developed in unit time on the total

surface of the particle. *A* decreases with increasing size of the Ag nuclei, and increases with decreasing concn. of nuclei, the no. of nuclei being const. *B* increases at the beginning of development, becoming later approx. const. The total amount of Ag developed is dependent only on the no. of nuclei, when their mass is $> 10^{-15}$ g., and when development is prolonged to 1—2 hr. J. L.

Increase of sensitivity of photographic emulsions by electrophoresis. A. CHARRIOU (Compt. rend., 1933, **196**, 1880—1882).—AgBr plates covered with a film of H_2O and subjected to d.c. of 30—40 milliamp. at 110 volts for 15 min. to 14 hr. gradually increased in sensitivity until after 4 hr. this was quintupled, and then declined, being only half the initial val. after 14 hr. Br, but no Ag, was found in the H_2O. C. A. S.

Photochemical behaviour of silver halide emulsions in relation to the constitution of new substances used as desensitisers and developers. G. KRAFT (Z. wiss. Phot., 1933, **31**, 329—364).—Many org. substances, including S compounds, have been tested for sensitising, desensitising, or anti-fogging properties, and for use as developers. The results are given in detail and discussed. Several substances new to photography have been found which should have practical val. as sensitisers, desensitisers, or anti-fogging agents. Kögel and Steigmann's "hydrogenation and dehydrogenation" theory of desensitisation is supported. J. L.

Eder's solution. F. KRAUSS and K. BERGE (J. pr. Chem., 1933, [ii], **136**, 257—287).—Ultra-violet irradiation of aq. $H_2C_2O_4$ causes no decomp.; CO_2 is produced when the solution contains a trace of $FeSO_4$ or, better, $FeCl_3$. A small amount of CO_2 is formed by irradiation of aq. $(NH_4)_2C_2O_4$; Fe salts again catalyse the decomp. The quantity of CO_2 produced from $(NH_4)_2C_2O_4$ is a min. in absence of O_2, indicating that O_2 is concerned in the above decomp. Solutions of $HgCl_2$ are also unaffected by irradiation; in presence of $FeSO_4$, small amounts of HgCl and H_2O_2 (which has no influence on the reaction) are produced. HgCl is similarly formed using Ru, Mo, and W salts (cf. A., 1930, 553). When solutions of $(NH_4)_2C_2O_4$ or $Na_2C_2O_4$ are heated, small amounts of HCO_2H are produced; $H_2C_2O_4$ and $K_2C_2O_4$ do not give HCO_2H. HCO_2H is produced during the oxidation of $H_2C_2O_4$ with $KMnO_4$ (cf. Oberhauser and Hensiger, A., 1928, 505). The experimental results of Dhar (J.C.S., 1917, **111**, 690, 700, 748; A., 1928, 720) are confirmed, but some of the work of Oberhauser *et al.* (*loc. cit.*; A., 1929, 793) is not; the "activated" $H_2C_2O_4$ of both authors is undoubtedly HCO_2H and their results are thus explicable. HgCl is not formed when the components [$HgCl_2$; $(NH_4)_2C_2O_4$] of Eder's solution are irradiated separately and then mixed; the production of HgCl occurs only when the solution contains both salts and can be ascribed to the intermediate formation of HCO_2H. The reaction mechanism is discussed. Eder's solution is unsuitable for accurate and reproducible measurement of light quanta. H. B.

Photochemical oxidation of ethyl alcohol in presence of benzophenone. A. BERTHOUD (Helv. Chim. Acta, 1933, **16**, 592—600).—Kinetic study of the photochemical oxidation of EtOH by O_2 in presence of $COPh_2$ (Boeseken *et al.*, A., 1927, 769) shows that the reaction is preceded by a long induction period of variable duration according to (unprescribed) conditions, but only a feeble residual photochemical effect occurs after illumination is discontinued. The velocity of oxidation is proportional to the light intensity, decreases with increasing $[O_2]$, but is independent of $[COPh_2]$ when total absorption of light of active wave-length occurs. The temp. coeff. between 20° and 30° is 1·7. Contrary to Boeseken (*loc. cit.*) light in the visible region is inactive, greatest activity being observed at λ=366 mμ, and with this λ the yield calc. on the no. of O_2 mols. absorbed is 18%. A chain reaction mechanism is probable. J. W. B.

Dependence of quantum efficiency on the frequency of effective monochromatic radiation in photochemical reactions. J. C. GHOSH and R. M. PURKAYASTHA (J. Indian Chem. Soc., 1933, Ray No. 235—242; cf. A., 1930, 1260).—Photobromination of cinnamic acid in CCl_4 solution occurs for light between 5460 and 3660 Å., which is absorbed by Br, but not at 3130 Å., when only the acid absorbs light. Aq. mandelic acid is not brominated in presence of KBr by light of wave-length 3130 Å., which is absorbed only by the Br_3' ion. H. J. E.

Photochemical reaction between quinine and dichromic acid. III. Quinine derivatives and utilisation of absorbed quanta. G. S. FORBES and L. J. HEIDT (J. Amer. Chem. Soc., 1933, **55**, 2407—2413; cf. this vol., 359).—For light of wave-lengths between 436 and 313 mμ, the log. of the quantum efficiency, γ, of the oxidation of quinine and 12 derivatives by chromic acid is a linear function of the log. of the concn. of the excited alkaloid mols. The low vals. of γ ($< 0{\cdot}1$) are not due to loss of quanta owing to direct decomp. of quinine mols. The *sec.*-OH group of quinine and its derivatives reduces the chromic acid, and effective transmission of absorbed quanta to the reactive OH occurs only when various photochemically inactive groups are substituted for H on the opposite side of the quinoline group. The nature of this transmission process is discussed. J. G. A. G.

Photolysis of gaseous acetone and the influence of water. G. H. DAMON and F. DANIELS (J. Amer. Chem. Soc., 1933, **55**, 2363—2375).—Dry $COMe_2$ vapour is decomposed by ultra-violet light mainly into CO and C_2H_6 with some H_2 and CH_4. A trace of H_2O catalyses a photo-condensation probably to diacetone alcohol, which on photo-decomp. affords the same products as $COMe_2$. The no. of mols., γ, of $COMe_2$ vapour at 1 atm. reacting per quantum is 0·17 at 56° when the incident intensity is 10^5 ergs per sq. cm. per sec.; γ increases at low intensities, decreases at low pressures, and is independent of wave-length between 3130 and 2650 Å. The blue fluorescence of $COMe_2$ vapour in the presence of a trace of O_2 changes to the much more intense green fluorescence of pure $COMe_2$ when all of the O_2 has been removed in a photo-oxidation. The energy of fluorescence is $< 3\%$ of the energy absorbed. The nature of the reaction mechanisms is discussed. J. G. A. G.

Photosynthesis in various portions of the spectrum. G. R. BURNS (Plant Physiol., 1932, **8**, 247—282).—Infra-red radiation (>1100 mμ) is detrimental to photosynthesis. With spruce the relative quantum yields in the wave-lengths 720—630, 720—560, and 470—390 mμ are 9·5, 10, and 5, and with pine, 9·5, 11·0, and 5, respectively. A. G. P.

Emission of Gurwitsch radiation by gaseous reactions. R. RUYSSEN (Bull. Acad. roy. Belg., 1933, [v], **19**, 535—542).—The Gurwitsch type of ultra-violet radiation was emitted in the combustion of coal gas, in that of a mixture of O_2 and H_2, and in the photosynthesis of HCl. N. M. B.

Reduction of chromate solutions by *X*-rays. H. FRICKE and E. R. BROWNSCOMBE (J. Amer. Chem. Soc., 1933, **55**, 2358—2363).—The reduction of $N/500$ to $N/9000$-$K_2Cr_2O_7$ in $0{\cdot}8N$-H_2SO_4 is independent of $[K_2Cr_2O_7]$ and proportional to the total dosage of *X*-rays. The temp. coeff. between 5° and 90° is unity. The reduction observed with $N/9000$-$K_2Cr_2O_7$ is min. when the acid is $10^{-3}N$ and becomes const. at high acidities. The reduction is due to the primary formation of H_2O_2 from the H_2O. Traces of inorg. substances are without effect, but fatty acids, alcohols, and aldehydes have marked catalytic effects which become sp. with increasing concn. J. G. A. G.

Action of radon on unsaturated hydrocarbons. III. Vinylacetylene and butadiene. G. B. HEISIG (J. Amer. Chem. Soc., 1933, **55**, 2304—2311).—The v.p. of butadiene (I) in the range 197—272° abs. is given by $\log_{10} P_{mm} = 1251{\cdot}8/T + 7{\cdot}543$ and the b.p. is −4·6°. The no. of mols. of vinylacetylene (II) and (I) condensing per α-particle from radon is 10·8 and 9, respectively. The yield of H_2+CH_4 is very small. (II) affords a white solid changing to yellow and (I) gives a pale viscous liquid. J. G. A. G.

Separation of the isotopic forms of water by fractional distillation. G. N. LEWIS and R. E. CORNISH (J. Amer. Chem. Soc., 1933, **55**, 2616—2617).—Differences of 60—80 p.p.m. have been observed between the *d* of H_2O obtained from the top and the bottom of a 20-ft. fractionating column. Calculations indicate a more effective separation by fractional distillation under reduced pressure. J. G. A. G.

Action of water vapour on alkali carbonates. C. KROGER and E. FINGAS (Z. anorg. Chem., 1933, **212**, 257—268).—The partial pressure of CO_2 obtained by heating Li_2CO_3, Na_2CO_3, or K_2CO_3 in a stream of H_2O vapour at 500—850° depends on the proportion of alkali hydroxide in the mixture, as well as on factors such as solution and diffusion. It is therefore a function of the duration of the experiment. The reaction with Na_2CO_3 at 1000—1165° is incomplete owing to vaporisation of the NaOH produced. F. L. U.

Action of carbon on alkali carbonates. C. KROGER and E. FINGAS (Z. anorg. Chem., 1933, **212**, 269—283; cf. preceding abstract).—Reaction pressures of CO in the reaction $M_2CO_3+2C=2M+3CO$ (M=Li, Na, K) have been determined at temp. up to 1060°. With Li_2CO_3 the pressures are reversible, but depend on the proportion of substance changed. They are irreversible with K_2CO_3 owing to the secondary formation of $(KCO)_6$, dissociation pressures of which have been measured. With Na_2CO_3 the pressures are reversible and reproducible. The heat of the reaction and of vaporisation of Na is calc. The results obtained in this and the preceding investigation indicate the following mechanism for the catalysis of water-gas formation by Na_2CO_3 or K_2CO_3: (1) $Na_2CO_3+2C=2Na(vapour)+3CO$; (2) $2Na+2H_2O=2NaOH+H_2$; (3) $2NaOH+2CO=2HCO_2Na$ $=Na_2C_2O_4+H_2=Na_2CO_3+CO+H_2$. F. L. U.

Decomposition of sodium sulphate by hydrogen. K. I. LOSEV and J. G. NAIDIS (J. Appl. Chem. Russ., 1933, **6**, 220—223).—Na_2SO_4 is reduced to Na_2S by H_2 at < 800°; at > 800° further reduction to NaOH and H_2S takes place. R. T.

Micro-determination of copper by the cysteine oxidation method. K. G. ANDRESEN and B. NIELSEN (Biochem. Z., 1933, **261**, 22—44).—Warburg's procedure (A., 1927, 985) gives unsatisfactory results. The cysteine oxidation method cannot thus be used for the determination of Cu, possibly because H_2O_2 is produced during the process. The effect of p_H on the decomp. of H_2O_2 has been investigated. W. McC.

Acetato-complexes of the alkaline-earth metals. J. V. DUBSKY and J. TRTILEK (Publ. Fac. Sci. Univ. Masaryk, 1932, No. 161, 3—30).—The following *compounds* have been prepared from aq. $CuCl_2$ and MR_2 (M=Mg, Ca, Sr; R=OAc), or alternatively from AcOH, acid, and MCO_3, or by the action of salts on complexes of the type $[M_2R_2]Cl_2$: $[Mg_2R_2]Cl(R),5$ and $6H_2O$; $[Sr_2R_2]Cl_2,SrCl_2,14H_2O$; $[Sr_2R_2]Cl_2,4H_2O$; $[Ca_2R_2]X_2,10H_2O$ (X=Cl, Br, and I); $[Sr_4R_4]Cl_3(R),7H_2O$; $[Ca_2R_2][C_6H_3(NO_2)_3O]_2,6H_2O$; $[Ca_2R_2]CrO_4,AcOH$; $[Ca_2R_2]CrO_4,2H_2O$; $[Ca_2R_2](NO_3)_2,CaR_2,3H_2O$; $[Ca_4R_6]S_2O_3,4H_2O$; $[Ca_2R_3]CNS,3H_2O$; $[Ca_2R_2](NO_3)_2,2H_2O$; $[Ca_3R_4](NO_2)R,Ca(NO_2)_2,5H_2O$; $[Ca_4R_6](NO_3)_2,CaR(NO_3)_2,5H_2O$. R. T.

Hydrates of calcium sulphate. C. S. GIBSON and S. HOLT (J.C.S., 1933, 638—640).—$CaSO_4,2H_2O$ (I) undergoes gradual change up to 73°±2°. Between 73° and 92°±2°, dehydration to $CaSO_4,0{\cdot}5H_2O$ (II) occurs. There is no higher discontinuity in dehydration curves, indicating that H_2O in (II) is zeolitically held. Dehydration of (I) proceeds by way of (II).

Synthesis of calcium silicates. V. S. NAGAI and K. MURAKAMI (J. Soc. Chem. Ind. Japan, 1933, **36**, 264—268B).—Examination of the products obtained by heating 2 : 1, 2·3 : 1, 2·7 : 1, and 3 : 1 mixtures of $CaCO_3$ and SiO_2 at 1300°, 1350°, and 1400° indicated: (1) complete combination of 2 : 1 mixture by heating at 1300° for 3 hr., (2) increase in $3CaO,SiO_2$ formation with increased $CaCO_3$ content of the original mixture, with higher temp., and by repeated heating, grinding, and mixing, a 99·55% yield being obtained from a 3 : 1 mixture by four such repetitions at 1400° for a total heating time of 12 hr. V. P. P.

Laboratory preparation of chloride of lime. A. B. JAFET (Chimica, 1933, **1**, 100).—Dry HCl-free Cl_2 is passed through a stirred mixture of dried slaked

lime and CCl_4 at 40—45°. After 11 hr. the mass is cooled to 20°, and the CCl_4 is distilled off at 25—30°/620 mm. The product contains 40% of active Cl, and has only a very slight odour of Cl_2. E. L.

Change of constitution of tricalcium orthophosphate after fusion. A. Travers and Bauer (Compt. rend., 1933, **196**, 1802—1804).—$Ca_3(PO_4)_2$ on fusion is transformed into a mixture of $Ca(PO_3)_2$, $Ca_4P_6O_{19}$, and CaO with loss of P_2O_5. In one case 4·2% of the P_2O_5 was found as $Ca(PO_3)_2$, with 3·36% CaO, whilst the loss of wt. was equiv. to 1·2% P_2O_5. This explains the increased solubility of the fused substance in 2% citric acid. C. A. S.

Hydrated hexagonal calcium aluminates. H. Lafuma (Compt. rend., 1933, **196**, 1671—1672).—On mixing at room temp. aq. Al_2O_3,CaO and aq. $Ca(OH)_2$ there are formed, according to the amount of $Ca(OH)_2$, $Al(OH)_3$ and/or one or more of the hexagonal Ca_2, Ca_3, or Ca_4 aluminates, all of which are rapidly transformed in the mother-liquor at 80°, or slowly in the cold in presence of saturated aq. $Ca(OH)_2$, *e.g.*, after <1 year, into cubic $3CaO,Al_2O_3,6H_2O$. The same result occurs on heating with additional $Ca(OH)_2$, but much more slowly in the case of Ca_2 aluminate. If warm solutions are used initially the transformation into the Ca_3 aluminate is much more rapid, and instantaneous with large proportions of $Ca(OH)_2$. The only stable aluminate is the cubic $3CaO,Al_2O_3,6H_2O$. C. A. S.

Separation of elements 88 (Ra), 89 (Ac), and 90 (Th) by means of organic solvents. M. Haissinsky (Compt. rend., 1933, **196**, 1788—1789).—The method is based on the comparative solubilities in EtOH and precipitabilities from such solution by C_5H_5N of Th-$X(NO_3)_2$, Ms-Th-$2(NO_3)_3$, and $Th(NO_3)_4$. An aq. solution of 3—4 mg. of $Ba(NO_3)_2$ containing Ms-Th-1, Ms-Th-2, Rd-Th, Th-*X*, and active deposit, together with 3—5 mg. $La(NO_3)_3$, is evaporated to dryness and extracted with 4 c.c. of EtOH. The insol. portion contains the Ba, Ms-Th-1, and Th-*X*, with 5—10% of the Ms-Th-2, and 2% of the Rd-Th. To the filtrate are added 3 mg. of cryst. Th nitrate, and 4—5 c.c. C_5H_5N, when Th and Rd-Th with 7% of the Ms-Th-2 are pptd., leaving in the filtrate La and most of the Ms-Th-2. Two or three repetitions complete the separation. Active deposit passes mainly into the filtrate; to separate it $Pb(NO_3)_2$ is added to the EtOH–C_5H_5N solution and H_2S passed in; the La and Ms-Th-2 are separated as hydrate or oxalate. Th-*X* is converted into iodide, dissolved out by $COMe_2$, and deposited electrolytically on a Ni or Pt cathode. C. A. S.

Formation of C_xO_y by wet oxidation of carbon. Y. Oshima, Y. Fukuda, and S. Takashima (J. Soc. Chem. Ind. Japan, 1933, **36**, 148—149B).—From the changes in properties (increase in wt., calorific power, volatile matter content) of C black on oxidation with HNO_3 and aqua regia, it is deduced that O is fixed as a physico-chemical complex, for which formulæ are suggested. J. S. A.

Mechanism of activation of carbon. N. Bach and I. Levitin (Kolloid-Z., 1933, **64**, 22—30).—The adsorptive power of natural graphite for crystal-violet and PhOH is diminished by treatment with CO_2 at 1000°, whilst that of artificial graphite is increased slightly. Natural graphite shows cementation and increase in size of the particles after the treatment; it is estimated that the mean thickness is increased by 2—3 times and the surface by 8 times. Microscopical examination at various stages shows that throughout the course of oxidation the particles acquire a smoother surface and a simpler geometrical form. The results indicate that the activation of C is due not to changes in the crystals, but to oxidation of org. impurities. E. S. H.

Acid-soluble oxidising material from charcoal. M. A. Mayers (J. Amer. Chem. Soc., 1933, **55**, 2435—2436).—Evidence previously adduced to show the existence of an acid-sol. peroxide of C is inconclusive (cf. A., 1931, 316). Traces of $Fe^{...}$ in the charcoal liberate I from KI. J. G. A. G.

Silicates. I, II. E. Thilo (Z. anorg. Chem., 1933, **212**, 369—376, 377—384).—I. When pyrophyllite, $Al_2(OH)_2Si_4O_{10}$, is heated at 750—800° with anhyd. $MgCl_2$, HCl is evolved and the residual product contains $1Mg : 4SiO_2$. The same result is obtained if ignited pyrophyllite (anhyd.) is heated with MgO, but not if it is heated, in the absence of O_2, with $MgCl_2$. The cryst. structure is unchanged, indicating an exchange of H_2O for MgO in the lattice.

II. $CoCl_2$, and probably $NiCl_2$ and $FeCl_2$ also, react similarly to $MgCl_2$. $CuCl_2$ and $CdCl_2$ do not react. CuO forms a different product of undetermined composition. $ZnCl_2$ and ZnO form Zn spinel and Zn_2SiO_4. $MnCl_2$, CdO, $CaCl_2$, and CaO completely destroy the cryst. structure. F. L. U.

Action of hydrogen and oxygen on blue ultramarine. K. Leschewski and H. Möller (Z. anorg. Chem., 1933, **212**, 420—424; cf. A., 1932, 351).—When ultramarine is heated at 400° or 500° alternately with H_2 and O_2 decreasing amounts of H_2O are given off, whilst the colour alternates between light and dark blue. The lattice remains intact. F. L. U.

Recovery of blue ultramarine from a colourless degradation product. K. Leschewski [with H. Möller, J. Barrollier, and E. Podschus] (Z. anorg. Chem., 1933, **212**, 425—428; cf. preceding abstract).—Ultramarine is first treated with boiling $CH_2Cl{\cdot}CH_2{\cdot}OH$, which extracts most of the alkali, leaving a white amorphous product. The latter, after fusion with $NaNO_3$ at 550°, is heated in air for 12 hr. at 700°, whereby a blue cryst. substance having the ultramarine lattice, but deficient in S, is obtained. When heated at 400° with excess of S the substance assumes the appearance and composition of the original material. The observations are discussed with reference to the origin of the blue colour. F. L. U.

Double decomposition between germanium halides, and halides of quadri-, ter-, and bivalent elements. T. Karantassis (Compt. rend., 1933, **196**, 1894—1896).—On distilling GeI_4 with $AsBr_3$ or $AsCl_3$, $GeBr_4$ or $GeCl_4$ passes over at 183—200° or 83—86·5°, followed by AsI_3 at 394—414°, both reactions being complete. $GeCl_4$ and AsI_3 do

not react at 200°. GeI_4 heated with $SbCl_3$, $BiCl_3$, $SnCl_4$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, or $PbCl_2$ gives $GeCl_4$ and the corresponding iodide; with $SbCl_5$ free I is also formed. GeI_4 does not react with PCl_3, $SiCl_4$, $TiCl_4$, $ZrCl_4$, or $ThCl_4$, but $GeCl_4$ and PI_3 or TiI_4 give GeI_4 and PCl_3 or $TiCl_4$; in the latter case the reaction is vigorous. C. A. S.

Lead oxides. Y. KATO and R. TAKASE (J. Soc. Chem. Ind. Japan, 1933, **36**, 173B).—Red PbO may be obtained by crystallisation from conc. alkali or by low-temp. oxidation of Pb by $NaNO_3$. Green PbO is a solid solution of Pb in PbO. J. S. A.

Sulphide mirrors. I. Lead sulphide. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1933, **62**, 252—262; cf. A., 1930, 1246).—Boiling aq. PbS_2O_3,$3Na_2S_2O_3$ deposits stable films of PbS on glass dipped in aq. $SnCl_2$ and washed with H_2O. The films are transparent and yellowish to reddish-brown for thicknesses below 560 mμ. For films $<$ 160 mμ thick the transmitted light obeys the Lambert–Beer law. Interference phenomena, reflecting properties, microscopic structure, and the action of HNO_3, H_2O_2, and heat are described. H. J. E.

Action of alkali borates on lead halides in aqueous solution. A. P. ROLLET and P. C. MING (Compt. rend., 1933, **196**, 1669—1670).—Conductometric determinations show that on adding aq. $K_2B_4O_7$,$4H_2O$ or NaB_5O_8,$5H_2O$ to aq. PbX_2 there is first formed PbO,PbX_2,B_2O_3, pptd. as monohydrate in white (X—Cl or Br), or yellow (X=I) crystals, which begin to lose H_2O at 100°, but are only completely dehydrated at 200°. Further addition of borate converts the halogeno-borate into PbB_2O_4,H_2O. C. A. S.

[Artificial] production of laurionite, and lead oxybromide. (MME.) N. DEMASSIEUX (Compt. rend., 1933, **196**, 1683—1684).—Saturated aq. $PbCl_2$ heated at 100—130° for 3—90 days gives crystals of Pb(OH)Cl identical with laurionite. Similarly $PbBr_2$ forms Pb(OH)Br. The reaction proceeds much more rapidly in hard than in Pyrex glass. C. A. S.

Compounds of hexamethylenetetramine. L. DEBUCQUET and L. VELLUZ.—See this vol., 813.

Action of sulphurous acid on arsenic and antimonic acids. A. KURTENACKER and E. FURSTENAU (Z. anorg. Chem., 1933, **212**, 289—304).—The rate of reduction of H_3AsO_4 by aq. SO_2 at room temp. is a max. in presence of 0·13*N*-HCl or 0·2—0·26*N*-H_2SO_4. With Sb^V solutions the velocity is a min. in about 5*N*-HCl, and increases more rapidly with decreasing acidity. The best conditions for the quant. reduction of As^V and Sb^V by SO_2 are given. F. L. U.

Action of sulphuryl chloride on inorganic compounds. II. H. DANNEEL and F. SCHLOTTMANN (Z. anorg. Chem., 1933, **212**, 225—232).—As, Sb, and sulphides of Na, Cu, Zn, Cd, Hg, Pb, Mn, Fe, Co, and Ni are converted into chlorides by SO_2Cl_2 vapour diluted with CO_2 at room temp.—350°, SO_2 being liberated. With the metal sulphides S is also formed, and production of S_2Cl_2 is noticeable only above 420°. Se and Te give, first Se_2Cl_2 and $TeCl_2$, then $SeCl_4$ and $TeCl_4$. Metal selenides and tellurides behave like the sulphides, except that the Se and Te separate as chlorides. White P is attacked with difficulty, red P easily, giving PCl_3. F. L. U.

Preparation of bismuthyl iodide by direct combination of bismuth iodide and oxide. Dissociation by heat. F. FRANÇOIS and (MLLE.) L. DELWAULLE (Compt. rend., 1933, **196**, 1731—1733).—$BiI_3+Bi_2O_3 \rightleftharpoons 3BiOI$ is an equilibrium reaction, beginning at 100° when about 12 hr. are required to attain equilibrium with formation of about 97% of BiOI. When heated at 620° BiOI loses all the I as sublimed BiI_3. BiOI is also formed by agitating Bi_2O_3 and BiI_3 in H_2O for several days, probably according to $BiI_3+H_2O=BiOI+2HI$, and $Bi_2O_3+2HI=2BiOI+H_2O$ (the reaction is not quite complete), or by agitating Bi_2O_3 in a solution of BiI_3 in aq. KI, pure BiOI being obtained if BiI_3 is in excess, although excess of Bi_2O_3 is required to remove all the BiI_3 from the solution. C. A. S.

Action of hydrogen sulphide on sulphides and polythionates. C. J. HANSEN (Ber., 1933, **66**, [*B*], 817—825).—Study of the interaction of trithionate (I) and H_2S in presence of NaOAc shows that the primary change is not $S_3O_6''+H_2S=2S_2O_3''+2H^{\cdot}$ but, probably, $S_3O_6''+H_2S=S_2O_3''+SO_3''+S+2H$, secondary actions involving the change $SO_3''\longrightarrow S_2O_3''+S_3O_6''$. Tetra- (II) and penta-thionate (III) react much more rapidly, yielding quantitatively $2S_2O_3''$ per mol. of H_2S when $<$ 1 mol. of the latter per mol. of polythionate is employed. The presence of AcOH and, particularly, of mineral acid retards the change. (II) and (III) react so readily with alkali sulphide that they can be titrated therewith, using Pb paper as external indicator: $S_4O_6''+S''=2S_2O_3''+S$ and $S_5O_6''+S''=2S_2O_3''+2S$. (I) and alkali sulphide liberate S, which is pptd. or forms polysulphide: the reaction is, probably, $S_3O_6''+S''=S_2O_3''+SO_3''+S$. H. W.

Sulphur monoxide. E. GRUNER (Z. anorg. Chem., 1933, **212**, 393—398; cf. A., 1932, 345).—Reduction of $SOCl_2$ by Ag, Mg, Na, or $SnCl_2$ gives rise to SO_2 and S, and SO can be detected in the condensed reaction gases, but the method is unsuitable for its prep. SO cannot be prepared from $Na_2S_2O_4$. F. L. U.

Polythionates. II. Formation of polythionates from thiosulphates and acids in presence and absence of compounds of arsenic. III. Behaviour of polythionates in alkaline and acid solution. C. J. HANSEN (Ber., 1933, **66**, [*B*], 1000—1008, 1009—1011).—II. The course of the reaction between $Na_2S_2O_3$ and H_2SO_3 in presence of $As^{\cdot\cdot\cdot}$ is shown by the equations: $As^{\cdot\cdot\cdot}+3S_2O_3''=As(S_2O_3)_3'''$; $As(S_2O_3)_3'''=AsS^{\cdot}+S_4O_6''+SO_3''$; $SO_3''+SO_2+H_2O=2HSO_3'$; $2SO+2H_2O-2H^{\cdot}=2HSO_3'$; $AsS^{\cdot}+2H^{\cdot}=As^{\cdot\cdot\cdot}+H_2S$; $4HSO_3'+H_2S=S_3O_6''+S_2O_3''+3H_2O$ (I) or, as sum, $2S_2O_3''+3SO_2=S_3O_6''+S_4O_6''$. In the presence of mineral acid, reaction follows a somewhat different course, since in consequence of the greater acidity HSO_3' is incapable of existence and the H_2S cannot therefore be consumed in the rapid reaction (I). It is therefore partly converted into S ($2H_2S+SO_2=3S+2H_2O$) and partly into polythionate by known processes. With increase in the ratio acid : $Na_2S_2O_3$, the pro-

duction of polythionates with increasing S content is favoured. It is assumed that a part of the S_2O_3'' is decomposed according to the equation $S_2O_3''+2H^{\cdot}=SO_2+S+H_2O$ and the rest forms polythionate, as described above. The total reaction is expressed: $5S_2O_3''+6H^{\cdot}=S_3O_6''+S_4O''+3S+3H_2O$. With a smaller proportion of acid ($H : S_2O_3''=1{\cdot}2$ to $0{\cdot}3$), the amounts of S_3O_6'' and S_4O_6'' increase with decreasing ratio and the production of polythionate (regardless of S content) is quant. It is considered that primarily formed $S{\cdot}SO_2O'$ ... (II) previous to dimerisation can add S to give $S_2{\cdot}SO_2O'$ ... (III). Union of (II) and (III) yields S_5O_6'', whereas dimerisation of (III) affords S_6O_6''. The action of other catalysts (Sb, Sn, Mo) is similarly explained; all form sulphides with several S atoms, and their formation therefore proceeds in stages. The yellow colour formed during the interaction of SO_2 and H_2S is attributed to the production of an additive compound of the substances. The assumption of the formation of sulphoxylic acid or a similar compound is unjustified.

III. The following explanations of the decomp. of polythionates in acid and alkaline medium are advanced. Dithionate is decomposed, $S_2O_6''+H_2O=SO_3''+SO_4''+2H^{\cdot}$. S_3O_6'' in acid or slightly alkaline solution behaves according to the scheme: $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$ (unsymmetrical or sulphate fission), and in more strongly alkaline solution, $2S_3O_6''+6OH'=S_2O_3''+4SO_3''+3H_2O$ (symmetrical or sulphite fission); the primary change is $S_3O_6''+2OH'=2SO_3''+S(OH)_2$ (not identical with sulphoxylic acid). In the cases of S_4O_6'' and S_5O_6'' the formation of S_3O_6'' and S_4O_6'', respectively, is regarded as evidence of primary sulphite fission. A similar decomp. is postulated for the yet readier separation of S from S_6O_6''. With S_5O_6'' and low concn. of alkali the final products are S_2O_3'' and SO_4''; with higher concn., S_2O_3'' and SO_3''. When such solutions are preserved, the separated S passes into solution owing to union with SO_3'' to S_2O_3''. The explanation of the decomp. of polythionates in acid or neutral solution is complicated by the immediate further change of the S_2O_3'' produced, but a simple conception is obtained by the assumption of sulphite fission. Polythionates may be classified as follows: $H_2S_2O_6$= disulpho-acid; $H_2S_3O_6$=thiodisulpho-acid; $H_2S_4O_6$ and onwards=true polythionic acids. H. W.

Chromium tanning. XVI. Action of acids on different chromium hydroxides. E. Stiasny and F. Tacheci (Collegium, 1933, 265—282).—Titration curves indicate that strongly "olated" $Cr(OH)_3$ is almost completely unaffected by acids. When feebly "olated" $Cr(OH)_3$ was treated with acids, it was dissolved by reaction of the non-olated (OH) groups and by the de-olation of those groups which are readily de-olated. Dissolved basic Cr salts were "olated" by ageing or heating, and acido-Cr-acids (I) were formed especially with $H_2C_2O_4$ and citric acid (II). The acid dissolving effect was accompanied by an increase in p_H, and the olation and formation of (I) were accompanied by a decrease in p_H. The citrato-Cr-acids formed by the action of (II) on feebly olated $Cr(OH)_3$ were stronger acids than (II) and the acidity was increased by adding $Cr(OH)_3$ to (II). The different degrees of olation obtained by different acids on $Cr(OH)_3$ offers an explanation of the detannisation of Cr leather by certain acids. D. W.

Triaquotrichlorochromium and tetra-aquohexachlorodichromium. A. Recoura (Compt. rend., 1933, **196**, 1853—1855; cf. A., 1932, 239).—The Et_2O solution of brown triaquotrichlorochromium $[Cr(H_2O)_3Cl_3]$ (I) is stable if perfectly dry, but a trace of H_2O causes pptn. of green tetra-aquodichlorochromic chloride, $[Cr(H_2O)_4Cl_2]Cl,2H_2O$ (II). On evaporation of the dry solution (I) is obtained as a brown amorphous solid rapidly transformed as above by H_2O, but first giving a yellowish-green solution therein. Its non-electrolytic character is shown by the facts that Et_2O solutions of (I) and $PbEt_4$ do not interact, and that an EtOH–H_2O solution at −15° is sufficiently stable to show no reaction with $AgNO_3$ for 15 min. *Violet tetra-aquohexachlorodichromium*, $[Cr(H_2O)_2Cl_3]_2$, sol. in Et_2O, is obtained when (I), or even (II), is kept in vac. for several years. When dissolved in H_2O it behaves as (I). By repeated evaporation of the Et_2O solution of (I), Cl, up to finally 1Cl per mol., is lost. C. A. S.

Supposed "selenium dioxide-oxalic acid." H. Stamm and M. Richter (Ber., 1933, **66**, [*B*], 941—942).—The substance obtained by dissolution of SeO_2 in conc. HCl, concn. of the solution, and addition of $K_2C_2O_4$, is KHC_2O_4. The solubility of $H_2C_2O_4$ in H_2O at 17° is little affected by addition of SeO_2. Solutions of SeO_2 and $H_2C_2O_4$ are stable in the dark, but slowly give red Se and CO_2 when irradiated; reaction is accelerated by $Fe^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$. H. W.

Heteropoly-compounds. IV. Boro- and meta-tungstates. M. A. Rakovski and A. V. Babaeva (J. Gen. Chem. Russ., 1933, **3**, 59—66).—Tensimetric determinations indicate that $5BaO,B_2O_3,24WO_3$ has two hydrates, one with 52·32—54·77H_2O, and the other with 20·66—22·89H_2O; the corresponding K salt forms only one well-defined hydrate, with 33·9—35·9H_2O. The hydrates of $BaO,4WO_3$ have 9·28—9·59 and 6·63—7·18H_2O. K, Na, and Ba boro- and meta-tungstates are not isomorphous. The limiting concns. of nicotine giving turbidity with various tungstates are: para- 1/14,200, meta- 1/42,800, phospho- 1/135,000, boro- 1/142,800, and silico-tungstate 1/285,700. R. T.

Action of alkaline potassium ferricyanide solutions on tungsten. J. A. M. van Liempt (Rec. trav. chim., 1933, **52**, 425—427).—The action of solutions containing NaOH and $K_3Fe(CN)_6$ on W, as measured by the loss of wt. of the W after immersion in the solution for 10 hr. at 20°, has been studied, the results being given in the form of a ternary diagram. The most active solution, suitable, *e.g.*, for the etching of W specimens, contains 305 g. of $K_3Fe(CN)_6$ and 44·5 g. of NaOH per litre of H_2O. The solution is suitable also for the etching of Mo. H. F. G.

Dissolution of tungsten by ammoniacal solutions of cupric hydroxide. T. Millner (Z. anorg. Chem., 1933, **212**, 284—288).—Powdered W reduces a solution of $Cu(OH)_2$ in aq. NH_3, first to the Cu^{I} stage, then to Cu, itself dissolving as $(NH_4)_2WO_4$.

If air is passed through the liquid, dissolution takes place as before, but at the expense of atm. O_2, the action of the solution being then purely catalytic. F. L. U.

Oxyacids of fluorine. II. L. M. DENNIS and E. G. ROCHOW (J. Amer. Chem. Soc., 1933, **55**, 2431—2434; cf. A., 1932, 485).—The high oxidising power of the product of interaction of F and cold conc. KOH is not due to K ozonate, O_3, H_2O_2, or F_2O. Electrolysis of a molten mixture of alkali hydroxides and fluorides affords MFO_3. $AgFO_3$ has been examined. J. G. A. G.

Simple preparation of pure dry hydrogen bromide. G. JUNG and W. ZIEGLER (Angew. Chem., 1933, **46**, 279).—H_2 is bubbled through Br at 20—25° and the mixed gases are passed over activated C at 80—150°. A. R. P.

Rhenium oxytetrachloride. A. BRUKL and E. PLETTINGER (Ber., 1933, **66**, [*B*], 971—973).—Cautious addition of H_2O to $ReOCl_3$ in CCl_4, $CHCl_3$, $COMe_2$, Et_2O, or C_6H_6 causes production of a blue non-homogeneous ppt. (Re : Cl approx. 1 : 2). Cautious treatment of $ReOCl_4$ with NH_3 affords the *compound* $ReO(NH_2)_2Cl$, which, with H_2O at 0°, yields *ReO(OH)*$_2$*(NH*$_2$*)*$_2$, passing at 100°/vac. into the *substance*, $ReO_2(NH_2)_2$. H. W.

Strongly magnetic ferric hydroxide. A. QUARTAROLI (Gazzetta, 1933, **63**, 279—280).—The green ppt. obtained by adding 1 c.c. of a 20% solution of NaOH to 20 c.c. of a solution of Mohr's salt (8 : 1000) is kept for 2 hr. and then 2 c.c. of 3% H_2O_2 are added. The resulting red ppt. of $Fe(OH)_3$ has $\chi \times 10^6 >$ 10,000. O. J. W.

Mechanism of formation of α-FeO·OH, and the influence of [H$^\cdot$] on the ageing of ferric hydroxide orthohydrate at higher temperatures. A. KRAUSE, H. ŁAKOSCIUKÓWNA, and J. CICHOWSKI (Rocz. Chem., 1933, **13**, 264—275).—Alkaline aq. ferric hydroxide orthohydrate (I) undergoes polymerisation when kept, the successive products being polyferric hydroxide orthohydrate (II), amorphous and cryst. polyferric acid (III), and goethite (α-FeO·OH) (IV). The mols. of (I) and (II) consist of chains of 4 and 40—50 atoms of Fe, respectively, those of (III) possess a cyclic structure, whilst those of (IV) consist of a network of rings. The above process is accelerated by heat and by OH′. The no. of mols. of constitutional H_2O per atom of Fe falls from 3 to 1 as aggregation increases from (I) to (IV). R. T.

Complex fluoro-salts of tervalent iron. H. REMY and H. BUSCH (Ber., 1933, **66**, [*B*], 961—969).—The following *salts* are obtained by addition of the substituted ammonium fluoride to a solution of FeF_3 in excess of HF, concn. of the solution until a skin forms, and crystallisation. The ratio of the components in the sequence FeF_3, NH_4F, HF is placed in parentheses: $[NH_3Me][FeF_4]$ (1 : 1 : 6, 1 : 1 : 15); $[NH_3Me]_2[FeF_5]$ (1 : 2 : 6, 1 : 3 : 6); $[NH_3Me]_3[FeF_6]$ (1 : 6 : 6, 1 : 6 : 15); $[NH_2Me_2][FeF_4],H_2O$ (1 : 1); $[NH_2Me_2][FeF_5],2H_2O$ (also H_2O) and $[NH_2Me_2][FeF_5],HF_2$ (1 : 2); $[NH_2Me_2]_3[FeF_6],2HF$ (1 : 3 : 6, 1 : 6 : 15); $[NHMe_3]_2[FeF_5],2HF$ (1 : 2, 1 : 3, 1 : 6); $[NMe_4][FeF_4],H_2O$ (1 : 1, 1 : 2, 1 : 3, 1 : 6); $[NH_3Et]_2[FeF_5],HF$ (1 : 2, 1 : 3); $[NH_3Et]_3[FeF_6],2HF$ (1 : 6); $[NH_3Pr^a]_2[FeF_5],HF$ (1 : 2, 1 : 3); $[NH_3Pr]_3[FeF_6],2HF$ (1 : 6); $[NH_3Bu][FeF_4],2H_2O$ (1 : 1); $[NH_3Bu]_2[FeF_5],HF$ (1 : 2, 1 : 3); $[NH_3Bu]_3[FeF_6],2HF$ (1 : 6). H. W.

Determination of very small amounts of material. F. EMICH (J. Indian Chem. Soc., 1933, Ray No., 189—192).—A review of experimental methods. H. J. E.

Colloid science and the mass-analytical problem. D. BALAREV (Kolloid-Z., 1933, **64**, 91—95).—A review of the bearing of the theory of inner adsorption (cf. A., 1932, 332) on analytical practice. E. S. H.

Drawing off and determination of very small quantities of gas. R. A. KOLLIKER (Chem. Fabr., 1933, **6**, 299—302).—A review.

Systematic analysis of inorganic anions. A. SCONZO (Annali Chim. Appl., 1933, **23**, 215—226).—A scheme for the qual. analysis of inorg. anions is based on their separation into the following groups: (1) Cd salts insol. in AcOH+NaOAc, (2) Ba salts insol. in AcOH+NaOAc, (3) Ag salts insol. in HNO_3, (4) Ca salts insol. in AcOH, (5) Ca salts sol. in AcOH but insol. in aq. NH_3, (6) anions not included in preceding groups. O. J. W.

Determination of the hydrogen-ion concentration of hypochlorite solutions with the glass electrode. G. F. DAVIDSON.—See B., 1933, 587.

Determination and detection of the halogens. A. J. MEE (Chem. and Ind., 1933, 520—523).—A review.

Aqueous ammonia as a reagent for chlorine and bromine in the presence of iodine. M. P. BABKIN (J. Gen. Chem. Russ., 1933, **3**, 134—136).—AgCl is sol. in *N*/250-, AgBr in *N*/32-, and AgI in *N*/2-aq. NH_3; the ppt. of Ag halides is shaken with *N*/64-aq. NH_3, and the filtrate is made acid with HNO_3, when a ppt. indicates AgCl, whilst AgBr in presence of AgI is detected similarly using *N*/16-aq. NH_3. R. T.

Volumetric determination of iodine in presence of alkali hydrogen carbonates, borates, and acetates. D. RAQUET and P. PINTE (J. Pharm. Chim., 1933, [viii], **17**, 508—514).—Titration of I by 0·1*N*-$Na_2S_2O_3$ in presence of $KHCO_3$ or Na borate leads to errors depending on the concn. of salt and the time of contact. Correct results are obtained after acidification, or, in presence of $KHCO_3$, by titration with 0·1*N*-As_2O_3, NaOAc is without effect. J. S. A.

Determination of small quantities of iodine. G. CSEGEZY (Magyar gogspz. Tars. Ert., 1932, **8**, 457—464; Chem. Zentr., 1933, i, 1171).—The I is liberated with dil. HNO_2, extracted with CCl_4, and oxidised to HIO_3 by Cl_2-H_2O in presence of HCl. H_2O is added, and the excess of Cl_2 and CCl_4 removed by boiling. The cold solution is acidified with H_3PO_4, and then treated with $KHCO_3$ and a little KI; after a short time it is titrated with 0·005*N*-$Na_2S_2O_3$.

0·05 mg. I in 100 g. of solution can be accurately determined. A. A. E.

Determination of iodine by the Carius method. A. GUERBET (J. Pharm. Chim., 1933, [viii], **17**, 556—559).—In the determination of I by the Carius method insufficient (< 50 times) dilution of the reaction mixture before boiling and filtering the AgI may lead to errors of 3%. S. C.

Determination of small quantities of iodides in the presence of large quantities of chlorides and bromides. V. A. SKOPINTZEV (J. Appl. Chem. Russ., 1933, **6**, 367—374).—To 5 c.c. of solution, containing $\lesssim$ 0·002 mg. of I, and $\gtrsim$1 g. of Cl and 0·05 g. of Br, 0·05 c.c. of 10*N*-KOH is added, and 0·1 c.c. of 0·1*N*-$KMnO_4$ is added to the boiling solution, which is then brought to p_H 2·5—3·0 by H_2SO_4, excess of $KMnO_4$ is removed by adding 0·1 c.c. of 0·1*N*-$H_2C_2O_4$, and the p_H is brought to 4·5 by adding 0·1 c.c. of 0·1*N*-NaOAc. IO_3' is then determined by adding KI and titrating liberated I with 0·01*N*-$Na_2S_2O_3$. R. T.

Analysis of alkali hydrogen sulphites. F. BALDRACCO.—See B., 1933, 587.

Determination of nitrate nitrogen. P. GRIGORIEV and E. NASTASKINA (Z. anal. Chem., 1933, **93**, 105—109).—NO_3' can be determined satisfactorily by boiling with an excess of $FeSO_4$ in dil. H_2SO_4 in an atm. of CO_2 and, after cooling, titrating the excess of $FeSO_4$ with $KMnO_4$; $MnSO_4$ must be added if Cl′ is present. A. R. P.

Determination of boron in silicate rocks and minerals. I. P. ALIMARIN and I. I. ROMM (Trans. Inst. Econ. Min., Russia, 1932, No. 53, 5—44).—Distillation as Me_3BO_3 into aq. NaOH and titration of the excess of NaOH with HCl is preferred. A few drops of HCl are preferably added to the Me_3BO_3 before distillation to neutralise (indicator) the CaO resulting from addition of $CaCl_2$. Alternatively, the NaOH fusion is extracted with hot H_2O and cations other than B are removed with $(NH_4)_2CO_3$. Fusion and extraction are repeated. Titration is completed as above. CH. ABS.

"Degea" carbon monoxide indicator. K. W. HETZEL (Gasmaske, 1933, 5, 39—44).—I_2O_5 is suspended in fuming H_2SO_4, which is impregnated in white pumice, which becomes coloured greenish to brownish or brownish-black ($I_2O_5+5CO=2I+5CO_2$). < 0·03 vol.-% CO gives no colour; > 0·06 vol.-% gives easily recognisable colours. CH. ABS.

Use of adsorption indicators in volumetric analysis. A. W. WELLINGS (Analyst, 1933, **58**, 331—333).—Diphenylcarbazide is used as an adsorption indicator in the determination of alkali cyanides by titration with $AgNO_3$. Fluorescein, dichloro- (I) and dibromo-fluorescein are used in the determination of $Pb(NO_3)_2$ and $Pb(OAc)_2$ by titration of NaOH with the Pb salt. (I) is used in the determination of borates by titration with $Pb(OAc)_2$. E. C. S.

Determination of potassium by the cobaltinitrite method. O. M. KOSMAN (J. Appl. Chem. Russ., 1933, **6**, 362—366).—K is quantitatively pptd. by Na cobaltinitrite as $K_2NaCo(NO_2)_6,H_2O$; other ions do not interfere. R. T.

Iodometric determination of sodium as sodium zinc uranyl acetate. R. LANG and G. MUCK (Z. anal. Chem., 1933, **93**, 100—102).—The ppt. of $NaZn(UO_2)_3(OAc)_9$ is dissolved in a few drops of H_2SO_4, 5 g. of $(NH_4)_2SO_4$, 2 g. of KI, and a little starch are added, and the Zn is titrated with $K_3Fe(CN)_6$ and $Na_2S_2O_3$ (cf. this vol., 799). A. R. P.

Potentiometric titration of sodium and calcium cyanamides. H. SINOZAKI (J. Soc. Chem. Ind. Japan, 1933, **36**, 145—146B).—Na_2CN_2 and $CaCN_2$ may be determined by potentiometric titration with $AgNO_3$ in alkaline solution. The method permits simultaneous determination of CN′ and CN_2''. J. S. A.

Detection of ammonium salts by drop reactions. F. FEIGL (Mikrochem., 1933, **13**, 129—135).—Using the procedure described, limiting concns. for the detection of NH_3 are by means of litmus, 2×10^{-7}; by the blackening of Hg_2Cl_2, 5×10^{-5}; by Nessler's solution, 2×10^{-6}; by reduction of Ag from $AgNO_3+CH_2O$, 10^{-6}; by pptn. of Ag+MnO_2 from $MnSO_4$ and $AgNO_3$ solution, 10^{-7}. J. S. A.

Potentiometric determination of small quantities of silver. R. SPYCHALSKI (Rocz. Chem., 1933, **13**, 236—244).—Dil. (0·001*N*) solutions of Ag can be titrated potentiometrically with 0·001*N*-KBr or -KI, in the presence of K_2SO_4 (mean error, 0·5—1%). The quantity of Ag rises in Ag hydrosols with dilution and with ageing. R. T.

Dithizone (diphenylthiocarbazone) reactions. H. WOLBLING and B. STEIGER (Angew. Chem., 1933, **46**, 279—281).—Dithizone in CCl_4 yields characteristic colour reactions with (*a*) Ag, Zn, Cd, Sn^{IV}, Pb, Mn, (*b*) Sn^{II}, Fe^{II}, (*c*) Sb, Bi, (*d*) Cu, (*e*) Au and the Pt metals, and (*f*) Hg. In acid solutions group (*a*) gives no reaction, oxidation in acid solution eliminates the effect of group (*b*), addition of tartaric acid that of group (*c*), and addition of HCO_2H that of Cu, whilst group (*e*) can be removed by reduction to metals, *e.g.*, by shaking with activated C. Hence the reaction can be made sp. for Hg; sensitivity 0·01 mg. In a mixed solution the Hg and precious metals can be pptd. with Cu and the Hg extracted from the ppt. with HNO_3 before making the test. A. R. P.

Drop test to distinguish calcite and aragonite. F. FEIGL and H. LEITMEIER (Mikrochem., 1933, **13**, 136—138).—The OH′ resulting from hydrolysis of dissolved $CaCO_3$ is sufficient to cause pptn. of Ag+MnO_2 from $AgNO_3+MnSO_4$ solution. Aragonite produces a grey coloration within 1 min. in the cold, the less sol. calcite only after 6—10 min. J. S. A.

Spectrographic detection and determination of beryllium in minerals. W. KEMULA and J. RYGIELSKI (Przemysł Chem., 1933, **17**, 89—97).—The mineral is dissolved in aq. HF, the solutes are converted into chlorides, and the emission spectrum of the solution is excited by a high-frequency alternating arc discharge of high potential. In the absence of other elements, or in the presence of Na, K, Li, Cs, B, Ca, Ba, Mg, and Al, the line at 3131 Å. undergoes extinction when Be < 0·0001%. In the presence of

Fe, Ni, Co, Cr, Mn, Ti, Zr, W, V, and Mo the line at 2348·6 Å. has to be used, when extinction occurs at 0·001% Be, and, for the 2494 Å. line, at 0·01% Be. Alternatively, d.c. may be used for exciting the emission spectrum, and successive spectrographs are compared, when the intensity of various lines varies characteristically with time for given elements, owing to their different volatility; thus, alkali metals give diminishing, alkaline-earth metals increasing, and other elements const. intensity. Using this method, 0·01% Be may be detected in admixture with Na, K, Ba, Mg, Al, and Si, by observing the 3131 and 2348·6 Å. lines. The damping affect of a no. of elements on the emission of the Be lines at 3131 and 2348·6 Å. increases in the order: K<Na<Ba<Ca<Mg<Al<Si; this series is identical with that of the ionisation potentials of the same elements. R. T.

Iodometric determination of zinc by the ferricyanide method. R. Lang (Z. anal. Chem., 1933, **93**, 21—31).—The method previously described (A., 1930, 182) can be used satisfactorily in the presence of H_2SO_4 provided that 10 g. of $(NH_4)_2SO_4$ or K_2SO_4 are present and the H_2SO_4 is < the equiv. of 10 c.c. of 5*N*-acid. Under these conditions tartaric acid, AcOH, and H_3PO_4 do not interfere if the $K_3Fe(CN)_6$ and $Na_2S_2O_3$ are added alternately in small quantities to the $ZnSO_4$ containing 2 g. of KI and starch. Small quantities of Mn (< 0·02 g.) can be determined in the same solution by oxidation to $KMnO_4$ and iodometric titration of the latter; subsequent determination of the Zn leads to results which are only 0·2—0·3% too high. Interference of Mo in the Zn titration is prevented by addition of H_3PO_4. A. R. P.

Separation of lead from zinc and their subsequent determination. K. M. Sil (J. Indian Chem. Soc., 1933, **10**, 137—141).—The presence of Zn does not interfere with the determination of Pb by the method previously described (A., 1929, 286), and the former may be afterwards pptd. as $ZnNH_4PO_4$. F. L. U.

Diphenylthiocarbazide as reagent for detection of traces of heavy metals. H. Fischer (Angew. Chem., 1933, **46**, 442—446; cf. A., 1931, 328).—Tables show the min. quantities of Pb, Ag, Cd, and Cu necessary (10^{-7} to 10^{-8} g.) and the sensitivities of the test for these metals ($1:5\times10^5$ to $1:6\times10^6$) when applied in the presence of large excesses of other metals. Cu is particularly sensitive; $0{\cdot}015\times10^{-6}$ g. can be detected in the presence of 373,000-fold excess of Zn and the reaction can be applied colorimetrically for the determination of Cu in other metals in concns. < 10^{-3}%. The masking of other metals so as to render the reaction sp. is effected by addition of KI, KCN, KCNS, acid, or alkali. Oxidising agents must be removed. The test is best carried out by shaking vigorously one or several drops of the metal solution with a few drops of the reagent solution (2—4 mg. in 100 c.c. of CCl_4 or CS_2). The sensitivity is further increased by using smaller vols. of reagent and larger vols. of the test solution. S. M.

Separation and determination of copper and nickel. F. L. Vodret and M. Gallo (L'Ind. Chimica, 1933, **8**, 695—697).—Cu_2S is pptd. from acid solutions by means of $Na_2S_2O_3$, the Ni in the filtrate being determined as the dimethylglyoxime compound. T. H. P.

2 : 3-Diaminophenazine as a sensitive analytical reagent. T. Pavolini (L'Ind. Chimica, 1933, **8**, 692—694).—EtOH solutions of 2 : 3-diaminophenazine hydrochloride (I) (0·5%) give coloured ppts. with neutral solutions containing group II cations. With Cu ($1:6\times10^6$) or Hg ($1:10^5$) a red froth is formed. Fe and NH_4 salts disturb the reaction. The Cu complex formed is $C_{12}H_8N_4Cu$ and probably contains the grouping ·NH·Cu·N· in place of the two NH_2 groups of the phenazine. Satisfactory quant. results are obtainable with Cu if NaCl is added to prevent colloidal dispersion of the complex; the unwashed ppt. is dried at 100°, the filter-paper is burnt, and the residue treated with H_2O and passed through a tared filter. The weight of the dried ppt. is diminished by that of the ash left on incineration to obtain the Cu. The fact that, in EtOH, (I) has an orange-red, and the free base a yellowish-green, fluorescence, may be used to detect basic compounds. The change from red to green is observed with EtOH containing 0·1% of C_5H_5N. T. H. P.

Iodometric determination of copper, iron, zinc, and aluminium in presence of each other. R. Lang and J. Reifer (Z. anal. Chem., 1933, **93**, 161—172).—The mixed sulphates or nitrates (free from Cl′) are treated with conc. H_2SO_4, neutralised with aq. NH_3, KHF_2 and then KI are added, and Cu is determined by titration with 0·1*N*-$Na_2S_2O_3$. After adding dil. H_2SO_4, H_3BO_3, and KCNS, Fe is determined iodometrically. Similarly, Zn is determined after adding $K_3Fe(CN)_6$. Al is determined in an aliquot part by the hydroxyquinoline method. The procedure may be used for the rapid analysis of brass and bronze. E. S. H.

Potentiometric determination of small amounts of mercury. K. Schwarz and T. Kantor (Mikrochem., 1933, **13**, 225—234).—$Hg^{..}$ is reduced to $Hg^{.}$ by shaking with Hg. The solution is titrated potentiometrically with KI, best in presence of a few drops of 20% $HClO_4$ (*i.e.*, p_H approx. 1·5), using amalgamated Pt electrodes. Titration may be carried out down to Hg=$10^{-6}N$. J. S. A.

Colorimetric determination of aluminium with aurintricarboxylic acid. P. S. Roller (J. Amer. Chem. Soc., 1933, **55**, 2437—2438; cf. A., 1929, 1413).—A modified method whereby 0·0001 mg. of Al can be determined is described. *x* c.c. of Al solution at p_H 6·3 are diluted with (12—*x*) c.c. of H_2O and 5 c.c. of buffer (4*M*-NH_4OAc+HCl, p_H 6·3). 1 c.c. (per 0·01 mg. of Al) of 0·1% NH_4 salt of the dye is added and the colour compared after 15 min. with simultaneously prepared standards. $Fe^{...}$ must be eliminated. Interference by traces of $Cr^{...}$ is not serious. J. G. A. G.

Precipitation of rhenium sulphide from ammoniacal solution. Separation of rhenium and molybdenum. J. H. Muller and W. A. La Lande, jun. (J. Amer. Chem. Soc., 1933, **55**, 2376—2378).—The pptn. of Re as sulphide from 10% aq. NH_3 saturated with H_2S is slow but almost quant. In the

presence of a large proportion of Mo, complete separation is effected by re-pptn. J. G. A. G.

Brucine as internal indicator in dichromate titrations. S. MIYAGI (J. Soc. Chem. Ind. Japan, 1933, **36**, 146—147B).—A 1% solution of brucine in H_2SO_4 may be used as internal indicator provided the acidity is $> 3N$. The red colour developed is clearly visible in presence of $Cr^{\cdots}$. J. S. A.

Potentiometric determinations in alkaline solution. Determination of chromate and simultaneous determination of chromate and ferricyanide. C. DEL FRESNO and E. MAIRLOT (Z. anorg. Chem., 1933, **212**, 331—336).—CrO_4'' can be determined by potentiometric titration with $VOSO_4$ in 16% NaOH at 70°, and in an atm. of N_2. Since the end-point potentials in the reduction of CrO_4'' and of $Fe(CN)_6'''$ differ by 0·4 volt, these can be determined simultaneously under similar conditions. F. L. U.

Determination of chromium and vanadium in alloy steels. H. H. WILLARD and P. YOUNG.—See B., 1933, 550.

Indicators for determining chromium and vanadium in alloy steels. Oxidised diphenylaminesulphonic acid and oxidised diphenylamine. H. H. WILLARD and P. YOUNG.—See B., 1933, 550.

Determination of zirconium in steels. Selenious acid–phosphate method. S. G. SIMPSON [with W. C. SCHUMB].—See B., 1933, 550.

Determination of small amounts of bismuth in presence of large amounts of copper and chloride. N. KAMEYAMA and S. MAKISHIMA (J. Soc. Chem. Ind. Japan, 1933, **36**, 364—365B).—Bi is separated by adsorption on MnO_2 pptd. in the solution and is then redissolved and determined by the usual methods. A. G.

Spectro-analytical and electrical investigation of purest platinum. W. GERLACH and E. RIEDL (Physikal. Z., 1933, **34**, 516—522).—The application of emission spectrum analysis to the detection of impurities in metals is described. By its aid the smallest trace of impurity can be detected. Ordinary so-called physically pure Pt contains Ca, Sr, Cu, Ag, Pd, and Pb. The resistance of specimens of Pt was determined, at various temp. The purest Pt, tested in the above way, had a small residual resistance at 4—1·35° abs., independent of temp. A. J. M.

Constant-temperature apparatus. VI, VII. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1933, **36**, 134—137B).—VI. A low-temp. thermostat electrically controlled for the range 0° to −60° is described.

VII. An air-bulb thermoregulator and a thermocouple control system for an electric furnace are described. J. S. A.

System of temperature control. H. H. DARBY and C. B. BRIDGES (J. Franklin Inst., 1933, **215**, 723—729).—A thermostat const. to 0·05°, embodying an automatic control of the electrical heating unit by means of a telegraphic sounder and mercoid vac. tube, is described. N. M. B.

Portable cooling machine for laboratory use. L. RAMBERG (Svensk Kem. Tidskr., 1933, **45**, 113—116).—The machine is electrically driven and uses CCl_2F_2 as refrigerating liquid. It is automatically controlled to ±0·5° and the cooling effect is 200—300 kg.-cal. per hr. R. P. B.

New Rojahn–Heinrici colour and luminescence comparator. H. SCHNEIDER (Pharm. Zentr., 1933, **74**, 379—381).—An inexpensive apparatus for measuring colours on an arbitrary scale is described. D. R. D.

Measurement of fluorescence colours. E. GRUNSTEIDL (Mikrochem., 1933, **13**, 183—188).—The faint reddish-violet fluorescence frequently reported is probably due to reflected long-wave ultra-violet and deep red light, and is eliminated by observation through a KNO_2 filter, which is opaque to ultra-violet light. A KNO_2 filter should therefore be used during photometry of true fluorescence colours, to cut out surface reflexion. J. S. A.

Simple spectrograph and measurements of absorption bands in the infra-red part of the solar spectrum made in North Africa during 1926—1927. W. GORCZYNSKI (Bull. Acad. Polonaise, 1933, **A**, 40—52). A. B. D. C.

Quantitative spectrum analysis. I. Physical principles and methods. F. WAIBEL (Z. Metallk., 1933, **25**, 6—12).—A review of recent methods of spectrographic analysis and a discussion of the physical principles on which they are based. A. R. P.

Quantitative spectrographic analysis. O. FEUSSNER (Z. Metallk., 1933, **25**, 73—75).—A discussion of papers by Waibel (preceding abstract) and Findeisen with hints on the arrangement and manipulation of the electrical apparatus for obtaining sharp and reproducible spectra. A. R. P.

Artificial daylight illuminator. D. R. BARBER (Analyst, 1933, **58**, 337—338).—The lamp is used in titrating. E. C. S.

Colorimeter. R. LEGENDRE (Compt. rend., 1933, **196**, 1875—1877).—The essential feature consists of two parallelepipedal vessels containing the solution under examination alone and with addition of indicator, and of two pairs of wedge-shaped vessels, each pair arranged to point opposite ways. In the pair below the vessel containing solution only are indicator+acid and indicator+alkali, in the other pair H_2O. An arrangement enables the light through the solution with indicator to be placed in juxtaposition with that through various thicknesses of indicator+acid and +alkali, and so to be accurately matched. C. A. S.

Device for reducing grain effects in microphotometer records. F. K. RICHTMYER and F. R. HIRSH, jun. (Rev. Sci. Instr., 1933, [ii], 4, 353—354).—The method of photographically enlarging *X*-ray spectrograms while the image of the spectrogram is oscillated parallel to its spectral lines is extended to curved spectral lines by means of an integrating device. N. M. B.

Cooling of crystals for *X*-ray scattering measurements. P. S. WILLIAMS (Rev. Sci. Instr., 1933, [ii], **4**, 334—336).—An improved apparatus, used with liquid air, is described. N. M. B.

Spectrally pure light sources for photochemical and spectroscopic purposes. H. ALTERTHUM and M. REGER (Chem. Fabr., 1933, **6**, 283—285).—Spectrally pure light of 15 wave-lengths between 2537 and 6438 Å. may be obtained by the use of Cd, Zn, Na, Hg, and Tl lamps and suitable filters. A. G.

[Automatic] pressure regulator for gas-filled *X*-ray tubes. F. D. MILES (Trans. Faraday Soc., 1933, **29**, 788—789).—The variations in the primary current in the transformer are utilised to open and close the by-pass between the high and fore vac., instead of controlling the flow of gas through the main connexion between tube and pumps. D. R. D.

Null method of measuring electrical conductivity of the atmosphere. (MME.) O. THELLIER (Compt. rend., 1933, **196**, 1684—1686).—One electrode of an auxiliary condenser is connected with the inner electrode of a Gerdien aspirator; the potential of the other electrode of the auxiliary condenser is then raised so that the potential of the inner electrode of the aspirator is zero, and the amount by which it is raised is measured. C. A. S.

Electric heating units for microchemical work. E. W. BLANK (Mikrochem., 1933, **13**, 147—148). J. S. A.

Platinised glass electrode. H. MURAOKA and K. HIRUMA (J. Soc. Chem. Ind. Japan, 1933, **36**, 161B).—Platinised glass filter plates form suitable electrodes for electrodialysis experiments. J. S. A.

Easily constructed p_H-meter. H. H. EDWARDS (New Zealand J. Sci. Tech., 1933, **14**, 275—280).—A valve circuit, suitable for use in conjunction with H_2 or quinhydrone electrodes, is described. A. G. P.

Precision gas-holder for constant pressure. H. O. HOHL (Mikrochem., 1933, **13**, 189—200).—An all-glass gas-holder is described. J. S. A.

Glass wool cell for measuring aqueous vapour pressure. N. E. EDLEFSEN (Rev. Sci. Instr., 1933, [ii], **4**, 345—346).—A cell for the aq. v.p. of H_2O in granular media, the resistance depending on the amount of condensation on the fibres, is described. N. M. B.

Completely automatic distilling and concentrating apparatus especially for preparing distilled water. E. SPIEGELBERG (Chem. Fabr., 1933, **6**, 285—286).—The apparatus described distils about 1·5 litres per hr. from a glass flask fed automatically from a storage vessel, and so arranged that the burner is extinguished after any required vol. is distilled. A. G.

Wash-bottle for gases. A. M. BELOUSOV (J. Appl. Chem. Russ., 1933, **6**, 383).—A modification of the ordinary wash-bottle is described. R. T.

Pore viscosimeter and stalagmometer for measurement of molecule aggregation and degradation in solutions and simple liquids. H. WISLICENUS [with K. UEBEL] (Kolloid-Z., 1933, **64**, 96—99).—The apparatus described is particularly suitable for work with sugar solutions. E. S. H.

Viscosimeter. J. KADLEC.—See B., 1933, 527.

Porcelain stirrer. F. MAYER (Chem.-Ztg., 1933, **57**, 494).—In a robust two-arm type the joint between the stirrer and the revolving mechanism is protected by means of a cylindrical sleeve fixed to the former. J. G.

Micro-density determination of gases by direct weighing. E. W. BLANK (Mikrochem., 1933, **13**, 149—154).—Procedure using about 10 c.c. of gas is described. J. S. A.

Microbalance. J. DONAU (Mikrochem., 1933, **13**, 155—164; cf. A., 1931, 189).—An improved form of the balance is described. J. S. A.

Hot plate for drop reactions. E. FRANKEL (Mikrochem., 1933, **13**, 179—182). J. S. A.

Mass spectrograph giving parabolic lines of greater sharpness. H. LUKANOW and W. SCHÜTZE (Z. Physik, 1933, **82**, 610—619).—A modified Thomson mass spectrograph is described. A complex ion, probably a hydride, appeared with He, Ne, and A. A method for showing the H^2 isotope is indicated. A. B. D. C.

Improved crucible support. E. G. RADLEY (Analyst, 1933, **58**, 339). E. C. S.

New form of filter stick: its use in gravimetric analysis. E. J. KING (Analyst, 1933, **58**, 325—328). E. C. S.

Detection of small leaks in high-vacuum apparatus. F. R. TERROUX and W. H. WATSON (Canad. J. Res., 1933, **8**, 412—413).—A glass tube carrying an electrode is fitted over the seal to be tested, the joint being formed by means of a rubber washer and a layer of plasticene. The tube is evacuated and the pressure is estimated from the nature of the discharge obtained when the electrode is connected to an induction coil. If the rate of leakage in the main vac. system falls, the seal under test is faulty. A double seal, the outer evacuated, is suggested for use on systems in which very low pressure is to be maintained for a long period. H. F. G.

Capillary electrometer stand. A. M. BELOUSOV (J. Appl. Chem. Russ., 1933, **6**, 379).—A stand facilitating rapid change of the level of Hg in the capillary is described. R. T.

Instrument for facilitating measurement of the level of the meniscus of liquids. A. M. BELOUSOV (J. Appl. Chem. Russ., 1933, **7**, 380—382).—An instrument, consisting of a black and white screen, and a lens, adapted for reading the level of liquid in burettes, is described. R. T.

Combustion of substances containing chlorine in Berthelot's bomb. II. Determination of the correction for the nitric acid formed. L. SMITH (Svensk Kem. Tidskr., 1933, **45**, 110—113; cf. A., 1931, 1262).—In the method previously described, the HNO_3 in the bomb liquid can be determined colorimetrically with sufficient accuracy if pure O_2 is used. R. P. B.

Precise automatic apparatus for continuous determination of carbon dioxide in air. M. D. THOMAS.—See B., 1933, 574.

Two formulæ for replacing that of Fresnel in the calculations of crystallographic optics. G. CESARO (Bull. Acad. roy. Belg., 1933, [v], **18**, 753—758) Mathematical. C. W. G.

Date and place of Priestley's discovery of oxygen. I. R. M. CAVEN (Nature, 1933, **132**, 25). II. (SIR) P. J. HARTOG (*ibid.*, 25—26).—Historical. L. S. T.

Geochemistry.

Formaldehyde in terrestrial and solar atmospheres. N. R. DHAR and A. RAM (J. Indian Chem. Soc., 1933, **10**, 161—167).—A fuller account of work previously published (A., 1932, 792, 1106). F. L. U.

Variation in amounts of ammoniacal and nitric nitrogen in rain water of different countries and origin of nitric nitrogen in the atmosphere. N. R. DHAR and A. RAM (J. Indian Chem. Soc., 1933, **10**, 125—133).—NH_3 and HNO_3+HNO_2 have been determined in the rain H_2O collected during 2 months at Allahabad. A survey of analyses made in various places leads to the conclusion that both total N and the ratio nitric N/NH_3-N are greater in tropical than in temperate countries. The result is attributed to photo-oxidation of NH_3 and atm. N_2. F. L. U.

Mineral waters of Rogaska Slatina. II. Catalytic action. A. REZEK and T. PINTER (Bull. Soc. Chim. Yougoslav., 1933, **4**, 37—51).—The H_2O of various springs catalyses decomp. of H_2O_2, and gives the benzidine reaction; in certain cases these findings are attributed to $Fe^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$. R. T.

Chemical analysis and physico-chemical investigations of the thermal springs of Sardara. E. PUXEDDU, G. SANNA, and E. MOSS (Annali Chim. Appl., 1933, **23**, 193—214).—A detailed investigation of the hot mineral waters of Sardara (Cagliari) shows that they are the most conspicuous example of the radioactive alkaline H carbonate waters common in Sardinia; *d*, f.p., conductivity, and other data are given. O. J. W.

Boric acid in sea-water and its effect on the carbon dioxide equilibrium. K. BUCH (Finska Kem. Medd., 1933, **42**, 14—29).—A detailed account of work already noted (this vol., 691). Data are given showing the effect of H_3BO_3 on the CO_2 equilibrium of sea-H_2O. At p_H 8·0 the val. for total CO_2 differs by 2% from that given by the International Commission; at p_H 7·0—7·5 and 8·6—9·0 the vals. are the same. L. S. T.

Metalimnic oxygen minima. F. RUTTNER (Naturwiss., 1933, **21**, 401—404).—The factors controlling the amount of O_2 in the metalimnion are discussed. A. J. M.

Geometric method of rock analysis. (MLLE.) M. TURNAU (Bull. Acad. Polonaise, 1932 A, 396—411).—By measuring $\lessapprox$ 300 grains in a thin rock section the mineralogical composition can be determined with quant. accuracy. The application of the method to mineralogical problems is discussed. F. L. U.

Transition point of sea sand. K. BITŌ, M. KADONO, and M. MATSUI (J. Soc. Chem. Ind. Japan, 1933, **36**, 339—340B).—Sea sand changes from an α- to a β-form at 575°. A. G.

Alkaline massif of Haute-Ruvubu (Urundi). J. THOREAU (Bull. Acad. roy. Belg., 1933, [v], **18**, 877—883).—A petrographic description is given. C. W. G.

Origin of tektites. F. CHAPMAN (Nature, 1933, **131**, 876).—A criticism (cf. this vol., 252). L. S. T.

Origin of tektites. L. J. SPENCER (Nature, 1933, **131**, 876).—A reply to criticism (cf. preceding abstract). L. S. T.

Identity of mottramite and psittacinite with cupriferous descloizite. F. A. BANNISTER [with M. H. HEY] (Min. Mag., 1933, **23**, 376—386).—Chemical analyses and *X*-ray photographs prove the identity of mottramite (Roscoe, 1876), psittacinite, and cuprodescloizite, and that these are merely descloizites containing some Cu replacing Zn. For members of the group containing > 10% CuO the variety name mottramite is retained. The unit cell, *a* 6·05, *b* 9·39, *c* 7·56 Å., with space-group V_h^{16}, contains 4 mols. of Pb(Zn,Cu)(OH)(VO_4). Finely cryst. and powdery material may contain an excess of adsorbed H_2O. Details of the analysis of V minerals are given. H_2O was determined by the method of Dittler and Hueber (A., 1931, 325, 1023), and an improved form of wash-bottle is figured. L. J. S.

Dehydration of thomsonite. A. E. MOURANT (Min. Mag., 1933, **23**, 371—375).—Isobaric dehydration and rehydration curves of analysed thomsonite from Scotland are compared with those of Hey (A., 1932, 715). L. J. S.

Statistical characteristics of the chemism of trachytes. F. J. LEVINSON-LESSING (Bull. Acad. Sci. U.R.S.S., 1933, 101—109).—The compositions of rocks referred to by Washington ("Chemical Analyses of Igneous Rocks," U.S. Geol. Survey, 1917, No. 99) are treated statistically, the following "characteristic coeffs." being considered: (1) acidity coeff. α; (2) the RO coeff. in the magmatic formula; (3) the ratio R_2O : RO, and (4) the % of SiO_2. It is shown that, under the name trachyte, not only true trachytes, but also numerous acidotrachytes, are included. The characteristics of true trachytes are discussed. T. H. P.

Distinction between sedimentary and tectonic breccias. L. CAYEUX (Compt. rend., 1933, **196**, 1844—1847).—The cementing material in a sedi-

mentary breccia is usually of some foreign material, differing substantially from that of the breccia, whilst in a tectonic breccia it is always derived from the material of the breccia itself. Other methods, microscopic and petrographic, of distinguishing between the two varieties are enumerated. C. A. S.

Pedestal rocks of granite in the southern Piedmont. J. J. PETTY (J. Elisha Mitchell Sci. Soc., 1932, **48**, 119—122).—Chemical decomp. of the rocks is most rapid at the soil surface, where Na and K are diminished, probably owing to the action of humic acid. CH. ABS.

Synthesis of northupite, tychite, and new artificial minerals of the same group. T. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 35—39).—Details are given of the prep. of the *compound* $2MgCO_3,2Na_2CO_3,Na_2CrO_4$, northupite, tychite, and bromonorthupite (cf. A., 1932, 218). D. R. D.

Crystal structures of northupite, $2MgCO_3,2Na_2CO_3,2NaCl$, and tychite, $2MgCO_3,2Na_2CO_3,Na_2SO_4$. T. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 40—62).—Natural northupite is identical in crystal structure with the artificial material previously investigated (A., 1932, 12, 218). Measurements using a single crystal of tychite confirm the earlier data by the powder method. The structures are worked out in detail. D. R. D.

Vegetable origin of palæozoic calcium phosphates. L. CAYEUX (Compt. rend., 1933, **196**, 1564—1567).—From the amount (2—8%) of free C in palæozoic (but not in later) phosphate rocks it is concluded that the C and $Ca_3(PO_4)_2$ are derived from algæ, which are assumed to have been very numerous in palæozoic seas. R. S. C.

Change in the surface of chalk. B. BRAJNIKOV (Compt. rend., 1933, **196**, 1817—1819).—A discussion. C. A. S.

Soil profiles from Cyprus. I. Soils over limestone and serpentine. A. REIFENBERG and E. K. EWBANK (Empire J. Exp. Agric., 1933, **1**, 85—96).—Geological and analytical data are given and utilised in a discussion of the mechanism of formation of these soils. A. G. P.

Methods and scope of soil surveys in Western Canada. A. H. JOEL (Empire J. Exp. Agric., 1933, **1**, 33—42). A. G. P.

Microbiological study of podsol soil profiles. P. H. H. GRAY and N. B. MCMASTER (Canad. J. Res., 1933, **8**, 375—389).—The microbiological characteristics of the virgin upland podsol soil of Quebec are described. The three layers recognised are (*a*) the surface mulch of semi-decomposed org. matter (1—5 in.), (*b*) a second, leached, layer ($\frac{1}{2}$—3 in.), and (*c*) the underlying sandy loam. The biological activity of (*a*) is much > that of (*b*) or (*c*), the CO_2 evolution and nos. of bacteria and *Actinomyces* in (*b*) and (*c*) being about 4% of the vals. observed for (*a*), although the soil solutions obtained from all three layers contained sufficient nutrient for the same nos. of bacteria to be produced in a standard medium. Since mixing the various layers does not influence the activity of the aerobic or nitrifying bacteria, the relatively low activities of the lower layers are presumably the result of position and not of the presence of toxic substances. The CO_2 evolution of the virgin soil is < that of similar soil which has been cultivated, but the latter has a considerably greater bacterial count. H. F. G.

Origin of the vitrain in hard coals. E. STACH (Angew. Chem., 1933, **46**, 275—278).—Modern theories on the origin of coal are discussed in the light of recent petrographic research. Suitable etching, *e.g.*, with aq. CrO_3, of hard bituminous coal and anthracite reveals the characteristic cellular grain structure of wood in the vitrain (I); hence it is considered that neither the lignin nor the cellulose theory of the origin of (I) is of general validity. (I) produced from lignin and cellulose always contains resin. A. R. P.

Organic Chemistry.

Progress of stereochemistry in India, and significance of the doctrine of symmetry. B. K. SINGH (J. Indian Chem. Soc., 1933, Ray No., 321—330). H. B.

Oxidations and reductions of organic compounds. G. URBAIN (J. Chim. phys., 1933, **30**, 309—318).—Theoretical. Modern electronic ideas of oxidation and reduction are applied to org. chemistry. D. R. D.

Liquid ammonia as a medium for the study of organic compounds. E. W. MCCHESNEY (J. Elisha Mitchell Sci. Soc., 1932, **48**, 33—34). CH. ABS.

Stability of spatial configurations and the Walden inversion. R. KUHN (Inst. int. Chim. Solvay, Conseil Chim., 1931, **4**, 413—422; Chem. Zentr., 1933, i, 206—207).

Pyrolytic condensation and decomposition of ethane in presence of hydrogen. M. W. TRAVERS (J. Indian Chem. Soc., 1933, Ray No., 17—26).—See A., 1932, 701. H. B.

Trimethylpentanes. K. C. LAUGHLIN and F. C. WHITMORE (J. Amer. Chem. Soc., 1933, **55**, 2607—2608).—Physical data for ββγ- (I), ββδ-, βγγ-, and βγδ-trimethylpentanes are given. (I) of Clarke *et al.* (A., 1912, i, 150) contained olefine. R. S. C.

Synthesis of δ-*n*-propylnonadecane and ε-*n*-butyleicosane. S. LANDA, J. ČECH, and V. SLÍVA (Coll. Czech. Chem. Comm., 1933, **5**, 204—210).—Interaction of Et palmitate with Mg (2 equiv.) and Pr^nBr in Et_2O gives δ-*propylnonadecan*-δ-*ol*, m.p. 44·5°, and some (I), converted by $ZnCl_2$ at 110—115° into δ-n-*propyl*-Δ^γ-*nonadecene* (I), b.p. 204—

206°/10 mm., which with H_2 and Ni at 140°/90 atm. gives δ-n-*propylnonadecane*, m.p. 6·5°, b.p. 210—211°/10 mm. The constitution of (I) was proved by oxidation by $KMnO_4$ to Pr pentadecyl ketone and $EtCO_2H$. $COPr^{\alpha}_2$ was not detected. ε-n-*Butyleicosan*-ε-*ol*, m.p. 50°, ε-n-*butyl*-Δ^{δ}-*eicosene* (II), b.p. 219—221°/10 mm., and ε-n-*butyleicosane*, m.p. 8°, b.p. 222—223°/10 mm., are similarly prepared. Oxidation of (II) with $KMnO_4$ gives *Bu*$^{\alpha}$ *pentadecyl ketone*, m.p. 52°, and $Pr^{\alpha}CO_2H$. H. A. P.

Action of the silent discharge on ethylene. W. Szukiewicz.—See this vol., 791.

Action of the silent electric discharge on ethylene. III. R. Stratta and E. Vernazza (L'Ind. Chimica, 1933, **8**, 698—702).—The condensation of C_2H_2 in mixtures containing up to 20% of an inert gas is proportional to the concn. of C_2H_2; if the diluent is H_2, the C_2H_2 at first disappears more rapidly and then normally. The formation from C_2H_4 of acetylenic hydrocarbons by the silent discharge decreases rapidly with time, owing to (1) diminution in the concn. of the C_2H_4 and (2) a secondary condensation of the C_2H_2. The H_2 liberated during the formation of a hydrocarbon with a triple linking is fixed immediately at a double linking of the C_2H_4, with formation of saturated hydrocarbons (C_2H_6, CH_4, etc.). T. H. P.

Influence of temperature on the isomerisation of butenes in the presence of aluminium [oxide]. C. Matignon, H. Moureu, and M. Dodé (Compt. rend., 1933, **196**, 1560—1563).—The amount of Δ^{β}-butene produced by dehydration of $Bu^{\alpha}OH$ by Al_2O_3 is increased by previous heating of the catalyst to 450° or 650° or by elimination of adsorbed sulphates by heating to 650° rather than by neutralisation by alkali. By regulation of these and other factors (cf. this vol., 693) the Δ^{α}- or Δ^{β}-isomeride may be produced at will. R. S. C.

Behaviour of pentenes with branched chains towards hydrochloric acid and aluminium chloride at low temperatures. Preparation of γ-methyl-Δ^{α}-butene. J. J. Leendertse, A. J. Tulleners, and H. I. Waterman (Rec. trav. chim., 1933, **52**, 515—524).—Dehydration of commercial amyl alcohol by Al_2O_3 at 350—450° affords a mixture of pentenes (I), hydrogenated (Pd–C) to β-methylbutane. (I) with dry HCl at −80° during hr. affords, when fractionally distilled, mainly β-chloro-β-methylbutane; also γ-methyl-Δ^{α}-butene (II) [which reacts with dry HCl at −80° in presence of $AlCl_3$ to give γ-chloro-β-methylbutane and a monochloride mixture formed from the polymerides of (II) and HCl] and β-methyl-Δ^{α}-butene (III). (II) with $BaCl_2$ and soda-lime at 350—400° affords β-methyl-Δ^{β}-butene and (III). J. L. D.

Stereoisomeric methylethylenes. Dehydration of δ-methylpentan-β-ol by alumina. δ-Methyl-Δ^{β}-pentene. δ-Methyl-Δ^{α}-pentene and its derivatives. H. van Risseghem (Bull. Soc. chim. Belg., 1933, **42**, 219—228, 229—242).—Dehydration of δ-methylpentan-β-ol by Al_2O_3 at about 360° leads to a mixture of δ-methyl-Δ^{α}-pentene, b.p. 53·9—54·1° (dibromide, b.p. 80·5°/17 mm.), β-methyl-Δ^{β}-pentene, b.p. 66·8—67·6° [*nitrosochloride*, m.p. 74·05—74·2° when slowly heated; *nitrosate*, m.p. 93° (decomp.)], oxidised by $KMnO_4$ to $COMe_2$ and $EtCO_2H$, and *cis*- and *trans*-δ-methyl-Δ^{β}-pentene detected by their Raman spectra but not isolated.

Interaction of $CH_2{:}CH{\cdot}CH_2Br$ and $MgPr^{\beta}Br$ leads to δ-*methyl*-Δ^{α}-*pentene* (I), b.p. 53·8—54·2°/760 mm., and an unidentified hydrocarbon, b.p. 51·5—52·0°/760 mm., hydrogenated to *iso*hexane. (I) is reduced to *iso*hexane and converted by Br in $CHCl_3$ into αβ-*dibromo*-δ-*methylpentane*, b.p. 86·9°/22 mm., transformed by boiling KOH–EtOH into δ-*methyl*-Δ^{α}-*pentinene*, b.p. 61·1—61·2°/760 mm., f.p. −105°, and a *bromohexene*, b.p. 134—136·5°/750·2 mm. δ-Methyl-Δ^{α}-pentene and HBr yield β-*bromo*-δ-*methylpentane*, b.p. 68·6—69·2°/90 mm., f.p. −94·6°. H. W.

Structure of Malbot's di*iso*butylene. A. D. Petrov, L. I. Anzousse, and D. N. Andreev (Bull. Soc. chim., 1933, [iv], **53**, 327—330).—Fractionation of the di*iso*butylene (I) [Malbot *et al.* (A., 1889, 842; prep. improved by using high pressure at 300—330° with smaller amounts of $ZnCl_2$)] gives a fraction b.p. 108—112°/760 mm. which by reduction with H_2–NiO at 200° under pressure affords two fractions, b.p. 102—107° and b.p. 107—113°. Comparison of this result with those obtained by reduction of ββγ- (II) (Clarke and Jones, A., 1912, i, 150) and ββδ- (III) (A., 1930, 1553) -trimethyl-Δ^{γ}-*n*-pentene suggests that (I) is a mixture of (II) and (III). The acid products of oxidation of (I) appear similar to those from (II) and (III), but fractional crystallisation of the semicarbazone of the ketonic product from (I) indicates the presence only of $CMe_3{\cdot}CH_2Ac$, whereas absence of aldehyde or ketone products in oxidation of (II) with CrO_3 is explained by the predominance of the form $CMe_3{\cdot}CHMe{\cdot}CH{:}CH_2$ and the ease with which the aldehyde initially formed is further oxidised. J. W. B.

Structure of the acids obtained by oxidation of tri*iso*butylene. J. B. Conant and G. W. Wheland (J. Amer. Chem. Soc., 1933, **55**, 2499—2504).—Butlerow's acid, m.p. 66—70°, supposed to be $C_{11}H_{22}O_2$ (A., 1880, 230), obtained from tri*iso*butylene by $H_2Cr_2O_7$ (modified procedure), is a mixture of about equal quantities of two *acids*, $C_{12}H_{24}O_2$, (I) m.p. 88—89° [*chloride*, b.p. 120—123°/40 mm.; *Me* ester, b.p. 117—120°/40 mm.; p-*chloroanilide*, m.p. 187—187·5°; *amide*, m.p. 140—141°, resistant to NaOH–EtOH, but regenerates (I) with HNO_2, and with KOH–Br gives the *carbamide*, $CO(NH{\cdot}C_{11}H_{23})_2$, m.p. 164—165° (stable to boiling KOH–EtOH)], and (II), m.p. 129° [*chloride*, b.p. 128—133°/50 mm., regenerates (II) with aq. NH_3; *Me* ester, b.p. 115—120°/30 mm.; p-*chloroanilide*, m.p. 166·5—167°]. Both are highly substituted acetic acids, since they are very weak acids, only very slowly esterified, and cannot be brominated. If the Bu^{γ} groups are still intact, they are: (I) $CMe_3{\cdot}CH_2{\cdot}CMe(CMe_3){\cdot}CO_2H$, and (II) $(CMe_3)_2CEt{\cdot}CO_2H$. R. S. C.

Hydrogenation of mixtures of unsaturated hydrocarbons without addition of a catalyst. H. I. Waterman and C. van Vlodrop (Rec. trav. chim., 1933, **52**, 469—477).—Hydrogenation of

octene and of mixtures of unsaturated hydrocarbons does not occur even at 360°/110—120 kg. per sq. cm. if no catalyst is present, although some polymerisation occurs. Previous reports to the contrary are ascribed to the presence of impurities on the walls of the autoclave; with a new autoclave the result is completely negative. H. F. G.

Plant colouring matters. LI. Pure α-carotene. P. KARRER and O. WALKER (Helv. Chim. Acta, 1933, **16**, 641—643).—Complete separation of α- (I) from β- (II) -carotene is effected by filtration of its ligroin solution through air-dried $Ca(OH)_2$ or CaO, (II) being found in the dark reddish-yellow upper layer and (I), m.p. 187—188° (corr.), $[\alpha]_C^{18}$ +315°, bands at 509 and 477 mμ in CS_2, in the lower yellow layer. Other methods of separation are unsatisfactory. With $SbCl_3$ (I) gives only the 542 mμ, and (II) only the 590 mμ, band. J. W. B.

Isomeric forms of carotene and the further purification of vitamin-*A*. P. KARRER, O. WALKER, K. SCHOPP, and R. MORF (Nature, 1933, **132**, 26).—Chromatographic adsorption with CaO or $Ca(OH)_2$ separates α- (I) from β- (II) -carotene. (I), m.p. 187°, in $SbCl_3$ shows only one absorption band (542 mμ) and (II) only one band at 590 mμ. Highly conc. vitamin-*A* can be similarly purified and separates into a main fraction (III), $C_{20}H_{30}O$, which gives absorption at 328 mμ, and a smaller fraction (IV), at 270 mμ. Vitamin-*A* preps. purified by old methods give two bands in $SbCl_3$, but after purification by adsorption on $Ca(OH)_2$, (II) shows one band at 620 mμ and (IV) initially one at 580 mμ and then a second at 620 mμ. (III) yields geronic acid with O_3. L. S. T.

Hydrogenation of acetylene derivatives. XIX. Dependence of direction and course of hydrogenation on the chemical nature of the catalyst. J. S. SALKIND, M. N. VISCHNJAKOV, and L. N. MOREV (J. Gen. Chem. Russ., 1933, **3**, 91—113).—The process of hydrogenation is independent of the method of prep. of colloidal Pt or Pd, or of the nature of the substances taken as carriers for these catalysts. Colloidal Pd, stabilised by starch, gum arabic, gum tragacanth, Na protalbuminate, or casein, in all cases catalyses chiefly reduction of C:C to C·C in tetramethylbutinenediol (I), further reduction of C·C to C·C proceeding far more slowly. In the case of $CH{:}C{\cdot}CMe_2{\cdot}OH$, the velocities of the former and latter reactions are equal, whilst in the case of $CPh{:}CH$ that of the latter reaction is greater. Similar results are obtained in the presence of Pd deposited on $BaSO_4$, $CaCO_3$, C, $Fe(OH)_3$, SiO_2 gel, or Ni. Similar experiments with Pt catalyst gave analogous results, *i.e.*, no selective action on either reaction was in any case found. The relative yield of α-form of tetramethylbutylenediol from (I) is proportional to the velocity of reaction, which, again, depends on the concn. of catalyst, and on the nature of the solvent (EtOAc > EtOH > Et_2O). The catalytic action of Pd is a consequence of its chemical properties, and not of its state of dispersion, or of the nature of protective colloids or carriers present; Pd has, and Pt has not, a special affinity for triple linkings. R. T.

Chlorofluoroethylenes. H. S. BOOTH, P. E. BURCHFIELD, E. M. BIXBY, and J. B. MCKELVEY (J. Amer. Chem. Soc., 1933, **55**, 2231—2235).—The prep. is described of C_2ClF_3, m.p. −157·6°, b.p. −27·9°/760 mm., *s*-$C_2Cl_2F_2$, m.p. −112°, b.p. 20·9°/760 mm., and C_2Cl_3F, m.p. −82°, b.p. 70·0°/740·8 mm. These *compounds* are hydrolysed slowly by H_2O. J. G. A. G.

Peroxide effect in the addition of reagents to unsaturated compounds. I. Addition of hydrogen bromide to allyl bromide. M. S. KHARASCH and F. R. MAYO. **II. Addition of hydrogen bromide to vinyl bromide. III. Addition of hydrogen bromide to propylene.** M. S. KHARASCH, M. C. MCNAB, and F. R. MAYO (J. Amer. Chem. Soc., 1933, **55**, 2468—2496, 2521—2530, 2531—2533).—The peroxide content of $CH_2{:}CH{\cdot}CH_2Br$ (I) (modified prep.; 90—95% yield) controls the direction of addition of HBr. Ignorance of this factor invalidates all previous results. (I) slowly forms peroxides (NH_4CNS test) when kept or when O_2 is bubbled through it. Presence of peroxides (notably when an org. peroxide is added) causes reaction with HBr to give rapidly αγ-dibromopropane (II) (reaction *A*); in the absence of O_2 or, better, presence of antioxidants αβ-dibromopropane (III) is formed (reaction *B*); the amount of each product formed varies from 0 to 100%, according to the conditions. Solvents very greatly affect the velocity of the additions without altering the ratio of (II) and (III) in the product, but this effect bears no relation to the κ of the solvent (cf. lit.). Rise of temp. in presence or absence of solvent increases greatly the velocity of both reactions, but the temp. coeff. of reaction *A* is 1·5—2 times as great as that of *B*, so that even a low peroxide content leads to much (II). Light of all λ (including infra-red and ultra-violet), particularly that of short λ, increases greatly the rate of reaction *A*. Anhyd. $FeCl_3$ or $AlCl_3$ increases greatly the rate of reaction *B*, but Cu salts are almost without effect. The reaction is homogeneous, since glass, Pyrex, asbestos (freed from Fe), and SiO_2 gel surfaces are without effect. AcOH acts as antioxidant, thus leading to apparently anomalous results with this solvent. The amounts of (II) and (III) in the product are estimated within 5% by determining *n* [after removal of (I) by $NPhMe_2$ in EtOH] and controlled by the b.-p. range.

II. Results with $CH_2{:}CHBr$ (IV) and HBr confirm those obtained with (I) in all respects, $CHMeBr_2$ being the "normal" product, and $(CH_2Br)_2$ the product of the peroxide reaction. (IV) forms peroxides very rapidly, and their effect can be completely eliminated only by the use of powerful anti-oxidants.

III. $CHMe{:}CH_2$ does not readily form peroxides and with HBr gives "normally" $Pr^{\beta}Br$, but addition of BzO_2H or ascaridole leads to nearly 100% yields of $Pr^{\alpha}Br$. The results in general confirm those above. R. S. C.

Catalytic oxidation of butyl alcohol to butaldehyde. A. M. RUBINSCHTEIN, A. A. BALANDIN, B. A. DOLGOPLOSKA, K. A. MOROZOV, and L. I. VAGRANSKAJA (J. Appl. Chem. Russ., 1933, **6**, 278—288).—$Bu^{\alpha}OH$ is converted into $Pr^{\alpha}CHO$ and $Pr^{\alpha}CO_2H$ at 350—

380° in presence of catalysts, the activity of which increases in the order: $Cr_2O_3 < Cr_2O_3+Fe_2O_3 < MnO_2+Fe_2O_3 < MnO_2 < Fe_2O_3 < V_2O_5 <$ Ag gauze $<$ 42·5% Ag+7·5% Cu+50% asbestos (I) $<$ 40% Ag + 60% (I) $<$ 75% Ag + 25% (I). The most active catalysts, in which Ag is pptd. on (I) by CH_2O, may be used repeatedly without loss in activity. V_2O_5 differs from other catalysts in giving the highest relative yields of $Pr^{\alpha}CO_2H$, and in catalysing oxidation in an atm. of CO_2. R. T.

Preparation of butyl and hexyl alcohols from the by-products of synthesis of divinyl from ethyl alcohol. III. B. A. KAZANSKI, A. A. BALANDIN, I. M. TSERKOVNIKOV, K. A. IVANOVA, and E. N. STAROVJEROVA (J. Appl. Chem. Russ., 1933, **6**, 266—273).—Considerable quantities of by-products are obtained in the Lebedev process for prep. of divinyl from EtOH. Of these, the "butyl fraction," b.p. 115—120°, consisting chiefly of unsaturated alcohols, is readily hydrogenated at 120° (Ni catalyst) to yield practically pure $Bu^{\alpha}OH$; under similar conditions the "hexyl fraction," b.p. 153—160°, cannot be completely hydrogenated, and does not yield a homogeneous product. R. T.

Glycerol β-monobromohydrin. L. SMITH and J. LAUDON (Ber., 1933, **66**, [*B*], 899—901).—Treatment of allyl alcohol with Br-H_2O affords a mixture of glycerol α- (I) and β- (II) -bromohydrin containing about 65% of (I). Condensation of the mixture with $COMe_2$ containing 1% of HBr and finally with $COMe_2$–P_2O_5 preferentially removes (I), leaving (II), b.p. 106°/6 mm., in which about 2% of (I) remains. H. W.

Mobilities of alkyl radicals in their chlorosulphites. P. CARRÉ (Compt. rend., 1933, **196**, 1806—1809).—Action of $SOCl_2$ in C_5H_5N on $CH_2Ph{\cdot}OH$ and on allyl alcohol produces the chloro-derivatives directly below −10°, whilst the decomp. temp. of the chlorosulphites formed in small amounts in the same reaction fall in the expected order compared with other radicals (cf. A., 1932, 719). Substitution of Cl, Br, CO_2R, and Ph in various radicals gives chlorosulphites of greater stability in accordance with the increased negative character of the migrating groups. A. A. L.

Methylene disulphones. D. T. GIBSON (J. Amer. Chem. Soc., 1933, **55**, 2611—2612).—The reaction of $SO_2R{\cdot}CH_2Ac$ (*A*) with $SO_2R'{\cdot}SMe$ (*B*) gives $SO_2R{\cdot}CHAc{\cdot}SMe$ if *A* is in excess, and $SO_2R'{\cdot}CHAc{\cdot}SMe$ if *B* is in excess, provided that R and R′ are both alkyl or both aryl. Exchange takes place if R is alkyl and R′ aryl, but not *vice versa*. Exchange is of SO_2R for SO_2R', and not of R for R′. R. S. C.

Acid chlorides and diazomethane. Carbonyl and sulphonyl. F. ARNDT and H. SOHOLZ (Ber., 1933, **66**, [*B*], 1012—1014).—*p*-$C_6H_4Me{\cdot}SO_2Cl$ does not react with CH_2N_2 (I). $MeSO_2Cl$ causes slow, catalytic decomp. of (I), but itself remains unchanged. The action between acid chlorides and (I) ($R{\cdot}COCl+CH_2N_2=R{\cdot}CO{\cdot}CHN_2+HCl$) is not therefore simply double decomp., but involves the formation of a primary, additive compound such as $R{\cdot}SO_2Cl$ is incapable of producing. Similar additive compounds are considered to be formed from (I) and aldehydes or ketones. H. W.

Preparation of ethyl acetate from acetaldehyde. M. J. KAGAN and I. A. SOBOLEV (J. Chem. Ind. Russ., 1933, No. 2, 35—37).—The conversion of MeCHO into EtOAc is catalysed not only by $Al(OEt)_3$, but also by other more easily preparable Al alkyloxides. $Al(OBu^{\alpha})_3$ and $Al(OBu^{\beta})_3$ are prepared by dissolving commercial Al foil (pure Al does not dissolve) in the corresponding anhyd. alcohol, containing 2·5% of $AlCl_3$. Al *iso*amyloxide is prepared by dipping Al in aq. $HgCl_2$, when the amalgamated metal readily dissolves in the alcohol; the same method can be applied to $Bu^{\alpha}OH$ and $Bu^{\beta}OH$. Yields of 80% of EtOAc are obtained using catalyst solutions containing $AlCl_3$, as compared with about 50% in its absence. About 7 g. of Al and 2 g. of $AlCl_3$ are required to produce 1 kg. of EtOAc. R. T.

Characterisation of higher fatty acids as their monocarbamides. N. STENDAL (Compt. rend., 1933, **196**, 1810—1812).—The Et esters of fatty acids react with carbamide and conc. NaOEt–EtOH in the presence of C_5H_5N at room temp. to give the *carbamido*-derivatives (90—100% yield) of stearic, m.p. 176·8°, erucic, m.p. 161·5°, octoic, m.p. 191·3°, decoic, m.p. 187°, arachidic, m.p. 172°, oleic, m.p. 161°, and undecenoic acid, m.p. 175°, hydrolysed to the acids by KOH–EtOH. A. A. L.

Products of cracking of oleic acid in the presence of aluminium chloride. N. D. ZELINSKI and R. D. LEVINA (J. Appl. Chem. Russ., 1933, **6**, 20—30).—Oleic acid when heated at 150° during 2—3 hr. with 30% of $AlCl_3$ yields 61% of volatile products, of which 40% has b.p. 60—150°, and contains 25·6% of unsaturated aliphatic (I), 13·7% of unsaturated *cyclo*hexane (II), 17·8% of unsaturated *cyclo*pentane (III), 4·1% of aromatic (IV), 2·2% of saturated *cyclo*hexane (V), 1·7% of saturated *cyclo*pentane (VI), and 34·6% of paraffin (VII) hydrocarbons. The corresponding figures for the fraction, b.p. 150—200°, are: (I) 35·2, (II) 9·9, (III) 10·4, (IV) 8·1, (V) 3·1, (VI) 3·8, (VII) 29·5%, and for the fraction, b.p. 200—250°: (I) 19·6, (II+IV) 19·6, (III) 20, (V) 4, (VI) 8·3, (VII) 28·5%. R. T.

Ozonisation of oleic acid and linseed oil, and the gaseous ozonisation products. E. BRINER, C. DENZIER, and H. PAILLARD (Helv. Chim. Acta, 1933, **16**, 800—807).—O_3 acts as an oxidation catalyst for linseed oil (I) at 60°, but not at 20° or 100°, nor for oleic acid (II). The ozonide of (II) gives gases containing H_2 33, CO_2 20, CH_4 23·4, CO 4·6, and O_2 2·5%, and those from the ozonide of (II) contain H_2 55, CH_4 14, CO_2 12·5, O_2 1·0%, and unsaturated substances 0·5%. The formation of the ozonide of (II) is exothermic (+279 kg.-cal.). R. S. C.

Esterification. II. Esterification of olive oil and carboxylic acids. R. ODA (J. Soc. Chem. Ind. Japan, 1933, **36**, 292—296B).—The esterification of olive oil and $CH_2Cl{\cdot}CO_2H$ is accelerated by a small amount of H_2O and by rise of temp. to 170°. With Ac_2O, the esterification is not affected by addition of H_2O. Esterification with BuOH, $H_2C_2O_4$, and aromatic and OH-acids is also described. F. R. S.

Elæostearic acids. II. Polymerisation of the elæostearic acids. E. ROSSMANN (Fettchem. Umschau, 1933, **40**, 96—102, 117—123).—Polymerisation at < 300° does not proceed beyond the dimeric stage. The cyclo*monoelæostearic acid* (I), b.p. about 200°/4 mm. (= "elæolic acid" of Cloez, A., 1876, ii, 102), formed in variable amount during heating (or distillation) of α- and β-elæostearic acids, is characterised as η-2-*butyl*-$\Delta^{3:5}$-cyclo*hexadienyloctoic acid*. The corresponding Me ester is formed during the distillation of α- or β-Me elæostearate. These monocyclic isomerides are sol. in most org. solvents and give red or violet colorations with conc. HNO_3 or with H_2SO_4 and EtOH. Besides (I), a dimeride, cyclo*dielæostearic acid*, has been separated from tung oil that had been gelled and further heated at 290° for ½ hr. A tung oil gel that has not been overheated can be re-liquefied by heating to 350°; similarly, on heating the polymerised Me esters obtained from such a gel, some depolymerisation occurs at the expense of the dimeride, and polymeric esters of β-elæostearic acid and of (I) are formed. The isomerism of elæostearic acid into (I) is irreversible. In strongly heated tung oil gels, further *cyclo*polymerides are formed, which cannot be depolymerised by heat before the onset of excessive decomp.

E. L.

Polymerisation of the methyl esters of the higher unsaturated fatty acids. XII. Structure of the intramolecular reaction products of methyl clupanodonate. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 63—68; cf. A., 1930, 1272).—Me clupanodonate at 290—300° in H_2 during 20 min. affords a product, b.p. 214—221°/3·5 mm., which with O_3 in $CHCl_3$ gives succinic acid and probably $C_{11}H_{18}O_2$ (this vol., 145). J. L. D.

Alkaline decomposition of aliphatic β-hydroxy-acids. III. Disubstituted β-lactic acids. D. IVANOV (Bull. Soc. chim., 1933, [iv], **53**, 321—323).—When heated with 20% KOH in H_2O–EtOH the disubstituted β-OH-acids (cf. this vol., 157) decompose: $OH{\cdot}CHR{\cdot}CHAr{\cdot}CO_2H \longrightarrow R{\cdot}CHO + CH_2Ar{\cdot}CO_2H$, quant. data being given. If decomp. is effected in the presence of NH_2OH, the oxime of the aldehyde is obtained, thus preventing further action of KOH. J. W. B.

Alkylidene acetate pyruvates. A. KIRRMANN (Bull. Soc. chim., 1933, [iv], **53**, 295—301).—The products obtained by heating aldehydes with $AcCO_2H$ and Ac_2O at 100° have the structure $OAc{\cdot}CHR{\cdot}O{\cdot}COAc$, and not $OAc{\cdot}CHR{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$ as stated by Wohl and Maag (A., 1911, i, 13), since they contain no active H (Zerevitinov), do not form salts, and are readily hydrolysed to the parent aldehyde and acids; no condensation occurs with $AcCO_2Et$. Thus from the appropriate aldehydes are obtained *ethylidene* (I), b.p. 98°/11 mm. (*semicarbazone*, m.p. 179°; p-*nitrophenylhydrazone*, m.p. 195°); *propylidene* (II), b.p. 108—109°/16 mm. (*semicarbazone*, m.p. 168°; p-*nitrophenylhydrazone*, m.p. 199°); *butylidene*, b.p. 114°/10 mm. (*semicarbazone*, m.p. 132°; p-*nitrophenylhydrazone*, m.p. 177°); *heptylidene*, b.p. 145°/10 mm. (*semicarbazone*, m.p. 75°); and *allylidene*, b.p. 108—109°/19 mm., *acetate pyruvate*, accompanied by the corresponding diacetates (*butylidene diacetate*, b.p. 86°/12 mm.). The hydrolysis of (I) and (II) in 1% aq. solution at 25°, studied kinetically by (*a*) determination of the CO group by $NaHSO_3$ titration, and (*b*) a conductometric method, is complete in a few days. J. W. B.

Chemical and electrochemical oxidation of lævulic and ε-keto-*n*-octoic acids. F. FICHTER and S. LURIE (Helv. Chim. Acta, 1933, **16**, 885—891).—α-Angelicalactone, γ-chlorovalerolactone, and lævulyl chloride with H_2O_2 or BaO_2 give ketoperoxides. "Acetyl-lævulic acid," $OAc{\cdot}CMe<\begin{matrix}CH_2{\cdot}CH_2\\O\text{—}CO\end{matrix}$, and H_2O_2 (2 mols.) give the keto-peroxide, $(C_5H_8O_4)_2$. K lævulate with $K_2S_2O_8$ gives CO_2 (1·24 mol.), $COMeEt$, and resins. ε-Keto-*n*-octoic acid (I), m.p. 52°, b.p. 175—177°/15 mm. (modified prep.), $+C_6H_6$, m.p. 78—82° (formed only in presence of Ac_2O), gives by electrolytic oxidation CO_2 (75%) and γμ-*tetradecadione*, m.p. 72—74°, b.p. 125°/4 mm. [*disemicarbazone*, m.p. 181° (decomp.)], and with $K_2S_2O_8$ CO_2, $COEtBu^{\alpha}$ (*semicarbazone*, m.p. 99—100°), and resins; the Et ester, b.p. 125—127°/12 mm., and H_2O_2 give the *keto-peroxide*, $C_{20}H_{36}O_8$. (I) and $SOCl_2$ give a small amount of a *substance*, $C_8H_{13}O_2Cl$, b.p. 105°/5 mm., not an acid chloride. R. S. C.

***iso*Propylidene compounds of glyceric esters.** E. OTT and K. KRAMER (J. pr. Chem., 1933, [ii], **137**, 255—256).—Me and Et *iso*propylideneglycerate, b.p. 84°/14 mm. and 89°/13 mm., respectively, are prepared from $COMe_2$ and Me and Et glycerates in presence of anhyd. $CuSO_4$. H. A. P.

Degradation of perhydronorbixin to perhydrocrocetin. H. RAUDNITZ and J. PESCHEL (Ber., 1933, **66**, [*B*], 901—903).—Perhydronorbixin is converted into γηλπ-tetramethyloctadecane-ασ-dicarboxylic acid, transformed by P and Br into the αα dibromo-bromide and thence by KOH–EtOH into βρ-*dihydroxy*-γηλ-*tetramethyloctadecane*-ασ-*dicarboxylic acid* [*Me* ester (I), b.p. 190°/0·009 mm.]. (I) and MgMeI yield the corresponding diglycol, transformed by $Pb(OAc)_4$ in C_6H_6 into βζλο-*tetramethylhexadecane*-ατ-*dial* (II). Oxidation of (II) by CrO_3 in AcOH yields the corresponding acid, the diamide, m.p. 130—131°, of which is identical with that from perhydrocrocetin. H. W.

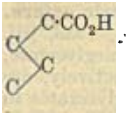
Preparation of *r*-tartaric acid. A. N. CAMPBELL, L. SLOTIN, and S. A. JOHNSTON (J. Amer. Chem. Soc., 1933, **55**, 2604—2605).—A method which avoids the use of Ca salts is described for the prep. of *r*- from *d*-tartaric acid. R. S. C.

Citric acid and its detection. G. D. ELSDON and A. LEES (Analyst, 1933, **58**, 328—331).—Citric acid monohydrate (I), stable in air of ordinary humidity at room temp., rapidly loses H_2O in dry air or on warming. In powder form it is completely dehydrated at 100° in a few hr. 0·01% of (I) in mixtures of tartaric acid and sucrose is detected by extracting with Et_2O and applying the Kunz pentabromacetone test (B., 1919, 435) to the extract. E. C. S.

Determination of citric acid by conversion into acetone. K. TAUFEL and F. MAYR (Z. anal. Chem., 1933, **93**, 1—20).—The method depends on the

oxidation of citric acid (I) by boiling with 0·05% $KMnO_4$, added dropwise to a solution buffered with a solution containing 49·03 g. of H_3PO_4 and 68·08 g. of KH_2PO_4 per litre (p_H 1·9—2·3). The $COMe_2$ formed is collected in ice-cold 2*N*-KOH, an excess of 0·1*N*-I is added, the solution acidified with H_2SO_4 after 30 min., and the excess of I titrated with $Na_2S_2O_3$. A modified method for the determination of (I) in urine is described. A. R. P.

Stereochemistry of sugar carboxylic acids. K. Rehorst (Annalen, 1933, **503**, 143—166).—l-*Ribonic acid* (I), m.p. 104—105° (shrinks 103°), and α-β-*glucoheptonic acid* (II), m.p. 134—135°, are prepared from their lactones by the method of A., 1930, 1407. (II) is converted into a mixture of lactones at 92°/vac. (but not below 92°) over P_2O_5. d-*Lyxonic acid* [*K* salt ($+1H_2O$, not lost at 78°/vac. over P_2O_5; cf. A., 1930, 1411)] is similarly prepared. These acids behave like *d*-talonic acid (A., 1930, 1407) in that, unlike the remaining corresponding carboxylic acids, they do not show the inflexion in the mutarotation curve regarded as due to δ-lactone formation. It is suggested that this is due to steric hindrance occasioned by the existence of the sugar chain in a "meander form" (annexed formula) in place of the commonly assigned coiled structure.



change of (I) into its γ-lactone as measured by mutarotation is slow enough to give the normal end-point for a monocarboxylic acid when rapidly titrated with aq. alkali. The γ-lactone is correspondingly stable to alkali. An aq. solution containing known amounts of lactone and acid, however, although it has normal vals. of [α], gives a high titre with alkali, the disparity being the greater the higher is the proportion of acid present. A similar behaviour is shown by the lactone in aq. H_2SO_4, and by the γ-lactone of (II). Care must be exercised, therefore, in the evaluation of [α] by methods involving titration of γ-lactone in presence of free acid. H. A. P.

Preparation of the free acids and abnormal lactones of the monobasic sugar acids. J. M. Brackenbury and F. W. Upson (J. Amer. Chem. Soc., 1933, **55**, 2512—2514).—Treatment of the Na salt with glacial AcOH gives the following unimol. acids: d-*galactonic*, m.p. 145—146°, $[\alpha]_D^{25}$ −13·09°; l-*rhamnohexonic*, m.p. 174—175°, $[\alpha]_D^{5}$ +19·15° ⟶ +60·3° in 12 days; d-*talonic*, m.p. 138—139°, $[\alpha]_D$ +18·71°; *d*-gluconic; *l*-arabonic; and the δ-lactones of *d*-gluconic, *l*-rhamnonic, and *d*-mannonic acids. R. S. C.

Derivatives of glycuronic acid. III. Synthesis of chlorodiacetylglycuron. W. F. Goebel and F. H. Babers (J. Biol. Chem., 1933, **101**, 173—177; cf. this vol., 698).—A mixture of α- and β-triacetylglycuron with AcCl and HCl gives l-*chlorodiacetylglycuron* (I) (83% yield), m.p. 107·5—108·5° (corr.), $[\alpha]_D^{22}$ +95·5° in $CHCl_3$, which with Ag_2CO_3 in dry Et_2O gives *diacetylglycuron* (II), m.p. 130—131° (corr.). (I) is stable, but (II) mutarotates in MeOH, α +1·60° ⟶ +0·85° in 25 min. (II) with hot H_2O gives an acid. R. S. C.

Substituted hydrazine derivatives of hexuronic acids. Phenylhydrazine and *p*-bromophenylhydrazine derivatives of *d*-galacturonic acid and *p*-bromophenylhydrazine derivatives of *d*-mannuronic acid. C. Niemann, E. Schoeffel, and K. P. Link (J. Biol. Chem., 1933, **101**, 337—358).—The following are prepared (adherence to detailed conditions and use of pure reagents essential): d-*galacturonic acid phenylhydrazone*, m.p. 140—141° (decomp.), $[\alpha]_D^{22}$ +1·0° in MeOH [*Ba*, chars < 250°, and $NH_2{\cdot}NHPh$, m.p. 133—134° (decomp.), $[\alpha]_D^{22}$ −10·4°, salts]; *Ba*, chars < 250°, and $NH_2{\cdot}NHPh$, m.p. 130—131°, $[\alpha]_D^{22}$ +2·40° in MeOH, d-*galacturonate phenylosazone*; d-*galacturonic acid* p-*bromophenylhydrazone*, m.p. 150—151°, $[\alpha]_D^{22}$ +11·5° in MeOH [*Ba* and p-*bromophenylhydrazine*, m.p. 145—146° (decomp.), $[\alpha]_D^{22}$ +9·0° in MeOH, salts; p-*bromophenylhydrazide*, m.p. 174—175° (decomp.), $[\alpha]^{22}$ +17·7° in C_5H_5N]; *Ba* and p-*bromophenylhydrazine*, m.p. 143—144°, $[\alpha]^{22}$ +48·5° in MeOH, salts, and p-*bromophenylhydrazide*, m.p. 174—175°, $[\alpha]_D^{22}$ +18·5° in C_5H_5N, of d-*mannuronic acid* p-*bromophenylhydrazone*; d-*mannuronolactone* p-*bromophenylhydrazone*, m.p. 160°, $[\alpha]_D^{2}$ +64·5° in MeOH. R. S. C.

Chemical constitution of aldehyde and ketone hydrogen sulphites. G. Schroetter (Ber., 1933, **66**, [*B*], 1038—1039).—Reinking's acid, from CH_2O–$NaHSO_3$ and NH_3, cannot be regarded as aminomethanesulphonic acid, since it behaves as a monobasic acid when titrated with 0·1*N*-NaOH in presence of phenolphthalein, whereas taurine is neutral in dil. solution and in conc. solution requires only 20% of the theoretically necessary amount of *N*-NaOH. Similarly, the compound from MeCHO and NH_4HSO_3 cannot be regarded as $NH_2{\cdot}CHMe{\cdot}SO_3H$, since it behaves definitely as a monobasic acid towards *N*-NaOH. The constitution of "aldehyde bisulphites" has not yet been established. H. W.

Formation of formaldehyde and reducing sugars from organic substances in light. N. R. Dhar and L. N. Bhargava (Nature, 1933, **132**, 30).—CH_2O (I) and reducing sugars are formed when aq. solutions of tartaric, citric, and lactic acids are exposed to direct sunlight in presence of air. (I) alone is formed in the case of glycine, malic acid, AcOH, and $COMe_2$, and aq. solutions of dyes such as methylene-blue, Me-violet, malachite-green, etc. L. S. T.

αβ-Ethylenic straight-chain aldehydes. R. Delaby and (Mme.) S. Guillot-Allègre (Bull. Soc. chim., 1933, [iv], **53**, 301—321).—A detailed account of work previously summarised (A., 1931, 1273). Alcohols $CHR{:}CH{\cdot}CH_2{\cdot}OH$ are best converted into the aldehydes $CHR{:}CH{\cdot}CHO$ (about 50% yield) by rapid oxidation with $K_2Cr_2O_7$+aq. H_2SO_4 at 5°, although dehydrogenation with Cu at 250° in presence of benzoquinone to prevent reduction to the saturated alcohol is also satisfactory. The following aldehydes and intermediates appear new: *vinyl*isoamylcarbinol (mixture of isomerides), b.p. 169—171°; Δ^{α}-n-*nonen*-β-*ol*, b.p. 193—194°, 92—95°/20 mm.; γ-iso*amyl*-*allyl bromide*, b.p. 70—75°/12 mm. (*acetate*, b.p. 87—94°/11 mm.; *alcohol*, b.p. 88—91°/12 mm.); α-*bromo*-

Δ^{β}-n-*nonene*, b.p. 105—110°/22 mm. (*acetate*, b.p. 118—122°/20 mm.; *alcohol*, b.p. 108—110°/17 mm.); Δ^{β}-*nonenal*, b.p. 100—102°/21 mm. (*semicarbazone*, m.p. 160—161°; p-*nitrophenylhydrazone*, m.p. 113°), and β-hexylacrylic acid (*Ag* and *Ba* salts). The compounds previously described as *p*-nitrophenylhydrazones (*loc. cit.*) are complex mixtures; the true p-*nitrophenylhydrazone*, m.p. 110—112°, of Δ^{β}-heptenal (I) is obtained by condensing 2 mols. of (I) with 1 mol. of the base. The behaviour of these aldehydes with various aldehydic reagents is investigated, and their role in plant metabolism discussed. Contrary to Curtius and Franzen (A., 1912, ii, 797), their formation in the plant is represented thus: $2MeCHO \longrightarrow OH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO \longrightarrow CHMe{:}CH{\cdot}CH{:}CH{\cdot}CHO$, which is reduced to $CHPr^{a}{:}CH{\cdot}CHO$ (II) by H_2 from the dehydrogenation of EtOH, and they are regarded as the precursors of essential oils. (II) condenses with $MgPr^{a}Br$ to give Δ^{ϵ}-*nonen*-δ-*ol*, b.p. 96—100°/35 mm. J. W. B.

Production of higher alcohols, aldehydes, and ketones. G. T. Morgan and D. V. N. Hardy (Chem. and Ind., 1933, 518—519).—The following CO compounds, prepared by the aldol condensation, are hydrogenated in presence of Ni–kieselguhr, Cu chromite, or Cu–Ba chromite catalysts: CHMe:CH·COMe, CHMe:CMe·CHO, CHEt:CMe·CHO, $CHPr^{a}{:}CEt{\cdot}CHO$, CMeEt:CH·CO·Et, *iso*phorone, and a mixture of condensation products from $COMe_2$ in presence of NaOH at 200°. In every case the ethylenic linking is first reduced giving a saturated aldehyde or ketone, which is then further reduced, although with difficulty in the case of the more complex compounds, to the carbinol. The following are new: sec.-*butyl*, m.p. 105·5°, β-*amyl*, m.p. 118°, δ-*methyl*-β-*amyl*, m.p. 95·5°, βζ-*dimethyl*-β-*heptyl*, m.p. 118°, and 3 : 3 : 5-*trimethyl*cyclo*hexyl*, m.p. 145°, p-*xenylcarbamates*; *ethylideneacetone*-, m.p. 155°, *tiglaldehyde*-, m.p. 206—207°, β-*methylbutan*-α-*al*-, m.p. 120·5°, β-*methylpentan*-α-*al*-, m.p. 160—161°, β-*methylpentan*-α-*al*, m.p. 103°, *diiso*butylketone-, m.p. 92°, 3 : 3 : 5-*trimethyl*cyclo*hexanone*-, m.p. 145—147°, and β-*ethyl*-Δ^{β}-*hexen*-α-*al*-, m.p. 124—125°, -2 : 4-*dinitrophenylhydrazones*. H. A. P.

Carbohydrates. XVI. Preparation of derivatives of *d*-glyceraldehyde from *d*-mannitol. P. Brigl and H. Grüner (Ber., 1933, **66**, [*B*], 931—936).—Mannitol 1 : 2 : 6-tribenzoate (I), m.p. 163°, $[\alpha]_D$ −44° in C_5H_5N, is converted by successive treatment with $COMe_2$ and conc. H_2SO_4 and BzCl in C_5H_5N into *d*-3 : 4-*iso*propylidenemannitol 1 : 2 : 5 : 6-tetrabenzoate, m.p. 122—123°, $[\alpha]_D$ +15·5° in PhMe, identical with the product obtained from Ohle's mannitol dibenzoate and from Fischer's *d*-mannitol 1 : 2 : 5 : 6-tetrabenzoate (II). Ac_2O and C_5H_5N transform (II) into d-*mannitol* 3 : 4-*diacetate* 1 : 2 : 5 : 6-*tetrabenzoate*, m.p. 127°, $[\alpha]_D$ +72·15° in $CHCl_3$, also obtained by the action of Ac_2O and $ZnCl_2$ on d-3 : 4-*benzylidenemannitol*, 1 : 2 : 5 : 6-*tetrabenzoate* (III), m.p. 127—128°, $[\alpha]_D$ −27·9° in $CHCl_3$. (II), PhCHO, and $ZnCl_2$ at room temp. yield d-3 : 4-*benzylidenemannitol* 1 : 2 : 6-*tribenzoate*, m.p. 140°, $[\alpha]_D$ −0·47° in $CHCl_3$, +11·8° in C_5H_5N, transformed by BzCl and C_5H_5N into (III), which is also derived from Ohle's benzylidenemannitol dibenzoate and from (II). The final proof of the position of the Bz groups in (II) is founded on its oxidation (Criegee) by $Pb(OAc)_4$ to d-*glyceraldehyde dibenzoate*, m.p. 80°, $[\alpha]_D$ −35·6° in C_6H_6, $[\alpha]_D$ −3·3° to +19·8° in $CHCl_3$ (containing EtOH), $[\alpha]_D$ +7·8° to +19·8° in EtOH (mutarotation due to formation of Et semiacetal); the (?) *hydrate*, unstable $NaHSO_3$ compound, m.p. 130—131° (decomp.), and the *semicarbazone*, m.p. 133° after softening at 131°, $[\alpha]_D$ +37·2° in EtOH, are described. The position of the :CHPh and $:CMe_2$ groups in the respective compounds follows from the established constitution of (II) unless wandering of Bz is assumed. H. W.

Keto-methylene condensation. U. Basu (J. Indian Chem. Soc., 1933, Ray No., 125—133).—The mechanism is discussed. H. B.

[Formation of] ketones. S. Araki (Mem. Coll. Sci. Kyoto, 1933, **A**, **16**, 137—159).—The yields of ketones formed from the Ca salts of AcOH, $EtCO_2H$, $Pr^{a}CO_2H$, $Bu^{\beta}CO_2H$, and palmitic acids at 600° are determined by isolation, and the loss by decomp. by determination of CO and CO_2 in the evolved gases. (Thermal decomp. of the ketones is assumed to be similar to $2COMe_2 \longrightarrow 2CH_4+C_2H_4+2CO$; $2CO \rightarrow CO_2+C$; it is also assumed that no $CaCO_3$ is decomposed.) The yields are in the order $C_1>C_2>C_3>C_{15}>C_4$, and the vals. of $CO+2CO_2$ are in the reverse order. In the prep. of mixed ketones by the distillation of an equinol. mixture the order is $C_2C_4>C_2C_{\ }>C_2C_3>C_3C_{15}$: $C_1C_3>C_1C_4>C_1C_{15}$. It is suggested that the yield of ketone is a measure of the affinity of the hydrocarbon radicals for the CO group, and that in the formation of mixed ketones those with radicals of similar affinity are formed in greater amount. H. A. P.

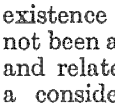
Purification of acetone and ether. E. A. Werner (Analyst, 1933, 58, 335—337).—Peroxides, aldehydes (I), and unsaturated compounds (II) are removed from Et_2O by shaking 500 c.c. with 4 g. of $AgNO_3$ in 30 c.c. of H_2O and 50 c.c. of 4% NaOH for 5—6 min. (I) and (II) are removed from $COMe_2$ by shaking 700 c.c. with 3 g. of $AgNO_3$ in 20 c.c. of H_2O and 20 c.c. of *N*-NaOH for 10 min. E. C. S.

Photolysis of gaseous acetone and the influence of water. G. H. Damon and F. Daniels.—See this vol., 792.

Halogenated pinacolones. G. A. Hill and E. L. Kropa (J. Amer. Chem. Soc., 1933, 55, 2509—2512).—Pinacolone, m.p. −49·8°, with Cl_2 in CCl_4 at 20° in light gives *chloropinacolone*, f.p. −12·6°, b.p. 60·5°/7 mm., and with Cl_2 and HgO in H_2O *trichloropinacolone*, b.p. 101—102°/8 mm. The preps. of pinacol hydrate (dried only by centrifuging), dichloro-, bromo- (I), m.p. −10·5°, b.p. 71·5—72°/10 mm., di- (II), m.p. 76·5°, b.p. 96·5—97°/12 mm., and tri-bromo-pinacolone, b.p. 116—117°/15 mm., cryst., are modified. (I) in ultra-violet light gives some (II), and with KI in MeOH *iodopinacolone*, an oil. The I_2-compound could not be prepared. R. S. C.

Spectrochemistry of keto–enols and the question of the existence of dienols of the allene type.

K. VON AUWERS (Ber., 1933, 66, [*B*], 955—960).—The apparently anomalous spectrochemical behaviour of $CH_2Ac{\cdot}CO_2Et$, $CH_2Bz{\cdot}CO_2Et$, $CH_2Ac{\cdot}COMe$, $CH_2Bz{\cdot}COMe$, $CH_2Ac{\cdot}CO{\cdot}CO_2Et$, and their *C*- and *O*-alkyl derivatives is explained by the unequal degree of enolisation of the individual compounds and the optical influence of OH and OAlk. at the end of a conjugation. Spectroscopic and chemical evidence does not warrant the denial of the possible existence of dienols for which certain evidence has not been adduced. It is improbable that αγ-diketones and related substances hitherto investigated contain a considerable proportion of dienol, but a small % is not excluded. H. W.

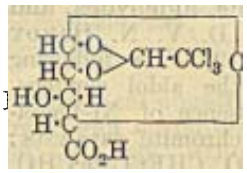
Reactions of reducing sugars. H. WUYTS (Compt. rend., 1933, 196, 1678—1680).—Aldehydes, RCHO, condense with thiobenzoylphenylhydrazide in 5% alcoholic HCl forming compounds  $CH{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}OH$. The *derivatives* of glucose, m.p. 147—148°, galactose, m.p. 178—179°, mannose, m.p. 198°, and arabinose, m.p. 222°, are characteristic, and give colour reactions with oxidising agents in H_2SO_4. Similar derivatives are not obtained from fructose or lactose. A. C.

Reducing sugars. II. W. GABRYELSKI and L. MARCHLEWSKI (Biochem. Z., 1933, 261, 393—410).—An amplification of previous work (A., 1932, 1020) and extension to mannose. The positions of the absorption bands are given using varying concns. of glucose and NaOH, and the interpretation of the change of spectrum with NaOH and on neutralising is discussed. P. W. C.

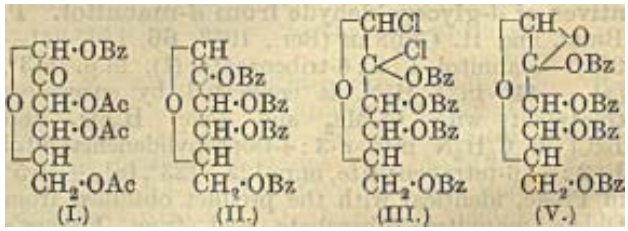
Determination of reducing sugars by titration with ferricyanide. S. W. COLE.—See this vol., 844.

Carbohydrates. XVII. Action of acetic anhydride on *iso*propylideneglucose in presence of zinc chloride. P. BRIGL and W. ZERRWECK (Ber., 1933, 66, [*B*], 936—940).—The action of $ZnCl_2$ and Ac_2O at 0° on mono- or di-*iso*propylideneglucose or their Ac derivatives (preferably *iso*propylideneglucose triacetate) leads to a reducing *compound*, m.p. 141°, $[\alpha]_D$ +60·5° in $CHCl_3$, provisionally designated *isopropylideneglucose penta-acetate* (I) $\left(?\,CMe_2\!<\!\begin{matrix}O{\cdot}CH{\cdot}[CH(OAc)]_3{\cdot}CH_2{\cdot}OAc\\O{\cdot}CH{\cdot}OAc\end{matrix}\right)$. The probability that an asymmetric centre is preserved at C_1 rests on the observation that similar treatment of *iso*propylideneglucose 6-benzoate yields two interconvertible isomerides $C_{21}H_{30}O_{12}$ (A), m.p. 138°, $[\alpha]_D$ −20·47° in $CHCl_3$, (B), m.p. 96°, $[\alpha]_D$ +63·4° in $CHCl_3$. (I) is very stable towards acids, by which it is ultimately converted into non-uniform products. Treatment with alkali removes :CMe_2 and Ac and leads only to such products as are obtained from glucose penta-acetate. H. W.

Structure of chloraloses; α- and β-glucochloralose. (MISS) A. WHITE and R. M. HIXON (J. Amer. Chem. Soc., 1933, 55, 2438—2444).—α-Glucochloralose (modified prep.), m.p. 187°, $[\alpha]_D^{28}$ −15·96°, with $CCl_3{\cdot}CHO$ (I) and conc. H_2SO_4 gives a poor yield of *dichloralglucose* E, m.p. 199°, and with AcCl and $ZnCl_2$ two Ac_5 derivatives, m.p. 174° and 151·5°, $[\alpha]_D^{19}$ −11·5° and +66·2° in $CHCl_3$, respectively, hydrolysis of which yielded indefinite products; an Ac_3 derivative could not be obtained. 3-Methylglucose di-*iso*propylidene ether affords methyldichloralglucose *A* and a new 3-*methyldichloralglucose*, m.p. 111°, $[\alpha]_D^{19}$ −10·8° in $CHCl_3$. Methylation of dichloralglucose *C* affords *methyldichloralglucose* C, m.p. 125°, $[\alpha]_D^{27}$ −26·97° in $CHCl_3$. β-Glucochloralose penta-acetate and 15% KOH–MeOH at room temp. give β-glucochloralose. β-Xylochloralose with AcCl and $ZnCl_2$ gives the Ac_4 derivative, a syrup. Dichloralglucose *D* with Ac_2O and C_5H_5N forms the *Ac* derivative, m.p. 95·5°, $[\alpha]$ 0. Dechlorination and hydrolysis of trimethyl-β-glucochloralose, trimethylglucose-chloro- and -dichloro-acetaldehyde gives trimethylglucoses (possibly mixtures) which could not be identified. These and previous results are best explained by assuming that (I) condenses to give true acetals, the first mol. entering the 1 : 2- and the second the 5 : 6- (or with pentoses the 4 : 5-) -positions. The Ac_5 derivatives are formed by fission of the *O*-ring. Trimethyl-β-glucochloralose is not identical with the condensation product of 3:5:6-trimethylglucose and (I), which, on the above assumption, must be explained by a change of the oxide ring. Chloralic acid has the annexed formula. R. S. C.



Derivatives of glucosone. K. MAURER and W. PETSCH (Ber., 1933, 66, [*B*], 995—1000).—Glucosone 2 : 3 : 4 : 6-tetra-acetate hydrate is converted by BzCl and C_5H_5N in $CHCl_3$ at 0° into *glucosone* 3 : 4 : 6-*triacetate* 1-*benzoate* (I), m.p. 116°, $[\alpha]_D^{19}$ +144·3° in $CHCl_3$, +156·4° in C_5H_5N, which reduces cold Fehling's solution and $KMnO_4$ in $COMe_2$ and does not yield kojic acid when treated with C_5H_5N. With HBr–AcOH (I) adds HBr to give an unstable *compound*, converted by C_5H_5N into $C_5H{\cdot}N,HBr$ and a halogen-free *substance*, $[\alpha]_D$ +212·2° in $CHCl_3$, +187° in C_5H_5N. Bromobenzoylglucose is transformed by $NHEt_2$ in C_6H_6 at room temp. into *oxyglucal tetrabenzoate* (II), m.p. 123°, $[\alpha]_D$ −77·0° in $CHCl_3$, which decolorises Br in $CHCl_3$ and $KMnO_4$ in C_5H_5N, reduces warm Fehling's solution, and is stable towards $NHPh{\cdot}NH_2.HCl$.



Addition of Cl_2 to (II) leads to a mixture of diehlorides (III) from which a stable *isomeride*, m.p. 156°, $[\alpha]_D$ +10·3° in $CHCl_3$, is isolated, transformed by C_5H_5N into dibenzoylkojic acid (IV), m.p. 136°, and by NaOAc in boiling AcOH into *glucosone* 1-*acetate* 3 : 4 : 6-*tribenzoate*, m.p. 131—132°, $[\alpha]_D$ +29·52° in C_5H_5N. The mixture of non-cryst. dichlorides (see above) passes under the influence of moist $NaHCO_3$ in C_6H_6 into the *osone benzoate* (V), m.p.

136°, $[\alpha]_D^{20}$ +7·05° in $COMe_2$, which reduces Fehling's solution and $KMnO_4$, does not decolorise Br in $CHCl_3$, and is quantitatively transformed by C_5H_5N into (IV). (V) gives a *glucosephenylosazone tribenzoate*, m.p. 193°, $[\alpha]_D$ −41·3° in C_5H_5N. The action of $NaHCO_3$ or Na_2HPO_4 on glucosone hydrate triacetate in H_2O at room temp. leads successively to glucosazone tri-, di-, and mono-acetate and ultimately to glucosazone; the production of kojic acid is not observed. H. W.

Fenton's reaction. A. T. KUCHLIN (Biochem. Z., 1933, **261**, 411—424).—The initial velocity of the oxidation of fructose by H_2O_2 in presence of $Fe^{\cdot\cdot}$ is max. at p_H 3·2—5·4, is proportional to the concn. of $Fe^{\cdot\cdot}$, is independent of the presence of $Fe^{\cdot\cdot\cdot}$, and is roughly proportional to the concn. of H_2O_2. The oxidation results in the formation of glucosone, keto- and probably diketo-gluconic acids. The mechanism of the reaction is discussed. P. W. C.

Two acetyl derivatives of sorbose. G. ARRAGON (Compt. rend., 1933, **196**, 1733—1735).—Acetylation of sorbose by Hudson's method yields *sorbose penta-acetate*, m.p. 99°, $[\alpha]_{5791}^{20}$ +2·75°, and *-tetra-acetate*, m.p. 96° (+$\frac{1}{2}Et_2O$, m.p. 65°), $[\alpha]_{5791}^{20}$ −21·63°. A. C.

Colour reaction of sucrose. H. W. RAYBIN (J. Amer. Chem. Soc., 1933, **55**, 2603—2604).—Diazouracil and sucrose or raffinose (but not a no. of other sugars and allied substances) in 0·05*N*-NaOH give a bluish-green colour in a few min.; addition of $Mg^{\cdot\cdot}$ gives a stable blue ppt. R. S. C.

Ketone sugar series. II. Preparation and structure of the hepta-acetate and methyl-glucosides of turanose. E. PACSU (J. Amer. Chem. Soc., 1933, **55**, 2451—2461; cf. A., 1932, 1115).—*Turanose hepta-acetate* (ortho-ester form) (I), dimorphic, m.p. 140—141° and 147°, $[\alpha]_D^{20}$ +47·2 in EtOH (stable) and +37° in $CHCl_3$ (⟶ 41·7° in 2 days), is prepared from stable bromoacetylturanose (II) by (i) Ag_2CO_3 in $COMe_2$ and a little H_2O, (ii) AgOAc in AcOH, or (iii) with β-*methylturanoside hepta-acetate* (ortho-ester form) (III), m.p. 162—164°, $[\alpha]_D^{20}$ +80° in $CHCl_3$, by Ag_2CO_3 in dry MeOH. (I) and 40% HBr–AcOH at room temp. re-form (II). (I), Ac_2O, and $ZnCl_2$ at 100° give two *turanose octa-acetates* (open-chain forms), m.p. 215—217° (IV) and 95—96°, respectively, but with Ac_2O–C_5H_5N a little (IV) only is formed. Unstable α-bromoacetylturanose and Ag_2CO_3 in aq. $COMe_2$ give turanose hepta-acetate, giving with Ac_2O and $ZnCl_2$ at 100° turanose octa-acetate. (I), MeI, and Ag_2O give β-*methylturanoside hepta-acetate* (normal form) (V), m.p. 188—189°, $[\alpha]_D^{20}$ +27·5° in $CHCl_3$, de-acetylated to a β-*methylturanoside*, amorphous, $[\alpha]_D^{20}$ +3·5° in H_2O. (III) is readily hydrolysed by acid (unimol. reaction) to (I), and by NH_3–EtOH or a trace of NaOMe in MeOH to "γ"-β-methylturanoside 3-acetate, which is very sensitive to acids. Methylation of ortho-acyl derivatives always, and generally of partly acetylated sugars, causes re-arrangements. Helferich's fructose tetra-acetate (A., 1928, 1224) may be an open-chain derivative. R. S. C.

Heteroside from *Betula alba*. A. SOSA (Compt. rend., 1933, **196**, 1827—1830).—The isolation of *betuloside*, $C_{16}H_{24}O_7$, m.p. 190° (corr.), $[\alpha]_D$ −44·3°, is described; it is hydrolysed by emulsin to *d*-glucose and a *phenol*, $C_{10}H_{14}O_2$, m.p. 81°. A. A. L.

Cardiac glucosides. I. Heart-activating substances of squill. Scillaren *A*. A. STOLL, E. SUTER, W. KREIS, B. B. BUSSEMAKER, and A. HOFMANN (Helv. Chim. Acta, 1933, **16**, 703—733).—From the pure mixed glucosides (two methods of prep. described) of squill, fractional pptn. from MeOH with H_2O and subsequent crystallisation from aq. MeOH affords the less sol. cryst. *scillaren* A, $C_{37}H_{54}O_{13}$ (I), m.p. indef. 270° (corr.), $[\alpha]_D^{20}$ −73·8° in 75% EtOH, and +MeOH+H_2O, m.p. 230—240° (corr.), which contains a lactone ring (homogeneity established), whilst *scillaren* B (II) (best prepared by another method) remains in aq. solution. Hydrolysis of (I) in MeOH with 2% H_2SO_4 affords amorphous *scillabiose* [Ac_6 derivative, m.p. 97° (corr.)], further hydrolysed to glucose, rhamnose (1 mol. each), and the aglucone *scillaridin* A, $C_{25}H_{32}O_3$ (III), darkens at 205°, m.p., indef., 245—250° (corr.), $[\alpha]_D^{20}$ −62·7° in $CHCl_3$–MeOH (4 : 1), which contains 1 OH (Zerevitinov) and a lactone ring. When squill emulsified with EtOAc is kept at 38° for 7 days enzymolysis of (I) occurs under the influence of *scillarenase* present in the plant, with fission of only the glucose mol., to give cryst. *proscillaridin* A (IV), $C_{31}H_{44}O_8$ +2MeOH and solvent-free, m.p. 213° (corr. decomp.), $[\alpha]_D^{20}$ −82·6° in MeOH, readily hydrolysed by MeOH–H_2SO_4 into 1 mol. of rhamnose and (III). When heated at 150—200°/high vac., (I), (III), and (IV) all yield a sublimate of *anhydroscillaridin* A, $C_{25}H_{30}O_2$, m.p. 208° (corr., decomp.), $[\alpha]_D^{20}$ −148·5° in $CHCl_3$, which still contains a lactone ring (no OH) and is best obtained by the action of MeOH–HCl on (III). (II), which has a higher physiological activity than (I), is probably a mixture of glucosides, and hydrolysis to the aglucone is accompanied by much resinification, only a small yield of a cryst. *substance*, $C_{15}H_{18}O_3$, being isolated. J. W. B.

Polysaccharide chemistry. H. PRINGSHEIM (J. Indian Chem. Soc., 1933, Rây No., 309—320).—An account of recent work (lit.) on the constitution of polysaccharides. H. B.

Constitution of starch. Method of acetylation. W. S. REICH and A. F. DAMANSKI (Compt. rend., 1933, **196**, 1610—1613).—Addition of natural starch to C_5H_5N–AcCl at −20° and warming to 70—80° gives a cryst. Ac_2 derivative (I); amylose gives similarly a Ac_3 derivative (II). Hydrolysis of (I) gives unchanged starch, and (II) gives amylose. Starch grains consist mainly of amylopectins with some amylose derived from the former by hydrolysis or stereochemical change. R. S. C.

Action of acetic anhydride on starch in the presence of sulphuric or phosphoric acid. R. SUTRA (Compt. rend., 1933, **196**, 1608—1610).—Acetylation of starch and glycogen in Ac_2O–H_2SO_4 or –H_3PO_4 gives partly degraded products (cf. lit.). R. S. C.

Plant colloids. XXXII. Swollen starch. XXXIII. Alteration of starch through oxidising introduction of acid groups. M. SAMEC and M.

BLINC (Kolloid-Beih., 1933, **38**, 40—47, 48—56; cf. this vol., 149).—XXXII. In swollen starch the grains are ruptured completely. The amylopectin portion is partly peptised, although insufficiently to nullify the ability to form a paste. Part of the starch becomes oxidised.

XXXIII. Investigations of viscosity, electrical conductivity, mol. wt. (by osmometry), and behaviour towards I show that when maize-starch is oxidised by hypochlorites a change occurs in the direction of smaller particle size. The introduction of acid groups into the mol. causes the hydrophilic properties to be enhanced. The relation of consistency and other properties of starch to the structure of the particle is discussed. E. S. H.

Determination of iodine value of cellulose derivatives. I. SAKURADA (J. Soc. Chem. Ind., Japan, 1933, **36**, 279—280B).—The determination of I val. (Bergmann, Machemer) is unsuitable for the characterisation of cellulose preps. V. E. Y.

Ethylation of cellulose by means of ethyl chloride. N. I. NIKITIN and T. I. RUDNEVA (J. Appl. Chem. Russ., 1933, **6**, 45—59).—Max. ethylation (3 Et per $C_6H_{10}O_5$) is obtained when excess of EtCl is added to cellulose suspended in 44% NaOH at 100°. Under these conditions 9·5% of the NaOH enters into hydrolytic reaction with EtCl, as compared with 57·5% when 13% NaOH is used; if excess of NaCl be added to the reaction mixture, the side reaction of hydrolysis is largely suppressed, 19% of 23% NaOH being used for hydrolysis, as compared with 32% in its absence. The % of NaOH used for hydrolysis rises rapidly with temp., and the velocity of this reaction falls with time, probably as a result of increasing concn. of NaCl in the mixture. The results obtained are substantially the same whether Fe or bronze autoclaves are used. The solubility in org. solvents of the ethylcelluloses (I) obtained rises with their Et content. (I) containing <1·5 Et per $C_6H_{10}O_5$ possess a fibrous structure, which is absent from products containing 2·5 Et groups. R. T.

Benzylcelluloses. N. I. NIKITIN (J. Appl. Chem. Russ., 1933, **6**, 60—74).—Benzylcelluloses (I) containing up to 2·5 $O{\cdot}CH_2Ph$ per $C_6H_{10}O_5$ unit are obtained by adding excess of CH_2PhCl (II) to a suspension of mercerised cellulose in 25% NaOH at 100°. Repeated benzylation of (I) only very slightly raises its $O{\cdot}CH_2Ph$ content. The reaction is completed within 8—10 hr. Addition of small quantities of xylene to the reaction mixture gives a product of slightly higher $O{\cdot}CH_2Ph$ content, whilst larger quantities reduce the reaction velocity. From 3 to 9% of the NaOH present is neutralised by HCl arising from hydrolysis of (II); this reaction is catalysed by Cu. Concn. of NaOH < 25% involves greater % neutralisation as a result of the hydrolytic reaction, whilst using > 25% NaOH the velocity of benzylation is reduced; the best results are obtained by adding fresh NaOH 3—4 hr. after the beginning of the reaction. Raising the temp. from 100° to 125° increases the velocity of reaction without adversely affecting benzylation; a certain degree of depolymerisation, however, takes place, whilst at 150° this becomes considerable, and the $O{\cdot}CH_2Ph$ content falls. 10% LiOH may be substituted for 25% NaOH. (I) is sol. in C_6H_6, C_6H_6–EtOH, $C_2H_2Cl_4$, and other org. solvents. Cotton-, sulphite-, or wood-cellulose may be used for benzylation, and yields products suitable for the manufacture of films. R. T.

Colloidal combination of cellulose with ether and alcohol. S. H. MEIHUIZEN (Chem. Weekblad., 1933, **30**, 385—387).—No reaction takes place between dry cellulose (filter-paper) and dry (over Na) Et_2O, but in presence of a trace of H_2O about 2·45% of Et_2O, calc. on the wt. of the cellulose, combines; under similar conditions about 1·7% of EtOH combines with the cellulose. In dry air the compounds are stable at > 100°, but in moist air they decompose readily. H. F. G.

Cellulose hydroxyethyl ether and its acetate. P. SCHORIGIN and J. RYMASCHEVSKAJA (Ber., 1933, **66**, [*B*], 1014—1016).—Alkali-cellulose does not react with $C_2H_4Br_2$ at 131° and becomes extensively decomposed at 160°. Mercerised cotton is transformed by $(CH_2)_2O$ in $COMe_2$ at 30° into the *β-hydroxyethyl ether*, $C_6H_7O_2(OH)_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, which with Ac_2O and H_2SO_4 affords the *triacetate*, $C_6H_7O_2(OAc)_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$, m.p. about 192—194° (decomp.), $[\alpha]_D^{15}$ about −5° in $CHCl_3$. H. W.

Raw ramie. E. OTT and D. A. WILSON (J. Amer. Chem. Soc., 1933, **55**, 2608—2609).—Raw ramie, or H_2O in which it has been steeped, gives an insol. *Pb* salt with characteristic *X*-ray diagram. R. S. C.

Chemical composition of wood. I. Cellulose content of wood of various origins. F. KOMAROV (J. Appl. Chem. Russ., 1933, **6**, 303—310).—A comparison of analyses of wood (pine, larch, ash) indicates that the method of Kürschner and Hoffer gives a higher Cu val. and pentosan content, and a lower cellulose content, than does that of Cross and Bevan. The content of H_2O-extractable substances and of reducing sugars in various types of wood is: pine, trunk and branches 2·31—3·38 and 0·22—0·46; larch, trunk 1·75—1·97 and 0·08—0·13, branches 6·65 and 0·20, bark 22·5 and 6·49; ash, trunk 2·40—2·57 and 0·13—0·27, branches 4·93 and 0·55; beech 2·60 and 0·22; willow 5·81 and 1·13%. R. T.

Constitution of optical isomerides containing quinquevalent nitrogen and geometrical inversion. P. NEOGI (J. Indian Chem. Soc., 1933, Ray No., 177—184).—Evidence in favour of the author's tetrahedral formula for N^V (A., 1919, i, 312) is reviewed. The mechanism of geometrical inversion (cf. A., 1930, 550) is discussed. H. B.

Nitrogen trichloride and Grignard reagents. G. H. COLEMAN and M. A. BUCHANAN (Proc. Iowa Acad. Sci., 1931, **38**, 168).—NCl_3 reacts with Grignard reagents to produce primary amines, NH_3, and a small quantity of *sec.*, but no *tert.*, amines. CH. ABS.

Quaternary ammonium salts from dimethyl-halogenoalkylamines. III. Dimethyl-ω-bromo-heptyl-, -octyl-, -nonyl-, and -decyl-amines. M. R. LEHMAN, C. D. THOMPSON, and C. S. MARVEL

(J. Amer. Chem. Soc., 1933, **55**, 1977—1981).—The following are prepared by the method previously described (A., 1930, 349): *θ-phenoxyoctyl*, b.p. 178°/5 mm., *ι-phenoxynonyl*, b.p. 141—143°/3 mm., and *κ-phenoxydecyl*, b.p. 170—176°/3 mm., m.p. 32·5°, *bromides*. The following intermediates are new: *Et ζ-phenoxyhexylmalonate*, b.p. 222—225°/7 mm.; *Et η-phenoxyoctoate*, b.p. 172—174°/3 mm.; *θ-phenoxyoctyl alcohol*, b.p. 177°/4 mm., m.p. 41—42°. The above bromides and $NHMe_2$ give *dimethyl-θ-phenoxyoctylamine*, b.p. 159—161°/5 mm. (*chloroplatinate*, m.p. 94—95·5°; *picrate*, m.p. 97—98°), *-ι-phenoxynonylamine*, b.p. 147—148°/5 mm. (*hydrobromide*, m.p. 114—115°; *chloroplatinate*, m.p. 136—137°), and *-κ-phenoxydecylamine*, b.p. 173—176°/3 mm. (*hydrobromide*, m.p. 105°; *chloroplatinate*, m.p. 104°), which are then converted (cf. *loc. cit.*) into dimethyl-θ-bromo-octylamine (I) (*chloroplatinate*, m.p. 91—92°), *-ι-*bromononylamine (II) (*chloroplatinate*), and *-κ-*bromodecylamine (III) (*hydrobromide*), respectively. When (I), (II), and (III) are kept (alone or in Et_2O) or heated under various conditions, *polymerides* of the type.
$\{Br(CH_2)_n\cdot NMe_2[\cdot(CH_2)_n\cdot NMe_2]_x\cdot(CH_2)_n\cdot NMe_2\}Br_{x+1}$, are formed; these are hygroscopic, basic, contain non-ionic Br, and are undoubtedly mixtures. They range from viscous gums to amorphous solids and their mol. wt. calc. from the ratio of non-ionic to total Br varies from 3350 to 28,000. Contrary to the previous statement (*loc. cit.*), dimethyl-η-bromoheptylamine (*chloroplatinate*) does not polymerise to *NN*-dimethylheptamethyleneiminium bromide, but gives a product of the above type. H. B.

Compounds of hexamethylenetetramine. L. Debucquet and L. Velluz (Compt. rend., 1933, **196**, 1809—1810).—Sol. Ca and Mg salts with $(CH_2)_6N_4$ and alkali chromates or dichromates give the following *compounds*: $2MgCrO_4,3(CH_2)_6N_4,15H_2O$, $MgCr_2O_7,2(CH_2)_6N_4,5H_2O$, $CaCr_2O_7,2(CH_2)_6N_4,7H_2O$. The *compounds* $Mg_2Ca[Fe(CN)_6]_2,4(CH_2)_6N_4,24H_2O$ and $3MgCa[Fe(CN)_6],4(CH_2)_6N_4,40H_2O$ are obtained from Ca and Mg compounds previously described (A., 1930, 752). A. A. L.

***cis–trans* Isomerism of salts, $MX_2,2A$.** J. Dubsky and V. Dostal (Pub. Fac. Sci. Univ. Masaryk, 1932, No. 160, 3—20).—The following compounds have been prepared from the corresponding salts and bases: $CuCl_2$,en, m.p. 242—245°, $CuBr_2$,en, m.p. 217°, $CuCl_2$,2 en,H_2O, m.p. 210°, $CuBr_2$,2 en,H_2O, m.p. 224°, $CuCl_2$,3 en,$4H_2O$, m.p. 130—145°, $CuBr_2$,3 en,$2·5H_2O$, m.p. 122°, *CuBr,en,2HBr*, m.p. 238°, $CuCl_2,2C_5H_5N$, m.p. 235°, $4CuCl_2,Cu(OH)Cl,9C_5H_5N$, m.p. 270°, *$CuCl_2$,2quinoline*, m.p. 232—233°, *$CuCl_2$,2quinoline,HCl,$2H_2O$*, m.p. 160°, *$CuCl_2$,2papaverine*, m.p. 145—147°. No definite evidence of *cis–trans* isomerism of the hydrochlorides of the above compounds was obtained, the same products being obtained by addition of CuX_2 to hydrochloride of base as from HCl and double compound. R. T.

Detection of tri(hydroxyethyl)amine and a new reaction of cobaltous salts. F. Garelli and A. Tettamanzi (L'Ind. Chimica, 1933, **8**, 577—578).—Solutions of $CoCl_2$ or $CoSO_4$ give with $N(C_2H_4\cdot OH)_3$ an intense violet-pink colour. This can be used to detect the base at concns. as low as 1 : 2000. The base can also be used to detect 1 part of Co^{II} in 15,000 parts of solution. O. J. W.

Preparation and properties of *n*-alkyl ethers of β-*n*-alkylcholine salts. R. T. Major and J. K. Cline (J. Amer. Chem. Soc., 1933, **55**, 2504—2509).—The following *β-alkoxy-n-alkyl bromides*, $OR'\cdot CHR\cdot CH_2Br$, were prepared: (i) R′=*Me*; R=*Me*, b.p. 72·5—73·5°/145 mm., *Et*, b.p. 54—55°/30 mm., *Pr*, b.p. 65°/30 mm., *Bu*, b.p. 65°/9 mm. (not isolated pure); (ii) R′—*Bu*; R=*Me*, b.p. 65°/7 mm. (not isolated pure), *Et*, b.p. 86°/20 mm., *Pr*, b.p. 95—97°/11 mm., *Bu*, b.p. 101·5—203°/10 mm.; (iii) R′=*amyl*; R=*Pr*, b.p. 99—101°/8 mm. From these by NMe_3 in C_6H_6 at about 115—125° are produced varying amounts of NMe_4Br and dimethyl-β-alkoxy-*n*-alkylamine, and mostly the following *ethers* of β-n-*alkylcholine bromides*, $OR'\cdot CHR\cdot CH_2\cdot NMe_3Br$, the groups named being R and R′ (? R′ and R), respectively; the m.p. in parentheses are those of the corresponding *chlorides*: *Me*, *Me*, m.p. 116—118° (135—136°); *Et*, *Me*, m.p. 122—124° (101—103°); *Pr*^{a}, *Me*, m.p. 101—103° (112—114°); *Bu*^{a}, *Me*, m.p. 98—100° (101—103°); *Me*, *Et*, m.p. 130—132° (132—134°); *Et*, *Et*, m.p. 159—160° (160—162°); *Pr*^{a}, *Et*, m.p. 147—149° (148—150°); *Bu*^{a}, *Et*, m.p. 148—149° (132—134°); *Et*, *Pr*^{a}, m.p. 147—149° (148—150°); *Me*, *Bu*^{a}, m.p. 101—103° (an oil; corresponding *sulphate*, m.p. 100—102°); *Et*, *Bu*^{a}, m.p. 128—130° (133—134°); *Pr*^{a}, *Bu*^{a}, m.p. 109—112° (95—97°); *Bu*^{a}, *Bu*^{a}, m.p. 95—97° (an oil); and *Pr*^{a}, n-*amyl*, m.p. 105—107° (101—103°). Impure *β-amyloxy-n-amyldimethylamine chloroplatinate* has m.p. 224·5° (decomp.). R. S. C.

Urethanes. VI. Acyl monourethanes and their reactions with ammonia and amines. S. Basterfield and (Miss) M. E. Greig (Canad. J. Res., 1933, **8**, 450—457; cf. A., 1931, 830).—*Chloroacetylurethane* [from urethane (I) and $CH_2Cl\cdot COCl$ at 100°], m.p. 129°, with NH_3–EtOH at room temp. gives $CH_2Cl\cdot CO\cdot NH_2$ and with NH_2Ph at 100° or 190° s-N-*phenylglycylphenylcarbamide*, $NHPh\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NHPh$, m.p. 195°, also prepared from *bromoacetylurethane*, m.p. 119° [obtained with allophanic acid from (I) and $CH_2Br\cdot COCl$]. Phenylacetylurethane (II) with NH_3–EtOH gives very slowly $CH_2Ph\cdot CO\cdot NH_2$, also obtained more rapidly with $CH_2Ph\cdot CO\cdot NH\cdot CO\cdot NH_2$ by means of aq. NH_3; with aq. NH_2Et at room temp. N-*ethylphenylacetamide*, m.p. 75°, and a little of a substance, m.p. 75°, probably N-*phenylacetyl-N′-ethylcarbamide*, are formed; with NH_2Ph at 100°, or, better, 150°, *N*-phenylacetyl-*N′*-phenylcarbamide is formed, which at 170° with NH_2Ph gives $CO(NHPh)_2$ (III) and $CH_2Ph\cdot CO\cdot NHPh$, both obtained also from (II) at 190°. *p*-$NO_2\cdot C_6H_4\cdot CO_2H$, (I), and $POCl_3$ at 90° give a little p-*nitrophenylacetylurethane*, m.p. 175°, and more (?) *Et* p-*nitrophenylacetylallophanate*, m.p. 190°; the urethane, best obtained from the *acid chloride* (prepared by $SOCl_2$), m.p. 49—50°, and (I) at 100°, gives with aq. NH_3 p-*nitrophenylacetamide*,

m.p. 191°, and p-*nitrophenylacetylcarbamide*, m.p. 235°; the acetamide together with a little *p*-$NO_2 \cdot C_6H_4 \cdot CO_2Et$ (IV) was formed by NH_3–EtOH. Aq. NH_2Et gives N-*ethyl*-p-*nitrophenylacetamide*, m.p. 155°, whereas in EtOH only (IV) was obtained; this urethane does not react with NH_2Ph at 100°, but gives at 150° (III) (12%), p-*nitrophenylacetanilide* (12%), m.p. 198°, and N-p-*nitrophenylacetyl*-N′-*ethylcarbamide* (80%), m.p. 220°, the first two products only being obtained at 190°. (I) and BzCl at 100° give only Et benzoylallophanate, but in C_5H_5N benzoylurethane, m.p. 111°, is also formed in 42% yield; the latter with aq. NH_3 gives $NH_2 \cdot CO \cdot NHBz$, with aq. NH_2Et $NHEt \cdot CO_2Et$ and NH_2Bz, and with NH_2Ph (i) at 150° $NHBz \cdot CO \cdot NHPh$ (98%; a trace only at 100°) and (ii) at 190° (III) and NHBzPh. p-*Nitrobenzoylurethane*, m.p. 152° [from *p*-$NO_2 \cdot C_6H_4 \cdot COCl$ and (I) in C_6H_6; gives *Et* p-*nitrobenzoylallophanate*, m.p. 194°, in hot EtOH], with NH_3 gives p-*nitrobenzamide*, m.p. 189°, with NH_2Et p-*nitrobenzoylethylamine*, m.p. 149°, and with NH_2Ph at 100° or 190° (III) and *p*-nitrobenzanilide. *m*-$NO_2 \cdot C_6H_4 \cdot COCl$ and (I) at 100° give *Et* m-*nitrobenzoylallophanate*, m.p. 128°, partly converted into m-*nitrobenzoylcarbethoxybiuret*, m.p. 140°, by hot EtOH, whereas in C_6H_6 the product is *Et* NN′-*di*-m-*nitrobenzoylallophanate*, m.p. 164°. Thus, with a given amine the tendency to amide as compared with carbamide formation is more marked with the acylurethanes from stronger acids, whilst with a given urethane amide formation occurs more readily with the stronger bases. NH_3 and NH_2Et cause ammonolysis more markedly in H_2O than in EtOH.

R. S. C.

Decolorisation of the solution in the preparation of *d*-glutamic acid hydrochloride by hydrolysis of wheat gluten. C. L. Tseng and E. J. H. Chu (Sci. Quart. Nat. Univ. Peking, 1932, **3**, 69—74).—Japanese active C gave the best results.

Ch. Abs.

Optimum conditions for preparing *d*-glutamic acid hydrochloride from wheat gluten. II. Effect of purity of acid, time of reaction, climatic conditions, and other experimental circumstances. C. L. Tseng and E. J. H. Chu (Sci. Quart. Nat. Univ. Peking, 1932, **3**, 53—68).—The purity of the HCl and the use of pressure had little effect; the optimum time of heating is 7 hr. Preliminary digestion (9 hr.) slightly improved the yield. Powdered sun-dried gluten gave the best results.

Ch. Abs.

Sullivan's reaction for the determination of cysteine and cystine. J. W. H. Lugg (Biochem. J., 1933, **27**, 668—673).—Cystine (I) and NaCN react at p_H 9·5 and the final colour is developed at p_H 12·5. Diminution in colour occurs if an excess of Na β-naphthaquinonesulphonate (II) is used; 2 mols. of (I) appear to react with 1 mol. of (II). The quantity of NaCN used also requires control. (I) or cysteine may be determined in pure solution with an accuracy of 1—2%.

P. G. M.

Oxidation of cysteine with iodine. Formation of a sulphinic acid. (Miss) D. G. Simonsen (J. Biol. Chem., 1933, **101**, 35—42).—Addition of cysteine to dil. I–HI affords a solid, probably a sulphinic acid, since it reduces two further equivs. of I.

R. S. C.

Decompositions and reactions of carbamide. II. Reactions of carbamide with acids, anhydrides, etc. J. M. Das-Gupta (J. Indian Chem. Soc., 1933, **10**, 117—123).—The products obtained when $CO(NH_2)_2$ is heated with various mono- (amide + NH_4 salt) and di- (imide) -basic acids and with acid anhydrides (imides) at 150—170° are tabulated and the reaction mechanisms are discussed. Esters and amides do not react at this temp. The corresponding reactions in H_2O, EtOH (50% and 90%), AcOH, and glycerol are compared. When heated in AcOH phenylcarbamide affords $CO(NHPh)_2$.

J. W. B.

New method of halogenation. I. Chlorination with dichlorocarbamide. II. Bromination with dichlorocarbamide and potassium bromide. M. V. Lichoscherstov. **III. Iodination with dichlorocarbamide.** M. V. Lichoscherstov and B. I. Tzimbalist (J. Gen. Chem. Russ., 1933, **3**, 162—171, 172—176, 177—182).—I. Dichlorocarbamide (I) acts as a chlorinating agent, particularly in acid solution; it chlorinates C_6H_6 in presence of I, AcOH in presence of S, EtOH, and NH_2Ph; NH_2Ph is also oxidised, but NHAcPh readily gives *o*- and *p*-Cl-derivatives. Resorcinol (II) and (I) (2 : 1) in dil. HCl give 4-chlororesorcinol, b.p. 259·5°, m.p. 102·5°, identical with the product from (II) and SO_2Cl_2 (A., 1878, 222); some 2-chlororesorcinol may also be formed. With more (I), 4 : 6-dichlororesorcinol, m.p. 68° (hydrated), 113·2° (anhyd.), is produced; and finally 2 : 4 : 6-trichlororesorcinol. 4-Bromoresorcinol similarly gives 6-chloro-, m.p. 108·5°, and 2 : 6-dichloro-, m.p. 78·5°, -4-bromoresorcinol. It is suggested that in these reactions (I) is hydrolysed to $CO(NH_2)_2$ and HOCl, which is the chlorinating agent.

II. (I) in aq. solution in presence of KBr acts as a brominating agent, probably owing to the formation of HOBr; it has a strong oxidising action in neutral, but not in acid, solution. Thus, (II) yields 4-bromo-, m.p. 99°, 4 : 6-dibromo-, m.p. 115°, and 2 : 4 : 6-tribromo-, m.p. 110°, -resorcinol; 4 : 6-dichloro- gives 4 : 6-dichloro-2-bromo-resorcinol, m.p. 101°.

III. (I) in presence of KI, preferably with the addition of H_2SO_4, acts as an iodinating agent; the acid prevents oxidation, although an excess is harmful owing to the formation of free I. Moreover, in neutral solution the reaction cannot be made to yield mono- and di-substitution products. In this way, 4-iodo-, m.p. 63° (hydrated), 100° (anhyd.), and 2 : 4 : 6-triiodo-resorcinol, m.p. 154°, are obtained. 4 : 6-Diiodoresorcinol, m.p. 84°, is prepared in AcOH solution. 4-Chlororesorcinol yields 4-chloro-2 : 6-di-iodo-, m.p. 106°, in neutral solution and 4-chloro-6-iodo-, m.p. 71·4°, -resorcinol, in presence of H_2SO_4. Iodination of 4 : 6-dichlororesorcinol gives the 2-iodo-compound, m.p. 94°, and 4-iodo- and (I) in AcOH give 2 : 6-dichloro-4-iodo-resorcinol, m.p. 92·6°. 6-Bromo-4-iodoresorcinol, m.p. 65° (monohydrate), 87·6° (anhyd.), results from the consecutive iodination and bromination of (II), and 2 : 6-dibromo-4-iodoresorcinol, m.p. 112·2°, is similarly prepared.

G. A. R. K.

Salts of guanylcarbamide and diguanidine. L. A. DESHUSSES and J. DESHUSSES (Helv. Chim. Acta, 1933, **16**, 783—792).—The following are prepared: *guanylcarbamide* (I) *picrate*, m.p. 260°, *styphnate*, m.p. 224° (decomp.), *picrolonate*, m.p. 253° (decomp.), *fluosilicate*, *phosphomolybdate*, $3B,H_3PO_4,12MoO_3,5H_2O$, *phosphotungstate*, $3B,H_3PO_4,12WO_3,5H_2O$, *silicotungstate*, $4B,SiO_2,12WO_3,5H_2O$ (loses $3H_2O$ at 100°), *arsenotungstate*, and 6-*chloro*-5-*nitro*-m-*toluenesulphonate*; *diguanidine* (II) *phosphotungstate*, $3B',2H_3PO_4,24WO_3,9H_2O$, and *phosphomolybdate*, $3B',2H_3PO_4,24MoO_3,12H_2O$, in which B=(I) and B'=(II). These salts are not suitable for analytical purposes. R. S. C.

Action of diazomethane on imides. I. G. LABRUTO (Gazzetta, 1933, **63**, 266—269).—Phthalimide and succinimide are converted by CH_2N_2 into their *N*-Me derivatives. E. W. W.

Refractometric examination of normal saturated nitriles. R. MERCKX, J. VERHULST, and P. BRUYLANTS (Bull. Soc. chim. Belg., 1933, **42**, 177—198).—MeCN and EtCN are prepared from KCN and Me_2SO_4 or Et_2SO_4. Higher nitriles with an even no. of C atoms are obtained from the acids through the chlorides (PCl_3) and amides, which are dehydrated with $SOCl_2$. Those with an odd no. of C atoms are derived from the alcohols through the bromides, which are treated with KCN; if necessary the nitriles are transformed into the amides, which are subsequently distilled with P_2O_5 under diminished pressure. B.p., d_4, d^{15}, and d_4^{20}, and n^{18} for the He_{red}, H_α, D, He_{yellow}, H_β, Hc_{violet}, and Hg lines are recorded for the series $MeCN—C_{13}H_{27}\cdot CN$. H. W.

Methylmercury derivatives. A. PERRET and R. PERRET (Helv. Chim. Acta, 1933, **16**, 848—857).—The following *HgMe* salts are prepared from HgMe·OH and the appropriate acid, the NH_3 *complexes* being given in parentheses: *thiocyanate* . *fluoride*, sublimes > 200°, *chromate*, explodes at 255—260°, *perchlorate*, deflagrates at 180° after melting, *formate*, m.p. 43°, decomp. > 60° to $HgMe_2$, HCO_2H, Hg, and CO_2, *H sulphide*, m.p. 143° (decomp.), *azide*, m.p. 130·5°, explodes about 200° (+NH_3), chloride (+NH_3), bromide (+0·66NH_3), and iodide (+0·5NH_3) (unstable). R. S. C.

Organomercuri-acetylides and their use in the identification of organomercuri-halides. R. J. SPAHR, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1933, **55**, 2465—2468).—Passing C_2H_2 into a solution of the appropriate organomercuri-halide in 10% aq. KOH gives 80—90% yields of *di(organomercuri)-acetylides*, $(R\cdot Hg\cdot C:)_2$, in which R is *Me*, m.p. 232—233° (decomp.), *Et*, m.p. 195—196°, *Pr*, m.p. 150—151°, *Bu*, m.p. 125·5—126·5°, *amyl*, m.p. 91—92°, *hexyl*, m.p. 104—105°, *Ph*, m.p. 179—180° (decomp.), o-, m.p. 205—206°, and p-*tolyl*, m.p. 190—191°, and *benzyl*, m.p. 110—111°. The alkyl and arylalkyl derivatives are unstable to atm. H_2O. The $CH_2Ph\cdot CH_2\cdot$ compound decomposes into $CH_2Ph\cdot CHO$ immediately on formation. 0·1 g. of halide in 10 c.c. of aq. KOH gives sufficient acetylide for identification. The compounds are sol. in org. solvents and volatile. R. S. C.

Stereoisomeric 1 : 2-dimethyl*cyclo*hexanes O. MILLER (Bull. Soc. chim. Belg., 1933, **42**, 238—242; cf. A., 1932, 837).—*o*-$C_6H_4Me_2$ is hydrogenated in presence of Ni–Al_2O_3 or Pt(Vavon)–asbestos to *trans*- (I), b.p. 123·70°±0·05°(corr.)/760 mm., m.p. −89·4°, and *cis*- (II), b.p. 130·04°±0·02°(corr.)/760 mm., m.p. −50·1°, -1 : 2-dimethyl*cyclo*hexane. The proportion of (I) increases with rise in temp. of hydrogenation. H. W.

Products of slow combustion of benzene. J. AMIEL (Compt. rend., 1933, **196**, 1896—1898).—In the liquid products obtained during the slow combustion of C_6H_6 (this vol., 600), PhOH and *p*-benzoquinone could be detected, but no aldehydes or peroxides. J. W. B.

Chlorine derivatives of *p*-xylene. H. WAHL (Compt. rend., 1933, **196**, 1900—1902).—In the presence of Fe filings at 10—15°, Cl_2 converts *p*-$C_6H_4Me_2$ into 2-*chloro*-p-*xylene*, b.p. 184°, m.p. 1·6°, converted by HNO_3–H_2SO_4 into its 5-NO_2-derivative (I), b.p. 135—136°/13 mm., m.p. 77°, and 30% of an isomeric NO_2-derivative (II), b.p. 127—137°/13 mm., which may not be pure. Reduction of (I) with Sn–HCl or Zn–AcOH affords the 5-NH_2-derivative (III) (Wheeler and Morse, A., 1925, i, 22) [*Bz* derivative, m.p. 163°; *picrate*, m.p. 195° (decomp.)]. Reduction of (II) gives some (III), but fractional crystallisation of the hydrochlorides of the liquid portion affords an isomeric *chloro*-p-*xylidine*, b.p. 132—133°/15 mm., m.p. 40° [*Ac*, m.p. 171°, and *Bz*, m.p. 177°, derivatives; *picrate*, m.p. 171—172° (decomp.)]. J. W. B.

Auto-racemisation and velocity of electrolytic dissociation. E. BERGMANN and M. POLANYI (Naturwiss., 1933, **21**, 378—379).—Auto-racemisation is due to removal of ions or groups from the asymmetric mol. The half-val. period of the activity in the case of CHPhMeCl (I) in liquid SO_2 is 18 hr. and the auto-racemisation is strictly unimol. This is due to electrolytic dissociation of (I) into $CHPhMe^+$ (II) and Cl^-. Each (II) undergoes very frequent change of configuration before its next combination with a Cl^-, so that the probability of the end product having the original configuration is 0·5. The electrolytic dissociation of (I) in liquid SO_2 proceeds at such a rate that in 18 hr. half the substance is converted into ions. A. J. M.

Reaction of a free radical, triphenylmethyl, with ethers, esters, and acetone. A. A. MORTON and L. V. PEAKES (J. Amer. Chem. Soc., 1933, **55**, 2449—2451).—CPh_3 with Et_2O and Cu or CuCl at 80° (without Cu reaction is much slower at 110°) gives $CPh_3\cdot OH$ (I), $CHPh_3$ (II), *p*-benzhydryltetraphenylmethane (III), oily products, CO, CH_4, and other gases. With EtOAc (I), (II), and a little peroxide (IV) are formed, and with $COMe_2$ (I). With other esters and ethers, oily products, sometimes containing (IV), (III), or (I), were obtained. $CPh_3\cdot OEt$ may be an intermediate product in the reaction with Et_2O. R. S. C.

Preparation of styrenes. D. GAUTHIER and P. GAUTHIER (Bull. Soc. chim., 1933, [iv], **53**, 323—326).—Good yields (in parentheses) of substituted styrenes $CHAr{:}CRR'$ are obtained by slow distill.

ation of the carbinols OH·CHAr·CHRR′ with 5% of $NaHSO_4$, and thus are prepared: CHPh:CH_2 (75%), CHPh:CHMe (85%), *p*-C_6H_4Me·CH:CH_2, *p*-C_6H_4Et·CH:CH_2 (80%), CHPh:CHEt (78%); CPhMe:CH_2 and 1-phenyl-Δ^1-*cyclo*hexene are similarly obtained from the *tert.* alcohols. J. W. B.

Oxidation of disubstituted acetylenes by selenium dioxide. R. Truohet (Compt. rend., 1933, **196**, 1613—1614).—CPh·CMe and SeO_2 in EtOH give a Se complex, stable to dil. acids, but decomposed by NaOH to give 10—12% of COPhEt. CPh:CEt, however, gives 25% of CPh·C·CHMe·OH. R. S. C.

Sensitivity of aromatic nitro-compounds to light. I. *peri*-Derivatives of 1-nitronaphthalene. R. E. Steiger (Helv. Chim. Acta, 1933, **16**, 793—799).—1-*Nitro*-8-*methylnaphthalene*, m.p. 65°, and its 5-*sulphonamide*, m.p. 236°, but not 1-nitronaphthalenesulphon-amide, m.p. 236°, or *-anilide*, m.p. 123°, are sensitive to light, which is attributed to the spatial proximity of the Me and NO_2 groups in the former pair. All m.p. are corr. R. S. C.

Catalytic oxidation of acenaphthene in solution. H. Paillard and R. Duckert (Helv. Chim. Acta, 1933, **16**, 773—783).—Acenaphthene and $Mn(NO_3)_2$ in *o*-$C_6H_4Cl_2$ and O_2 at 3 kg. per sq. cm. initially and finally 44 kg. and 310° give 24% of naphthalic acid and acenaphthenequinone. Other catalysts, solvents, or conditions give lower yields. R. S. C.

Chlorination of acenaphthene. H. Paillard and P. Favarger (Helv. Chim. Acta, 1933, **16**, 614—623).—The effects of solvent, temp., catalyst, concn. and amount of Cl_2 on the yields of monochloroacenaphthene have been studied. Hydroxylic solvents are best, the yields on acenaphthene (I) consumed (I catalyst) being as follows: fused 55·7, $CHCl_3$ 51·7, CCl_4 49·3, C_6H_6 58·3, PhCl 52·8, *o*-$C_6H_4Cl_2$ 54·7, EtOH 78·9, MeOH 83·8, AcOH 82·7, and PhOH 78%. In AcOH temp. (25—115°) has little effect, a very flat max. being observed at 80°. Traces of I or $SbCl_5$ are the best catalysts, $FeCl_3$ promoting polychlorination. Up to an optimum concn. of 38·5 g. of (I) in 100 g. of AcOH the yield increases with concn., and then decreases only slightly unless very high concn. are used. Prolonged passage of Cl_2 (> 0·5 hr.) decreases the yield and increases the proportion of resinous products. The Cl in 3-chloro- and 3-chloro-4-nitro-acenaphthene is only slightly labile, very little replacement by NH_2 or OH occurring under usual conditions. J. W. B.

Use of potassium dichromate and sodium nitrite in aromatic nitrosations. F. P. J. Dwyer, D. P. Mellor, and V. M. Trikojus (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 315—331).—Diazo- and NO-derivatives are readily obtained from amines and a mixture of $K_2Cr_2O_7$ and $NaNO_2$ in H_2O–MeOH: NH_2Ph and *o*- and *p*-toluidines give diazoaminobenzenes, NMe_2Ph and thymol form NO-derivatives, and NH_2Ph and β-naphthol together yield 1-benzeneazo-β-naphthol. p_H measurements (glass electrode) show that the initial val. is 4·5, rising rapidly on addition of NH_2Ph, the main reaction taking place at p_H 6·35—7·41. K_2CrO_4 in a current of CO_2 may replace $K_2Cr_2O_7$. F. R. S.

Additive compounds of phenylnitroamines and anilines. G. Owen (Mem. Manchester Phil. Soc., 1931—1932, **76**, 10—18).—The salts are pptd. by addition of light petroleum, b.p. 60—80°, to solutions of the components in $CHCl_3$. All are unstable, but respond to the aromatic ·NH·NO_2 test with conc. H_2SO_4. 2 : 4 : 6-Tribromophenylnitroamine gives *compounds* with NH_2Ph, m.p. 77°, *p*-C_6H_4Me·NH_2, m.p. 92—93°, *o*-C_6H_4Me·NH_2, granules or needles, m.p. 102°, *p*-C_6H_4Cl·NH_2, m.p. 93°, and *p*-C_6H_4Br·NH_2, m.p. 106°, whilst 2 : 4-dichlorophenylnitroamine yields *salts* with NH_2Ph, plates or needles, m.p. 88°, *o*-C_6H_4Me·NH_2, m.p. 77—78°, *p*-C_6H_4Cl·NH_2, m.p. 58°, *p*-C_6H_4Br·NH_2, m.p. 68°, and 2 : 4 : 6-NO_2·$C_6H_2Cl_2$·NH_2, m.p. 77°. H. W.

Interaction of aromatic thiocarbamides with bromine. R. F. Hunter (J. Indian Chem. Soc., 1933, Rây No. 73—79).—A review. H. B.

Comparative stability of isomerides relative to their absorption spectra. Isomerisation of arylamines. (Mme.) Ramart-Lucas and (Mlle.) Wohl (Compt. rend., 1933, **196**, 1804—1806).—The absorption curves of $NPhMe_2$, methyl-*o*- and *-p*-toluidine, and *m*-4-xylidine hydrochlorides fall in the order predicted by the rule previously enunciated (A., 1928, 760). Curves are also recorded for the free bases in EtOH and C_6H_{14}. A. A. L.

Condensation of methyl- and ethyl-*o*-toluidines with chloral hydrate. A. N. Meldrum and A. H. Advani (J. Indian Chem. Soc., 1933, **10**, 107—110).—Methyl-*o*-toluidine condenses with CCl_3·CH(OH)$_2$ (anhyd. $AlCl_3$) to give p-(βββ-*trichloro*-α-*hydroxyethyl*)*methyl*-o-*toluidine*, m.p. 104—105° [*hydrochloride*, m.p. 207—208° (decomp.); N-*Ac* derivative, (I), m.p. 187°; Ac_2 derivative (II), m.p. 111°; *NO*-derivative, m.p. 172—173° (decomp.)]. Reduced with Zn+AcOH (I) or (II) affords p-(ββ-*dichlorovinyl*)-N-*acetmethyl*-o-*toluidide*, b.p. 204°/11 mm., m.p. 107—108°. Oxidation with 1·5% $KMnO_4$ in dil. KOH converts (II) into the *Ac* derivative, m.p. 232°, of 6-methylamino-*m*-toluic acid, which is obtained by hydrolysis with 40% aq. KOH at 150°. p-(βββ-*Trichloro*-α-*hydroxyethyl*)*ethyl*-o-*toluidine*, m.p. 107° [*hydrochloride*, m.p. 210—212° (decomp.); Ac_2 derivative, m.p. 106—107°; *NO*-derivative, m.p. 138° (decomp.)], is obtained similarly. J. W. B.

α-Naphthylthiocarbimide as a reagent for primary and secondary aliphatic amines. C. M. Suter and E. W. Moffett (J. Amer. Chem. Soc., 1933, **55**, 2497—2499).—α-$C_{10}H_7$·NCS (modified prep.) gives the following N-α-*naphthyl*-N′-*alkylthiocarbamides*: Me, m.p. 191—192° (depends on rate of heating); Et; Pr^a, m.p. 102—103°; Bu^a, m.p. 108—109°; *n*-amyl, m.p. 102—103°; n-*hexyl*, m.p. 78—79°; n-*heptyl*, m.p. 68—69°; n-*octyl*, m.p. 71·5—72·2°; Pr^β, m.p. 142—143°; *iso*amyl, m.p. 96·5—97·5°; iso*hexyl*, m.p. 78·5—79·5°; Bu^β, m.p. 136—137°; α-*methylhexyl*, m.p. 101—102°; α-*methylheptyl*, m.p. 82—83°; i-*amyl*, m.p. 133—134°; cyclo*hexyl*, m.p. 141—142°; *benzyl*, m.p. 171—172°; Me_2, m.p. 167—168°; Et_2, m.p. 107—108°; $Pr^a{}_2$, m.p. 160—

161°; *Bu*$^{a}_{2}$, m.p. 122—123°; *diisoamyl*, m.p. 117—118°; and *dibenzyl*, m.p. 130—131°. These give satisfactory depressions of the m.p., when mixed. R. S. C.

New method of introducing the thiocyano-group into aromatic compounds with dichlorocarbamide. M. V. LICHOSCHERSTOV and A. A. PETROV (J. Gen. Chem. Russ., 1933, **3**, 183—197).—Dichlorocarbamide (I) reacts with NH_4CNS in $COMe_2$, H_2O, or MeOH giving the unstable dithiocyanocarbamide, hydrolysed to hypothiocyanous acid, which then undergoes further decomp. This reaction is utilised for the introduction of the CNS group with aromatic compounds possessing groups which assist halogenation. The CNS group enters the *p*-position. $COMe_2$, AcOH, or EtOH, with or without H_2O can be used as solvent; a few drops of H_2SO_4 are beneficial. Thus, $NPhMe_2$ in $COMe_2$ gives *p*-thiocyanodimethylaniline, NH_2Ph in MeOH *p*-thiocyanoaniline and 2 : 4-dithiocyanoaniline, m.p. 108° (80% yield). α-$C_{10}H_7$·NH_2 in MeOH yields 4-thiocyano-, m.p. 146°, and in $COMe_2$ and excess of reagent 2 : 4-dithiocyano-α-naphthylamine, m.p. 204°. *m*-$C_6H_4(NH_2)_2$ in AcOH gives 4-thiocyano-(II), m.p. 160—161°, and 4 : 6-dithiocyano-*m*-phenylenediamine, m.p. 170—172°. (II) is brominated with (I) and KBr to the 6-Br-derivative. Benzidine in AcOH gives a $(CNS)_2$-compound, m.p. 250°, which is readily tetrazotised. Anthranilic acid in $COMe_2$ gives the 4-CNS-compound, m.p. 168—170°; *m*-aminobenzoic acid gives a product which decomposes on heating. The group cannot be introduced into monohydric phenols; quinol and pyrocatechol are oxidised to quinones and resorcinol gives a $(CNS)_1$-derivative. α-Naphthol yields the known mono- and di-thiocyano-compounds. G. A. R. K.

Nitro-compounds as oxidising agents. W. A. FLETCHER and K. LEWIS (Trans. Kansas Acad. Sci., 1932, **35**, 146—148).—*o*-, *m*-, and *p*-Azoxy-phenetole and -anisole were prepared by the action of CH_2Ph·ONa on the corresponding NO_2-derivatives. The yield of BzOH and azoxy-derivative was increased by excess of alkali. CH. ABS.

Oxanilhydrazides. G. TIERIE (Rec. trav. chim., 1933, **52**, 533—537; cf. this vol., 598).—Et oxanilate in warm EtOH with N_2H_4,H_2O affords *oxanilhydrazide*, m.p. 217°, which readily condenses with aldehydes and ketones in warm H_2O. The following are prepared: *benzaldehyde*-, m.p. 270°; 4-*methoxy*-, m.p. 272°, 3 : 4-*methylenedioxy*-, m.p. 274°, and 3-*methoxy*-4-*hydroxy-benzaldehyde*-, m.p. 267°; *furfuraldehyde*-, m.p. 258° (decomp.); *hydroxymethylfurfuraldehyde*-, m.p. 219° (decomp.); *acetone*-, m.p. 210°, and *acetophenone-oxanilhydrazone*, m.p. 237°. Similarly, Et *p*-nitro-oxanilate (*ibid.*, 704) affords p-*nitro-oxanilhydrazide*, m.p. 293°, which with PhCHO and $COMe_2$ gives *benzaldehyde*-, m.p. 325° (decomp.), and *acetone*-p-*nitro-oxanilhydrazone*, m.p. 310°, respectively. Interaction of Et 2 : 4-di- or Et 2 : 4 : 6-tri-nitro-oxanilate and N_2H_4,H_2O in boiling $CHCl_3$ affords 2 : 4-di- and 2 : 4 : 6-tri-nitroaniline, respectively. J. L. D.

Alkyl derivatives of halogenophenols and their bactericidal action. I. Chlorophenols. E. KLARMANN, V. A. SHTERNOV, and L. W. GATES (J. Amer. Chem. Soc., 1933, **55**, 2576—2589).—The following are prepared (*a*) in the *o*-alkyl series by re-arrangement of the *p*-chlorophenol esters by $AlCl_3$ and subsequent Clemmensen reduction, and (*b*) in the *p*-alkyl series by rearrangement of the phenol ester, Clemmensen reductions and chlorination by SO_2Cl_2: (i) *o*-substituted p-*chlorophenols*: Me, m.p. 45°, b.p. 220—225°, Et, b.p. 98—102°/2·5 mm., *Pr*^{a}, b.p. 105°/2 mm., *Bu*^{a}, b.p. 140°/18 mm., n-*amyl*, b.p. 122°/3 mm., sec.-*amyl*, b.p. 120—123°/3 mm., m.p. 61·5°, n-*hexyl*, b.p. 132°/3 mm., cyclo*hexyl*, b.p. 152—156°/4 mm., m.p. 57·5°, n-*heptyl*, b.p. 150—152°/3 mm., n-*octyl*, b.p. 165°/3 mm., and sec.-*octyl*, b.p. 155—160°/3 mm.; (ii) *p*-substituted o-*chlorophenols*: Me, b.p. 195—196°, *Et*, b.p. 214—216°, *Pr*^{a}, b.p. 228—230°, *Bu*^{a}, b.p. 247—248°, n-*amyl*, b.p. 115—116°/2 mm., tert.-*amyl*, b.p. 105—110°/2 mm., n-*hexyl*, b.p. 139—142°/6 mm., and n-*heptyl*, b.p. 147°/6 mm.; (iii) 3-*methyl*-6-*ethyl*-, b.p. 102°/3 mm., m.p. 73·2°, -6-n-*propyl*-, b.p. 115°/2 mm., m.p. 49·5°, -6-iso*butyl*-, b.p. 120—123°/3 mm., -6-β-*ethylpropyl*-, b.p. 128°/2 mm., -2-*ethyl*-6-iso*propyl*-, b.p. 132°/2 mm., and -6-sec.-*octyl*-, b.p. 155—159°/2 mm., -4-*chlorophenol*, 2-*chloro*-3 : 5-*dimethyl*-4-n-*propylphenol*, b.p. 125—130°/3 mm., m.p. 81·7°; 4-*chloro*-3 : 5-*dimethyl*-2-*ethyl*-, m.p. 97·5°, -2-iso*propyl*-, b.p. 125°/3 mm., -2-iso*butyl*-, b.p. 131—133°/2 mm., -2-β-*ethylpropyl*-, b.p. 141—142°/3 mm., -2-sec.-*amyl*-, b.p. 142—145°/2 mm., and -2-sec.-*octyl*-, b.p. 160—163°/3 mm., -*phenol*; 5-*chloro*-2-*hydroxy-aceto*-, b.p. 97—99°/2 mm., m.p. 54°, -propio-, m.p. 59·7°, -butyro-, b.p. 108—112°/3 mm., m.p. 50·5°, and -*valero*-, b.p. 120—125°/2 mm., -*phenone*; 5-*chloro*-2-*hydroxyphenyl* n-*amyl*, m.p. 56·5°, n-*hexyl*, b.p. 140—144°/3 mm., m.p. 43·5°, and n-*heptyl*, m.p. 63°, *ketones*; 5-chloro-2-hydroxy-4-methyl-aceto-, m.p. 71°, and -propiophenone, m.p. 65·3°, b.p. 110—115°/3 mm.; 5-chloro-2-hydroxy-4 : 6-dimethyl-, m.p. 89·7°, and o-*chloro*-2-*hydroxy*-6-*methyl*-3-iso*propyl*-*acetophenone*, b.p. 127—135°/3 mm.; 4-chlorophenyl acetate, b.p. 90—92°/2·5 mm., propionate, b.p. 76—78°/2 mm., butyrate, b.p. 96—98°/3 mm., *valerate*, b.p. 113—118°/2 mm., n-*hexoate*, b.p. 125—130°/2 mm., n-*heptoate*, b.p. 135°/2 mm., and n-*octoate*, b.p. 154—156°/2 mm.; 6-chloro-*m*-tolyl acetate, b.p. 94—96°/2·5 mm., and propionate, b.p. 102—104°/3·5 mm.; 4-*chloro*-3 : 5-*dimethylphenyl acetate*, b.p. 102°/2·5 mm., m.p. 48·7°; and 4-chloro-3-methyl-6-*iso*propylphenyl acetate, b.p. 112—114°/2 mm. The phenols are strongly antiseptic to *Eberthella typhi* and *paradysenteriæ*, *Staph. pyogenes aureus*, *Streptoccoccus* (hæmolytic), *Mycobacterium smegmatis*, and *Trichophyton rosaceum*, several being as effective as any known substance. In general, the *p*-C_6H_4Cl·OH derivatives are more potent than the *o*-series. Typical examples of quasi-specificity are shown. The variation of efficacy with length of the alkyl chain varies in the different series and according to the nature of the organism used. R. S. C.

Condensation of formaldehyde with *p*-nitrophenol. F. D. CHATTAWAY and R. M. GOEPP (J.C.S., 1933, 699—700).—Interaction of CH_2O (1 mol.) with *p*-NO_2·C_6H_4·OH (2 mols.) in H_2SO_4–H_2O at

75—80° affords 5 : 5′-dinitro-2 : 2′-dihydroxydiphenylmethane, m.p. 268° (lit., 230°) (*Ac*$_2$ derivative, m.p. 153°), which with fuming HNO_3 at 0—5° affords 3 : 3′ : 5 : 5′-*tetranitro*-2 : 2′-*dihydroxydiphenylmethane*, m.p. 253°. CH_2O (2 mols.) and *p*-NO_2·C_6H_4·OH (1 mol.) in H_2SO_4–H_2O at 15° afford 6-mtrobenzdioxin (I), halogenated in AcOH to 8-*chloro*- (II), m.p. 152—153°, and 8-*bromo*-6-*nitrobenzdioxin* (III), m.p. 165—166°. (II) and (III) with CrO_3 afford 8-*chloro*-, m.p. 125—126°, and 8-*bromo*-6-*nitro*-4-*ketobenzdioxin*, m.p. 120—121°, hydrolysed to 3-*chloro*-, m.p. 202—203°, and 3-*bromo*-5-*nitrosalicylic acid*, m.p. 223—224°, respectively. Reduction of (I) and diazotisation followed by Cu_2Cl_2 (or Cu_2I_2) affords 6-*chloro*-, m.p. 98—99°, and 6-*iodo-benzdioxin*, m.p. 58°. Interaction of CH_2O (> 3 mols.) and p-NO_2·C_6H_4·OH (1 mol.) in H_2SO_4–H_2O at 75—80° affords *di*-8-(6-*nitrobenzdioxinyl*)*methane*, m. p. 225°, oxidised by boiling CrO_3–AcOH to *di*-8-(6-*nitrobenzdioxinyl*) *ketone*, decomp. > 285°, further oxidised by $K_2Cr_2O_7$ in cold H_2SO_4 to *di*-8-(6-*nitro*-4-*ketobenzdioxinyl*) *ketone*, m.p. 314°, easily hydrolysed (20% KOH) to CH_2O and 5 : 5′-*dinitro*-3 : 3′-*ketodisalicylic acid*, m.p. > 330°. J. L. D.

Crystallisation under the microscope. β-Naphthyl benzoate. A. Glazunov and K. Šefl (Coll. Czech. Chem. Comm., 1933, **5**, 222—232).—An apparatus for the measurement of rapidity of crystallisation by visual observation of the substance on a heated microscope slide is described and illustrated by measurements of the rate of crystallisation and nucleus formation of the labile, m.p. 97°, and stable, m.p. 110°, forms of β-$C_{10}H_7$·OBz. H. A. P.

Stereochemistry of cyclic compounds. W. H. Mills (Inst. int. Chim. Solvay, Conseil Chim., 1931, 4, 1—60; Chem. Zentr., 1933, i, 217—218).

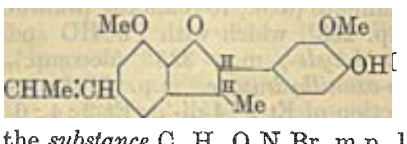
Constitution of laccol. G. Bertrand and G. Brooks (Ann. Inst. Pasteur, 1933, **50**, 763—777).—A detailed account of work already noted (A., 1932, 943).

Nitrosation of phenols. XV. Resorcinol mono-*n*-butyl ether. H. H. Hodgson and H. Clay (J.C.S., 1933, 660—661).—Nitrosation of *m*-OH·C_6H_4·OBu^n (I) (cf. A., 1931, 1153) affords a mixture of 4- (II) (34%), m.p. 155—156° (decomp.), and 6-*nitroso*-3-n-*butoxyphenol* (III), m.p. 79°, and thereby continues the abnormal increase in 4-nitrosation noted in the case of the Pr$^\beta$ ether (A., 1932, 509). The strong positive electromeric effect of the OBu^n group on the *p*-NO-group results in easy chelation which accounts for the high solubility of (III) in C_6H_6. (III) with dil. HNO_3 or alkaline $K_3Fe(CN)_6$ affords 6-*nitro*- (IV), m.p. 43—44°, and (II) affords 4-*nitro*-3-n-*butoxyphenol* (V), m.p. 96°; a mixture of these phenols is obtained by nitration of (I). (IV) and (V) suffer debutylation by HBr to 4-nitroresorcinol, indicating the absence of a 2-NO_2-group. *m*-NO_2·C_6H_4·OH and Bu^{n}I afford m-*nitrophenyl* n-*butyl ether*, b.p. 273—274°, reduced (Fe–HCl) to m-n-*butoxyaniline*, b.p. 264—265°, methylated by Me_2SO_4 at 100° to m-n-*butoxydimethylaniline*, b.p. 267—268°, which with $NaNO_2$ in HCl at 0—5° affords 4-*nitroso*-3-n-*butoxydimethylaniline hydrochloride*, m.p. 145—146° (*base*, m.p. 92—93°), converted by boiling 5% NaOH into (II). J. L. D.

Detection of polyhydric phenols. P. K. Bose (J. Indian Chem. Soc., 1933, Ray No., 65—66).—*o*- and *p*-$C_6H_4(OH)_2$, pyrogallol, gallic and tannic acids, catechin, and quercetin give violet colorations with EtOH–*o*-$C_6H_4(NO_2)_2$ and aq. Na_2CO_3 or NaOH (cf. A., 1932, 499); *m*-$C_6H_4(OH)_2$, phloroglucinol, and orcinol give brown colorations. H. B.

Structure of the dimeric modifications of propenylphenol ethers. Synthesis of di*iso*eugenol methyl ether and di*iso*eugenol. J. Haraszti and T. Széki (Annalen, 1933, **503**, 294—300).—The dibromide of *iso*eugenol Me ether is converted by Cu powder in anhyd. C_6H_6 into the saturated dimeric *compound* (I), $C_{22}H_{27}O_4Br$, m.p. 153°, in which Br is in aliphatic union, since (I) and KOH–MeOH yield the substance $C_{22}H_{26}O_4$, m.p. 122°. (I) is transformed by Zn dust in boiling EtOH–H_2O into di*iso*eugenol Me ether, m.p. 106°, identical with that obtained by the action of mineral acid on the propenylphenol ether. *iso*Eugenol dibromide similarly yields an intermediate *product*, $C_{20}H_{23}O_4Br$, m.p. 198° after decomp., whence di*iso*eugenol (II), m.p. 180—181°. The observations are reconciled with difficulty with an anthracene structure for (II) (cf. Haworth *et al.*, A., 1931, 954) and the possibility of the *cyclo*butane constitution is revived. H. W.

Dehydrogenations in the coniferyl series. II. Dehydrodi*iso*eugenol. H. Erdtman (Annalen, 1933, **503**, 283—294; cf. this vol., 390).—Dehydrodi*iso*eugenol Me ether (I) is oxidised by boiling HNO_3 (*d* 1·42) to 4 : 5-dinitroveratrole and $H_2C_2O_4$ and by fuming HNO_3 at room temp. to trinitroveratrole, m.p. 144—145° (also obtained from acetoveratrone, 3 : 4-dimethoxypropiophenone, and veratril, but not from eugenol or its Me ether, which yield only resins). Ozonolysis of (I) leads to MeCHO in amount indicating the presence of 1 CHMe:CH· group. Oxidation of (I) by $KMnO_4$ in cold $COMe_2$ leads to the *acid* CO_2H·$C_{15}H_{19}O(OMe)_3$, m.p. 134—135°, oxidised by boiling aq. $KMnO_4$ to veratric acid and converted by HNO_3 (*d* 1·42) at 100° into the $(NO_2)_2$-compound $C_{15}H_9O(NO_2)_2(OMe)_3$, m.p. 194—195°. Hydrogenation of (I) (PtO_2 in EtOH) affords *dihydrodehydrodi*-iso*eugenol Me ether* (II) m.p. 98—99°, which gives a pale yellowish-brown colour with $C(NO_2)_4$ and is converted by HNO_3 in AcOH into *dinitrodihydrodehydrodi*iso*eugenol Me ether*, m.p. 140—142°. With gradually increasing amounts of Br- (II) affords successively a mixture of isomeric Br_1-derivatives, the Br_2-compound, m.p. 89—90°, and the Br_3-derivative (III), $C_{21}H_{23}O_4Br_3$, m.p. 137—138°, oxidised by $KMnO_4$ in C_5H_5N–H_2O at 90—100° to $PrCO_2H$ and 6-bromoveratric acid, m.p. 184—185°. (II) and HNO_3 (*d* 1·42) at 50—55° give the *substance* $C_{21}H_{23}O_8N_2Br$, m.p. 122—123°. To dehydrodi*iso*eugenol (IV) the annexed constitution is assigned. The oily by-products of the prep. of (IV) when hydrogenated and treated with NaOH and Me_2SO_4 yield propylveratrole and (II). H. W.



p-Xylenolsulphone. J. ZEHENTER [with S. MAYR] (J. pr. Chem., 1933, [ii], **137**, 216—226).—Interaction of 1 : 4 : 2-$C_6H_3Me_2$·OH with conc. H_2SO_4 at 150—160° in an open vessel gives, in addition to the sulphonic acid, 4 : 4′-*dihydroxy*-2 : 5 : 2′ : 5′-*dimethyldiphenylsulphone*, m.p. 280—282°, sublimes 220—230°/10—12 mm. (a second form, m.p. 254—255°, obtained from MeOH or EtOH may be impure) *H* (aq. Na_2CO_3) and *Na*$_2$ (NaOEt) salts; *Ac*$_2$, m.p. 206—207°, *Bz*$_2$, m.p. 171—172°, and *Br*$_2$, m.p. 254° (Br in Et_2O), derivatives; 3-*sulphonic acid* (excess of cold, conc. H_2SO_4), m.p. 149—150° (*Na*, *Ba*, and *Pb* salts); *Me*, m.p. 171° (MeI and NaOH in EtOH), *Me*$_2$, m.p. 175° (Me_2SO_4), *Et*, m.p. 200—201°, and *Et*$_2$ *ethers*, m.p. 142—143° (both last with EtI)]. Br in H_2O in the cold and conc. H_2SO_4 at 100° both cause fission at the ·SO· linking giving 3 : 5- and 3 : 5 : 6-Br- and 5-SO_3H derivatives of the xylenol. H. A. P.

Manufacture of 4-amino-2 : 5-dialkoxydiphenyls and azo-dyes therefrom. I. G. FARBENIND. A.-G.—See B., 1933, 582.

Synthesis of di*iso*butyl-mono-, -di-, and -trihydric phenols. J. B. NIEDERL, S. NATELSON, and E. MCK. BEEKMAN (J. Amer. Chem. Soc., 1933, **55**, 2571—2575).—Addition of H_2SO_4, followed by the appropriate phenol, to "di*iso*butylene" (A., 1931, 1148) in AcOH affords *diisobutyl-pyrogallol*, m.p. 103°, *-pyrocatechol*, m.p. 109°, *-resorcinol*, m.p. 101—102°, b.p. 219°/23 mm., *-quinol*, m.p. 142°, b.p. 210—225°/7 mm., *-guaiacol*, b.p. 295—298°/760 mm., 138—144°/4 mm., *-phenol*, m.p. 83°, and *-o-cresol*, m.p. 49—50°. R. S. C.

β-Phenylethylamines. III. Synthesis of mescaline. K. H. SLOTTA and G. SZYSZKA (J. pr. Chem., 1933, [ii], **137**, 339—350).—Mescaline and similar substances are prepared by condensation of trialkoxybenzaldehydes with nitromethane, and electrolytic reduction of the resulting ω-nitrostyrenes in AcOH–EtOH–HCl. 3 : 4 : 5-*Trimethoxy-*, m.p. 169° (*chloride*, m.p. 77°, b.p. 185°/18 mm.; best prepared with $SOCl_2$), and 3 : 4 : 5-*triethoxy-benzoic acid*, m.p. 112° (*chloride*, b.p. 180°/12 mm.), are prepared from Na gallate and Me_2SO_4 or Et_2SO_4 in N_2; their chlorides are reduced (Rosenmund) to 3 : 4 : 5-*trimethoxy-*, m.p. 74°, and 3 : 4 : 5-*triethoxybenzaldehyde*, m.p. 68°. *Pyrogallol Et*$_3$ *ether*, b.p. 130°/9 mm., is converted (Gattermann) into 2 : 3 : 4-$C_6H_2(OEt)_3$·CHO (cf. A., 1931, 213). The following are also described: ω-*nitro*-2 : 3 : 4-*trimethoxy-*, m.p. 79°, and -3 : 4 : 5-*triethoxy-styrene*, m.p. 102°; 3 : 4 : 5-trimethoxy-β-phenylethylamine (mescaline), (yield 77·3% of theory); 3 : 4 : 5-*triethoxy-*, b.p. 181°/10 mm. (*hydrochloride*, m.p. 175°; *picrate*, m.p. 155°), 2 : 3 : 4-*trimethoxy-*, b.p. 170°/12 mm. (*hydrochloride*, m.p. 167°; *picrate*, m.p. 137°), and 2 : 3 : 4-*triethoxy*-β-*phenylethylamine*, b.p. 165°/11 mm. (*hydrochloride*, m.p. 185°; *picrate*, m.p. 142°). H. A. P.

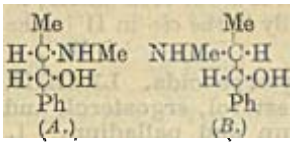
Humic substances. III. Oxidation of humic substances obtained from phenols. N. A. ORLOV and N. D. LIKHACHEV (J. Appl. Chem., Russia, 1932, **5**, 797—802).—The products resemble those obtained by oxidation of natural humic substances or humic substances from carbohydrates. The hydrogenation products include pyrene. CH. ABS.

Effect of auxochromes. M. HORIO.—See this vol., 763.

Optically active aminocyclanols. M. GODCHOT, M. MOUSSERON, and R. GRANGER (Compt. rend., 1933, **196**, 1511—1512).—*dl*-2-Ethylamino*cyclo*hexanol, b.p. 107—108°/16 mm., m.p. 35° (*hydrochloride*, m.p. 155°; *H* d- and l-*tartrates*, both m.p. 123—124°), is resolved by *d*- and *l*-tartaric acids (method; this vol., 499) into d-, b.p. 99—100°/16 mm., m.p. 38°, $[\alpha]_D$ +89·2° (*hydrochloride*, m.p. 150—151°; *H* d-*tartrate*, m.p. 148—149°; l-*tartrate*, m.p. 156—157°), and l-*forms*, b.p. 99—100°/16 mm., m.p. 38°, $[\alpha]_D$ −89·2° (*hydrochloride*, m.p. 150—151°; *H* d-*tartrate*, m.p. 156—157°; l-*tartrate*, m.p. 148—149°). dl-2-*Propylaminocyclohexanol*, b.p. 117—118°/16 mm., m.p. 39° (*hydrochloride*, m.p. 181—182°), from epoxy*cyclo*hexane and EtOH–NH_2Pr, is similarly resolved with difficulty into d- and l-*forms*, m.p. 45°, $[\alpha]_D$ +90·45° (d-*tartrates*, m.p. 151—152° and 160—161°, respectively), whilst dl-2-*methylamino*-4-*methyl*cyclo*hexanol*, b.p. 112—113°/16 mm. (*hydrochloride*, m.p. 115—116°; d-*tartrate*, m.p. 153—154°), gives d- and l-*forms*, b.p. 110—111°/16 mm., $[\alpha]_D$ ±52·5° (d-*tartrates*, m.p. 164—165° and 159—160°, respectively). *N*-Substitution in 2-amino*cyclo*hexanol increases the rotatory power in the order H < Me < Et < Pr; the dispersion ratio remains practically const. H. B.

Synthesis of β-hydroxy-β-phenylethylamine. D. RAFFAELI (L'Ind. Chimica, 1933, **8**, 575—577).—Aminoacetyl chloride is condensed ($AlCl_3$) with C_6H_6, and the aminoacetophenone hydrogenated catalytically to a 71% yield of pure OH·CHPh·CH_2·NH_2. E. W. W.

Nucleus-hydrogenated, optically active ephedrines. A. SKITA, F. KEIL, and H. MEINER (Ber., 1933, **66**, [*B*], 974—984).—Observations of the changes in sp. rotation caused by nuclear hydrogenation justify the configurations *A* and *B* for



(−)-ephedrine (I) and (−)-ψ-ephedrine (II). "Circuit processes" are detailed by which with a single quantity of (I) all the optically active stereoisomerides of mandelic acid and of ephedrine can be prepared. *r*-ψ-Ephedrine and (II) are prepared by transformation of *r*-ephedrine and (+)-ephedrine by PCl_5. The hexahydro-ephedrines and -ψ-ephedrines are obtained by resolution of the nucleus-hydrogenated racemates by optically active mandelic acids or by hydrogenation of the corresponding optically active bases. The following compounds appear new: r-*hexahydroephedrine*, m p. 64—65° (*hydrochloride*, m.p. 168—169°); r-*hexahydro-ψ-ephedrine*, m.p. 63—64° (*hydrochloride*, m.p. 142—143°; *picrate*, m.p. 138—139°); (−)-*hexahydroephedrine*, m.p. 61—62° (*hydrochloride*, m.p. 202°, $[\alpha]_D^{19\cdot5}$ −11·26° in H_2O); (+)-*hexahydroephedrine*, m.p. 61—62° (*hydrochloride*, m.p. 202—203°, $[\alpha]_D^{15}$ +11·94° in H_2O); (−)-*hexahydro-ψ-ephedrine*, m.p. 87—88° (*hydrochloride*, m.p. 152—153°, $[\alpha]^{20}$ +9·05° in H_2O); (+)-*hexahydro-ψ-ephedrine*,

m.p. 86—87° (*hydrochloride*, m.p. 152—153°, $[\alpha]_D$ +8·84° in H_2O). H. W.

Synthesis of perhydrovitamin-*A*. Purification of vitamin-*A* preparations. P. KARRER and R. MORF (Helv. Chim. Acta, 1933, **16**, 625—641).—Details of work already published (this vol. 605) are given. J. W. B.

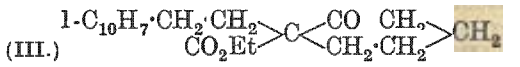
Preparation of aliphatic cholesteryl ethers and cholesterilene. E. MULLER and I. H. PAGE (J. Biol. Chem., 1933, **101**, 127—132).—Cholesterylphosphoric acid (I), m.p. 193—195°, $[\alpha]_D^{23}$ −35·64° in $CHCl_3$, when heated with the appropriate alcohol and 10% of H_2SO_4, gives *cholesteryl Me*, m.p. 84·5—85°, $[\alpha]_D^{20}$ −45·82° in $CHCl_3$, *Et*, m.p. 88·5°, $[\alpha]_D^{22}$ −39·37°, *Pr*$^{\alpha}$ (II), m.p. 100—100·5°, $[\alpha]_D^{23}$ −34·78°, and *Pr*$^{\beta}$, m.p. 132—132·5°, $[\alpha]_D^{1}$ −34·45° in $CHCl_3$, *ethers*. If heating be too long during the prep. of (II), or if cholesterol is heated with PrOH and 10% of H_2SO_4, there is formed a *substance*, $C_{54}H_{88}$, m.p. about 320°, possibly *dimeric cholesterilene*. (I) at 200° gives 40% of cholesterilene, m.p. 76—78°, $[\alpha]^{20}$ −68·99°, and a *substance*, amorphous, m.p. about 190°, possibly dicholesteryl ether. The former substance only, $[\alpha]_{\mathrm{H}}^{18}$ −77·53° (50% yield), is obtained from dicholesterylphosphoric acid (modified prep.), m.p. 203—203·5°, $[\alpha]_D^{23}$ −34·5° in $CHCl_3$. R. S. C.

Structure of the sterols and bile acids. I. M. HEILBRON, J. C. E. SIMPSON, and F. S. SPRING (J.C.S., 1933, 626—635).—A review of recent work on substances having a sp. bearing on constitutional problems related to the bile acids and sterols. J. L. D.

Ergostadienetriols. T. ACHTERMANN (Z. physiol. Chem., 1933, **217**, 281—284).—High-vac. distillation of ergostadienetriol II benzoate yields BzOH and dihydroergosterol (A), the diacetate of triol II affords AcOH and the acetate of (A), and ergostenetriol II is unchanged. When heated in C_5H_5N at 190—200°, ergostadienetriol I (*acetate*, m.p. 176—177°, decomp. begins 172°) gives (A). When a C_6H_6 solution of triol I is heated with maleic anhydride it yields triol II. Triols I and II are stereoisomeric; in I the OH-groups are probably in the *cis*- in II in the *trans*-position. J. H. B.

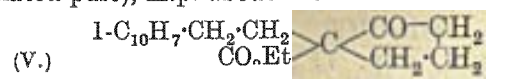
Polyterpenes and polyterpenoids. LXXXIII. Dehydrogenation of cholesterol, ergosterol, and cholic acid with selenium and palladium. L. RUZICKA, M. W. GOLDBERG, and G. THOMANN. LXXXIV. Synthesis of 1 : 2-*cyclo*pentanophenanthrene, its α- and β-methyl-derivatives, and chrysene. L. RUZICKA, L. EHMANN, M. W. GOLDBERG, H. HOSLI, and (in part) W. BOSSARD, E. SCHMID, H. WIRZ, and E. MULLER. **LXXXV. Transformation of abietic acid by oxidation into 1 : 3-dimethyl*cyclo*hexan-2-one and by dehydrogenation with palladium into retene.** L. RUZICKA and H. WALDMANN (Helv. Chim. Acta, 1933, **16**, 812—832, 833—841, 842—848; cf. this vol., 495).—LXXXIII. Polemical against Diels. Cholesterol and Pd-C at 325—340° give H_2 (4·7 mols.), CH_4 (1·2 mols.), and *hydrocarbons*, $C_{18}H_{14}$ (or $C_{18}H_{12}$), m.p. 250—255° [*compound* with 2 : 7-dinitroanthraquinone (I), m.p. 281—283°], and $C_{25}H_{24}$ or $(C_{26}H_{24})$, m.p. 220—221° after sintering at 219° [*compound*, with (I), m.p. 236—237°]; with Se, first at 280° and then at 330—360°, it gives hydrocarbons $C_{18}H_{16}$ (or $C_{17}H_{14}$), m.p. 124—125° [*compound* with (I), m.p. 151°], and $C_{25}H_{24}$ (or $C_{26}H_{24}$), m.p. 224—225° [*compound* with (I), m.p. 239—240°]. Ergosterol and Se at 330—360° give *hydrocarbons*, m.p. 126—127° after sintering at 125°, and (?) $C_{26}H_{26}$, m.p. 214—215° after sintering at 213° [*compound* with (I), m.p. 254—255°]. Cholic acid and Se at 260—340° give (?) $C_{18}H_{16}$ (II), m.p. 125° [picrate, m.p. 115°; *compounds* with $C_6H_3(NO_2)_3$ and (I), m.p. 146° and 230° (decomp.), respectively], and (?) $C_{21}H_{16}$, m.p. 345—347°. Cholatrienic acid or cholic acid and Pd-C at 300—350° give gases (CO_2 2, CO 11, CH_4 22, and H_2 65%), and hydrocarbons, including (II). Crystallographic data are given and formulæ suggested for the hydrocarbons. M.p. are corr.

LXXXIV. 1-(β-*Hydroxyethyl*)*naphthalene* (from 1-$C_{10}H_7$·MgBr and ethylene oxide), b.p. 125°/0·2 mm., gives 1-β-*bromoethylnaphthalene*, b.p. 114°/0·15 mm., which with Et *cyclo*hexanone-2-carboxylate and K in C_6H_6 at 100—110° gives *Et* 2-(β-1-*naphthylethyl*)-cyclo*hexan*-1-*one*-2-*carboxylate* (III), b.p. 208—212°/



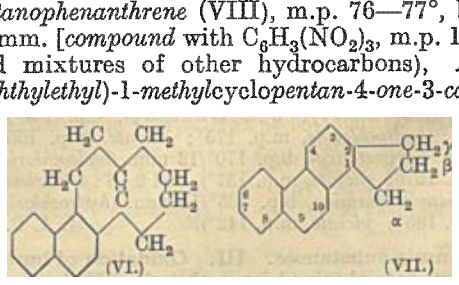
(III.)

0·3 mm. This with boiling 50% (vol.) H_2SO_4 gives *Et* *hexahydrochrysenecarboxylate* (IV), b.p. 170°/0·2 mm., m.p. 145—146°, affording with Pd at 230° chrysene [*compound* with (I), m.p. 306—307°]. *Et* 2-(β-1-*naphthylethyl*)cyclo*pentan*-1-*one*-2-*carboxylate* (V), similarly prepared, b.p. 188—189°/0·1 mm., gives with 10% KOH α-(β-1-*naphthylethyl*)*glutaric acid*, 1-$C_{10}H_7$·CH_2·CH_2·$C(CO_2H)$·$[CH_2]_3$·CO_2H, m.p. 153—154°, and with 50% H_2SO_4 the *hydrocarbon* (VI) (not isolated pure), m.p. about 100—105° and 1 : 2-cyclo-



(V.)

pentanophenanthrene (VII), m.p. 133—134° [*picrate*, m.p. 133—134°; *compounds* with $C_6H_3(NO_2)_3$ and $C_6H_2Me(NO_2)_3$, m.p. 165—166° and 101—101·5°, respectively]. Similarly were obtained *Et* 3-(β-1-*naphthylethyl*)-1-*methyl*cyclo*hexan*-2-*one*-3-*carboxylate*, b.p. 188—189°/0·1 mm., α-(β-1-*naphthylethyl*)-α'-*methylglutaric acid*, m.p. 149—150°, α-*methyl*cyclo*pentanophenanthrene* (VIII), m.p. 76—77°, b.p. 170°/0·2 mm. [*compound* with $C_6H_3(NO_2)_3$, m.p. 143—144°] (and mixtures of other hydrocarbons), *Et* 3-(β-1-*naphthylethyl*)-1-*methyl*cyclo*pentan*-4-*one*-3-*carboxylate*,



b.p. 179—181°/0·1 mm. [from Et 1-methyl*cyclo*hexan-4-one-3-carboxylate, b.p. 110—111°/14 mm. (? semicarbazone, m.p. 95°) (obtained by a Dieckmann

reaction from Et_2 β-methyladipate), and β-*methyl*-1 : 2-cyclo*pentanophenanthrene* (IX), m.p. 106·5—107° [*compound* with $C_6H_3(NO_2)_3$, m.p. 140—141°]. (VII), (VIII), and (IX) are not identical with dehydrogenation products of terpenoid substances. M.p. are corr.

LXXXV. Abietic acid (X) and alkaline $KMnO_4$ (40 O) give 1 : 3-dimethyl*cyclo*hexan-2-one (p-*nitrophenylhydrazone*, m.p. 163°; *phenylsemicarbazone*, two forms, m.p. 160—161° and 153—154°). (X) and Pd–C at 300—325° give 90% of nearly pure retene and CH_4 (1 mol.), H_2 (4 mols.), CO_2 (0·75 mol.), and CO (0·25 mol.); dehydrogenation thus proceeds mostly thus: $C_{20}H_{30}O_2 \longrightarrow C_{18}H_{18}+CH_4+CO_2+4H_2$, but partly also to give $C_{18}H_{18}+CH_4+CO+H_2O+3H_2$. The results of S and Se dehydrogenation are thus confirmed. R. S. C.

Benzonitrile. M. S. Roshdestvenski and L. A. Zepalova-Michailova (J. Appl. Chem. Russ., 1933, **6**, 274—277).—PhCN is obtained in 71% yield by the Sandmeyer reaction from PhN_2Cl and $K_2[CuNH_3(CN)_4]$. R. T.

Preparation and pyrolysis of dibenzyl ketone, phenylacetic anhydride, and diphenylacetic anhydride. C. D. Hurd, R. Christ, and C. L. Thomas (J. Amer. Chem. Soc., 1933, **55**, 2589—2592).—Phenylacetic anhydride (prepared from the acid by refluxing with Ac_2O) at 165—210°/14 mm., gives $(CH_2Ph)_2CO$ in 48—61% yield, which at 500—700° gives PhMe and a little anthracene (possibly by way of CHPh:CO). Diphenylacetic anhydride (similarly prepared), m.p. 98° (lit. 91·5—92°), at 270—285° gives CO, CO_2, CH_2Ph_2, $CHPh_2{\cdot}CO_2H$, and C_2Ph_4. Initial scission into radicals is assumed. R. S. C.

Maximum rotations of phenyl compounds. P. A. Levene and R. E. Marker (J. Biol. Chem., 1933, **100**, 685—694).—The max. rotations of the series $CHPhR{\cdot}CO_2H \longrightarrow CHPhR{\cdot}CH_2{\cdot}CO_2H \longrightarrow CHPhR{\cdot}CH_2{\cdot}OH$ (R=Me or Et) through the primary alcohols and bromides are tabulated from published vals. or calc. The following are found by resolution: l-β-*phenylbutyric acid*, $M[\alpha]_D^{25}$ −81·3°; l-α-*phenylpropionic acid*, $M[\alpha]^{25}$ −111·2°; d-α-*phenylbutyric acid*, $M[\alpha]^{25}$ +138·5°; d-β-*phenyl*-n-*valeric acid*, +84·3°. The apparent anomalies in the rotation vals. tabulated are probably connected with the distance of the functional group from the asymmetric centre (cf. this vol., 211). J. L. D.

Preparation of diarylacetic acids and their derivatives. J. Hoch (Compt. rend., 1933, **196**, 1617—1619).—$CHPhBr{\cdot}CO_2Me$ (I), $Et_2C_2O_4$, and Zn give $CH_2Ph{\cdot}CO_2Me$ (II) (40%), $CHPh(CO_2Me)_2$, and $(\cdot CHPh{\cdot}CO_2Me)_2$ (both forms). (I) and Zn in C_6H_6 (best in the proportions 1 mol. : 0·7 atom : 5—6 mols.) give (II) (25%), $CHPh_2{\cdot}CO_2Me$ (III) (40%), and some $(\cdot CHPh{\cdot}CO_2Me)_2$ (IV), m.p. 224°, the reactions assumed being: $2(I)+Zn \longrightarrow ZnBr_2+(IV)$; $(I)+C_6H_6(+ZnBr_2) \longrightarrow (III)+HBr$; $2HBr+Zn \longrightarrow ZnBr_2+H_2$; $(I)+H_2 \longrightarrow (II)+HBr$. Similar reactions occur with PhMe and PhOMe (giving *p*-derivatives). Use of $AlCl_3$ instead of Zn, and C_6H_6 or PhMe, *p*-$C_6H_4Me_2$, PhOMe, or $C_{10}H_8$ in CS_2 gives 70—80% yields of diarylacetic acids. $ZnCl_2$ gives 20% yields. $CH_2Ph{\cdot}CN$, C_6H_6, and $AlCl_3$ give a 69% yield of $CHPh_2{\cdot}CN$. R. S. C.

Asymmetric syntheses by hydrogenation with platinum-black. G. Vavon and (Mlle.) B. Jakubovicz (Compt. rend., 1933, **196**, 1614—1617).—When β-phenylcrotonic acid is esterified with the following active alcohols: menthol, neomenthol, *cis*- and *trans*-carvomenthol, β- and ε-cholestanol, the ester hydrogenated in presence of Pt-black and then hydrolysed, the resulting β-phenylbutyric acid has $[\alpha]_{5461}$ +12·0°, −4·9°, −3·2°, −1·8°, −3·0°, and −2·3°, respectively. R. S. C.

Synthesis of acyclic thiohydrazones from methylhydrazine and aromatic dithiocarboxylic acids. H. Wuyts and L. C. Kuang (Bull. Soc. chim. Belg., 1933, **42**, 153—162).—The action of a slight excess of $NHMe{\cdot}NH_2$ on aromatic dithiocarboxylic acids in warm Et_2O yields thioacylhydrazones of the general formula $R{\cdot}CS{\cdot}NMe{\cdot}N{:}CHR$. The following are described: *benzaldehyde-α-thiobenzoyl-α-methylhydrazone* (I), m.p. 124—125°; o-*tolualdehyde-α-thio-*o-*toluoyl-α-methylhydrazone*, m.p. 118—119°; 1-*naphthaldehyde-α-thio*-1-*naphthoyl*-α-*methylhydrazone*, m.p. about 159°. 2-Dithionaphthoic acid yields 2-*naphthaldehyde-α-thio*-2-*naphthoyl*-α-*methylhydrazone*, m.p. 149°, and (probably) dimeric β-thionaphthaldehyde. (I) is not hydrolysed by HCl in cold EtOH, but with 15% HCl at 80° it yields PhCHO (70% yield), $NHMe{\cdot}NH_2$,HCl, and (probably) $PhCS{\cdot}OH$. H. F. G.

Molecular rearrangements involving optically active radicals. IV. Hofmann rearrangement of the amide of an optically active 2 : 2′-disubstituted 6-carboxydiphenyl. E. S. Wallis and W. W. Moyer (J. Amer. Chem. Soc., 1933, **55**, 2598—2603; cf. this vol., 606).—*dl*-3 : 5-Dinitro-6-α-naphthylbenzoic acid, m.p. 185—187° (modified prep.; Et ester, m.p. 109°, b.p. 244—248°/1·5 mm.), is best resolved by crystallisation of the brucine salt from $COMe_2$ or $COMe_2$–$CHCl_3$, the salt of the pure *d*-acid having $[\alpha]_D^{20}$ +119·4°. The *dl*-amide with NaOBr at 70—80° gives dl-3 : 5-*dinitro*-6-α-*naphthylaniline*, m.p. 205—206°, and the d-*amide*, m.p. 157—158°, $[\alpha]_{5461}$ +37·3° in C_6H_6, gives the d-*amine*, m.p. 201—206°, $[\alpha]_{5461}$ +398° in EtOH. It follows that migration of the active group must be preceded by a loose combination of the N atom and cannot involve existence at any time of a free radical. R. S. C.

Catalytic reduction of mandelonitriles. J. S. Buck (J. Amer. Chem. Soc., 1933, **55**, 2593—2597).—Catalytic (PtO_2) hydrogenation at 50 lb. pressure in EtOH–HCl of mandelonitriles and their CO_2Et and CO_2Me derivatives gives the following substituted *phenylethylamines* in the yields stated; the m.p. in parentheses are those of the hydrochlorides and *p*-nitrobenzoyl derivatives, respectively (in italics, if the compounds are new): o-*OMe*-β-*OH*-, 59 (*184°*, *178°*); o-*Cl*-β-OH-, 41 (*197°*, *194°*); 2 : 3-$(OMe)_2$-β-*OH*-, 23·5 (*134°*, *178°*); o-*Cl*-, 94 (indef., about *204°*, *112°*); p-*NMe_2*-, 44 (decomp. 238°; *Bz* derivative, m.p. 130°); unsubstituted, from OH·CHPh·CN 8, from the CO_2Me and CO_2Et derivatives, 38 and 47, respectively (217°, *147°*); *p*-OMe-, from the nitrile 52, from the CO_2Et derivative 49 (indef. 210°; ? di-

morphic, 145° and 144°); 3 : 4-$(OMe)_2$-, 52 (151°, *147°*); p-*Cl*-, 50 [*195°* (decomp. 215°); *Bz* derivative, m.p. 147°]. Only the *o*-substituted derivatives give β-hydroxy-amines. The following *mandelonitriles* were prepared: o-*Cl*-, m.p. 47°; 2 : 3-$(OMe)_2$-, m.p. 79°; p-*Cl*-, m.p. 43°; CO_2Me, b.p. 136°/3 mm.; p-*methoxycarbomethoxy*-, b.p. 170°/2·1 mm.; and o-*chlorocarbomethoxy*-, b.p. 145°/1·4 mm. R. S. C.

Walden inversion. XII. Displacement of hydroxyl by chlorine in the optically active ethyl α-naphthylglycollates. A. McKenzie and (Miss) E. R. L. Gow (J.C.S., 1933, 705—714; cf. *ibid.*, 1911, **99**, 1910).—Interaction of (+)-α-naphthylglycollic acid (I) in Et(or Me)OH with boiling H_2SO_4 affords the ester, which suffers partial racemisation (cf. this vol., 273). The Ag salt of (I) and EtI afford *Et* (+)-α-*naphthylglycollate* (II), b.p. 203°/18 mm., $[\alpha]_{5893}$ +132·9° in $COMe_2$. Interaction of $SOCl_2$ (6 mols.) and (II) (1 mol.) in boiling Et_2O during 0·5 hr. affords 100% *Et* (+)-α-*naphthylchloroacetate*, b.p. 180—182°/7 mm., $[\alpha]_{5893}^{20\cdot7}$ +60·0° in $COMe_2$, partly racemised by heat. No change of sign occurs when $SOCl_2$, (II), and C_5H_5N react in Et_2O (cf. A., 1930, 598), although the extent of the chlorination depends on the quantities of the reactants; the reaction is hindered by excess of C_5H_5N, which forms a compound $(C_5H_5N)_2,SOCl_2$ with $SOCl_2$. Chlorination of the (−)-isomeride of (II) in $CHCl_3$ affords a Cl-compound, $[\alpha]_{5893}^{20}$ +4·0° in $COMe_2$. Hydrolysis of (II) with alcoholic KOH affords partly racemised (I). Theoretical considerations are utilised to explain these reactions. J. L. D.

Constitution of santenone and santenic acid. T. Enkvist (J. pr. Chem., 1933, [ii], **137**, 261—293).—In part a fuller description of previously published work (cf. this vol., 273). 2-*Hydroxy*-5-*methyl*cyclo*pentane*-1 : 4-*dicarboxylic acid*, m.p. 159—161° [not 2 : 3-$(OH)_2$-], is reduced by HI to *iso*santenenic acid. *trans*-Santenic acid is converted at 320° into santenic anhydride (I). The "isomeride," m.p. 104—106°, of α-santenol is santenone alcohol (cf. A., 1907, i, 1062). The constitution of santenone (II) is proved by the following relationships with santenic acid. Reduction of (I) with Ni–H_2 gives *santolide*, m.p. 41—42°, b.p. 141—148°/26 mm., which is converted by KCN into *homosantenonitrile*, m.p. 103°, also prepared from (II) by the action of $(CN)_2$ on its Na enolate (IV) followed by hydrolysis (cf. A., 1879, 329); this is hydrolysed by conc. HCl to *homosantenic acid* (III), m.p. 164·5—165·5° (*Et_2* ester, b.p. 147—148°/15 mm.). Interaction of (IV) with CO_2 gives *santenonecarboxylic acid*, m.p. 109°, the *Et* ester, b.p. 151—156°/23 mm., of which is converted by NaOEt into the Et_2 ester of (III). Distillation of the *Ca* salt of (III) gives (II). H. A. P.

Absorption in the ultra-violet of some β-arylacrylic acids and their derivatives. (Mlle.) R. M. da Costa (Compt. rend., 1933, **196**, 1815—1817; cf. this vol., 63).—Introduction of α- and β-Me into β-anisyl- and β-piperonyl-acrylic acids shifts the absorption curves towards the ultra-violet and reduces the intensity of absorption. Modification of the CO_2H group produces little change, except that α-substituted amides are more transparent. The following are described: β-*methyl*-, m.p. 163° (*Et* ester, b.p. 188—189°/13 mm., m.p. 50—51°; *amide*, m.p. 122°), and αβ-*dimethyl*-β-*piperonyl*-, m.p. 117—118°, and -β-*anisyl-acrylic acid*, m.p. 112—113°, β-*methyl*-, m.p. 145°, and α-*methyl*-β-*anisyl*-, m.p. 160°, and α-*methyl*-β-*piperonyl-acrylamide*, m.p. 157°, and β-*piperonylacrylonitrile*, m.p. 88°. A. A. L.

Reaction between malonic acid and naphthols in presence of zinc chloride. R. Sudzuki (Sci. Rep. Tôhoku, 1933, **22**, 176—181).—Fusion of 1 mol. of α-$C_{10}H_7$·OH with 1 mol. of $CH_2(CO_2H)_2$ (I) and 3 mols. of $ZnCl_2$ at 160—170° affords the *lactone*, m.p. 275° (decomp.), of 1-hydroxy-2-naphthoylacetic acid (II) (*Ag* salt), together with 1 : 2-OH·$C_{10}H_6$·COMe, also obtained by hydrolysis of (II) with 10% KOH, or by heating its Ag salt at 200—250°. Contrary to Witt (A., 1888, 486), β-$C_{10}H_7$·OH does not react with AcOH in presence of $ZnCl_2$, but with (I) the *lactone*, m.p. 275°, of 2-hydroxy-1-naphthoylacetic acid (*Ag* salt) is obtained and is similarly converted into 2 : 1-OH·$C_{10}H_6$·COMe. J. W. B.

Phthaloylation. G. B. Crippa and P. Galimberti (Gazzetta, 1933, **63**, 81—96).—*o*- (I), *m*-, and *p*-Phthalimidobenzoic acids with HNO_3 (*d* 1·42) and H_2SO_4 give 5-*nitro*-2- (identified through *p*-NO_2·C_6H_4·NH_2), 6-*nitro*-3-, and 3-*nitro*-4-*phthalimidobenzoic acids*, m.p. 263°, 285°, and 300°, respectively; 5-*nitro*-2-β-*naphthylamine*- and 5-*nitro*-2-β-*naphtholazobenzoic acids* have m.p. 232° and > 325°, respectively. A *sulphonic acid* is prepared from (I). 3-*Phthalimidoacenaphthene*, m.p. 229°, with AcOH and $Na_2Cr_2O_7$ yields the corresponding *-quinone*, m.p. 319° [condenses with *o*-$C_6H_4(NH_2)_2$], and, on prolonged boiling, 4-*phthalimidonaphthalic acid*, hydrolysed (KOH) to 4-*benzamidonaphthalene*-1 : 8 : 2′-*tricarboxylic acid* (re-condenses at 200°) and (HCl) to 4-aminonaphthalic acid. 3 : 4-Diaminoacenaphthene and phthalic anhydride form phthaloaceperinone (A., 1911, i, 960) and 3 : 4-*diphthalimidoacenaphthene*, which are oxidised to *phthaloaceperinonedicarboxylic acid* and 4 : 5-*diphthalimidonaphthalic acid*, respectively; the last three all have m.p. > 300°. 3 : 3′-Dinitrobenzidine with phthalic anhydride forms 3 : 3′-*dinitro*-4 : 4′-*diphthalimidodiphenyl*, m.p. > 310°, reduced (Fe + AcOH) to the 3 : 3′-*diamino*-compound, which when heated in Ac_2O gives 1 : 2 : 1′ : 2′-*bis*-*o*-*benzoylene*-5 : 5′-*dibenziminazolyl*, m.p. > 300°, hydrolysable to the *dicarboxylic acid*. 2 : 2′-*Dinitro*-4 : 4′-*diphthalimidodiphenyl*, m.p. > 300°, is prepared and reduced to the $(NH_2)_2$-compound. *Me*, m.p. 113°, Et, *Pr*$^{\alpha}$, m.p. 105°, and *Bu*$^{\beta}$, m.p. 64°, *phthalimidoacetates* are prepared from the acid, and, from the first, *phthalimidoacetamide*, m.p. 261°, which when heated with phthalic anhydride did not further condense. E. W. W.

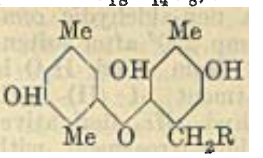
Steric hindrance in the Hoesch reaction. II. M. Yamashita (Sci. Rep. Tôhoku, 1933, **22**, 167—175).—Condensation of phloroglucinol (I) with *m*-$C_6H_4(CN)_2$ in the presence of HCl–Et_2O and $ZnCl_2$ (Hoesch, A., 1915, i, 820) gives, after hydrolysis, 2 : 4 : 6-*trihydroxybenzophenone*-3′-*carboxylic acid*, m.p. 269—270·5°. With resorcinol (II) *p*-$C_6H_4(CN)_2$

similarly affords 2 : 4-*dihydroxybenzophenone-4'-carboxylic acid*, m.p. 293°, but with (I) a mixture of 2 : 4 : 6-*trihydroxybenzophenone-4'-carboxylic acid*, m.p. 240·5—242°, and 2 : 4 : 6 : 2' : 4' : 6'-*hexahydroxy*-p-*dibenzoylbenzene*, m.p. above 360°, is obtained. As in the case of the corresponding NO_2-compounds (A., 1928, 1136), *o*-$C_6H_4(CN)_2$ does not react, but with $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ all three isomerides react. Thus *o*-$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ with (II) gives 2 : 4-*dihydroxyphenyl* o-*cyanobenzyl ketone*, m.p. 173·5—174°, and with (I) affords 2 : 4 : 6-*trihydroxyphenyl* o-*cyanobenzyl ketone*, sinters 238°, decomp. 240·5° (hydrolysed by 70% aq. KOH to homophthalic acid), and, in small yield, a *substance* $C_{15}H_{11}O$-, m.p. 255·5° (corresponding 2'-CO_2H derivative less $1H_2O$). With (II) *m*-$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ affords 2 : 4-*dihydroxyphenyl* m-*cyanobenzyl ketone*, m.p. 170—170·5°, and with (I), m-2 : 4 : 6-*trihydroxyphenacylbenzoic acid*, m.p. 273°, is obtained. Similarly, *p*-$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ and (I) give 2 : 4 : 6-*trihydroxyphenyl* p-*cyanobenzyl ketone*, m.p. 248·5—249°. J. W. B.

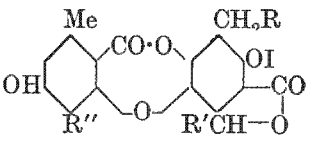
Preparation of dibenzoyl-*d*-tartaric acid. C. L. Butler and L. H. Cretcher (J. Amer. Chem. Soc., 1933, **55**, 2605—2606).—The prep. is modified to give a 93% yield. R. S. C.

Constitution of caperatic acid. I. M. Asano and Z. Ohta (Ber., 1933, **66**, [*B*], 1020—1023).—Extraction of *Parmelia caperata*, L., with Et_2O at room temp. affords usnic acid, m.p. 200—203°, $[\alpha]_D^0$ +470·4° in $CHCl_3$, (?) capraric acid, decomp. about 260° after darkening at 240°, and caperatic acid (I), $C_{21}H_{38}O_7$ (instead of $C_{22}H_{38}O_8$), m.p. 132—133·5°, $[\alpha]_D^0$ −3·85° in $CHCl_3$, which does not give a colour with $FeCl_3$, does not reduce $KMnO_4$ or react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. *Me*$_2$ *caperatate*, m.p. 56·5—57·5° [from (I) and CH_2N_2], gives a *Cl*-compound, m.p. 52—53°, with $SOCl_2$ and is hydrolysed by KOH–EtOH to norcaperatic acid (II), $C_{20}H_{36}O_7$, m.p. 138—139°, and palmitic acid (anilide, m.p. 90·5°). (II) is also obtained by hydrolysis of (I). Treatment of (II) with conc. H_2SO_4 at 100° leads to Me pentadecyl ketone, m.p. 47—48° (semicarbazone, m.p. 126·5—127°). Thermal fission of (II) at 155—160° followed by reduction of the product and treatment with NH_2Ph at 220° yields (?) *methyltetradecylsuccinanil*, m.p. 63·5—64·5°. H. W.

Lichen substances. XXIII. Salazic acid. II. Y. Asahina and J. Asano. **XXIV. Methyl norbarbatate.** Y. Asahina and T. Tukamoto (Ber., 1933, **66**, [*B*], 893—897, 897—899; cf. this vol., 713).—XXIII. The compound (I) $C_{18}H_{14}O_7$ [second reduction product of salazic acid (*loc. cit.*)] is converted by boiling 50% KOH in H_2 atm. into *hyposalazinol* (II), $C_{16}H_{18}O_5$, m.p. 197° [*Me*$_3$ *ether*, (III), m.p. 146°], converted by KOH at 250—300° into β-orcinol (IV) and 3 : 5-dihydroxy-*p*-toluic acid (V). Hydrogenation of (II) (Pd–C in AcOH) affords *deoxyhyposalazinol* (VI), $C_{16}H_{18}O_4$ [*Me*$_3$ *ether*, m.p. 95°, also obtained by hydrogenation of (III)]. (IV) is not transformed into (V) by fusion with KOH, so that reductive fission of the ether linking is assumed during the treatment of (II). (II) and (VI) are therefore formulated according to *A* (R=OH and H, respectively), whereas (I), the first reduction product $C_{18}H_{14}O_8$, and salazic acid have the structure

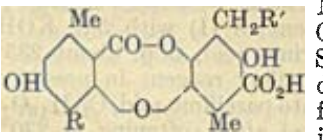


(*A*.)



(*B*.)

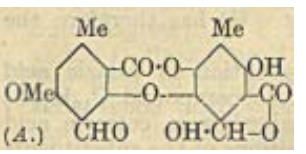
B (R=R'=H, R''=Me: R=H, R'=OH, R''=Me: R=R'=OH, R''=CHO, respectively). Since the reduction product (VII), $C_{18}H_{16}O_7$, from cetraric acid (VIII) is smoothly converted by 50% KOH into (VI) the formulæ *C* (R=Me, R'=H: R=CHO, R'=OEt, respectively) are assigned to (VII) and (VIII).



(*C*.)

XXIV. Catalytic hydrogenation (Pd–C in AcOH) converts atranorin into *Me norbarbatate* (I), m.p. 134° (decomp.), converted by incomplete action of CH_2N_2 into the Me_2 ether, m.p. 123°, identical with Me *O*-methylbarbatate of Robertson *et al.* (A., 1932, 850) and converted by KOH–EtOH into rhizonic acid and Me *iso*rhizonate. Protracted action of CH_2N_2 on (I) affords the Me_3 ether, m.p. 107°, identical with Me *O*-methyldiffractaate. H. W.

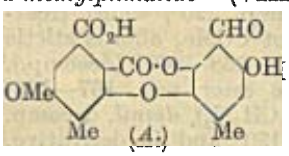
Lichen substances. XXV. Stictic acid. Y. Asahina, M. Yanagita, and T. Omaki. **XXVI. Psoromic acid.** Y. Asahina and H. Hayashi. **XXVII. Transformation of salazic acid into a derivative of cetraric acid.** Y. Asahina and J. Asano (Ber., 1933, 66, [*B*], 943—947, 1023—1030, 1031).—XXV. Extraction of the thalli of *Lobaria pulmonaria* from Central Japan with warm Et_2O yields gyrophoric acid (I), m.p. 220°, whilst treatment of the residue with hot $COMe_2$ affords stictic acid (II), $C_{19}H_{14}O_6,2H_2O$, m.p. 268—269° (decomp.), containing 1 OMe. The *Me* ester, m.p. 167—168° (obtained by short action of CH_2N_2), *dianil*, decomp. about 165° after softening at 130°, and Ac_4 derivative, m.p. 221—222°, are described. (II) is converted by dry distillation into *atranol Me ether*, m.p. 78°, prepared also from atranol, Ag_2O, and MeI in $COMe_2$. Catalytic reduction (Pd–C) of (II) gives the *substance* (III) $C_{19}H_{16}O_8$, decomp. 263—264°, the Me_2 derivative of which is identical with the Me_3 derivative of the first reduction product of salazic acid. Treatment of (III) with AcOH and Zn dust affords the *compound* $C_{19}H_{16}O_7$, m.p. 264° (decomp.), the Me derivative of which is identical with the Me_2 derivative of the second reduction product of salazic acid. (II) is therefore *A*. Extraction of the same lichen from South Sakhalin failed to yield (II) but gave (I) and an *acid* $C_{23}H_{34}O_5$, m.p. 298°, converted by CH_2N_2 in Et_2O–$COMe_2$ into the *Me* ester, m.p. 144°, which with Ag_2O and MeI affords its *Me ether*, m.p. about 110°.



(*A*.)

XXVI. Extraction of the thalli of *Alectoria sulcata*, Nyl, with Et_2O yields atranorin and psoromic (sulcatic) acid (I), $C_{18}H_{14}O_8$, m.p. 265° (decomp.)

after becoming discoloured at 262° (*anil*, decomp. 299°; *triacetate*, m.p. 198—199°). Catalytic reduction (Pd–C) of (I) leads to a non-aldehydic *compound* (II), $C_{18}H_{16}O_7,H_2O$, decomp. 230° after softening and darkening above 160°, from which H_2O is not removed at 110°. Treatment of (II) with CH_2N_2 in Et_2O gives the anhyd. Me_2 derivative, m.p. 200°, transformed by short treatment with KOH–MeOH into the *phenol* $C_{21}H_{24}O_8$, m.p. 153° (? opening of lactone ring), which when further methylated affords a neutral *substance* $C_{22}H_{26}O_8$, m.p. 136—137°. Treatment of (I) with 5% KOH at room temp. yields parinic acid, m.p. about 235° (decomp.), whereas the boiling reagent in presence of Na_2SO_3 transforms (I) into parellinic acid, C_1-$H_{16}O_7$, m.p. about 240 (decomp.) after softening at 230°. Dry distillation of (I) leads to atranol and 3-*hydroxy*-5-*methoxy*-4-*methylphthalic anhydride* (III), m.p. 206°, transformed by short action of CH_2N_2 in Et_2O into 3 : 5-*dimethoxy*-4-*methylphthalic anhydride*, m.p. 166°, and by boiling MeOH into *Me H* 3-*hydroxy*-5-*methoxy*-4-*methylphthalate* (IV), m.p. 189°. Short treatment of (IV) with CH_2N_2 in Et_2O at 0° affords Me_2 3-*hydroxy*-5-*methoxy*-4-*methylphthalate*, m.p. 117°, whereas prolonged action gives rise to Me_2 3 : 5-*dimethoxy*-4-*methylphthalate* (V), m.p. 67°, hydrolysed to 3 : 5-*dimethoxy*-4-*methylphthalic acid* (VI), m.p. 189—190°. Treatment of (III) with boiling HI (*d* 1·7) leads to 3 : 5-dihydroxy-*p*-toluic acid, m.p. 262° [*Me* ester, m.p. 190°; Me 3 : 5-dimethoxy-*p*-toluate (VII), m.p. 105°]. Treatment of (VII) with $CCl_3{\cdot}CH(OH)_2$ in 90% H_2SO_4 gives 3 : 5-*dimethoxy*-4-*methyltrichloromethylphthalide*, m.p. 134°, converted by 15% NaOH at 80° into 3 : 5-*dimethoxy*-4-*methylphthalidecarboxylic acid*, m.p. 175°, which loses CO_2 when heated above its m.p. and yields 3 : 5-*dimethoxy*-4-*methylphthalide* (VIII), m.p. 155°. (VIII) is oxidised by $KMnO_4$ and 15% KOH to 3 : 5-dimethoxy-4-methylphthalic acid, identical with (VI) [Me_2 ester identical with (V)]. The possibility that (III) is 5-hydroxy-3-methoxy-4-methylphthalic anhydride is excluded, since (III) gives in EtOH a solution with pale bluish-green fluorescence greatly accentuated by addition of a trace of alkali, but discharged by further addition. 3-Hydroxyphthalic anhydride is precisely similar in its behaviour, whereas the 5-OH compound is non-fluorescent. (I) has therefore the constitution *A*.



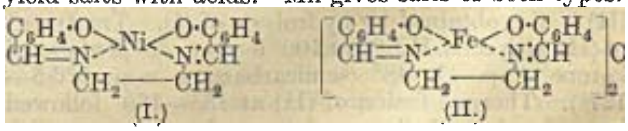
(A.)

XXVII. Catalytic hydrogenation of salazic acid (I) leads in poor yield to the compound $C_{18}H_{16}O_7$ (Me_3 ether, m.p. 170°) obtained from cetraric acid (II). The skeletons and positions of the substituents in (I) and (II) are therefore identical. H. W.

Decompositions and reactions of carbamide. I. Reactions of carbamide with hydrazines, aldehydes, ketones, etc. J. M. Das-Gupta (J. Indian Chem. Soc., 1933, **10**, 111—115).—The reaction between $CO(NH_2)_2$ (I) and PhCHO (II) at 150—160° is formulated, (I)+(II) $\longrightarrow$ OH·CHPh·NH·CO·NH_2 $\longrightarrow$ $CHPh<^{NH\cdot CO}_{NH\cdot CO}>NH+H_2O$, and similarly *p*-*dimethylamino*-, m.p. 264°, and *o*-*hydroxy*-, not melting below 280°, -*benzylidenebiuret* are obtained: (I) and COPhMe at 180—185° afford *methylbenzylidenecarbamide*, m.p. 176°. Since condensation of substituted hydrazines (III) with (I) (Pinner, A., 1887, 1042) also occurs at 100° in H_2O the reaction is probably between (III) and HNCO. Dinitrohalogenobenzenes and -phenols readily afford the corresponding NH_2-derivative when heated with (I) at 200°, and thus are obtained 2 : 4-, 2 : 6-, 3 : 5-, m.p. 158°, and 2 : 5-, m.p. 137°, -dinitroaniline. J. W. B.

Benzylbenzaldoxime. E. Wertheim (J. Amer. Chem. Soc., 1933, **55**, 2540—2543).—*p*-Benzoylbenzoic acid, m.p. 197—200° (rapid heating) (modified prep.), with HI and red P at 160—170° gives *p*-benzylbenzoic acid, m.p. 159—160°, whence were prepared successively the acid chloride, b.p. 193°/8 mm., *amide*, m.p. 172—173°, and nitrile, m.p. 50—52°. The nitrile, by a modified Stephen reaction, gives p-*benzylbenzaldehyde*, b.p. 189—190°/14 mm. (slight sweet taste) [syn-*oxime*, m.p. 89—91° (slight sweet taste) (*acetate*, m.p. 64—66°)]. Analogies of taste and m.p. between *p*-disubstituted benzene and 2 : 5-furan compounds are noted. R. S. C.

Tricyclic *ortho*-condensed co-ordinate valency rings. P. Pfeiffer, E. Breith, E. Lübbe, and T. Tsumaki (Annalen, 1933, **503**, 84—130).—Co-ordinate ring compounds are classified on the basis of the no. and arrangement of co-ordinate linkings in the ring. *o*-Hydroxy-aldehydes and -ketones condense with $C_2H_4(NH_2)_2$ or o-$C_6H_4(NH_2)_2$ and Ni salts to form co-ordinated compounds of type (I), in general sol. in org. solvents and stable to alkalis but not to acids. Similar compounds are given by Cu and other bivalent metals, and in the case of Cu the ring may be extended, *e.g.*, by use of the polymethylenediamines, *m*- (but not *p*-)$C_6H_4(NH_2)_2$, or benzidine. With Fe basic compounds of type (II) are formed which readily yield salts with acids. Mn gives salts of both types.



The following complex *salts* are described: $C_2H_4(NH_2)_2$ derivatives: salicylaldehyde {*Ni* (I), *Cu*, *Fe*^{III} *oxide* (II) [*acetate*, *benzoate* (dimorphous), *mandelate*, d-*camphor*-β-*sulphonate*, *chloride*, d-α-*bromocamphor*-α-*sulphonate*], *Mg*, *Zn* (+0·5$C_2H_8N_2$), *Cd*, *Co*, and *Mn*^{II} salts (+1$C_2H_8N_2$) (oxidised by O_2 in $CHCl_3$ to *hydroxide* [$C_{16}H_{14}O_2N_2Mn^{III}$]OH)}; 2-hydroxy-5-carboxybenzaldehyde {*Ni* salt [NH_4 salt (+0·25H_2O); stable to acids, loose to alkalis, gives ppts. with $BaCl_2$ and KCl]}; 2-hydroxy-4-carboxybenzaldehyde {*Ni* salt [NH_4 salt (+2H_2O)]}; resorcylaldehyde [*Ni* (*Bz* derivative) and *Cu* salts]; *o*-hydroxyacetophenone (*Ni*, *Cu* salts, and *Fe*^{III} *oxide*); resacetophenone [*Ni* (+1H_2O) (*Bz* and *phenylacetyl* derivatives) and *Cu* salts]; pæonol (*Ni* and *Cu* salts); quinacetophenone [*Ni* salt (+2H_2O) (*Bz* derivative)]; 2 : 4-dihydroxybenzophenone {*Ni* salt (+3H_2O) [*Me ether* (+0·8 dioxan)]}; 5-hydroxyxanthone [*Ni* salt (+2C_5H_5N)]; 1-hydroxyanthraquinone [*Ni* salt (+2C_5H_5N); the ethylenedi-

imine compound could not be prepared]; 2-hydroxy-1-naphthaldehyde (*Cu* salt); NH_3 derivatives: resacetophenone (*Ni* salt); 1-hydroxyanthraquinone [*Ni* salt (anhyd., $+2H_2O$)]; *Cu* salts of salicylaldehyde-propylenedi-imine, and -tri-, -tetra-, -penta-, and -deca-methylenedi-imines, -*o*-toluylene-, -*m*-phenylene-, and -4 : 4′-diphenylyl-di-imines: salicylaldehyde-*o*-phenylenedi-imine (*Ni* and *Cu* salts): *ferric acetylacetone*, and the *Cd* ($+1C_5H_5N$ and free) and *Co* salts of *o*-OH·C_6H_4·CHO. *o*-Hydroxyacetophenone (III) and $C_2H_4(NH_2)_2$ in presence of $Mn(OAc)_2$ give the Mn-free *di-imine*, m.p. 195°. The *Cu* and *Ni* ($+4H_2O$) salts, and the β-*aminoethylimine*, m.p. 122°, and *anil*, m.p. 113°, of benzylidene-*o*-hydroxyacetophenone (IV) are described. Action of $Ni(OAc)_2$ or $Cu(OAc)_2$ on (IV) gives the complex salts of (III), the CHPh group being hydrolysed away. p′-*Chlorobenzylidene*-o-*hydroxyacetophenone*, m.p. 150°, behaves similarly. H. A. P.

Alkoxyaldehydes. L. Palfray, S. Sabetay, and M. Rotbart (Compt. rend., 1933, **196**, 1508—1510).—CH_2Br·$CH(OEt)_2$ and the Na derivatives of cyclanols at 180° in absence of solvent give OR·CH_2·$CH(OEt)_2$, which are hydrolysed by aq. 1% H_2SO_4–AcOH to the alkoxyaldehydes (purified through their semicarbazones). The following are described: cyclo*hexyloxyacetaldehyde*, b.p. 71°/14 mm. [*acetal*, b.p. 115°/12 mm.; *semicarbazone*, m.p. 175° (all m.p. are on Maquenne block)]; 2-, b.p. 85—88°/12 mm. (*acetal*, b.p. 124—126°/18 mm.; *semicarbazone*, m.p. 152—152·5°), 3-, b.p. 84—86°/14 mm. (*acetal*, b.p. 120—121°/12 mm.; *semicarbazone*, m.p. 175°), and 4- (*acetal*, b.p. 125—126°/12 mm.; *semicarbazone*, m.p. 187—188°) -*methyl*cyclo*hexyloxyacetaldehydes*. H. B.

Reactions catalysed by aluminium chloride. V. Compounds formed by the condensation of *cyclo*hexane and acetyl chloride. C. D. Nenitzescu and J. Chicos (Ber., 1933, **66**, [*B*], 969—971).—Re-examination of the fraction, b.p. 160—200°, of the product formed from *cyclo*hexane and AcCl in presence of $AlCl_3$ and comparison of the consts. of the ketones in question confirms the absence of ketones with 6-membered ring in appreciable amount. Physical consts. are recorded for the following: stable 2-acetyl-1-methyl*cyclo*pentane, b.p. 169·5° (corr.)/755 mm. (semicarbazone, m.p. 167°); 2-acetyl-1-methyl-Δ^1-*cyclo*pentene, b.p. 189—190° (corr.)/760 mm. [semicarbazone, m.p. 220—221° (decomp.)]; labile 2-acetyl-1-methyl*cyclo*pentane, b.p. 63°/16·5 mm. (semicarbazone, m.p. 166·5—167°); acetyl-Δ^1-*cyclo*hexene, b.p. 201—202° (corr.)/760 mm., [semicarbazone, m.p. 220—221° (decomp.)]; *cyclo*hexyl Me ketone, b.p. 179·5—180·5° (corr.)/755 mm., (semicarbazone, m.p. 174°). H. W.

Acetylenic carbinols from optically active 3-methyl*cyclo*hexanone and their conversion into unsaturated ketones. H. Rupe, R. Haecker, E. Kambli, and N. Wassieler (Helv. Chim. Acta, 1933, **16**, 685—700).—3-Methyl-1-ethinyl*cyclo*hexanol (I) (A., 1928, 297) (*Bz*, m.p. 39°, and p-NO_2·C_6H_4·*CO*, m.p. 84—85°, derivatives) with Ac_2O–B_2O_3 affords its *borate*, hydrolysis of which gives the pure solid form of (I). Heated with 86% HCO_2H (I) (mixture of solid and liquid forms) gives a mixture of ketones, fractional crystallisation of the semicarbazone, m.p. 205°, of which gives a *semicarbazone* (II; 75%), m.p. 213°, and a *semicarbazone* (III; 25%), m.p. 195·5°, together with 3-methyl*cyclo*hexanonesemicarbazone. From (II) is obtained a *ketone* (IV), b.p. 89·2°/9 mm. $[\alpha]_D^{20}$ +183·2° (*oxime*, m.p. 81°), which consists mainly of 5-methyl-Δ^1-*cyclo*hexenyl Me ketone, since it is reduced (H_2–Ni) to 3-*methyl*-cyclo*hexyl Me ketone* (V), b.p. 75°/10 mm. $[\alpha]_D^{20}$ +1·83° [*semicarbazone*, m.p. 166° (identical with a specimen prepared from active 3-methyl*cyclo*hexanone by Darzens' method, A., 1907, i, 627)], and on ozonolysis in CCl_4 affords β-methyladipic acid together with a small yield of ε-keto-*n*-heptoic acid, indicating the presence of a little of the Δ^5-isomeride in (IV). From (III) is obtained a *ketone* (VI), b.p. 87·5°/9 mm., $[\alpha]_D$ +97·93°, which appears to be a mixture of (IV) and the Δ^6-isomeride. With O_3 (VI) gives AcOH and a methyladipic acid, and with $KMnO_4$ a similar mixture of α- and β-methyladipic acids is obtained from which the anilide of the α-acid is isolated. Catalytic reduction of (VI) gives (V). With MgEtBr (IV) gives 2-*ethyl*-5-*methyl*cyclo*hexyl Me ketone*, b.p. 81°/14 mm., $[\alpha]_D^{20}$ +100·3° (*semicarbazone*, m.p. 182—186°), a little 5-*methyl*- -cyclo*hexenylmethylethylcarbinol*, b.p. 95°/11 mm., and (mainly) (?) β-(5-*methyl*-Δ^1-cyclo*hexenyl*)-Δ^β-n-*butene*, b.p. 76°/11 mm., $[\alpha]_D$ +64·51°. J. W. B.

Reaction of some carbonyl and thiocarbonyl compounds with phenylhydrazine. L. C. Raiford and W. T. Daddow (Proc. Iowa Acad. Sci., 1931, **38**, 171). Ch. Abs.

Polyhalogen derivatives of acetophenone. M. Jastrzebski and J. Suszko (Rocz. Chem., 1933, **13**, 293—297).—*o*-$C_6H_4Cl_2$ and chloroacetyl chloride yield in the presence of $AlCl_3$ ω : 3 : 4-*trichloroacetophenone* (I), m.p. 43°, b.p. 171—173°/15 mm. (*oxime*, m.p. 119°). 3 : 4-*Dichloro*-ω-*bromoacetophenone* (II), m.p. 58°, b.p. 180°/15 mm. (*oxime*, m.p. 122°), is prepared by brominating 3 : 4-dichloracetophenone (*oxime*, m.p. 107°). The oximes of (I) and (II) yield by the Beckmann transformation respectively 3 : 4-*dichloro*-*chloro*-, m.p. 105°, and -*bromo*-, m.p. 103°, -*acetanilide*. (I) and (II), but not their oximes, irritate the skin and mucous membranes. R. T.

Preparation of β-chloropropiophenone [and its homologues]. C. F. H. Allen, H. W. J. Cressman, and A. C. Bell (Canad. J. Res., 1933, **8**, 440—446).—The prep. of CH_2Bz·CH_2Cl from BzCl, C_2H_4, and $AlCl_3$ (good quality or + 1% of $FeCl_3$) in EtBr is modified and the apparatus described. A yield of 87—92% is obtained. The following *p*-substituted β-*chloropropiophenones* are prepared from CH_2Cl·CH_2·CO_2H in the yield given in parentheses: *F*-, m.p. 50° (60); *Cl*-, m.p. 48° (38); *Br*-, m.p. 35° (35); *Me*-, m.p. 75° (80); *Et*-, m.p. 55° (69); *MeO*-, m.p. 55° (60); *EtO*-, m.p. 45° (82); *PhO*-, m.p. 62° (99); Ph-; 3 : 4-Me_2-, m.p. 68° (60). R. S. C.

Uranium tetrachloride, tungsten hexachloride, and molybdenum pentachloride in organic syntheses. L. I. Kaschtanov (J. Gen. Chem. Russ.,

1933, **3**, 229—233).—The chlorides of U, W, and Mo behave like $TiCl_4$ in promoting reaction between C_6H_6 and $CH_2Ph{\cdot}OEt$ (I). UCl_4 and C_6H_6 give 21—22% yields of $COPhMe$ and $COPh_2$ with AcCl and BzCl, respectively, and with (I) $CHPh_2$ and p-$C_6H_4(CH_2Ph)_2$; with $CH_2Ph{\cdot}OBz$ *m*- and p-$C_6H_4(CH_2Ph)_2$; no reaction takes place with *iso*amyl benzoate or acetate. WCl_6 and C_6H_6 give $COPh_2$ with BzCl and *m*- and p-$C_6H_4(CH_2Ph)_2$ with (I); $MoCl_5$ also promotes the latter reaction. G. A. R. K.

Ketoneimine dyes and their derivatives. D. F. J. Lynch and J. D. Reid (J. Amer. Chem. Soc., 1933, **55**, 2515—2520).—4 : 4′-Tetramethyldiaminothiobenzophenone, best prepared by boiling $CH_2[C_6H_4{\cdot}NMe_2(p)]_2$ and S in $C_{10}H_8$, is converted by NH_3 and NH_4Cl in boiling $C_{10}H_8$ (10% yield) or liquid NH_3 in dry EtOH at 100° (17% yield) into auramine base (I), also obtained from phenylauramine and liquid NH_3 in dry EtOH at 100° (50% yield) or (method *A*) from Michler's ketone by $POCl_3$ in hot PhMe, followed by liquid NH_3 at 100° (75% yield). 4 : 4′-*Tetraethyldiaminobenzophenoneimine* (II), similarly prepared (50% yield by *A*), has m.p. 67—68°. $COPh_2$ and $POCl_3$, followed by liquid NH_3 in hot PhMe, give benzophenoneimine (*benzoate*, m.p. 182°). 4 : 4′-*Tetraethyldiaminothiobenzophenone*, m.p. 158°, prepared from 4 : 4′-tetraethyldiaminobenzophenone (III), $POCl_3$, and S, gives with NH_2OH,HCl the *oxime*, m.p. 135°, of (III), also prepared directly from (III). The following are prepared : *anthranilate*, m.p. 172°, p-*toluate*, m.p. 147°, *salicylate*, m.p. 205°, 3 : 5-*dinitrobenzoate*, m.p. 198°, p-*hydroxybenzoate*, m.p. 184°, and *benzoate*, m.p. 156°, of (I); *benzoate*, m.p. 191°, p-*toluate*, m.p. 175°, and *anthranilate*, m.p. 168°, of 4 : 4′-diaminobenzophenoneimine; *hydrochloride*, m.p. 262°, *benzoate*, m.p. 155°, *anthranilate*, m.p. 157°, *salicylate*, m.p. 170°, and p-*toluate*, m.p. 158°, of (II). R. S. C.

Preparation of disubstituted fluorenones by the action of heat on the corresponding substituted diphenic acids or their derivatives. E. H. Huntress and I. S. Cliff (J. Amer. Chem. Soc., 1933, **55**, 2559—2567).—Diazotised 6-chloroanthranilic acid and ammoniacal Cu^I NH_4 sulphite give 3 : 3′-*dichlorodiphenic acid* (I), m.p. 304—305° (decomp.) [*anhydride* (II), m.p. 257—258°], which with conc. H_2SO_4 at 125° gives 1 : 6-*dichlorofluorenone*-5-*carboxylic acid* (III), m.p. 242·5° (*chloride*, m.p. 180—181°; *amide*, m.p. 281°), which at 350° gives 1 : 6-*dichlorofluorenone* (IV), m.p. 218—219° [*oxime*, m.p. 230° (decomp.)]. (II) at 310° gives 1 : 8-*dichlorofluorenone* (V), m.p. 254° [*oxime*, m.p. 217° (decomp.)], and (in one experiment) a little of a *substance*, m.p. 218—219°. Heating (I) above its m.p. gives (IV) and (V), and in single, separate experiments, small amounts of (III) and 3 : 3′-*dichlorodiphenyl*-1-*carboxylic acid*, m.p. 152·5°. 5 : 5′-Dichlorodiphenic anhydride is stable at 310°, but at 400° gives 3 : 6-*dichlorofluorenone*, m.p. 301° [*oxime*, m.p. 237° (decomp.)]. All m.p. are uncorr. R. S. C.

Fluorene group. Syntheses of ketones and hydrocarbons derived from 2-benzyl- and 2-benzoyl-fluorene. K. Dziewonski, M. Dominikówna, L. Gałuszkówna, and L. Muz (Rocz. Chem., 1933, **13**, 283—292; cf. A., 1930, 1586).—2 : 7-*Dibenzoylfluorenedioxime*, m.p. 235°, gives by the Beckmann transformation 2 : 7-*dibenzamidofluorene*, m.p. 316°, also prepared by benzoylating 2 : 7-diaminofluorene, which on diazotisation and coupling with β-$C_{10}H_7{\cdot}OH$ yields *fluorene*-2 : 7-*bisazo*-(1 : 1′)-β-*naphthol*, m.p. 185°. 7-*Aceto*-2-*benzylfluorene*, m.p. 130—131° [*phenylhydrazone*, m.p. 195° (decomp.); *oxime*, m.p. 164—165°], is obtained from 2-benzylfluorene and AcCl in CS_2 in the presence of $AlCl_3$. 7-*Benzoyl*-2-*benzylfluorene*, m.p. 126—127°, b.p. 340—350°/15 mm. (*oxime*, m.p. 180—182°, yielding 7-*benzamido*-2-*benzylfluorene*, m.p. 215—216°, by the Beckmann change), is prepared analogously, and yields on oxidation 2 : 7-dibenzoylfluorene (I), which on reduction with Na in $C_5H_{11}{\cdot}OH$ gives 2 : 7-*dibenzyltetrahydrofluorenone*, m.p. 90—91°. 2 : 7-Dibenzylfluorene, prepared by reducing (I), or by condensing fluorene with CH_2PhCl in presence of $AlCl_3$, yields 7-nitro-2-benzoylfluorene on nitration. R. T.

Steric hindrance in the acyl*cyclo*pentanone series. (Mlle.) S. Grateau (Compt. rend., 1933, **196**, 1619—1621).—2-*p*-Toluoyl*cyclo*pentanone and MgEtBr give approx. equal quantities of 2-α-p-*tolylpropylidene*cyclo*pentanone*, $CH_2{-}CO$ / $CH_2{\cdot}CH_2$ >C:CEt·C_6H_4Me (I), and Δ¹-1-p-*toluoyl*-2-*ethyl*cyclo*pentene*, $CH_2{\cdot}CH_2$ / $CH_2{\cdot}CEt$ >C·CO·C_6H_4Me (II), b.p. of both 175°/20 mm. (I) is hydrolysed during the reaction to *p*-tolyl Et ketone (III) and *cyclo*pentanone; when oxidised by $KMnO_4$ (I) gives (III) and glutaric acid, whilst (II) gives terephthalic, *p*-toluic, and δ-keto-*n*-heptoic (IV) acids. 2-2′ : 5′-Dimethylbenzoyl*cyclo*pentanone and MgEtBr, owing to steric hindrance, give only p-*xylyl* Δ¹-2-*ethyl*-1-cyclo*pentenyl ketone*, b.p. 174°/15 mm., oxidised to 4-methyl*iso*phthalic and 3 : 5-dimethylbenzoic acids, (IV), $C_6H_3Me_2{\cdot}CO{\cdot}CO_2H$, and probably αβζ-*triketo*-n-*octyl*-p-*xylene* (giving a mixture of *di*- and *tri*-*semicarbazones*). R. S. C.

Anionotropic and protropic changes in cyclic systems. I. Hydroxy*cyclo*pentenones. H. Burton, C. W. Shoppee, and C. L. Wilson (J.C.S., 1933, 720—731).—$COMePr^\beta$ (p-*nitrophenylhydrazone*, m.p. 103·5°) and Bz_2 (cf. *ibid.*, 1901, **79**, 1038) afford 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (I) (2 : 4-*dinitrophenylhydrazone*, m.p. 217—218°), which is not acetylated in the normal manner, but with Pt–H_2 in AcOH at 60° affords the *dihydro*-derivative, m.p. 120·5°, and 4-*acetoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone*, m.p. 128—129° [hydrolysed to (I)], which with boiling Ac_2O–H_2SO_4 affords 2-acetoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ³-*cyclo*pentenone (II) (cf. *ibid.*, 1909, **95**, 2131), as does (I) with boiling Ac_2O during 20 hr. (II) with hot 1·45*N*-NaOEt or $COMe_2$–HCl affords 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (III) (cf. J.C.S., 1909, **95**, 2131) [2 : 4-*dinitrophenylhydrazone*, m.p. 194—195°; 2 : 4-*dinitrophenylosazone*, (IV), m.p. 243°], the acetate (V) of which is hydrolysed to (III). (III) with NaOMe and MeI affords the 2-OMe-derivative [2 : 4-*dinitrophenylhydrazone* (VI),

m.p. 234°]. Similarly prepared, 2-*ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone* has m.p. 70·5—71° [2 : 4-*dinitrophenylhydrazone* (VII), m.p. 205°], which (together with the OMe compound) is converted into (III) by boiling 50% H_2SO_4. (II) in 96% EtOH with H_2–Adams' catalyst at 15° affords 3(or 4)-*cyclo*hexyl-4(or 3)-phenyl-5 : 5-dimethyl*cyclo*pentanone (an oil) [2 : 4-*dinitrophenylhydrazone*, m.p. 194°, also obtained from the reduction product of (V)]. Reduction of (I) with boiling AcOH–Zn affords 3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone* (VIII), m.p. 95—96° [2 : 4-*dinitrophenylhydrazone*, m.p. 246° (decomp.); *benzylidene* derivative m.p. 160—161°], also obtained from (I) or (II) with boiling HI. (VIII) is reduced (Clemmensen) to an oil (*semicarbazone*, m.p. 224°, isomeric with 3 : 4-diphenyl-5 : 5-dimethyl*cyclo*pentanonesemicarbazone, m.p. 230°) together with 1 : 2-*diphenyl*-3 : 3-*dimethyl*cyclo*pentane*, a high-boiling oil. Oxidation of (II) with CrO_3–AcOH at room temp. affords BzOH, αβ-oxido-αβ-diphenyl-γγ-dimethylglutaric acid (IX) [previously obtained (J.C.S., 1903, **83**, 306) by oxidation of (I)] and 2-*hydroxy*-3 : 4-*oxido*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-cyclo*pentanone*, m.p. 124° (*semicarbazone*, m.p. 159—160°). With O_3 in AcOH (II) affords BzOH and a *substance*, m.p. 132°. (II) with 2 : 4-dinitrophenylhydrazine sulphate in EtOH (or MeOH) affords 2-*ethoxy*- (X), m.p. 182° (decomp.), and 2-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone*, m.p. 196° (decomp.), respectively, different from (VI) and [(XI), see below]. (X) differs from (VII). The evidence of the 2 : 4-dinitrophenylhydrazones supports the mechanism advocated for these interconversions. (I) when boiled with EtI and Ag_2O for 140 hr. affords 4-*ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*, m.p. 80—80·5°, which with 2 : 4-dinitrophenylhydrazine sulphate in EtOH affords a *compound*, $C_{25}H_{22}O_5N_4$, m.p. 204° (decomp.), which contains no OEt and may be the 2 : 4-dinitrophenylhydrazone of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone. Similarly, (I) with boiling MeI in 10 days affords 4-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*, m.p. 148° [2 : 4-*dinitrophenylhydrazone* (XI), m.p. 196° (decomp.)]. $COEtPr^{\beta}$ (p-*nitrophenylhydrazone*, m.p. 133·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 109—109·5°) and Bz_2 afford 4-hydroxy-3 : 4-diphenyl-2 : 5 : 5-trimethyl-Δ^2-*cyclo*pentenone (J.C.S., 1901, **79**, 1039) [2 : 4-*dinitrophenylhydrazone*, m.p. 184—185° (decomp.)], which with boiling Ac_2O–H_2O affords 3 : 4-*diphenyl*-5 : 5-*dimethyl*-2-*methylene*-Δ^3-cyclo*pentenone*, m.p. > 290°, ozonised to CH_2O, BzOH, and a ketonic substance. (I) with boiling $SOCl_2$ during 0·5 hr. affords 4-chloro-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone (XII), m.p. 133° (cf. this vol., 67) [2 : 4-*dinitrophenylhydrazone*, m.p. 197° (decomp.)], and 2-*chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone* (XIII), m.p. 126—127°. (XII) is fairly resistant to 2% alcoholic KOH, whilst 2*N*-KOH converts it into (III). (XII), AgOAc, and boiling AcOH afford (II). (XII) with AgOAc and boiling MeOH in 10 min. affords a mixture of isomerides, m.p. 125—135° (lit., 144°), from which 4-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone (see above) can be isolated; the other compound is probably 2-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone. (XII) with AgOAc and boiling EtOH affords no (I), but the product contains OEt [*bisdinitrophenylhydrazone*, m.p. 245°, isomeric with (IV); *dinitrophenylhydrazone*, m.p. 252°]. (XIII) gave identical results. (VIII) and Cl_2 at 100° afford (XIII) together with 3(or 4)-*phenyl*-4(or 3)-p-*chlorophenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*, m.p. 121°.



(XII.) (XIII.)

(XII) or (XIII) with boiling Ac_2O or PhCN during 1—2 hr. affords a *compound* (XIV) m.p. 300°, oxidised by $KMnO_4$ in warm $COMe_2$ to the anhydride of (IX). Mesityl oxide is also isolated as its 2 : 4-*dinitrophenylhydrazone*, m.p. 201°, and arises from the $COMe_2$. The formation of (XIV) supports the view that (XII) and (XIII) form a mobile anionotropic system. J. L. D.

Carvacrol. I. 5-Acetocarvacrol. II. 3-Acetocarvacrol. H. John (J. pr. Chem., 1933, [ii], **137**, 351—364, 365—376).—I. The yields of 5-acetocarvacrol (I) (*acetate*, m.p. 66°) obtained by the Friedel–Crafts reaction and from carvacryl acetate and $AlCl_3$ are only approx. 40% and 23%, respectively (cf. A., 1928, 1010). With HNO_3 (*d* 1·4) in AcOH at —5° to 0° (I) gives the 3-NO_2-derivative (II), m.p. 157° [*acetate*, m.p. 75° (from EtOH), 95° (from C_6H_6); *Me*, m.p. 66°, *Et* (III), m.p. 90°, iso*amyl*, m.p. 73°, and *benzyl*, m.p. 103°, *ethers*], which on further nitration gives the 3 : 6-$(NO_2)_2$-derivative, m.p. 55°. Reduction of (II) with Sn and HCl or, better, alkaline $Na_2S_2O_4$ gives the 3-NH_2-compound, m.p. 100° [*hydrochloride*, m.p. 199—200° (decomp.); N-*Ac* derivative, m.p. 144° (6-NO_2-derivative, m.p. 162°); *oxazole*, m.p. 46° (HCO_2H); *Et ether* (IV), m.p. 57° (N-*Ac* derivative, m.p. 76°) {reduction of (III)}]. Diazotisation of (IV) and subsequent heating at 135—145° in presence of much H_2SO_4 gives 3-*hydroxy*-2-*ethoxy*-5-*aceto*-p-*cymene*, m.p. 88°.

II. In the prep. of (I) by the Friedel–Crafts reaction 3-*acetocarvacrol* (V), m.p. 100° (*acetate*, b.p. 293°; ω-*CHPh*: derivative, m.p. 104°), is also formed. Its proportion of the total reaction product is increased slightly by use of more $AlCl_3$ and considerably by addition of PCl_3 or $POCl_3$; in presence of $POCl_3$ and a little $MgCl_2$ it reaches 56%. Nitration as above gives 5-NO_2-, m.p. 151° (*acetate*, m.p. 87°; *Et ether*, m.p. 43°), and 5 : 6-$(NO_2)_2$-, m.p. 119°, -derivatives. The 5-NH_2-derivative, m.p. 117° [N-*Ac* derivative, m.p. 120° (*Et ether*, m.p. 148°); Ac_2 derivative, m.p. 96°], is also prepared as before. Condensation of (V) with isatin in 33% aq. KOH gives 6′-*hydroxy*-2-*phenyl*-5′-*methyl*-2′-iso*propylquinoline*-4-*carboxylic acid*, m.p. 288° (decomp.). H. A. P.

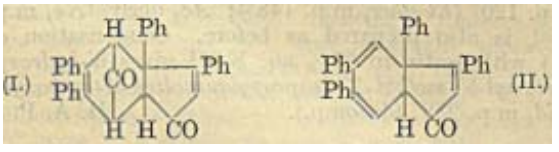
Condensation of phenols with benzotrichloride in presence of sodium hydroxide. C. Hamada (Sci. Rep. Tohoku, 1933, **22**, 55—60).—PhOH (2 mols.) in aq. NaOH condenses with 1 mol. of $Ph·CCl_3$ to give a 14·5% yield of *o*-hydroxybenzophenone and some PhOBz. Similarly with *o*- and *p*-cresols are obtained 4-hydroxy-3- (22% yield,

with *p*-tolyl benzoate and BzOH) and 2-hydroxy-5-methyl- (33·2% yield) -benzophenone, whereas *m*-cresol affords 2- (7·4% yield) and 4-hydroxy- (6·2% yield) -2-methylbenzophenone, separated by steam-distillation. J. W. B.

Action of phosphorus pentachloride on indan-1 : 3-dione. W. H. HUNTER and R. E. JACKMAN (J. Amer. Chem. Soc., 1933, **55**, 2567—2570).—Indan-1 : 3-dione (modified prep.) and PCl_5 give 1 : 1 : 3-tri- and 1 : 1 : 3 : 3-*tetra-chloroindane*, m.p. 104—105·5° [readily hydrolysed, *e.g.*, by NaOEt or NaOH–EtOH, to 1 : 1 : 3-*trichloroindene*, m.p. 77—78° (*Br*$_x$-derivative, m.p. 92—94°)], a little 3 : 3-*dichloroindone*, m.p. 85—86° [*oxime*, m.p. 190—191° (decomp.) after sintering at 178—182°], and other products. R. S. C.

Synthesis of substances related to the sterols. I. Derivatives of chrysene. G. R. RAMAGE and R. ROBINSON (J.C.S., 1933, 607—610).—Me meso-$\beta\gamma$-diphenyladipate (I) (A., 1930, 1435) in hot H_2SO_4 (cf. A., 1927, 1084) affords *trans*-2 : 11-diketo-1 : 2 : 9 : 10 : 11 : 18-hexahydrochrysene (II) (*bis-semicarbazone*, m.p. 352°), which with EtOH–HCl does not afford Et diphenyladipate (cf. A., 1931, 1407). (II) is reduced by Zn–Hg and HCl to trans-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*, m.p. 115° (different from the hexahydrochrysenes described in A., 1931, 1407), and dehydrogenated by Se to chrysene (III). The *r*-form of (I) similarly affords the *cis*-form of (II), reduced to cis-*hexahydrochrysene*, m.p. 75°, and dehydrogenated to (III). Et (or Me) 4-methoxycinnamate in moist Et_2O with Al–Hg affords β-anisylpropionic ester and *Et*, m.p. 110°, or *Me* $\beta\gamma$-*dianisyladipate*-a, m.p. 153°, hydrolysed to the *acid*, m.p. 250°, which affords a chloride, m.p. 162°, cyclised by $AlCl_3$ in $C_2H_2Cl_4$ to 2 : 11-*diketo*-5 : 14 - *dimethoxy* - 1 : 2 : 9 : 10 : 11 : 18 - *hexahydro* - *chrysene*-a, m.p. 285°, which with Zn–Hg, conc. HCl, and anisole affords 5 : 14-*dimethoxy*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 185°. J. L. D.

Structure of the diketone obtained from anhydroacetonebenzil [4-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone]. C. F. H. ALLEN and E. W. SPANAGEL (Canad. J. Res., 1933, **8**, 414).—The compound, $C_{34}H_{24}O_2$, described by Japp and Burton (J.C.S., 1887, **51**, 426; cf. this vol., 67), is probably (I), and arises by "dien"-addition of 2 mols. of 3 : 4-diphenyl*cyclo*pentadienone. When it is heated (cf. *loc. cit.*), CO is eliminated and the ketone (II) or 2 : 3 : 5 : 6-tetraphenylhydrindone (III) is pro-



duced; (III) results when (II) is heated for a longer time or to a higher temp. The structure of (III) is determined by a series of degradation reactions ultimately giving *o*-$C_6H_4Ph_2$. Tetraphenyl*cyclo*pentadienone and maleic anhydride give an adduct containing an *endo*-CO group. H. B.

Benzoylphenacylcarbinol. H. W. DUDLEY and S. OCHOA (J.C.S., 1933, 625—626).—Prep. of phenylglyoxal (I) by Riley's method (A., 1932, 833) also affords *benzoylphenacylcarbinol*, m.p. 98° (II) (*Ac* derivative, m.p. 120°) [also obtained by interaction of (I) and boiling COPhMe], which is not oxidised to the tetraketone. (II), NH_2OH,HCl and $BaCO_3$ in EtOH afford some diphenacyldioxime, m.p. 206—208° (cf. A., 1889, 147); with NH_2OH and K_2CO_3, some diphenacyl is obtained. J. L. D.

Composition of the mother-liquor of the dimethyl acetal of α-hydroxy-β-methoxy-β-phenylpropiophenone. R. RANKIN (Trans. Kansas Acad. Sci., 1932, **35**, 158—160). CH. ABS.

Synthesis of derivatives of 4′-amino-2 : 4 : 6-trimethoxybenzophenone. Improved synthesis of 4′-amino-2 : 4 : 6-trimethoxybenzophenone. M. YAMASHITA (Sci. Rep. Tôhoku, 1933, **22**, 156—162).—Reduction of 4′-nitro- to 4′-amino-2 : 4 : 6-trimethoxybenzophenone (I) is best effected by NaHS in hot EtOH. By the Sandmeyer reaction (I) affords the corresponding 4′-*CN*-derivative, m.p. 171—172°, hydrolysed by KOH–EtOH to the 4′-*CO*$_2$*H*, m.p. 233—235°. By diazotisation and treatment with EtO·CS_2K and hydrolysis of the product with KOH–EtOH (I) gives the 4′-*SH* compound, m.p. 161—163°. J. W. B.

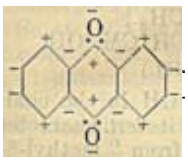
Action of zinc chloride on 4′-amino-2 : 4 : 6-trimethoxybenzophenone. M. YAMASHITA (Sci. Rep. Tôhoku, 1933, **22**, 163—166).—When 4′-amino-2 : 4 : 6-trimethoxybenzophenone is heated with anhyd. $ZnCl_2$ and a little H_2O at 134—138° the products are *s*-$C_6H_3(OMe)_3$ (I), *p*-NH_2·C_6H_4·CO_2H (II), and NH_2Ph (III). At 210—230° or fused with $ZnCl_2$, no (II) is obtained, the yield of (III) being increased. Some demethylation of (I) also occurs. J. W. B.

Constitution of so-called aromatic *o*-hydroxyazo-compounds. A. BURAWOY and I. MARKOWITSCH (Annalen, 1933, **503**, 180—202).—1 : 2-Naphthaquinone-2-phenylhydrazone (I) ("benzeneazo-α-naphthol") has an absorption spectrum totally different from that of β-benzeneazo-α-naphthol Me ether (II), but very similar to 1 : 2-naphthaquinone-2-diphenylhydrazone in an indifferent solvent; in conc. H_2SO_4, however, the spectra are similar owing to formation of the salt [$^+$NHPh:N·$C_{10}H_6$·OR]X$^-$. Analysis of the absorption spectra of (I) and (II) in hexane and MeOH confirms the quinonoid structure of (I) and the azoic structure of (II). Similar methods are applied to 1 : 2-naphthaquinone-1-phenylhydrazone, its -8-carboxylic acid, and -8-nitrile, and -1-α-naphthylhydrazone, *o*-benzoquinonephenylhydrazone, and *o*-toluquinonephenylhydrazone. 1 : 2-Naphthaquinone-2-phenylmethylhydrazone could not be prepared (cf. J.C.S., 1909, **95**, 1809). H. A. P.

Acenaphthenequinonesulphonic acids. K. DZIEWOŃSKI and S. PIASECKI (Bull. Acad. Polonaise, 1933, **A**, 108—115).—Oxidation of Na acenaphthene-3-sulphonate with $Na_2Cr_2O_7$ in AcOH at 105° affords *Na acenaphthenequinone-3-sulphonate* (*phenylhydrazone*), which with PCl_5 at 190—200° gives 7 : 7-*dichloro*-

8-ketoacenaphthene-3-sulphonyl chloride, m.p. 191°, whilst its $NaHSO_3$ additive *compound* condenses with β-hydroxythionaphthen (I) in NaOH to give *Na 2-thionaphthen-8′-acenaphthene-indigo-3′-sulphonate* $C_6H_4<^{CO}_{S}>C{:}C<^{CO}_{C_{10}H_5\cdot SO_3Na}$ Similar oxidation of Na acenaphthene-1-sulphonate affords *Na acenaphthenequinone-1-sulphonate* (II) (*NH_2Ph* salt, darkens at 200°, not melting at 400°; *phenylhydrazone*), separated as its $NaHSO_3$ additive *compound* (III) from a small amount of the *anhydride* of 2-sulphonaphthalene-1 : 8-dicarboxylic acid (*phenylhydrazone* of Na salt), and converted by PCl_5 into two isomeric 7(or 8)-*dichloro*-8(or 7)-*ketoacenaphthene-1-sulphonyl chlorides* (*a*-chloride, m.p. 194—195°, *b*-chloride, m.p. 180°). With (I), (III) gives *Na 2-thionaphthen-8′-acenaphthene-indigo-1′-sulphonate*. With *o*-$C_6H_4(NH_2)_2$ (II) gives *Na acenaphthaphenazine-1-sulphonate*, $C_6H_4<^{N:C}_{N:C}>C_{10}H_5\cdot SO_3Na$. J. W. B.

Constitution and reactivity. VII. Theory of substitution in anthraquinone. K. Lauer (J. pr. Chem., 1933, [ii], **137**, 161—178).—The substitution and oxidation reactions of anthraquinone are expressed by the annexed formula. β-Sulphonation is then normal, α-sulphonation in presence of Hg being the result of prior entry of Hg into the α-position. α-Nitration is not abnormal (unpublished work). Substitution by an anionoid residue activates the substituted nucleus and further substitution is homonuclear. Progressive weakening of the anionoid character of the substituent leads to progressive increase in 4-substitution instead of 2-substitution. This is evident in the nitration of 1-aminoanthraquinone and its acyl derivatives (cf. this vol., 395); a similar behaviour is shown by NH_2Ph and a series of acylanilides from acids of increasing strength. A cationoid substituent inactivates the nucleus it occupies and leads to heteronuclear substitution; the disubstituted product then resists further substitution, and vigorous attack by reagents results in replacement of substituents, oxidation (as in the disulphonic acids; cf. this vol., 277), or destruction of the mol. A cationoid residue in the 1-position weakens the polar character of the 9-CO group and strengthens that of the 10-CO group; in the 2-position it exercises the reverse effect. Fresh experimental evidence in support of this is provided by the sulphonation of 1-$C_{14}H_7O_2\cdot SO_3H$ in absence of Hg [68% 1 : 6-, 32% 1 : 7-$(SO_3H)_2$] and of 2-$C_{14}H_7O_2\cdot SO_3H$ in presence of Hg [41% 1 : 6-, 59% 1 : 7-$(SO_3H)_2$], the nitration of 1- and 2-$C_{14}H_7O_2\cdot SO_3H$ and of 1- and 2-$C_{14}H_7O_2\cdot NO_2$, and by the sulphonation in presence of Hg of 1-$C_{14}H_7O_2\cdot NO_2$. H. A. P.



Synthesis of anthraquinones occurring in nature. P. C. Mitter (J. Indian Chem. Soc., 1933, Ray No., 285—292).—Various methods (lit.) are summarised. H. B.

Potassium atractylate and the work of Wunschendorff and Braudel. T. Ajello (Gazzetta, 1933, **63**, 289—296).—The formula of the above authors (A., 1931, 1341) is criticised, and the following equation suggested for acid hydrolysis of K atractylate: $C_{30}H_{48}O_{18}S_2K_2+4H_2O\longrightarrow 2C_5H_{10}O_2+2KHSO_4+C_6H_{12}O_6+C_{14}H_{22}O_4$. If hydrolysis is prolonged the amount of valeric acid formed decreases. E. W. W.

Constitution of tasmanol. V. M. Trikojus and D. E. White (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 279—283).—Tasmanol (cf. Robinson and Smith, B., 1915, 1270) appears to be an acid, $C_{13}H_{22}O_3$, containing OMe and forming a *p*-toluidide, m.p. 88—89°. F. R. S.

Constituents of the kawa root. XIII. Substances from technical kawa resin. W. Borsche and B. K. Blount (Ber., 1933, **66**, [*B*], 803—806; cf. A., 1932, 748).—The purified resin is hydrolysed with 3*N*-NaOH. The cold solution deposits crude Na kawaate (I) mixed with "neutral resin" (II), a further portion of which is obtained by extraction with Et_2O. *N*-AcOH ppts. the "solid acids" (III) from the alkaline solution at 0°, whilst subsequent addition of *N*-H_2SO_4 causes separation of the "resinous acids" (IV). (I) yields kawaic (V), dihydrokawaic (VI), methystic (VII), and dihydromethystic (VIII) acids. (III), m.p. 115—117° after softening at 100°, consists mainly of (V) and (VI) contaminated with (VII) and (VIII) and containing ψ-kawaic acid mixed with ψ-methystic acid. (IV) decomposes when distilled in vac., evolving CO_2; the distillate deposits a little *p*-methoxycinnamic acid, but consists mainly of liquids which give red, ill-defined ppts. with 2 : 4-dinitrophenylhydrazine. (II) is amorphous, but contains a small amount of cryst. material, m.p. 135°. When distilled in vac. it yields (*a*) a liquid resembling physiologically Lewin's "α-resin" and yielding a *dinitrophenylhydrazone*, $C_{15}H_{14}O_6N_4$ or $C_{15}H_{12}O_6N_4$, m.p. 228—229°; (*b*) a gelatinous fraction which deposits stearyl alcohol, m.p. 59°, and (*c*) a yellowish-brown syrup from which separates a saturated *alcohol* of the sterol group, $C_{23}H_{40}O$, m.p. 133°, $[\alpha]_D$ −36·6° in $CHCl_3$. The active principle of kawa is presumed to be present in (II). H. W.

Ouabain. II. Degradation of *iso*ouabain. W. A. Jacobs and N. M. Bigelow (J. Biol. Chem., 1933, **101**, 15—20; cf. A., 1932, 856).—*iso*Ouabain (I) with Ac_2O and $ZnCl_2$ gives resins, but with Ac_2O and H_2SO_4 at 70° affords CH_2O and an *acetyltrianhydrohydroxylactone* (II), $C_{24}H_{28}O_3$, m.p. 244—246°, $[\alpha]_D$ −22·7° in C_5H_5N (neutralises 2 equivs. of hot NaOH), which with hot 0·5*N*-NaOH gives a *hydroxytrianhydrolactone* (III), $C_{22}H_{26}O_4$, m.p. 256—258°, $[\alpha]_D^{25}$ +29·1° in C_5H_5N (possibly, therefore, rearranged), hydrolysed by alkali to an oily acid, the *Me* ester, $C_{23}H_{30}O_5$, m.p. 214—216° (decomp.), $[\alpha]_D^{23}$ +1·6° in C_5H_5N, of which is oxidised by CrO_3 to the *Me* ester, $C_{23}H_{26}O_5$, m.p. 210—213°, $[\alpha]_D^{23}$ +172·5° in C_5H_5N, of a *ketoanhydrolactone*. (II) absorbs 3 mols. of H_2 in AcOH, but it and (III) resist hydrogenation in EtOAc. Previous analyses are confirmed and the presence of the following grouping in (I) is proved.

CH_2—CH·CHMe·CH·
CO·O·CH— O—C< R. S. C.

Elemic acid from manila-elemi resin. VII. Methyl ether and bromo-derivatives of α-elemolic and α-elemonic acids. H. Lieb and M. Mlade-

NOVIĆ [with A. REŽEK and M. SOBOTKA] (Monatsh., 1933, **62**, 232—240; cf. this vol., 278).—Elemolic acid or its Ac derivative with 4% H_2SO_4 in MeOH at the b.p. gives *α-elemolic acid Me ether* (I), m.p. 242° (*Ac* derivative, m.p. 224°), by addition of MeOH at the double linking. This is confirmed by the action of Br, which gives an OMe-free *Br*-compound, $C_{30}H_{49}O_3Br$, m.p. 219°, and of HBr, which gives a similar *Br*-compound, m.p. 234°. The OMe group is, however, unaffected by conc. aq. alkali. Oxidation of (I) with CrO_3 in AcOH gives *α-elemonic acid Me ether*, m.p. 282° (*oxime*, m.p. 243°). Bromination of α-elemonic acid in $CHCl_3$ gives a Br_2-derivative (II), m.p. 235°, also obtained by oxidation of dibromoelemolic acid. *Bromo-α-elemonic acid*, m.p. 273°, is similarly obtained from bromo-α-elemolic acid (III) (*Ac* derivative, m.p. 260°), or by action of KOH in MeOH on (II). Hydrogenation of (III) (Pd–C in EtOH) gives dihydro-α-elemolic acid, m.p. 238°; similarly (IV) gives *dihydro-α-elemonic acid*, m.p. 291°. H. A. P.

Oxidation product of α-elemolic acid. M. MLADENOVIĆ (Bull. Soc. Chim. Yougoslav., 1933, **4**, 31—36).—α-Elemolic acid yields on oxidation (CrO_3 in AcOH) α-and β-elemonic acids; the latter, which is an unsaturated keto-acid, is identical with Ruzicka's δ-elemic acid (A., 1932, 750), and was probably present in the original resin. R. T.

Saponin series. IV. Saponin of *Fatsia japonica*, decne et plane. M. KOTAKE, K. TAGUCHI, and T. OKAMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 100—103).—The roots gave α-, $C_{42}H_{72}O_{16}$, m.p. 250—253°, hydrolysed to hederagenin, and β-*prosaponin*, $C_{41}H_{68}O_{13}$ or $C_{42}H_{70}O_{13}$, m.p. 260—261°, hydrolysed to panaxsapogenin. The leaves yielded only the β-compound. F. R. S.

[**Sapotalin.**] E. SPATH (Helv. Chim. Acta, 1933, **16**, 624).—A reply to Ruzicka (this vol., 69). Prior independent investigation of sapotalin is claimed (A., 1932, 603). J. W. B.

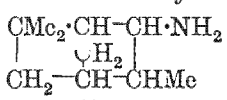
[**Sapotalin.**] L. RUZICKA (Helv. Chim. Acta, 1933, **16**, 625).—A reply to Spath (preceding abstract). J. W. B.

Sulphur compounds of terpenes. V. Action of sulphur on various types of monoterpene hydrocarbons. A. NAKATSUCHI (J. Soc. Chem. Ind. Japan, 1933, **36**, 254—255B).—Δ^3-*p*-Menthene when heated with S gives a compound, $C_{10}H_{18}S$, which with $AuCl_3$ forms $C_{10}H_{18}SAu$, m.p. 92—96°. Menthene similarly affords $C_{10}H_{18}SAu$, decomp. 170°; α-phellandrene and terpinolene yield *p*-cymene, whilst linaloolene behaves like linalyl acetate. F. R. S.

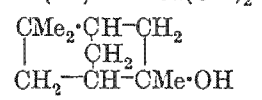
Reaction of sulphur with terpenes, and the use of this reaction for the preparation of a solution of gold. P. BUDNIKOV (Compt. rend., 1933, **196**, 1898—1899).—With MeI the derivative $C_{10}H_{16}S$ (I) (A., 1922, i, 944; best obtained by the action of N_4S_4 on terpenes) affords a small yield of the *methiodide* which forms stable complexes with metallic chlorides. The prep. of Au solutions for ceramics (Au, 12—16%) from (I) and $KAuCl_4$ in MeOH is described. J. W. B.

Chlorinated derivatives of cineole. A. GANDINI (Gazzetta, 1933, **63**, 151—159).—Cineole with Cl_2 in CCl_4, in presence of $CaCO_3$ and H_2O, and in sunlight, forms 2-*chlorocineole*, b.p. >200° (decomp.), 78—80°/3 mm., which is not easily hydrolysed or reduced, and is oxidised ($KMnO_4$) to terebinic, teracemic, homoterpenilic, and terpenilic acids. E. W. W.

Fenchene series. III. γ-Fenchene and β-fenchene hydrate. G. KOMPPA and S. BECKMANN (Annalen, 1933, **503**, 130—142; cf. A., 1929, 1076).—Hydration of γ-fenchene (I) (*nitrosate*, decomp. 146—147°) with H_2SO_4–AcOH gives *iso*fenchyl acetate. An *adduct*, m.p. 165—170° (decomp.: sinters 145°), is given by (I) with PhN_3; δ-fenchene is inert under the conditions studied. The *nitrosochloride* of (I), m.p. 150° (decomp.) (EtO·NO and HCl in MeOH), is reduced by Zn and AcOH to β-fenchene (identified by oxidation to β-fenchocamphorone and β-hydroxyfenchenic acid), a *base* (*chloroplatinate*), probably (II), an *azine*, $C_{20}H_{30}N_2$, m.p. 115—116°, and *β-fenchene hydrate* (III), m.p. 66·5—67·5° (*phenylurethane*, m.p. 101—102°; *p*-NO_2·C_6H_4·COCl gives fenchene and *p*-NO_2·C_6H_4·CO_2H). (III) is also obtained from *iso*fenchyl chloride (IV) and $Ca(OH)_2$ or



(II.)



(III.)

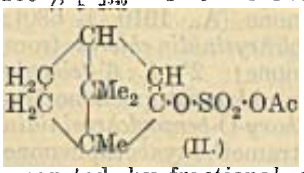
NaOH at 70°, or with Na and EtOH in the cold. Its formula is assigned on account of its *tert.* character and mode of formation. It differs from "methyl-β-fenchocamphorol" of the same formula (cf. Komppa and Roschier, A., 1918, i, 445) and is probably a stereoisomeride. It is also obtained from β- and *cyclo*fenchene hydrochlorides with $Ca(OH)_2$; the latter would be expected to give α-fenchene, and it is supposed that the addition of HCl to *cyclo*fenchene gives an equilibrium mixture of two chlorides. Na and warm EtOH convert (IV) into a *difenchane*, b.p. 194—196°. H. A. P.

Action of Japanese acid clay on terpene compounds. III. Dimerisation of camphene. T. KUWATA (J. Soc. Chem. Ind. Japan, 1933, **36**, 256—258B).—Camphene is dimerised by Japanese acid clay in C_6H_6 to *dicamphene*, b.p. 176—178°/15 mm. (*hydrochloride*, m.p. 68·5—69°). F. R. S.

Preparation of camphor by dehydrogenation of borneol and *iso*borneol using metallic catalysts. F. K. SIVOV, M. M. KOROTAEVA, and M. P. KOTSCHNEVA (J. Chem. Ind. Russ., 1933, No. 3, 52—56).—Cu is not a satisfactory catalyst for conversion of borneol (I) or *iso*borneol into camphor (II); max. yields of (II) (68—84%) are obtained at 220—240°, using 5—8% of Cu. Ni catalyst gives 85% yields of (II), containing ≯ 3% of (I); using 2% of Ni the reaction is complete at 260° in 5 hr., the greater part of (I) being converted during the first 2 hr. The catalyst loses about 2% of its activity during each operation, and this amount of fresh Ni should be added before repeating the process. R. T.

Acetylsulphate and hydrogen sulphate of camphor. FREREJACQUE (Compt. rend., 1933, **196**

1513—1515).—Dilution of the Ac_2O–H_2SO_4 mother-liquors from the prep. of *d*-camphor-10-sulphonic acid with H_2O gives (cf. Reychler, A., 1899, i, 445) camphor (I) and a mixture (*A*) of the *compound* (II), m.p. about 150° (then blackens and decomp. about 160°), $[\alpha]_{546}^{20}$ −32·5° in $CHCl_3$, −29·1° in EtOH, and its dl-*isomeride* (III), m.p. about 167° (decomp.); (*A*) is separable from (I) through its sparing solubility in light petroleum, whilst (II) and (III) are separated by fractional crystallisation from EtOH.



(II.)

(II) is hydrolysed by H_2O at 100° to AcOH and the amorphous *H sulphate* (IV) (II, OAc=OH), $[\alpha]_5^{25}$ −40° in H_2O, an aq. solution of which when heated for a long time at 100° or for several hr. at 125° gives a dextrorotatory solution [probably owing to isomerisation of (IV) to a sulphonic acid]. Hydrolysis (cold EtOH–KOH; dil. aq. alkali at 100°) of (II) affords a sulphonic acid, $[\alpha]_{546}$ +57·5° (calc.) in H_2O. (IV) and Ac_2O give (II). H. B.

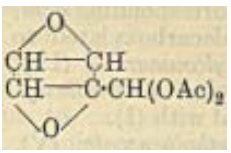
Dehydrogenation of the sesquiterpenes of *Wintera colorata*. J. Melville (J. Amer. Chem. Soc., 1933, **55**, 2462—2465).—This oil (a mixture) absorbs 4 H in presence of Pd. With Pd at 200°, Se at 260°, or S (< 1 mol.) at 250°, 2, 3, and 5%, respectively, of azulene (I) (picrate, m.p. 121°) (? guiazulene) are formed; with Br, I, or anhyd. $CuSO_4$ (I) is not formed. With > 1 mol. of S cadalene is also obtained. R. S. C.

Amber. L. Schmid and A. Erdos (Annalen, 1933, **503**, 269—276).—Amber is separated into portions sol. (I) and insol. (II) in EtOH. (I) is subdivided by light petroleum into a sol. portion, from which are derived, after hydrolysis, succinic acid (III), a compound, m.p. 131°, and borneol, and an insol. portion, from which are obtained succinoxyabietic acid, succinoabietinolic acid, and a neutral compound. (II) is hydrolysed to a resin (IV), (III), and two substances (V and VI) sol. and insol., respectively, in EtOH. Dehydrogenation of (IV), (V), or (VI) by Se leads to the *hydrocarbon* $C_{13}H_{14}$, m.p. 28° (*picrate*, m.p. 139·5°), probably a trimethylnaphthalene, and 1 : 7-dimethylphenanthrene, m.p. 86° (picrate, m.p. 131°). H. W.

Difuryl-butadiene and -hexadiene. A. Mironescu, G. Ioanid, and I. Nicolescu (Bul. Soc. Chim. Romania, 1933, **14**, 187).—Furil and MeMgI give $\beta\gamma$-*di*-2-*furylbutadiene*, m.p. 145°; MgEtI affords $\gamma\delta$-*di*-2-*furyl*-$\Delta^{\beta\gamma}$-*hexadiene*, m.p. 128°. F. R. S.

Molecular transposition accompanying the dehydration of tetrahydrofurfuryl alcohol. R. Paul (Compt. rend., 1933, **196**, 1409—1411).—Dehydration of tetrahydrofurfuryl alcohol over Al_2O_3 at 370—380° gives 2 : 3-dihydropyran (I), b.p. 86—87°, reduced (H_2, Pt-black) to tetrahydropyran, b.p. 87—88°, which with HBr affords $\alpha\varepsilon$-dibromopentane, b.p. 222—223°/766 mm. (I) is hydrolysed slowly to (probably) δ-hydroxyvaleraldehyde. 2-Bromomethyltetrahydrofuran and dry KOH give the unstable $\beta\varepsilon$-oxido-Δ^{α}-pentene, b.p. 82—83°, readily hydrolysed to γ-acetylpropyl alcohol (*semicarbazone*, m.p. 155—157°). H. B.

Action of perbenzoic acid on furfuraldehyde diacetate. H. Scheibler, J. Jeschke, and W. Beiser (J. pr. Chem., 1933, [ii], **137**, 322—326).—Action of BzO_2H on furfuraldehyde diacetate in $CHCl_3$ gives a *monoxide*, m.p. 118—119° (sinters 115°), b.p. 120°/2 mm., to which on account of its unreactivity towards Br and H_2–Pt the annexed formula is assigned. No identifiable products were isolated as a result of acid hydrolysis.



H. A. P.

Reaction between keten and mercurials. H. Gilman, B. L. Woolley, and G. F. Wright (J. Amer. Chem. Soc., 1933, **55**, 2609).—Keten and RHgCl or R_2Hg give 2- and 3-*furyl Me ketone*, b.p. 84°/21 mm. (*semicarbazone*, m.p. 150°), 2 : 5-*diacetylfuran*, m.p. 94° (*dioxime*, m.p. 187°), and $COPh_2$ in 20—50% yields. The CO group in some carbimides may react similarly. R. S. C.

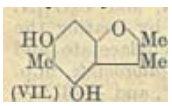
Synthesis of chromones. K. Venkataraman (J. Indian Chem. Soc., 1933, Ray No., 27—36).—Various methods are reviewed. H. B.

Some 4-styrylcoumarins. H. S. Mahal and K. Venkataraman (J.C.S., 1933, 616—617).—4-*Styrylcoumarin*, m.p. 143°, is prepared from coumaryl-4-acetic acid, PhCHO, C_5H_5N, and $C_5H_{11}N$. The coumarins have been obtained by heating the appropriate chalkones with Na phenylacetate and Ac_2O: 3-*phenyl*-4-*styryl*-, m.p. 174° (*dibromide*, m.p. 198°), -4-(4′-*methoxystyryl*)-, m.p. 170°, and -4-(3′ : 4′-*methylenedioxystyryl*)-, m.p. 172°, 7 : 8-*dimethoxy*-3-*phenyl*-4-(4′-*methoxystyryl*)-, m.p. 195°, and -4-(3′ : 4′-*methylenedioxystyryl*)-*coumarin*, m.p. 203°; 3-*phenyl*-4-*styryl*-, m.p. 210°, -4-(4′-*methoxystyryl*)-, m.p. 196°, and -4-(3′ : 4′-*methylenedioxystyryl*)-1 : 2-α-*naphthapyrone*, m.p. 215°. Similarly, 3-*phenyl*-4-*methylcoumarin*, m.p. 153° (*o*-hydroxyacetophenone), 3 : 3′-diphenyl-4 : 4′-dimethyldicoumarin (4 : 6-diacetylresorcinol), and the corresponding 3 : 3′-di-*p*-nitrodiphenyl compound have been prepared. F. R. S.

Usnic acid. II. Usneol. F. H. Curd and A. Robertson (J.C.S., 1933, 714—720).—Methylation of usneol (MeI–K_2CO_3) gives the O-*Me*$_2$ *ether* (I), b.p. 168—172°/5 mm. (*picrate*, m.p. 87—88°), and ethylation the O-*Et*$_2$ *ether* (II), b.p. 164—175/20 mm., m.p. 123—124° (*picrate*, m.p. 82—83°). *Et* α-3-*methoxyphenoxypropionate*, b.p. 164—167°/21 mm., is obtained from resorcinol Me ether and Et α-chloro-α-methylacetoacetate, but the ether and γ-chlorobutan-β-one (III) [improved prep.; *semicarbazone*, m.p. 138—139° (decomp.)] afford *Me* α-3-*methoxyphenoxyethyl ketone*, b.p. 157—158°/24 mm. (*semicarbazone*, m.p. 126—127°), which with H_2SO_4 gives 6-*methoxy*-2 : 3-*dimethylcoumarone*, b.p. 145°/21 mm. (*picrate*, m.p. 76—77°). (III) and Na salt of phloroglucinol Me_2 ether yield *Me* α-3 : 5-*dimethoxyphenoxyethyl ketone*, b.p. 167°/13 mm. (*semicarbazone*, m.p. 167—168°), cyclised to 4 : 6-*dimethoxy*-2 : 3-*dimethylcoumarone*, m.p. 55° (*picrate*, m.p. 129—130°); (III) and methylphloroglucinol α-Me_2 ether give *Me* α-3 : 5-*dimethoxy*-2-*methylphenoxyethyl ketone*, b.p. 151—152°/1 mm. (*semicarbazone*, m.p. 172—173°), cyclised to 4 : 6-*dimethoxy*-2 : 3 : 7-*trimethylcoumarone*,

m.p. 68° (*picrate*, m.p. 110—111°); (III) and Me 2 : 4-dihydroxy-6-methoxy-3-methylbenzoate form *Me* 6-*hydroxy*-4-*methoxy*-2 : 3 : 5-*trimethylcoumarone*-7-*carboxylate*, m.p. 123—134°, the corresponding *acid*, m.p. 215—216° (decomp.), being decarboxylated to 6-*hydroxy*-4-*methoxy*-2 : 3 : 5-*trimethylcoumarone* (IV), m.p. 133°. Methylation of (IV) gives 4 : 6-*dimethoxy*-2 : 3 : 5-*trimethylcoumarone*, identical with (I).

Me 2 : 6-*dihydroxy*-4-*ethoxy*-3-*methylbenzoate* (V), m.p. 108—109° (ethylation by diazoethane), is methylated to the 2-*hydroxy*-6-*methoxy*-ester, m.p. 134°, and the 2 : 6-*dimethoxy*-ester, m.p. 93°. Ethylation of 2 : 4-*dihydroxy*-6-*methoxy*-3-*methylbenzaldehyde*, m.p. 243—244° (from methylphloroglucinol α-Me ether), gives the 4-*ethoxy*-compound, m.p. 126—127° [*acetate* (VI), m.p. 116—117°], which with acetylanisole forms 5 : 4′-*dimethoxy*-7-*ethoxy*-8-*methylflavylium ferrichloride*, m.p. 169—170°. (VI) is oxidised to 2-*hydroxy*-6-*methoxy*-4-*ethoxy*-3-*methylbenzoic acid*, m.p. 167—168°, decarboxylated to 4-*methoxy*-6-*ethoxy*-o-*cresol*, m.p. 79—80°. (V) and (III) give *Me* 6-*hydroxy*-4-*ethoxy*-2 : 3 : 5-*trimethylcoumarone*-7-*carboxylate*, m.p. 100—101°, hydrolysed to the *acid*, m.p. 191—192° (decomp.), which is decarboxylated to 6-*hydroxy*-4-*ethoxy*-2 : 3 : 5-*trimethylcoumarone*, identical with (II). Condensation of Me 2 : 4 : 6-trihydroxy-3-methylbenzoate and (III) has given



Me 4 : 6-*dihydroxy*-2 : 3 : 7-*trimethylcoumarone*-5-*carboxylate*, m.p. 130—131° (*picrate*, m.p. 104—105°), and in one experiment, an isomeric *compound*, m.p. 98—99° (*picrate*, m.p. 84—85°). Usneol must be (VII). F. R. S.

Formula of crocin. P. Karrer and H. Salomon (Helv. Chim. Acta, 1933, **16**, 643).—After drying at 100° (loss of $1H_2O$) analysis of crocin corresponds with $C_{44}H_{64}O_{24}$, a digentiobiose ester of crocetin. J. W. B.

Dye of acacia wood. K. C. Gulati and K. Venkataraman (J. pr. Chem., 1933, [ii], **137**, 294; cf. this vol., 719).—Hydroxyfisetin penta-acetate, m.p. 225°, and Me_5 ether, m.p. 148°, from acacia wood are identical with the corresponding derivatives of 3 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone. H. A. P.

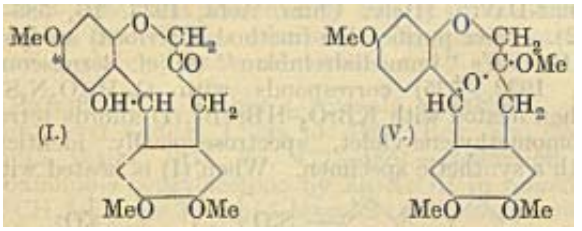
Spectrography of benzopyrylium pigments. I. Influence of substitution in the side phenyl group. K. Hayashi (Acta Phytochim., 1933, **7**, 117—141).—*O*-Benzoylphloroglucinaldehyde and COPhMe in EtOAc saturated with HCl yield O-*benzoylchrysinidin chloride*, $C_{22}H_{15}O_4Cl,1{\cdot}5H_2O$ (cf. A., 1927, 1083). Similarly are prepared 2′-*hydroxy*-O-*benzoylchrysinidin chloride* from *o*-acetoxyacetophenone (A., 1897, i, 424); O-*benzoylapigenidin chloride* from *p*-acetoxyacetophenone; 2′-*methoxy*-O-*benzoylchrysinidin chloride* from *o*-methoxyacetophenone; O-*benzoylacacetinidin chloride* from *p*-methoxyacetophenone; 3′-*hydroxy*-O-*benzoylchrysinidin chloride* from *m*-acetoxyacetophenone (A., 1901, i, 103); 2′ : 4′-*dimethoxy*-O-*benzoylchrysinidin chloride* from resacetophenone Me_2 ether (J.C.S., 1908, **93**, 1108); 2′ : 5′-*dimethoxy*-O-*benzoylchrysinidin chloride* from quinacetophenone Me_2 ether (A., 1881, 811); 2′ : 6′-*dimethoxy*-O-*benzoyl*-4′-*methylchrysinidin chloride* from orcacetophenone Me_2 ether (A., 1907, i, 75); 4′-*hydroxy*-3′-*methoxy*-O-*benzoylchrysinidin chloride* from acetovanillone (A., 1927, 565); 3′ : 4′-*methylenedioxy*-O-*benzoylchrysinidin chloride* from acetopiperone; 2′ : 3′ : 4′-*trimethoxy*-O-*benzoylchrysinidin chloride* from gallacetophenone Me_3 ether (A., 1903, i, 644); 3′ : 4′ : 5′-*trimethoxy*-O-*benzoylchrysinidin chloride* from 3 : 4 : 5-trimethoxyacetophenone (A., 1910, i, 680); 2′ : 4′ : 5′-*trimethoxy*-O-*benzoylchrysinidin chloride* from 2 : 4 : 5-trimethoxyacetophenone; 2′ : 4′ : 6′-*trimethoxy*-O-*benzoylchrysinidin* from phloracetophenone Me_3 ether; 2′ : 3′ : 4′ : 6′-*tetramethoxy*-O-*benzoylchrysinidin chloride* from 2 : 3 : 4 : 6-tetramethoxyacetophenone (A., 1932, 388). Absorption spectra of the above pigments and of acacetinidin chloride (0·0001*M* in EtOH) show two general absorption bands, one in the visible and the other in the ultra-violet (cf. A., 1927, 918). The relations between absorption spectra and constitution are discussed. F. O. H.

Anthoxanthins. XV. Experiments on the synthesis of garcinin. R. Robinson and R. C. Shah (J.C.S., 1933, 610—612).—In an attempt to synthesise garcinin, *Et* 5 : 6-*dimethoxy*-1-*hydrindone*-2-*glyoxylate*, m.p. 158—159° (*acid*, m.p. 245—247°), prepared from 5 : 6-dimethoxyhydrindone (I) and $Et_2C_2O_4$, has been condensed with phloroglucinol Me_2 ether and HCl to the pyrylium salt, decomp. > 300°, purified through the *colour-base* of 7-*hydroxy*-5 : 5′ : 6′-*trimethoxy*-4-*carbethoxy*-2 : 3(3′ : 2′)-*indenobenzopyrylium chloride*, m.p. 220—225°; the corresponding acid cannot be oxidised to the γ-pyrone. Me 2 : 4 : 6-trimethoxybenzoate (improved prep.) does not condense with (I). 1-Hydrindone forms the 2-*Bz* derivative, m.p. 104°. F. R. S.

Attempted synthesis of demethoxymatteucinol. S. Fujise and T. Nishi (Ber., 1933, **66**, [*B*], 929—931).—Phloroglucinol and cinnamic anhydride in presence of $PhNO_2$, Et_2O, and $AlCl_3$ afford 5 : 7-dihydroxyflavanone, in poor yield, which is not improved by use of CS_2 or decahydronaphthalene as solvent or by replacement of $AlCl_3$ by $SnCl_4$. 2 : 4-Dimethylphloroglucinol, cinnamyl chloride, and $AlCl_3$ in $PhNO_2$ yield 5 : 7-*dihydroxy*-6 : 8-*dimethylflavanone* (I), m.p. 201—202°, which does not appreciably depress the m.p. of demethoxymatteucinol (II) from natural sources. The Me ether of (I) has m.p. 130°, whereas that of (II) has m.p. 108—109° (mixed m.p. 109—120°). The presence of the isomeric 6 : 7-dihydroxy-5 : 8-dimethylflavanone in (II) appears improbable, but its synthesis from hydroxy-β-orcinol could not be effected. 5-*Hydroxy*-7-*acetoxy*-6 : 8-*dimethylflavanone* has m.p. 162°. H. W.

Brazilin and hæmatoxylin. XII. Trimethylbrazilonol and derivatives. P. Pfeiffer, R. Hilpert, and P. Schneider (J. pr. Chem., 1933, [ii], **137**, 227—254).—The H_2-derivative (I), m.p. 153·5° (cf. A., 1928, 647), obtained by catalytic reduction of trimethylbrasilone (II), is also obtained, mixed with α- (III), m.p. 277° (+xC_5H_5N, lost at 150°) [*bis*-m-, m.p. 80°, and -p-*nitrobenzoyl* derivative, m.p. 190° (+xC_5H_5N)], and β-*trimethylbrazilopinacone* (IV), m.p. 294° (decomp.) (+xC_5H_5N, lost <150°) (Ac_2, m.p. 298°, and *bis*-p-*nitrobenzoyl* derivative, decomp. 300°), by reduction with Mg and AcOH. (III) and (IV) are identified by mol. wt. and by oxidation to (II)

by CrO_3–AcOH; (IV) also gives (I) on further reduction with Mg–AcOH. Their isomerism is regarded as the result of pinacone formation at different CO groups. (I) is unimol. and gives *Ac*, m.p. 121°, and *p-nitrobenzoyl*, m.p. 104°, derivatives, and α-, m.p. 167°, and β-*oximes*, m.p. 114°. It is oxidised by CrO_3 to dihydrobrazilinic acid (J.C.S., 1908, **93**, 514) [*Me* ester, m.p. 183° (CH_2N_2); Et ester, m.p. 156° (*Br*-derivative, m.p. 212°)], and is therefore *trimethylbrasilonol* (annexed formula). With Me_2SO_4 and



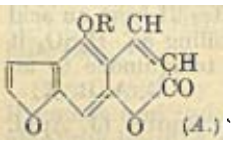
NaOH it gives a OH-free *Me ether*, m.p. 156—157°, which on account of its freedom from active H is assigned the cyclic acetal formula (V). Oxidation of (V) with CrO_3–AcOH gives a *compound*, $C_{20}H_{20}O_7$, m.p. 180·5—181° [*sulphonic acid*, m.p. 191—192° (decomp.)], which contains no active H and gives no oxime or semicarbazone.

The following are prepared by direct bromination: bromotrimethyl-brazilone (VI), m.p. 224—225° (decomp.); *-deoxybrazilin* (VII), m.p. 165°; *-brazilonol* (VIII), m.p. 220—221° (and some Br_2-derivative, m.p. 178—181°); and *-brazilonol Me ether* (IX), m.p. 187—188°. (VI) is also formed from (VII) and CrO_3 in AcOH, (VIII) from (VI), Mg, and AcOH, or from (IX) by demethylation with H_2SO_4, and (IX) from (VIII) and Me_2SO_4. Oxidation of (VI) with $KMnO_4$ gives *m*-hemipinic acid. Fuming HNO_3 at the b.p. gives $H_2C_2O_4$ and 4 : 6-*dinitro*-3-*methoxyphenoxyacetic acid*, m.p. 211—212° (*Ag* salt; *Me* ester, m.p. 141°), identified by conversion by 40% HBr into 2-bromo-4 : 6-dinitroresorcinol, and by synthesis by nitration of 3-OMe·C_6H_4·O·CH_2·CO_2H. The Br is therefore assigned to the position marked * in formula (I).

H. A. P.

Synthesis of αß-dinaphtho-γ-pyrone (1 : 2 : 7 : 8-dibenzoxanthone). II. K. Dziewoński and (Mlle.) Z. Zalewska (Bull. Acad. Polonaise, 1933, A, 116—118).—One mol. of β-$C_{10}H_7$·OH (I) heated with 1 mol. of PhNCO (II) and $AlCl_3$ at 40—50° affords β-*naphthyl phenylurethane*, m.p. 157—158° [the substance, m.p. 230°, obtained by Leuckart and Schmidt, A., 1885, 1224, is its decomp. product $CO(NHPh)_2$], converted by heating at 220° into the anil of 1 : 2 : 7 : 8-dibenzoxanthone (A., 1932, 859), which is obtained directly when 2 mols. of (I) are heated with 1 mol. of (II) at 220—230°. J. W. B.

Vegetable fish poisons. IV. Constitution of oxypeucedanine from *Imperatoria Ostruthium*. E. Späth and K. Klager (Ber., 1933, **66**, [*B*], 914—922; cf. this vol., 614).—Oxypeucedanine (I), m.p. 142—143°, α —0·03° in $CHCl_3$ (l=2, c=10) is $C_{16}H_{14}O_5$ (cf. Butenandt *et al.*, A., 1932, 751). It is converted by fusion with KOH into phloroglucinol in good yield and is transformed by successive hydrogenation (Pd–C in AcOH) and oxidation with HNO_3 (d 1·52) into succinic acid, thus indicating a coumarin structure. (I) does not contain OMe or active H, and does not react with ketonic reagents, hence the remaining 3 O are in ether-like union. Oxidation of (I) with H_2O_2 in alkaline solution affords furan-2 : 3-dicarboxylic acid (II), m.p. 223° (Me ester, m.p. 33—36°). The possibility that the production of (II) is due to oxidative ring contraction is excluded by companion experiments with umbelliferone. Treatment of (I) with boiling AcOH containing a little conc. H_2SO_4 followed by methylation leads to bergapten, thus leading to the structure *A* (R=C_5H_9O) for (I) is not affected by short treatment with Ac_2O alone, whereas its hydrate (III) [from (I) and $H_2C_2O_4$ in boiling H_2O] affords a diacetate, m.p. 132—133°. Oxidation of (III) with CrO_3 yields $COMe_2$. Treatment of (I) with P_2O_5 in boiling PhMe yields *iso*oxypeucedanine (IV), m.p. 146° (oxime, m.p. 184°), oxidised by H_2O_2 in alkaline solution to *iso*butyric acid. Oxidation of (III) with chromic acid also yields oxypeucedanic acid (V), m.p. 265° (Me ester, m.p. 185—185·5°). In (I), (III), (IV), and (V) R is therefore ·CH_2·CH<$\overset{CMe_2}{O}$>, ·CH_2·CH(OH)·CMe_2·OH, ·CH_2·COPr^s, and ·CH_2·CO_2H, respectively.



H. W.

2-Methylindone. N. Kijner (J. Gen. Chem. Russ., 1933, **3**, 201—207).—2-Bromo-2-methylhydrindone (A., 1915, i, 562) when boiled with C_5H_5N gives 2-methylindone (I), yellow plates, m.p. 47—47·5°, b.p. 99—100°/6 mm. (*p-nitrophenylhydrazone*, m.p. 195—197°; *p*-bromophenylhydrazone, m.p. 122—123°; cf. *loc. cit.*), giving a blue solution in H_2SO_4 and in alkali and oxidised by $KMnO_4$ to *o*-$C_6H_4(CO_2H)_2$. (I) readily undergoes condensation, especially with alkali. HBr, preferably in AcOH, gives the *bromide*, $C_{20}H_{17}O_2Br$, m.p. 170—171° (II), which is quantitatively transformed by alkalis into the saturated *compound* $C_{20}H_{16}O_2$, m.p. 197—198°, probably dimethyltruxone, which slowly passes into (II) when heated with HBr in AcOH. G. A. R. K.

Dinaphthylene dioxide. II. R. Pummerer, A. Rieche, G. von Krudener, H. Pfeiffer, E. Prell, W. Tuchmann, and H. Wilsing (Annalen, 1933, **503**, 40—60; cf. A., 1926, 1135).—Oxidation of dinaphthylene dioxide (I) with Caro's acid or CrO_3 in AcOH gives the -4 : 4′-*quinone* (II), m. p. > 400° (sublimes 320°/high vac.), reduced by Zn and AcOH to the 4 : 4′-(*OH*)$_2$-compound (*Na* salt, Ac_2 derivative). Action of BzO_2H on (I) in C_6H_6 gives 4-*benzoyloxy*-, m.p. 237° {free *OH*-compound [*acetate*, sublimes 230° (decomp.)]}, and 4 : 4′-*dibenzoyloxy-dinaphthylene dioxide*; both give (II) with conc. H_2SO_4, but the product from the former is very impure. The *di*-*m*-*nitrobenzoate* and *-α-naphthoate* are similarly prepared. All these products are vat dyes with good affinity for cotton. The constitution of (II) is proved by conversion of 4-amino-β-naphthol, m.p. 211° (lit. 185°), into its *phthalimido*-derivative, m.p. 242°; oxidation of this with PbO_2 in PhCl to 2 : 2′-*dihydroxy*-4 : 4′-*bisphthalimido*-1 : 1′-*dinaphthyl*, ring closure with Ag_2O or Cu_2O in $PhNO_2$ to 4 : 4′-*bisphthalimidodinaphthylene*

dioxide, and hydrolysis of this to (II) with 30% KOH in MeOH. *Di-α-naphthoyl peroxide*, explodes 92°, is prepared from H_2O_2 and $C_{10}H_7\cdot COCl$ in C_5H_5N. H. A. P.

Compound of methylenedihydrofuran with benzoquinone. N. KIJNER (J. Gen. Chem. Russ., 1933, **3**, 198—200).—Methylenedihydrofuran (I), the labile isomeride of methylfuran (A., 1932, 857), combines with 2 mols. of *p*-benzoquinone (II) in C_6H_6 to a ruby-red *compound* $C_{17}H_{14}O_5$ (III), which dissociates in solution. Equimol. quantities of (I) and (II) give a brown oil which passes into (III) on adding more (II). 1 mol. of (III) liberates 2I from an acid solution of KI; with SO_2 and boiling aq. H_2SO_4 it gives quinol. (I) combines with toluquinone to an oily additive product. G. A. R. K.

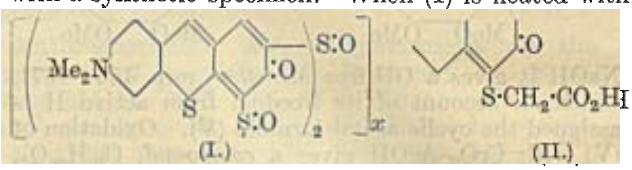
Synthesis of thiophen. A. S. BROUN (J. Appl. Chem. Russ., 1933, **6**, 262—265).—The most active catalyst for synthesis of thiophen (I) from C_2H_2 and H_2S at 350° is $NiCO_3$, containing a trace of $MgCO_3$, both pptd. from the nitrates on pumice. Amongst the reaction products are the Me, Me_2, Et, and Pr derivatives of (I). R. T.

Thiophen derivatives. II. I. J. RINKES (Rec. trav. chim., 1933, **52**, 538—548).—*5-Nitrothiophen-2-carboxyl chloride*, m.p. 52—53° [from the acid (I) and $SOCl_2$], and $CH_2Ac\cdot CO_2Et$ (Na derivative) in boiling Et_2O in 1 hr. afford a product, hydrolysed by $EtOH$–H_2SO_4 to *5-nitro-2-acetothienone* (II), m.p. 106—107°. Similarly, 4-nitrothiophen-2-carboxylic acid (III) (improved prep.; cf. this vol., 73) affords *4-nitro-2-acetothienone*, m.p. 125—126°, identical with one product of nitration of 2-acetothienone (A., 1917, i, 277). The other product (m.p. 88°) affords an *oxime*, m.p. 189°, identical with the oxime of (II) and hydrolysed to (II) by 10% HCl. 2-Methyl-3 : 5-dinitrothiophen, prepared by extensive nitration of 2-methylthiophen, with PhCHO and piperidine affords *3 : 5-dinitro-2-styrylthiophen*, m.p. 205°. *5-Iodo-2-methylthiophen*, b.p. 90°/16 mm., yields a Grignard compound which with CO_2 gives 2-methylthiophen-5-carboxylic acid (this vol., 73), the Me ester of which is nitrated by HNO_3 (*d* 1·51) in Ac_2O < 0° to *Me 3-nitro-2-methylthiophen-5-carboxylate*, m.p. 79—80°. This reacts with PhCHO and piperidine at 120° in 20 min. to give *Me 3-nitro-2-styrylthiophen-5-carboxylate*, m.p. 110°, hydrolysed to the *acid*, m.p. 222°, decarboxylated to *3-nitro-2-styrylthiophen*, m.p. 87—88°. The Me ester of (I) with HNO_3–H_2SO_4 at −5° to −10° during 1 hr. affords a product, hydrolysed to *3 : 5-dinitrothiophen-2-carboxylic acid*, m.p. 135—136°, easily decarboxylated to 2 : 4-dinitrothiophen, identical with the product of nitration of 2-nitrothiophen (*ibid.*, 512). (III) is decarboxylated much less readily. Orientation in the thiophen series is discussed. J. L. D.

Relationship between the structure of antigens and the specificity of antibodies. VII. H. ERLENMEYER, E. BERGER, and M. LEO (Helv. Chim. Acta, 1933, **16**, 733—738).—Condensation of the chloride of thiophen-2-carboxylic acid with $p\text{-}NO_2\cdot C_6H_4\cdot NH_2$ gives the p-*nitroanilide*, m.p. 220°, from which the corresponding NH_2-derivative, $C_4H_3S\cdot CO\cdot NH\cdot C_6H_4\cdot NH_2$ (I), m.p. 171°, is obtained. Similarly, from β-naphthoyl chloride are obtained the p-*nitroanilide*, m.p. 196°, and the NH_2-compound $C_{10}H_7\cdot CO\cdot NH\cdot C_6H_4\cdot NH_2$ (II), m.p. 167°. The mols. (I), (II), and $NHBz\cdot C_6H_4\cdot NH_2$ (III) have similar cryst. forms, and hence similar mol. fields, and, in agreement with the authors' hypothesis (A., 1932, 1054), no serological distinction is possible between antigens produced from (I), (II), or (III). J. W. B.

Blue sulphur dyes. E. KELLER and H. E. FIERZ-DAVID (Helv. Chim. Acta, 1933, **16**, 585—592).—After purification (method described) analysis of Gnehm's "immedialreinblau" (I) (cf. Bernasconi, A., 1932, 525) corresponds with

When heated with $KBrO_3$–HBr–Br (I) affords tetrabromomethylene-violet, spectroscopically identical with a synthetic specimen. When (I) is heated with



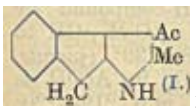
glucose and KOH (in N_2) the SO groups are reduced to SH, and subsequent treatment with $CH_2Cl\cdot CO_2H$ affords a small yield of the *thioglycollic acid* (II), whence the structure (I) is assigned to the original dye, dissolution in Na_2S arising from reduction of the quinone groups to the leuco-compound and fission of the disulphoxide groups. J. W. B.

Symmetrical dithio*spiro*heptane. H. J. BACKER and K. J. KEUNING (Rec. trav. chim., 1933, **52**, 499—514; cf. A., 1931, 1054).—Interaction of K_2S and $C(CH_2Br)_4$ in boiling EtOH during 20—24 hr. affords *2 : 6-dithio-4-spiroheptane* (I), m.p. 31·5° [*methiodide*, m.p. 143° (decomp.); *mercurichloride*], oxidised by $KMnO_4$ or excess of H_2O_2 to *2 : 6-dithio-4-spiroheptane 2 : 2 : 6 : 6-tetraoxide* (II), m.p. 244·5°, whereas with smaller amounts of H_2O_2 in AcOH the following are obtained: *2 : 6-dithio-4-spiroheptane 2 : 6-dioxide*, m.p. 146° [*bismercurichloride*, m.p. 185° (decomp.)], also obtained from (I) and HNO_3 or from (I) and excess of CrO_3, and reduced by boiling HCl–AcOH and Zn to (I); the *2-oxide*, m.p. 81·5° (+ $1\frac{1}{2}HgCl_2$, decomp. when heated), also from (I) and CrO_3 at room temp.; and the *2 : 2 : 6-trioxide* (III), m.p. 156° [+$1HgCl_2$, m.p. 186—187° (decomp.)], all of which afford (II) on extensive oxidation. Interaction of (I) with excess of Br in C_6H_6 at room temp. affords *1 : 5-dibromo-2 : 6-dithio-4-spiroheptane 2 : 6-dioxide*, m.p. 126·5°, whereas I affords a I_4-additive compound, decomp. about 100°. Reduction of (III) (Zn, hot HCl) affords *2 : 6-dithio-4-spiroheptane 2 : 2-dioxide*, m.p. 116·5° (+$1HgCl_2$, m.p. 177—178°). J. L. D.

Synthesis and physiological action of α-substituted *N*-methylpyrrolidines. L. C. CRAIG (J. Amer. Chem. Soc., 1933, **55**, 2543—2550).—*N*-Methyl-2-pyrrolidone gives by the Grignard reaction and subsequent reduction by Mg and HCl 2-phenyl-, b.p. 106°/20 mm., 217·5° (uncorr.)/760 mm. (*oxalate*, an oil; *picrate*, m.p. 146°; *chloroplatinate*, +$3H_2O$, m.p. 122°), 2-p-*chlorophenyl-*, b.p. 118°/9 mm. (*oxalate*, an oil; *picrate*, m.p. 173°), and 2-p-*anisyl*-N-

methylpyrrolidine (I), b.p. 130—131°/9 mm. (*oxalate*, an oil; *picrate*, m.p. 155°). (I) with HI gives 2-*p-hydroxyphenyl*-N-*methylpyrrolidine*, m.p. 157° (*picrate*, m.p. 181°). 2-Methyl-, b.p. 96° (picrate, m.p. 235°), 2-ethyl-, b.p. 123°, 2-*n*-propyl-, b.p. 147°, and 2-*n*-butyl-*N*-methylpyrrolidine, b.p. 170° (*oxalate*, an oil; *picrate*, m.p. 114°), are best prepared by electrolytic reduction of the corresponding pyrrolines. Analogous compounds could not be obtained from the Grignard reagents of pyrrole or thiophen. The dissociation consts. of these and similar bases (which are recorded) bear a close, and the toxicity and pharmacological activity bear some, relationship to the electron-sharing ability of the substituent. R .S. C.

Extension of Knorr's pyrrole synthesis. G. Bondietti and F. Lions (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 477—485).—Reduction of α-oximino-α-benzylacetone by Zn–AcOH in presence of CH_2Ac_2 gives 3-*acetyl*-5-*benzyl*-2 : 4-*dimethylpyrrole*, m.p. 165—166°, with $CH_2Ac{\cdot}CO_2Et$, *Et* 5-*benzyl*-2 : 4-*dimethylpyrrole*-3-*carboxylate*, m.p. 119°, and with dimethyldihydroresorcinol, 4-*keto*-2-*benzyl*-3 : 6 : 6-*trimethyl*-4 : 5 : 6 : 7-*tetrahydroindole*, m.p. 197°, are obtained in small yield. Similarly, oximinoacetone and dimethyldihydroresorcinol afford 4-*keto*-3 : 6 : 6-



: 5 : 6 : 7-*tetrahydroindole*, m.p. 156°, whilst α-oximino-α-methylacetone yields the 2 : 3 : 6 : 6-*Me*$_4$ derivative, m.p. 228°. Oximino-α-hydrindone and CH_2Ac_2 form 3-*acetyl*-2-*methyl*-4 : 5-*indeno*-(1 : 2)-*pyrrole* (I), m.p. 254°. F. R. S.

Action of ozone on heterocyclic compounds. II. M. Freri (Gazzetta, 1933, **63**, 281—289; cf. A., 1932, 1142).—The action of O_2+O_3 on tripyrrole yields pyrrole-blacks; on thiophen, polymerides, with a *compound* $C_{35}H_{23}O_2S_{10}$ (?), and an *ozonide*, decomposing to CO_2, H_2SO_4, $H_2C_2O_4$, and glyoxal; on furan, glyoxal and a *polymeride*, $C_{12}H_{12}O_{10}$ (?). E. W. W.

Dehydrogenation of pyridine by anhydrous metallic chlorides. G. T. Morgan and F. H. Burstall (J. Indian Chem. Soc., 1933, Ray No., 1—16).—The chief products formed in the dehydrogenation of C_5H_5N with the following salts (method; A., 1932, 284) are identified: $[CoCl_2,4C_5H_5N]Cl$; $CuCl_2,2C_5H_5N$; WCl_6; $MoCl_5$; $SnCl_4$; $C_5H_5N,HFeCl_4$. The following are described: α- and β-2 : 2′-*dipyridylplatinous chloride*; 2 : 2′-*dipyridylpalladous chloride*; *tris*-2 : 2′-*dipyridylmanganous chloride* (anhyd. and $+8H_2O$), *bromide* ($+7H_2O$), and *iodide* ($+6H_2O$); *tris*-2 : 2′-*dipyridylcupric chloride* ($+6H_2O$). H. B.

Molecular association of pyridine and iodine. M. Chatelet (Compt. rend., 1933, **196**, 1421—1423).—When a conc. solution of I in C_5H_5N is allowed to evaporate in air, an unstable complex, probably $2C_5H_5N,I_2$, separates. H. B.

Iodine–pyridine–water complexes. M. Chatelet (Compt. rend., 1933, **196**, 1607—1608).—Addition of a little H_2O to an I–C_5H_5N solution (*A*) ppts. the *complex* $I_2,(C_5H_5N)_4,24H_2O$; addition of (*A*) to much H_2O ppts. the *complex*, $I_2,C_5H_5N,6H_2O$. The C_5H_5N is determined after removal of I by pptn. as Reineckate in acid solution. R. S. C.

Tri-(2-pyridyl)amine. J. P. Wibaut and G. L. C. La Bastide (Rec. trav. chim., 1933, **52**, 493—498).—Interaction of 2-iodo- (I) or 2-bromo-pyridine and 2-aminopyridine (II) in presence of K_2CO_3 and Cu-bronze during 16 hr. in boiling mesitylene affords tripyridylamine (III), m.p. 130° (cf. A., 1928, 75) [$+1MeI$, m.p. 204—206° (decomp.); $+HgCl_2,HCl$, m.p. 180°; *picrate*, m.p. 150—151°], also formed from dipyridylamine (IV) and (I) as above, or from the Na derivative of (II) and 2-chloropyridine in paraffin oil at 170—180° during 3 hr. p_H and λ vals. in EtOH + H_2O of (II), (III), and (IV) show that (III) is the least basic. J. L. D.

[Syntheses by means of magnesylpyrroles.] Pyrroles and indoles. Series II. XVI. Action of alkyl halides on magnesylindole. B. Oddo. XVII. Syntheses of 2 : 3-dialkylindoles. B. Oddo and C. Alberti (Gazzetta, 1933, **63**, 234—235, 236—242).—XVI. A claim for priority (A., 1911, i, 486) against Hoshino (A., 1932, 952; this vol., 164).

XVII. When 2-methylindole is heated at 210—220° with ROH and RONa, where R=Me, Et, etc., the following are obtained: 2 : 3-dimethyl-, 2-methyl-3-ethyl-, -3-*n*-propyl-, -3-n-*butyl*-, b.p. 220—222°/80 mm. (*picrate*, m.p. 134—135°), -3-sec.-*butyl*-, b.p. 188—192°/15 mm. (*picrate*, m.p. 139—140°), and -3-iso*amyl*-, b.p. 222—224°/60 mm. (*picrate*, m.p. 147—149°), -indole. The reaction does not take place with indole or skatole. E. W. W.

Indoles. III. Application of the Japp–Klingemann reaction to cyclic β-keto-acids. F. Lions (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 516—525).—Addition of PhN_2Cl and NaOAc to Et *cyclo*hexanone-2-carboxylate in aq. KOH–EtOH, previously kept at 0° for 24 hr., gives *cyclo*hexane-1 : 2-dionemonophenylhydrazone, cyclised by heating with HCl–AcOH to 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole. The following have been similarly prepared: cyclo*pentane*-1 : 2-*dionehydrazonephenylhydrazone*, m.p. 126°, cyclised to cyclo*pentane*-1 : 2-*dione*-1 : 1′-*ketazine*-2 : 2′-*diphenylhydrazone*; cyclo*hexane*-1 : 2-*dione*-*mono*-β-*naphthylhydrazone*, m.p. 173° (cyclo*hexane*-1 : 2-*dione*-1 : 1′-*ketazine*-2 : 2′-*di*-β-*naphthylhydrazone*, m.p. 205°, being formed with N_2H_4), cyclised to 8-*keto*-8 : 9 : 10 : 11-*tetrahydro*-β-*naphthacarbazole*, m.p. 204—205°; cyclo*hexane*-1 : 2-*dionemono*-p-*tolylhydrazone*, m.p. 187°, cyclised to 1-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m.p. 195—196°; and cyclo*hexane*-1 : 2-*dionemono*-α-*naphthylhydrazone*, m.p. 133°, cyclised to 10-*keto*-7 : 8 : 9 : 10-*tetrahydro*-αβ-*naphthacarbazole*, m.p. 238—240°. F. R. S.

Attempted fission of quinoline oxide; stereochemistry of tervalent nitrogen. J. Meisenheimer (Ber., 1933, **66**, [*B*], 985—988).—The non-resolvability of quinoline oxide by optically active acids is regarded as evidence against Phillips' hypothesis that a co-ordinatively tervalent atom can be a centre of asymmetry if it is attached to three different groups and carries a positive charge. The question of the invariable ability of the co-ordination no. 3 to inhibit a plane arrangement of attached groups is

discussed. The normal *tartrate*, needles, m.p. 121°, or leaflets, m.p. 138°, $[\alpha]_D^{\dot{}}$ +5·62° in H_2O, and the *α-bromo-d-camphor-π-sulphonate*, m.p. 134—135° (*mono-*, m.p. 92° and, after re-solidification, about 125°, $[\alpha]_D$ +57·6° in H_2O, and *di-*, m.p. 107—112°, $[\alpha]_D$ +44·3° in H_2O, *-hydrate*), of quinoline oxide are described. H. W.

Alkali salts of 8-hydroxyquinoline. P. Sue and G. Wetroff (Compt. rend., 1933, **196**, 1813—1815).—The prep. of the *Li*, decomp. 125°, *Na*, *K* (+KOH), decomp. 50°, and NH_4 (+NH_3), decomp. at room temp., salts of 8-hydroxyquinoline is described. A. A. L.

***iso*Quinoline derivatives.** H. J. Harwood and T. B. Johnson (J. Amer. Chem. Soc., 1933, **55**, 2555—2559).—Homoveratrylamine (modified prep.) and 10% aq. NaOH with furylacryloyl chloride in $CHCl_3$ give *N-(3 : 4-dimethoxyphenylethyl)furylacrylamide*, m.p. 108—109°, which with $POCl_3$ in PhMe gives *6 : 7-dimethoxy-1-furylvinyl-3 : 4-dihydroisoquinoline*, m.p. 94—96° after sintering at 90°, unstable (*picrate*, m.p. 210—211°; *H sulphate*, m.p. 243·5—244°; *hydrochlorides*, 1 mol. base+1 mol. HCl, m.p. 183—184°, and 3 mols. base+4 mols. HCl, m.p. 167·5—168·5° after sintering at 160°), which gives indefinite products when reduced. Ring-closure of *N-(β-phenylethyl)furylacrylamide*, m.p. 124—125°, similarly prepared, could not be accomplished. *N*-(β-Phenylethyl)chloroacetamide and P_2O_5 in boiling xylene give *1-chloromethyl-3 : 4-dihydroisoquinoline*, an unstable oil (*picrate*, m.p. 173—174°; *hydrochloride*, m.p. 164—165°), in which Cl could not be replaced by OH or ester groups. R. S. C.

Synthesis of bases allied to coniine. I. Preparation and pyrolysis of allyl ethers of *N*-heterocyclic enols. B. Mander-Jones and V. M. Trikojus (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 300—314).—Pyrolysis of 4-allyloxyquinaldine (I), b.p. 152—153° [picrate, m.p. 188°; *methiodide*, m.p. 165° (decomp.); hydrochloride, m.p. 171—172°], prepared from the Ag salt and allyl bromide, gives *4-hydroxy-2-methyl-3-allylquinoline* (II), m.p. 273° (*Bz* derivative, m.p. 87—88°), also obtained from Et β-anilino-α-allylcrotonate, b.p. 161—162°/2 mm., by elimination of EtOH. The methiodide of (I) is converted by heating into *N*-methyl-4-quinaldone with loss of allyl iodide. (II) forms through the Cl-derivative *4-methoxy-2-methyl-3-allylquinoline*, b.p. 147—149°/1·6 mm. (*picrate*, m.p. 143°), reduced to the tetrahydro-derivative. *4-Allyloxy-2 : 3-dimethylquinoline*, m.p. 161°, is pyrolysed to *4-hydroxy-2 : 3-dimethyl-5(?)-allylquinoline*, m.p. 249—250°. *8-Allyloxyquinoline*, b.p. 143—144°/0·6 mm. (*picrate*, m.p. 148—149°), forms *8-hydroxy-7-allylquinoline* (II), m.p. 46° (*picrate*, m.p. 190°), which, heated with allyl bromide and KOMe, gives an oil, b.p. 140°/3 mm. (picrate, m.p. 135°), pyrolysed to *8-hydroxy-5 : 7(?)-diallylquinoline*, m.p. 83°, also obtained along with (II). *8-Methoxy-7-allylquinoline*, b.p. 176—177°/16 mm. (*picrate*, m.p. 148—149°), is converted by heating with NaOEt into the iso*allyl* compound (*picrate*, m.p. 200°). F. R. S.

Action of phosphoryl chloride on the toluene-*p*-sulphonyl derivative of β-anilinopropionic acid. O. G. Backeberg (J.C.S., 1933, 618—619).—Interaction of $POCl_3$ with the toluene-*p*-sulphonyl derivative of β-anilinopropionic acid affords (contrary to A., 1924, i, 1103) 4-chloro-1-toluene-*p*-sulphonyl-1 : 2-dihydroquinoline, together with 4-chloroquinoline (also obtained from 4-hydroxyquinoline and $POCl_3$), which with Na in MeOH under pressure affords 4-methoxyquinoline. The corresponding compounds from *m*- and *p*-toluidino-, *p*-anisidino-, and *p*-phenetidinopropionic acids (cf. A., 1926, 76) should be formulated as the 1-toluene-*p*-sulphonyl derivatives of 5-, 7-, and 6-methyl-, 6-methoxy-, and 6-ethoxy-4-chloro-1 : 2-dihydroquinoline. J. L. D.

New method of preparation of compounds of the quinoline group. I. K. Dziewonski and J. Moszew (Bull. Acad. Polonaise, 1932, **A**, 383—395).—When heated with either $CS(NHPh)_2$ or $CO(NHPh)_2$ at 180—210°, COPhMe affords a 60% yield of 4-anilino-2-phenylquinoline (I), m.p. 190° [John (A., 1928, 528) gives m.p. 182°; *hydrochloride*, m.p. 265—266°; *nitrate*, m.p. 195° (decomp.); *NO*-derivative, m.p. 203° (decomp.); *Ac* derivative, m.p. 160°; additive *compound* with $C_2H_4Br_2$, m.p. 297—298°], which gives the 4-OH-compound by fusion with KOH, is reduced by Na+C_5H_{11}·OH to the *tetrahydro*-derivative, m.p. 138—139° (*picrate*, m.p. 163°), and with HNO_3–H_2SO_4 in AcOH is converted into its 6-NO_2-derivative, m.p. 219—220° [*sulphate*, m.p. 313—314° (decomp.)]. Since (I) is also obtained by heating together CPhMe:NPh and PhNCS the reaction mechanism is formulated: $CX(NHPh)_2 \longrightarrow NH_2Ph + PhNCX$; NH_2Ph + COPhMe $\longrightarrow$ CPhMe:NPh $\longrightarrow$ NPh:CPh·CH:C:NPh $\longrightarrow$ (I) (X=O or S). Similarly $CS(NH\cdot C_6H_4Me\text{-}p)_2$ affords *4-p-toluidino-2-phenyl-6-methylquinoline*, m.p. 162° [*hydrochloride*, m.p. 324°; *nitrate*, m.p. 171° (decomp.); *picrate*, m.p. 241°; *NO*-derivative, m.p. 189° (decomp.); *Ac* derivative, m.p. 154°; additive *compound* with $C_2H_4Br_2$, m.p. 262—263°], reduced to its *tetrahydro*-compound, m.p. 113° (*picrate*, m.p. 203°), and giving the 4-OH-compound by fusion with KOH. J. W. B.

Derivatives of 2-phenylquinoline. I. Preparation of "atophans" from veratraldehyde. II. "Atophans" with substituent basic groups. III. Derivatives of polyhydroxy-"atophans." (Miss) M. G. Holdsworth and F. Lions (J. Proc. Roy. Soc. New South Wales, 1933, **66**, 273—278, 459—472, 473—476).—I. Condensation of veratraldehyde and $AcCO_2H$ with amines has yielded the following: *2-veratryl-5 : 6-benzo-*, m.p. 142—143° (with β-$C_{10}H_7$·NH_2), *2-veratryl-*, m.p. 235° (with NH_2Ph; also obtained from isatin, acetoveratrone, and KOH), *2-veratryl-8-methoxy-*, m.p. 116° (*o*-anisidine), *-7-methoxy-*, m.p. 222° (*m*-anisidine), *-6-methoxy-*, m.p. 257° (*p*-anisidine), *-7-hydroxy-*, m.p. > 300° (*m*-aminophenol), *-6-hydroxy-*, m.p. > 300° (*p*-aminophenol), and *7-dimethylamino-quinoline-4-carboxylic acid*, m.p. 259° (*m*-NMe_2·C_6H_4·OH); and *αα'-diveratrylphenanthroline-γγ'-dicarboxylic acid*, m.p. 191° [*m*-$C_6H_4(NH_2)_2$].

II. Condensation as above using varying aldehydes has given: from *m*-aminophenol, *7-hydroxy-2-(4'-dimethylaminophenyl)quinoline-4-carboxylic acid*, m.p.

$>300°$ (with *p*-$NMe_2·C_6H_4·CHO$); from *m*-$NMe_2·C_6H_4·OH$, 7-*dimethylamino*-2-(4′-*methoxyphenyl*)-, m.p. 315° (anisaldehyde), 7-*dimethylamino*-2-(3′ : 4′-*methylenedioxyphenyl*)-, m.p. $>300°$ (piperonal), and 7-*dimethylamino*-2-(4′-*dimethylaminophenyl*)-*quinoline*-4-*carboxylic acid*, m.p. $>300°$ (*p*-$NMe_2·C_6H_4·CHO$); from *m*-$C_6H_4(NH_2)_2$, αα′-*dianisyl*-, m.p. 210° (anisaldehyde), αα′-*dipiperonyl*-, m.p. 205—206° (piperonal), and αα′-*di*-(p-*dimethylaminophenyl*)-m-*phenanthroline*-γγ-*dicarboxylic acid*, m.p. 234° (*p*-$NMe_2·C_6H_4·CHO$); from ($·CH_2·NH·C_6H_4·NH_2$-*m*)$_2$, s-*bis*-(2-*phenyl*-, m.p. 280° (decomp.) (PhCHO), -(2-*anisyl*-, m.p. 276° (anisaldehyde), -(2-*veratryl*-, m.p. 264° (veratraldehyde), -(2-*piperonyl*-, m.p. 290° (piperonal), -(2-*vanillyl*-, m.p. 256° (vanillin), and -(2-p-*dimethylaminophenyl*-4-*carboxy*-7-*quinolylamino*)*ethane*, m.p. 260° (*p*-$NMe_2·C_6H_4·CHO$); from 1 : 4-*di*-(m-*aminophenyl*)-*piperazine*, m.p. 102°, 1 : 4-*di*-(2-*phenyl*-, m.p. 265° (PhCHO), -(2-*anisyl*-, m.p. 217°, -(2-*veratryl*-, m.p. 242°, -(2-*piperonyl*-, m.p. 236°, -(2-*vanillyl*-, m.p. 242°, and -(2-p-*dimethylaminophenyl*-4-*carboxy*-7-*quinolyl*)*piperazine*, m.p. 278°. Colour reactions of the acids and their salts are described.

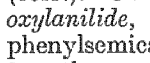
III. The following have been similarly obtained: 2-(3′ : 4′-*dihydroxyphenyl*)-, m.p. $>300°$ (NH_2Ph and protocatechualdehyde), 7-*hydroxy*-2-(2′-*hydroxyphenyl*)-, m.p. $>300°$ (*m*-aminophenol and salicylaldehyde), and 7-*hydroxy*-2-(3′ : 4′-*dihydroxyphenyl*)-*quinoline*-4-*carboxylic acid*, m.p. $>300°$. Isatin and α-hydroxy-3 : 4-dimethoxyacetophenone give 2-(2′-*hydroxy*-3′ : 4′-*dimethoxyphenyl*)*quinoline*-4-*carboxylic acid*, m.p. 245°, and 2 : 3 : 4-trimethoxyacetophenone affords the corresponding -2′ : 3′ : 4′-(OMe)$_3$-derivative, m.p. 196°. F. R. S.

4-Acyl derivatives of antipyrine. E. Benary (Ber., 1933, **66**, [*B*], 924—927).—Antipyrine, $CH_2Cl·COCl$, and $AlCl_3$ in CS_2 yield 4-*chloroacetyl*-1-*phenyl*-2 : 3-*dimethylpyrazol*-5-*one* (I), m.p. 166—167°, converted by NaI in $COMe_2$ into the 4-*iodoacetyl*, m.p. 140—141°, by NH_3–EtOH at 100° into the 4-*aminoacetyl*, decomp. about 265°, and by piperidine–EtOH into the 4-*piperidinoacetyl*, m.p. 139—141°, derivative [reduced by Zn dust and AcOH to 4-acetylantipyrine, m.p. 150—151° (*phenylhydrazone*, m.p. 208—210°)]. The following -1-*phenyl*-2 : 3-*dimethylpyrazol*-5-*ones* are analogously prepared: 4-α-*bromopropionyl*-, m.p. 145—146°; 4-α-*aminopropionyl*-, m.p. about 315° (decomp.); 4-α-*piperidinopropionyl*-, m.p. 125—126°; 4-α-*bromobutyryl*-, m.p. 127—128°; 4-α-*bromoisobutyryl*-, m.p. 152—153°; 4-α-*bromoisovaleryl*-, m.p. 129—130°; 4-*trichloroacetyl*-, m.p. 181—182°; 4-n-*butyryl*-, m.p. 113—114°; 4-iso*valeryl*-, m.p. 103—104°; 4-p-*nitrobenzoyl*-, m.p. 165—168°, whence 4-p-*aminobenzoyl*-, m.p. 254—255°. (I) and KOAc in EtOH yield the 4-*acetoxyacetyl* compound, m.p. 173—174°. The 4-α-*acetoxybutyryl* compound, m.p. 142—143°, is described. H. W.

Pyrazoles. II. Acylation of pyrazole. Q. Mingoia (Gazzetta, 1933, **63**, 242—247).—Mg pyrazole when treated with the appropriate acyl chloride gives N-*propionyl*-, b.p. 149—150°/4·8 mm. (good yield only under pressure), N-*chloroacetyl*-, b.p. 170—172°/52 mm., and N-*ethyloxalyl*-, b. p. 155—156°/16 mm. (*picrate*, m.p. 100°), -*pyrazole*. E. W. W.

Synthesis of methylcaffeidine. A. Heymons (Ber., 1933, **66**, [*B*], 1017—1019).—4-Nitro-1-methylglyoxaline-5-carboxylamide is converted by conc. HCl at 100° into 4-nitro-1-methylglyoxaline-5-carboxylic acid, m.p. 172° (decomp.) (*Et* ester, m.p. 10·1°), transformed by the successive action of $SOCl_2$ and NH_2Me into 4-*nitro*-1-*methylglyoxaline*-5-*carboxylmethylamide*, m.p. 196°, which is reduced by Sn and 2*N*-HCl at 0° to norcaffeidine (I), m.p. 150° (*picrate*, m.p. 221°; *hydrochloride*, m.p. 222°). (I), MgO, and MeI at 40° afford *methylcaffeidine methiodide*, m.p. 166° [corresponding *picrate*, m.p. 153°; *monohydrate*, m.p. 166° (decomp.) after softening at 90—95°, identical with the "hydriodide" of Biltz and Rakett], which yields methylcaffeidine, m.p. 84—88° (picrate, m.p. 158°), when distilled at 150°/12 mm. H. W.

5-Substituted derivatives of 3-phenyl-1-methylbarbituric acid. B. Hepner and S. Frenkenberg (Rocz. Chem., 1933, **13**, 276—282).—3-Phenyl-1-methylbarbituric acid (I) with PhCHO gives the corresponding 5-*benzylidene* derivative, m.p. 102—104°, with PhN_2Cl 3-*phenyl*-1-*methylalloxan*-5-*phenylhydrazone*, m.p. 210—214°, with amyl nitrite 3-*phenyl*-1-*methylvioluric acid*, $+H_2O$, m.p. 91° (decomp.), which with HCO_2H and Zn gives the 5-*formamido*-derivative of (I), m.p. 248° (decomp.), and with Br its 5-*Br*-derivative, m.p. 161° [5-*Pr*^{α}, m.p. 89°; 5-*Pr*^{α} derivative (II), m.p. 95°]. (II) when heated with aq. NH_3 in EtOH gives N-*phenyl*-N-*methyl*-C-iso*propylhydantoin*, m.p. 170° (C-*Br*-derivative, m.p. 127°). 3-Phenyl-1-methyl-5-allyl-5-*n*-propyl- and -5 : 5-diallyl-barbituric acid give with Br respectively the corresponding 5-β*γ*-*dibromopropyl*, m.p. 118—120°, and 5 : 5-*bis*-β*γ*-*dibromopropyl* derivative, m.p. 168°. NHPh·CS·NHMe is conveniently prepared from PhCNS and NH_2Me, and S is readily eliminated from it by the action of H_2O_2 in alkaline solution. R. T.

Transformation of esters of γ-keto-acids into pyridazine and pyrazoline derivatives. H. Machemer (Ber., 1933, **66**, [*B*], 1031—1033).—Catalytic hydrogenation (Pd sponge in AcOH) of the semicarbazone of lævulic acid, m.p. 184° (corr.), or its Me ester, m.p. 151° (corr.), leads to 3-*keto*-6-*methylhexahydropyridazine*-2-*carboxylamide*, m.p. 183° (corr.). 3-*Keto*-6-*methylhexahydropyridazine*-2-*carboxylanilide*, m.p. 186°, is derived from Me lævulate phenylsemicarbazone, m.p. 117° (corr.), whereas Me δ-methoxymethyl-lævulate semicarbazone, m.p. 117° (corr.) (similarly or in presence of PtO_2), yields 3-*keto*-6-β-*methoxyethylhexahydropyridazine*-2-*carboxylamide*, m.p. 147° (corr.). Me δ-methoxymethyl-lævulate is converted by successive treatment with PCl_5 and $NaHCO_3$–ice mainly into *Me* δ-*hydroxymethyl-lævulate* (I), b.p. 110—115°/6 mm., transformed by NH_2Ph into *Me* γ-*anilo*-ε-*hydroxyhexoate*, m.p. 58°. (I) and $NHPh·NH_2$ yield the compound (?)  , m.p. 69°, hydrolysed by HCl to the corresponding *acid*, m.p. 112° (corr.). H. W.

o-Aminoazo-derivatives. Quinoxalines and *N*-arylidoiminazoles. G. B. Crippa [with T. Cessi

and G. PERRONCITO] (Gazzetta, 1933, **63**, 251—261).—α-Benzeneazo-β-naphthylamine and β-$C_{10}H_7$·COMe with HCl as catalyst at 165—180° form 6-β-*naphthyl*-2 : 3-αβ-*naphthoquinoxaline*, m.p. 162° (strong depression when mixed with 6-Ph analogue); with α-$C_{10}H_7$·COMe, the 6-α-*naphthyl* compound, m.p. 161·5°, is formed, and with COPhMe, the 6-*phenyl*-5-*methyl* compound (I), m.p. 121°, and a *substance*, m.p. 280°. With PhCHO and C_6H_4Me·CHO, (I) forms the 6-*styryl*-5-*methyl*, m.p. 166°, and 6-p-*methylstyryl*-5-*methyl*, m.p. 178°, compounds. With $AcCO_2H$ the product is not a quinoxaline, but 4-anilino-5-methyl-2 : 3-αβ-naphthoiminazole, with an acid *product*. Bis-β-naphthylamine-α-azo-*pp'*-diphenyl and PhCHO yield *pp'*-bis-(*C*-phenylnaphthoiminazolylamino)diphenyl, m.p. 245°; the C-o-*nitrophenyl* analogue has m.p. 260°. E. W. W.

Behaviour of heterocyclic compounds towards ozone. M. MILONE (Gazzetta, 1933, **63**, 329—333).—2-Phenyl-4-methyl- (I), -4 : 5-dimethyl- (II), -5-methyl-4-ethyl- (III), and -4-methyl-5-ethyl- (IV) -1 : 2 : 3-triazole 1-oxides react in CCl_4 with O_2+O_3 giving *ozonides*, decomposed when heated with H_2O to form HNO_3 and (I) AcCHO, (II) Ac_2, (III and IV) AcCOEt. Under similar conditions the triazoles themselves are not attacked. E. W. W.

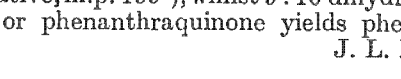
2-α- and 2-β-Pyridylbenziminazole. II. A. LEKO and G. VLAINATZ (Bull. Soc. Chim. Yougoslav., 1933, **4**, 17—21).—$HgCl_2$ yields a *compound* with 1 mol. of 2-α- and with 2 mols. of 2-β-pyridylbenziminazole. R. T.

Heterocyclic compounds obtained by the interaction of benzoins and hydrazine hydrochloride. III. J. VAN ALPHEN (Rec. trav. chim., 1933, **52**, 525—532; cf. this vol., 286, 724).—1 : 3 : 4 : 6-Tetraphenyl-Δ^2-[dehydro]trimidine (I) with conc. HNO_3 at −10° in 15 min. gives 1 : 3 : 4 : 6-*tetra*-(p-*nitrophenyl*)-Δ^2-[*dehydro*]*trimidine*, m.p. about 340° (decomp.), reduced in 2 hr. by boiling conc. HCl and Sn to the (p-NH_2)$_4$-*compound*, m.p. 248° (+1*EtOH*, m.p. 168°; Ac_4 derivative, m.p. 268°). (I) with excess of Br in sunlight yields a Br_2-derivative, m.p. 270°, with Br in the *p*-position in two Ph nuclei. Anisoin, N_2H_4,2HCl, and boiling EtOH during 5 hr. afford anisilazine (A., 1930, 90) and 1 : 3 : 4 : 6-*tetra*-(p-*methoxyphenyl*)-Δ^2-[*dehydro*]*trimidine*, m.p. 233° (5 : 7-Ac_2, and 5 : 7-Bz_2 derivatives, m.p. 132° and 211°, respectively; *di*-p-*bromobenzoyl* derivative, m.p. 174°). Similarly, toluoin (crude prep.) gives 1 : 3 : 4 : 6-*tetra*-(p-*tolyl*)-, m.p. 250° (5 : 7-Bz_2 derivative, m.p. 167°), and cumoin (A., 1905, i, 653) gives *tetra*-(p-iso*propylphenyl*)-Δ^2-[*dehydro*]*trimidine*, m.p. 207° (5 : 7-Bz_2 derivative, m.p. 199°), whilst 9 : 10 dihydroxyphenanthrene or phenanthraquinone yields phenanthoxazine. J. L. D.

Structure of theophylline *l*-arabinoside. J. PRYDE and R. T. WILLIAMS (J.C.S., 1933, 640—642).—Methylation of theophylline arabinoside [2 : 6-dioxy-1 : 3-dimethylpurine-(7)-β-*l*-arabinoside] gives the Me_3 derivative, m.p. 125°, $[\alpha]_{5461}^{19}$ +61·97°, oxidised by HNO_3, the products isolated being *mononitrotheophylline* (+0·5H_2O), m.p. 275°, and Me *d*-arabotrimethoxyglutarate. F. R. S.

Constitution of purine nucleosides. J. M. GULLAND and T. F. MACRAE (J.C.S., 1933, 662—669).—The prep. of 4-methylglyoxaline (I) from AcCHO (cf. Bernhauer, A., 1929, 939) gives also a *substance* $C_5H_7N_2Cl$, m.p. 207° (5-chloro-2 : 4-dimethylglyoxaline?). 3-*Tetra-aceto*-β-*glucosido*-4-*methylglyoxaline*, m.p. 176° [prepared from the Ag salt of (I)], forms through the *methiodide*, m.p. 232° (decomp.), a methochloride, hydrolysed by aq. HCl to 3-β-*glucosido*-4-*methylglyoxaline methochloroaurate*, m.p. 144—145°, and by conc. HCl at 150° to 1 : 4-dimethylglyoxaline, isolated as the chloroaurate. Theophylline tetra-aceto-β-glucoside (improved prep.) and MeI at 150° yield the periodide of caffeine methiodide and at 125° the same product and an *iodide*, m.p. 208° (decomp.); with CH_2PhCl theophylline-*d*-glucoside and CH_2Ph·OAc are formed. Xanthosine, obtained from guanosine, is methylated to 3 : 9-*dimethylxanthine hydriodide* (*chloropalladite*) in good yield, whilst xanthine gives only a small yield. Theophylline is methylated to 1 : 3 : 7-trimethylxanthine hydriodide, whilst xanthosine in presence of $BaCO_3$ forms 3 : 7-dimethylxanthine and its methiodide [*theobromine methochloride*, m.p. 320—340° (decomp.)]. It is suggested that the pentose mol. is probably attached to position 7 of xanthosine and of guanosine. Neither guanosine nor xanthosine is oxidised by xanthine dehydrogenase of milk. F. R. S.

Reactions of diacyhydrazide chlorides with sodium azide. R. STOLLÉ [with O. KRAMER, E. SCHICK, and H. ERBE] (J. pr. Chem., 1933, [ii], **137**, 327—338).—The reactions previously described with dibenzhydrazide chloride (cf. A., 1922, i, 690) are extended to its di-*p*-Me, -*o*-Cl-, -*m*-NO_2-, and -*p*-NO_2-derivatives. *Di*-p-*tolu*- (I), m.p. 138°, *di*-o-*chlorobenz*-, m.p. 106°, and *di*-m-*nitrobenz*-*hydrazide chloride*, m.p. 193°, are prepared by chlorinating the hydrazides with Cl_2 in CCl_4 or with PCl_5; in the case of the *o*-Cl-compound I is a necessary catalyst. Interaction of the hydrazide chlorides with NaN_3 in boiling 5% EtOH gives *di*-p-*tolu*-, m.p. 145° (decomp.), *di*-m-*nitrobenz*-, m.p. 156° (decomp.), and *di*-p-*nitrobenzhydrazide azide*, decomp. 161°. At the same time are formed 5 : 1′-*di*-p-*tolyl*-, m.p. 184° (decomp.) [*Na*, *Ag*, and *Me*, m.p. 163° (decomp.), derivatives], 5 : 1′-*di*-o-*chlorophenyl*-, m.p. 166° (decomp.) [*Ag*, *Me*, m.p. 175° (decomp.), and *Et*, m.p. 122°, derivatives] (accompanied by *substances*, m.p. 222°, and 202°), 5 : 1′-*di*-p-*nitrophenyl*-, m.p. 202°, and 5 : 1′-*di*-m-*nitrophenyl*-1 : 5′-*ditetrazolylamine*, m.p. 204° (decomp.). These are formed in almost quant. yield by use of excess of NaN_3 in boiling EtOH, and have markedly acidic properties. The alternative formula



is suggested and is supported by fission of the di-Cl-*o*-derivative by HCl at the b.p. into *o*-C_6H_4Cl·NH_2 and 1-amino-5-*o*-chlorophenyltetrazole. By boiling with a large excess of abs. EtOH, (I) is converted slowly into N-p-*tolyl*-N′-5-p-*tolyl*-1-*tetrazolyl*-O-*ethyl*isocarbamide, m.p. 143° (15% in 12 hr.). The corresponding (?) *Me* compound has m.p. 137°. H. A. P.

Chlorophyll-*a*. V. Its phase-positive derivatives and allomerisation. A. STOLL and E.

WIEDEMANN (Helv. Chim. Acta, 1933, **16**, 379—772; cf. this vol., 515).—Polemical against H. Fischer. Chlorophyll-*a* and -*b*, m.p. 150—153° (decomp.) and 183—185° (decomp.), respectively, have Willstatter's formulæ. Details are given for the prep. and previously recorded properties of benzoyl- (I), benzoylmethyl-, benzylphytyl-, and methyl-phæophorbide-*a* (oxime), allomerised phæophorbide-*a* (II) (oxime), protophæoporphyrin-*a* [Bz derivative, also prepared from (I); oxime] [by catalytic reduction of (II) and HI–AcOH reduction of allomerised (I)] and its allomerisation product (=phæoporphyrin-a_5) (oxime). New spectroscopic data and the method of obtaining them in test-tubes are described. R. S. C.

Chlorophyll-*b*. II. H. FISCHER, S. BREITNER, A. HENDSCHEL, and L. NUSSLER (Annalen, 1933, **503**, 1—40; cf. A., 1932, 1264; Stoll and Wiedemann, *ibid.*, 1265).—Rhodinporphyrin-g_3 Me ester (I) gives an *oxime*, m.p. 276°, readily dehydrated by Ac_2O and KOAc to a *substance*, $C_{33}H_{35}O_2N_5$, m.p. 265° (*Cu* and *Fe* salts), which could not be hydrolysed to a dicarboxylic acid and may be an oxazole. (I) also adds HCN; the *cyanohydrin* thus formed is readily hydrolysed to a *dicarboxylic acid* (*Me*$_2$ ester, $C_{35}H_{49}O_5N_4$, m.p. 207°), but HBr in AcOH at 120° gives in addition some phylloporphyrin; the stability of the acid indicates that the CO group is in the side-chain. Fusion of the Fe salt of (I) or its semicarbazone with resorcinol at 190—200° gives phylloporphyrin hæmin; a similar result is obtained with (I) in Ph_2 at 255°. Methylphæophorbide-*b* (II) gives a *monoxime* without absorption of O_2; this does not react further with NH_2OH. It also gives a *Me*$_2$ *acetal* with $CH(OMe)_3$, also unaffected by NH_2OH, and hydrolysed to its components by 0·5% HCl. Phæophorbide-*b* gives a *cyanohydrin* (III), as also do (II) and methylchlorophyllide-*b*. (III) is unaffected by NH_2OH and semicarbazide, converted into rhodin-*g* by $Ba(OH)_2$, and into phæoporphyrin-a_5 (?) by HI–AcOH. Rhodin-*g* gives an *oxime* in the cold, hydrolysed by HCO_2H to rhodinporphyrin-g_3. Its Me_3 ester also gives an *oxime*, m.p. 238° (previous sintering), and a *cyanohydrin*, m.p. 230°, which readily loses its HCN with NaOH in C_5H_5N, and with HI in AcOH gives a *porphyrin* (*Me* ester, m.p. 259°), spectroscopically similar to chloroporphyrin-e_6, and reduced by H_2–PtO_2 merely to a *leuco-compound*, readily reoxidised by air; it is possible therefore that the $[CH_2]_2{\cdot}CO_2H$ residue has been converted into a OH-acid. Phæoporphyrin-b_6 (IV) (*Me* ester, m.p. 256°) is split by KOH in MeOH to chloroporphyrin-e_6 at room temp. and phyllo- and pyrro-porphyrins at 150°. Fusion of its Fe salt with resorcinol at 190—200° gives a *substance* (*Me* ester, m.p. 232°) closely resembling phylloerythrin (not analysed). HCO_2H converts (IV) at the b.p. into *phæoporphyrin*-b_5 [*Me*$_2$ ester, m.p. 243° (*oxime*)] and a *porphyrin* (*Me* ester, $C_{34}H_{36}O_4N_4$, m.p. 262°). The phase-test differs considerably in the *a* and *b* series. Phæophorbide-*b* takes up O_2 in EtOH, but the phase-test is still positive after 7 days at room temp. and a further 8 at the b.p., and small additions of alkali have no effect. Allomerisation with I in AcOH gives a negative phase-test after 24 hr., not restored by reducing agents. Addition of HCN restores the phase-test, and I in AcOH does not destroy it in the cyanohydrin. Phæophytin is allomerised by benzoquinone, but after hydrolysis the separated phæophorbides-*a* and -*b* give a positive test. H. A. P.

Nitrosocarbohydrazines. A. QUILICO (Gazzetta, 1933, **63**, 269—279).—The compound $C_4H_2O_3N_4$ (I) (A., 1931, 194) is 1 : 2-*oxazolyl*-5-*nitrosocarbohydrazine* (cf. this vol., 59) and with $C_5H_{11}N$ forms 1 : 2 : 5 - *oxazolylnitrosohydrazinecarbopiperidide*, R·N(NO)·NH·CO·NC$_5$H$_{10}$, decomp. 100° to give 1 : 2 : 5-*oxazolyl-azocarbopiperidide*, R·N:N·CO·NC$_5$H$_{10}$, reduced to the *-hydrazinecarbopiperidide*, m.p. 185°. Similarly phenylnitrosocarbohydrazine (II) (*ibid.*) yields *phenylnitrosohydrazinecarbopiperidide*, decomposed at 100° to *phenyl-azocarbopiperidide*, m.p. 78—79°, reduced to the *-hydrazinecarbopiperidide*, m.p. 182°; p-*nitrophenylazocarbopiperidide* has m.p. 132°. NHPh·NH$_2$ and (I) form s-1 : 2 : 5-*oxazolylphenylcarbazide*, m.p. 180—185° (decomp.) (*K* salt); with (II), *s*-diphenylcarbazide is formed. E. W. W.

Derivatives of furfuraldehyde. A. MIRONESCU, G. IOANID, and I. NICOLESCU (Bul. Soc. Chim. Romania, 1933, **14**, 183—186).—Condensation of furfuraldehyde with PhCHO cyanohydrin gives β-phenyl-α′-furanoxazole, sublimes at 212°, and with anisaldehyde cyanohydrin the corresponding *OMe*-derivative, m.p. 220°. Furfuraldehyde cyanohydrin and PhCHO give *α′-phenyl-β-furanoxazole*, m.p. 216°, and furfuraldehyde and anilinoacetonitrile afford *β-phenyl-α-furaniminazole*, m.p. 132°. F. R. S.

Polymorphism of the substituted thiazole, 3-phenyl-2 : 4-thiazolidione. I. R. E. GIBSON and K. S. MARKLEY. **II. Optical crystallography of 3-phenyl-2 : 4-thiazolidione.** H. E. MERWIN (J. Amer. Chem. Soc., 1933, **55**, 2399—2406, 2406—2407).—I. 3-Phenyl-2 : 4-thiazolidione exists in two polymorphic (enantiotropic) modifications. The form, m.p. 143—144°, usually obtained from glacial AcOH solution is stable at room temp., whilst the form, m.p. 147—148°, obtained from aq. solution is stable above 100° (approx.).

II. Data are recorded. J. G. A. G.

Synthesis of new heterocyclic compounds. 3-Aryldihydrothiodiazoles. H. WUYTS and (MLLE.) A. LACOURT (Bull. Acad. roy. Belg., 1933, [v], **19**, 543—560).—Condensation of β-thioacetyl-α-phenylhydrazine and MeCHO gives 3-*phenyl*-2 : 5-*dimethyl*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m.p. 80°, and with CH_2O, the corresponding *-5-methyl* derivative, m.p. 75°. Similarly, 3-*phenyl*-5-*benzyl*-, m.p. 68° (CH_2O and β-phenylthioacetyl-α-phenylhydrazine), 3 : 5-*diphenyl*-, m.p. 97° (CH_2O and β-thiobenzoyl-α-phenylhydrazme), 3-*phenyl*-2-*methyl*-5-α-*naphthyl*-, m.p. 102° [β-(α-thionaphthoyl)-α-phenylhydrazine and paraldehyde], 2 : 3-*diphenyl*-5-*benzyl*-, m.p. 92° (β-phenylthioacetyl-α-phenylhydrazine and PhCHO), 2 : 3 : 5-*triphenyl*-, m.p. 97° (β-thiobenzoyl-α-phenylhydrazine and PhCHO), 2 : 3-*diphenyl*-5-α-*naphthyl*-, m.p. 147° [β-(α-thionaphthoyl)-α-phenylhydrazine and PhCHO], 3-*phenyl*-2 . 2 : 5-*trimethyl*-, b.p. 108—109°/1 mm. (β-thioacetyl-α-

phenylhydrazine and $COMe_2$), *5-phenyl-3-p-bromophenyl-2 : 2-dimethyl-*, m.p. 74° (β-thiobenzoyl-α-*p*-bromophenylhydrazine and $COMe_2$), and 2-spirocyclohexane-*5-phenyl-3-p-bromophenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, $\begin{matrix}CPh\text{———}S\\ N{\cdot}N(C_6H_4Br)\end{matrix}>C<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}>CH_2$, m.p. 97° (*cyclo*hexanone), have been obtained. The properties and colour reactions of the compounds are given and the mechanism of their formation is discussed. F. R. S.

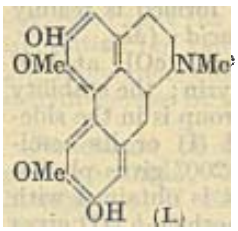
***Sophora* alkaloids. III. Alkaloids of the foliage of *Sophora alopecuroides*.** A. Orekhov (Ber., 1933, **66**, [*B*], 948—951; cf. this vol., 617).—The finely-divided material is moistened with 10% NH_3 and percolated with C_6H_6. The solution is extracted with 5% HCl, the bases are liberated by NaOH (0·75% of material) and extracted with Et_2O. After removal of Et_2O the oily residue is extracted with light petroleum (b.p. 60—90°), giving a sol. (*A*) and an insol. (*B*) portion. After removal of the solvent, *A* slowly deposits *sophoridine* (I), $C_{15}H_{26}ON_2$ (possibly $C_{15}H_{24}ON_2$), m.p. 109—110°, $[\alpha]_D$ −63·57° in H_2O, which does not contain OH or OMe and slowly discharges the colour of $KMnO_4$ in H_2SO_4. The salts of (I) with mineral acids are freely sol. and hygroscopic; the *chloroaurate*, m.p. 189—190°, *picrolonate*, m.p. 226—228° (decomp.), *picrate*, and *methiodide*, m.p. 234—236°, are described. *B* is treated with EtOH followed by EtOH–HCl; the pptd. hydrochloride yields *sophoramine* (II), $C_{15}H_{20}ON_2$, m.p. 164—165°, $[\alpha]_D$ −90·85° in EtOH, which does not contain OH or OMe. The *hydrochloride*, m.p. 247—248° (decomp.), *hydriodide*, m.p. 294—296°, *chloroaurate*, m.p. 183—184° (decomp.), *chloroplatinate*, m.p. 245—247° (decomp.), *picrate*, m.p. 229—231° (decomp.), and *picrolonate*, m.p. 173—175° (decomp.), are described. (I) and (II) are strong, monacid, *tert.* bases. (I) is indifferent to acids and bases. H. W.

Pyridylnitropyrazole, an oxidation product of nicotine. Position of the nitro-group. H. Lund (J.C.S., 1933, 686—687).—The nitro-5-(3-pyridyl)pyrazole (I) (cf. Gough and King, this vol., 616), obtained during the oxidation of nicotine with HNO_3, is probably the 3-NO_2-derivative (4-*Br*-derivative, m.p. 240—242°; *Bz* derivative, m.p. 169°), and not the 4-compound. Oxidation of (I) with $KMnO_4$ gives nicotinic acid, and reduction affords the corresponding NH_2-compound (*Ac* derivative, m.p. 308°), which forms an *azo-dye* and *3-iodo-5-(3-pyridyl)pyrazole*, m.p. 180°. Pyridylpyrazole is nitrated to the 4-NO_2-derivative, m.p. 220° (*hydrochloride*). F. R. S.

Yohimbine (quebrachine). IV. Harman, a degradation product. G. Barger and C. Scholz (J.C.S., 1933, 614—615).—Indole-2-carboxylic acid has been identified in the degradation products of yohimbine (cf. Warnat, A., 1927, 681). Fusion of yohimbic acid with KOH gives 3-ethylindole, m.p. 37°. The base "$C_{13}H_{12}N_2$" obtained by Warnat (*benzylidene* derivative, m.p. 200°) is identical with harman and has the formula $C_{12}H_{10}N_2$. F. R. S.

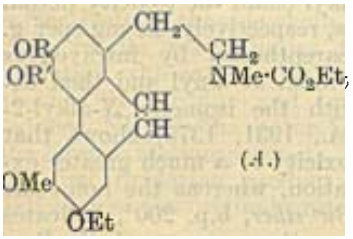
Micro-optical properties of cocaine hydrochloride and novocaine. C. van Zijp (Pharm. Weekblad, 1933, **70**, 606—609).—Cocaine hydrochloride forms poorly defined rhombic crystal fragments showing angles of 141° and 90°. With convergent light a faint black cross is observed, which soon disappears on rotation. Novocaine forms well-defined crystals; angles 120°. Well-defined interference figures are obtained, convergent light giving a double axis figure, which persists on rotation; the angle between the optical axes is 62°. The two substances are readily differentiated. S. C.

Constitution of boldine. E. Späth and K. Tharrer (Ber., 1933, **66**, [*B*], 904—914).—Boldine (I), m.p. 162—163°, is converted by CH_2N_2 into its Me_2 ether, m.p. 117—118°, identical with glaucine, and from which only $H_2C_2O_4$ could be obtained by oxidation with $KMnO_4$ in alkaline solution. (I) and $CHMeN_2$ yield the non-cryst. *boldine Et₂ ether*, which gives a non-cryst. *methiodide* from which the methine base (II) is obtained. (II) with MeI in EtOH yields the *methiodide* (III), $C_{25}H_{34}O_4NI$, m.p. 252—253°, accompanied by NMe_3 and 4 : 6-*dimethoxy*-3 : 7-*diethoxy*-1-*vinylphenanthrene* (IV), m.p. 112—113°, also obtained by the Hofmann degradation of (III). (IV) is oxidised by $KMnO_4$ in $COMe_2$ to 4 : 6-*dimethoxy*-3 : 7-*diethoxyphenanthrene*-1-*carboxylic acid*, m.p. 202—203° (vac.), decarboxylated by Cu powder in boiling quinoline to 4 : 6-*dimethoxy*-3 : 7-*diethoxyphenanthrene* (V), m.p. 133—134°.



The synthesis of the following phenanthrenes is recorded. 2-Nitrovanillin is converted by NaOH and EtI in EtOH into its *Et ether*, m.p. 106—107°, which is transformed by Na 4-methoxy-3-ethoxyphenylacetate (VI) and Ac_2O into 2-*nitro*-3 : 3′-*dimethoxy*-4 : 4′-*diethoxystilbene*-7′-*carboxylic acid*, m.p. 186—187°, reduced by $FeSO_4$ and NH_3 to the corresponding NH_2-acid, m.p. 126—127°, which is diazotised and treated with Cu powder, thereby yielding 4 : 6-*dimethoxy*-3 : 7-*diethoxyphenanthrene*-9-*carboxylic acid*, m.p. 224—225° [decarboxylated to (V)], and 4 : 6-*dimethoxy*-3 : 5-*diethoxyphenanthrene*-9-*carboxylic acid*, m.p. 193—195°, whence 4 : 6-*dimethoxy*-3 : 5-*diethoxyphenanthrene*, m.p. 88—88·5°. 2-*Nitro*isovanillin *Et ether*, m.p. 76—77°, (VI), and Ac_2O at 110—120° afford 2-*nitro*-4 : 4′-*dimethoxy*-3 : 3′-*diethoxystilbene*-7′-*carboxylic acid*, m.p. 165—166°, whence the NH_2-acid, m.p. 141—142°, and 3 : 6-*dimethoxy*-4 : 7-*diethoxyphenanthrene*-9-*carboxylic acid*, m.p. 208—209° (3 : 6-*dimethoxy*-4 : 7-*diethoxyphenanthrene*, m.p. 139—140°), with 3 : 6-*dimethoxy*-4 : 5-*diethoxyphenanthrene*-9-*carboxylic acid*, m.p. 176—178° (3 : 6-*dimethoxy*-4 : 5-*diethoxyphenanthrene*, m.p. 126—128°). Similarly, from 3-*methoxy*-4-*ethoxyphenylacetic acid*, m.p. 118·5—119°, is derived 2-*nitro*-3′ : 4-*dimethoxy*-3 : 4′-*diethoxystilbene*-7′-*carboxylic acid*, m.p. 176—177°, whence the corresponding NH_2-acid, m.p. 158—159°, and 3 : 7-*dimethoxy*-4 : 6-*diethoxyphenanthrene*-9-*carboxylic acid*, m.p. 165—166° (3 : 7-*dimethoxy*-4 : 6-*diethoxyphenanthrene*, m.p. 96—98°), with 3 : 5-*dimethoxy*-4 : 6-*diethoxyphenanthrene*-9-*carboxylic acid*, m.p. 188—190° (3 : 5-*dimethoxy*-4 : 6-*diethoxyphenanthrene*, m.p. 79—83°). H. W.

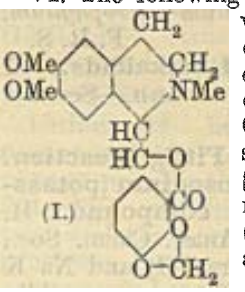
Constitution of boldine and synthesis of its *r*-diethyl ether. E. SCHLITTLER (Ber., 1933, **66**, [*B*], 988—995).—Oxidation of boldine (I) (see preceding abstract) with $KMnO_4$ yields only $H_2C_2O_4$. (I) is transformed by $CHMeN_2$ in EtOH–Et_2O into its non-cryst. Et_2 ether (II), oxidised by $KMnO_4$ to nor-*m*-hemipinic acid ether. With $ClCO_2Et$ and NaOH in $CHCl_3$ the hydriodide of (II) affords the *compound A* (R=Et, R′=Me), (III), m.p. 115—116° (non-cryst. *Bz* derivative; corresponding vinyl compound, $C_{12}H_{24}O_4$, m.p. 113°).



3-*Methoxy*-4-*ethoxycinnamic acid*, m.p. 200—201°, from ethylvanillin and $CH_2(CO_2H)_2$ in C_5H_5N, is hydrogenated to β-3-*methoxy*-4-*ethoxyphenylpropionic acid*, m.p. 130°, the chloride of which yields β-3-*methoxy*-4-*ethoxyphenylpropionamide*, m.p. (indef.) 128°, transformed by NaOCl into β-3-methoxy-4-ethoxyphenylethylamine (III), b.p. 156°/11 mm. Similarly, 4-*methoxy*-3-*ethoxycinnamic acid*, m.p. 176°, is converted successively into β-4-*methoxy*-3-*ethoxyphenylpropionic acid*, m.p. 105·5°, *Et* β-4-*methoxy*-3-*ethoxyphenylpropionate*, b.p. 187°/16·5 mm., β-4-*methoxy*-3-*ethoxyphenylpropionamide*, m.p. 123°, and β-4-methoxy-3-ethoxyphenylethylamine (IV), b.p. 158°/12·5 mm. Treatment of (III) with 6-nitro-4-methoxy-3-ethoxyphenylacetyl chloride (V) affords 6-*nitro*-4-*methoxy*-3-*ethoxyphenylacet*-β-3′-*methoxy*-4′-*ethoxyphenylethylamide*, m.p. 164·5—165°, whence 6-*methoxy*-7-*ethoxy*-1-6′-*nitro*-4′-*methoxy*-3′-*ethoxybenzyl*-3 : 4-*dihydro*isoquinoline, m.p. 177—178° [*methiodide*, m.p. 198—199° (decomp.)], reduced to 6-*methoxy*-7-*ethoxy*-1-6′-*amino*-4′-*methoxy*-3′-*ethoxybenzyl*-2-*methyltetrahydro*isoquinoline, the *dipicrolonate* of which is transformed by $Ba(NO_2)_2$ into 3 : 6-dimethoxy-2 : 5-diethoxyaporphine (VI) in poor yield. (VI) and $ClCO_2Et$ yield the *compound* A (R=Me, R′=Et), m.p. 106—107°, not identical with the similar substance derived from (I). Starting from (IV) and (V) there are obtained in similar sequence: 6-*nitro*-4-*methoxy*-3-*ethoxyphenylacet*-β-4′-*methoxy*-3′-*ethoxyphenylethylamide*, m.p. 157·5°, 7-*methoxy*-6-*ethoxy*-1-6′-*nitro*-4′-*methoxy*-3′-*ethoxybenzyl*-3 : 4-*dihydro*isoquinoline, m.p. 163·5° [*methiodide*, m.p. 188° (decomp.)], 7-*methoxy*-6-*ethoxy*-1-6′-*amino*-4′-*methoxy*-3′-*ethoxybenzyl*-2-*methyltetrahydro*isoquinoline (*dipicrolonate*), 3 : 5-dimethoxy-2 : 6-diethoxyaporphine hydriodide, and the compound *A* (R=Et; R′=Me), m.p. 114—115°, identical with that derived from (I). H. W.

Alkaloids of fumaraceous plants. V. Constitution of adlumine. VI. *Corydalis sempervirens* (L.), Pers. R. H. F. MANSKE (Canad. J. Res., 1933, **8**, 404—406, 407—411).—V. Adlumine (this vol., 728) is (I) since hydrolytic oxidation (dil. HNO_3) gives 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde and 3 : 4-methylenedioxybenzaldehyde-2-carboxylic acid [not isolated, but reduced (Na–Hg, dil. H_2SO_4) to 3 : 4-methylenedioxyphthalide]. (I) is thus closely related to hydrastine and bicuculline (*loc. cit.*).

VI. The following alkaloids are isolated from the whole plant using the procedure previously described (*loc. cit.*): protopine, cryptopine, bicuculline, *bicucine*, probably $C_{20}H_{19}O_7N,H_2O$ [previously described (this vol., 105) as alkaloid β], *capnoidine*, $C_{19}H_{17(15)}O_6N$, m.p. 235° [isomeric with adlumine (see above)], and a trace of an alkaloid (γ), m.p. 201°.



H. B.

Lupin alkaloids. VII. Structure of lupinane and sparteine. G. R. CLEMO and R. RAPER (J.C.S., 1933, 644—645).—The structure of lupinane and sparteine is discussed in the light of the conclusions reached by Ing (cf. this vol., 727). F. R. S.

So-called 1 : 2-dihydropapaverine. J. S. BUCK (J.C.S., 1933, 740).—4-Hydroxy-6 : 7 : 3′ : 4′-tetramethoxy-1 : 2 : 3 : 4-tetrahydroprotopapaverine and homoveratro-β-veratrylethylamide are identical, as are 6 : 7 : 3′ : 4′-tetramethoxy-9-keto-1 : 2-dihydroprotopapaverine and 6 : 7 : 3′ : 4′-tetramethoxy-1-benzoyl-3 : 4-dihydro*iso*quinoline (cf. this vol., 514). F. R. S.

***Strychnos* alkaloids. LXXIV. Complete hydrogenation of derivatives of strychnine and a transition from the brucine to the strychnine series.** H. LEUCHS and H. S. OVERBERG (Ber., 1933, **66**, [*B*], 951—955).—Treatment of strychnidine (I) with BzOH and BzO_2H in $CHCl_3$ gives strychnidine-diamine oxide [*perchlorate* (II) $C_{21}H_{24}O_3N_2,2HClO_4$]. Hydrogenation of (II) in H_2O (PtO_2) leads to octahydrostrychnidine (III) (*perchlorate*, $C_{21}H_{32}ON_2,2HClO_4$, $[\alpha]_D^{20}$ +16·7°/*d*), also obtained from (I). Brucidine in *N*-HCl is hydrogenated to dihydrobrucidine and thence to (III). Tetrahydrostrychnine is hydrogenated (PtO_2) to dodecahydrostrychnine ($C_{21}H_{34}O_2N_2,HCl,HClO_4$, $[\alpha]^{20}$ (?) +1·3°/*d*). H. W.

Sinomenine. XXXVI. New dihydroxythebainone. K. GOTO and Y. SHIBASAKI (Annalen, 1933, **503**, 277—283).—Catalytic reduction of sinoneminone leads to *α-dihydrosinomeninone* (I), m.p. 128° or m.p. 202° after preservation during 2 months, $[\alpha]^{20}$ +64·65° (*methiodide*, m.p. 284°; *oxime*, m.p. 170°; Bz_2 derivative, m.p. 141°), and the β-*compound* (II), m.p. 104° after softening below 100° (*methiodide*, m.p. 281°; *oxime*, m.p. 145—150°, or m.p. 107° from H_2O, 80° after softening at 75° from MeOH). Dihydrosinomenine is hydrolysed by 25% HBr to an intimate mixture of (I) and (II). (I) passes into (II) when boiled with 25% HBr, with 5% NaOH, or when heated at 204°; the reverse transformation could not be effected. The behaviour of (I) and (II) towards Br is described. Catalytic hydrogenation of (—)-bromosinomeninone (Pd–$BaSO_4$) leads to (—)-α-*dihydrosinomeninone* (7-*hydroxydihydrothebainone*), m.p. 127° or m.p. 202° after preservation, $[\alpha]_D$ −64·64° in $CHCl_3$ (*methiodide*, decomp. 276°; Bz_2 derivative, m.p. 135—140°; *oxime*, m.p. 170°), converted by admixture with an equal quantity of (I) into dl-α-*dihydrosinomeninone*, m.p. 226°. H. W.

Isolation of crystalline atisine. J. P. C. CHANDRASENA (J.C.S., 1933, 740).—Atisine, m.p. 314°

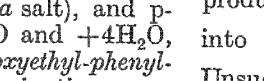
(decomp.), $[\alpha]_{61}^{29}$ +16·6° (*perchlorate*, m.p. 199°), has been isolated from tubers of *Aconitum heterophyllum*. F. R. S.

Antioxygenic properties of alkaloids. C. ACHARD, A. BOUTARIC, and J. BOUCHARD.—See this vol., 789.

Mechanism of the Wurtz–Fittig reaction. Direct preparation of an organosodium (potassium) compound from an RX compound. H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1933, 55, 2893—2896).—3-Iodofuran (I) and Na–K alloy at 30 mm. at room temp. or more rapidly at 115° give 3-sodio-(or -potassio-)furan, which with CO_2 before or after removal of unchanged (I) gives a little 3-furoic acid. Mechanisms of the Wurtz–Fittig reaction involving free radicals and organometallic compounds are thus supported. R. S. C.

Alcoholic arsinic acids. E. FOURNEAU and (MME.) Y. DE LESTRANGE (Bull. Soc. chim., 1933, [iv], 53, 330—340).—By reduction of the appropriate NO_2-derivative, diazotisation of the NH_2-compound, and application of the Bart reaction, the following hydroxyalkylphenylarsinic acid has been prepared: o- (as its internal anhydride), m- (*Na* salt), and p- (*Na* salt) -*hydroxymethyl*-; o-, $+2H_2O$ and $+4H_2O$, and p-, $+2H_2O$ (*Na* salt), -β-*hydroxyethyl-phenylarsinic acid*. Treatment of the *Ac* derivative, m.p. 102°, of *p*-aminobenzyl acetate with fuming HNO_3 at 10—15° affords the 3-NO_2-derivative, m.p. 82—83°, hydrolysed (with difficulty) by NaOH in H_2O–EtOH to 3-*nitro*-4-*aminobenzyl alcohol*, from which is obtained 2-*nitro*-4-*hydroxymethylphenylarsinic acid*, reduced by $FeSO_4$ in aq. NaOH to the 2-NH_2-compound (0·01; 0·005) [*Na* salt; *Ac* derivative (*Na* salt)] from which the 2-*OH*-derivative (0·02; 0·005) (*Na* salt, $+4H_2O$) is obtained. By similar series of reactions are prepared 6-*nitro*-3-*acetamidobenzyl acetate* (I), m.p. 111°; 6-*nitro*-3-*aminobenzyl alcohol*, m.p. 143°, 4-*nitro*- and 4-*amino*- (0·030; 0·010) (*Na* salt; *Ac* derivative) -3-*hydroxymethylphenylarsinic acid*; o-*acetamidobenzyl acetate*, m.p. 95°, and its 5-NO_2-derivative (II), m.p. 128—129°; o-*nitro*-2-*aminobenzyl alcohol*, m.p. 141° (III); 4-*nitro*- and 4-*amino*-2-*hydroxymethylphenylarsinic acid*. Reduction of (I) and (II) gives the same 2 : o-*diaminobenzyl alcohol*, m.p. 114° (*Ac* derivative, m.p. 185°), and replacement of NH_2 by OH in (III) affords the known 5-nitro-2-hydroxybenzyl alcohol. Similarly are obtained β-(p-*acetamidophenyl*)*ethyl acetate*, m.p. 93° (*alcohol*, m.p. 108°), and its 3-NO_2-derivative, m.p. 80—82° (*alcohol*, m.p. 90°); β-(3-*nitro*-4-*aminophenyl*)-*ethyl alcohol*; 2-*nitro*- and 2-*amino*- (*Na* salt) -4-β-*hydroxyethylphenylarsinic acid*. The trypanocidal activity of these arsinic acids is high, the vals. of the tolerated and curative doses for intramuscular injection being given in parentheses. J. W. B.

Alkoxypyridinearsinic acids. A. BINZ, H. MAIER-BODE, and K. MORISAWA (Angew. Chem., 1933, 46, 349—350).—By the action of NaOR on 2-chloropyridine-5-arsinic acid the following alkoxy-derivatives are prepared: 2-*methoxy*- (*Na* salt, 1·67; 1); 2-*ethoxy*- (*Na* salt, 0·1; 0·05); 2-n-*propoxy*- (*Na* salt, 0·05; 0·025); 2-n-*butoxy*- (*Na* salt, 0·025; 0·01), m.p. < 260° [reduced by HI–SO_2 to 2-n-*butoxy-pyridine*-5-*arsinic oxide*, m.p. 186° (*Na* salt, 0·01, 0·005)]; 2-i-*amyloxy*-, m.p. 115° (*Na* salt, 0·005; 0·0025); 2-sec-*octyloxy*-, m.p. < 260° (*Na* salt, 1·67; 1), and 2-*dodecyl*-, m.p. < 275° (*Na* salt, 0·5; 0·25), -*pyridine*-5-*arsinic acid*. With increasing length of the alkyl chain the toxicity (lethal and max. tolerated doses, respectively, in mg. per g. mouse are given in parentheses) by intravenous injection increases to a max. at amyl and then decreases. Comparison with the isomeric *N*-alkyl-2-pyridonearsinic acids (A., 1931, 1375) shows that *O*-alkylation increases toxicity to a much greater extent than does *N*-alkylation, whereas the non-toxic character of 2-*pyridyl Bu*$^{\alpha}$ *ether*, b.p. 200°, indicates that the As residue is the active group. J. W. B.

Attempted synthesis of heterocyclic compounds containing antimony or phosphorus in the nucleus. H. LECOQ (Bull. Soc. chim. Belg., 1933, 42, 199—214).—$PPhCl_2$, b.p. 224·9°, is reduced by gaseous HI to *di-iodophenylphosphine hydriodide*, which is distilled in a current of H_2, thus giving *phenylphosphine* (I), b.p. 159·7°. (I) reacts with MgEtBr with quant. evolution of C_2H_6 and the product, $PPh(MgBr)_2$, is converted by $O(CH_2{\cdot}CH_2I)_2$ into the *substance*  PPh, m.p. 135°. Unsuccessful attempts to reduce phenylstibinic acid to $SbPhH_2$ are recorded. H. W.

Aryl selenohalides. III. Relationship between m.p. and mol. wt. O. BEHAGEL and H. SEIBERT (Ber., 1933, 66, [*B*], 922—924; cf. this vol., 619).—Rectilinear graphs are obtained by plotting mol. wt. of $SePhCl_3$, $SePh_2Cl_2$, and $SePh_3Cl$ or the corresponding bromides against the m.p. The point of intersection of the graphs is probably the m.p. of $SePh_4$. Similar observations are recorded for $GePh_4$, $GePh_3Cl$, and $GePh_2Cl_2$ and for $SiPh_4$, $SePh_4$, $SnPh_4$, and $PbPh_4$. H. W.

Oxidation of caseinogen and serum-albumin by potassium permanganate. F. LIEBEN and B. BAUMINGER (Biochem. Z., 1933, 261, 374—386).—A no. of NH_2-acids, caseinogen (I), and serum-albumin were oxidised with $KMnO_4$ (the proteins in two stages) under comparable conditions and the NH_3 liberated was determined. Tyrosine, phenylalanine, and cystine give notably small amounts of NH_3. Nitration of the first oxidation product of (I) gives a substance containing no NO_2 groups, tyrosine and tryptophan having been destroyed. Iodination of (I) and its first oxidation product gives substances containing 9·3 and 4·5% I, respectively. Thus in spite of the destruction of aromatic rings, half of the I is still combined with the oxidation product. Considerable loss of arginine occurs, part being completely degraded and part broken down to ornithine and urea. The free NH_2-N of the first oxidation product is much <, and of the second oxidation product is >, in (I), and since the elimination of NH_3 is small, the initial decrease of NH_2-N is probably due to ring closure. A table summarises the melanin-, NH_3-, basic, and mono-NH_2-acid-N of (I) and its two oxidation products. P. W. C.

Action of sodium hypochlorite on amino-acids and proteins. F. LIEBEN and B. BAUMINGER (Bio

chem. Z., 1933, **261**, 387—392).—Oxidation with NaOCl led to the liberation of much greater amounts of NH_3 than with $KMnO_4$ (preceding abstract), the amounts for glycine, alanine, leucine, phenylalanine, tyrosine, and histidine being 22, 51, 65, 50, 64, 73%, respectively, of the side-chain-N. Oxidation of protein gave results very similar to those with $KMnO_4$ oxidation, the early oxidation products showing an absence of tyrosine and tryptophan and a much reduced NH_2-N, the latter being again increased in the later oxidation products. The cystine content of the first oxidation product of serum-albumin was half that of the original protein. P. W. C.

Casein. II. E. Cherbuliez and F. Meyer (Helv. Chim. Acta, 1933, **16**, 600—613).—Casein (I) (cows' milk) is separated by fractional pptn. from NaOH–NH_4Cl solution (cf. A., 1932, 762) by HCl and $COMe_2$, with controlled p_H, into α_1- (p_H 4·6—4·2), α_2- (as for α_1 but $COMe_2$ added), γ- ($p_H < 3·6$), and δ- (only in presence of excess of $COMe_2$) -fractions, which, since they resemble homogeneous substances on repptn. and their proportions vary widely with different samples of (I), are probably present in (I) and not formed by its degradation. The analytical data, % of humic, NH_3-, and arginine-N obtained on hydrolysis, and % of tryptophan present, in the fractions are, respectively, α_1-, C 50·4, H 7·4, N 15·2, P 0·65, S 0·78, 0·11, 1·05, 2·18, and 0·5; α_2-, 52·5, 7·0, 14·9, 0·55, 0·70, 0·07, 0·39, 1·43, and 2·2; γ-, 51·4, 7·0, 15·7, 0·69, 0·51, 0·16, 1·77, 0·12, and 0·5; δ-, 52·5, 6·8, 15·1, 1·93, 0·26, —, —, —, and 0·2%. The fractions also differ in their coagulation by rennin, α_2 being most readily coagulated. Similar fractions can be separated directly from the milk. J. W. B.

State of combination of phosphorus in phosphoproteins. I. Serinephosphoric acid from caseinogen. II. Nature of the linking between protein and phosphoric acid. F. Lipmann (Biochem. Z., 1933, **262**, 3—8, 9—13; cf. A., 1932, 1269).—I. Serinephosphoric acid (Ba and Ag salts) is obtained from caseinogen (I) by prolonged acid hydrolysis at 100°. Very probably all the P in (I) is combined thus.

II. Removal of H_3PO_4 from phosphoproteins (and from serinephosphoric acid) by acid hydrolysis is a unimol. reaction, the reaction const. being approx. the same in all cases (cf. A., 1929, 208). The purity of ichthylin from cod roe has been checked by examining its stability towards acid and alkali. W. McC.

Adenylic acid and adenine nucleotide. II. R. Klimek (Biochem. Z., 1933, **262**, 1—2; cf. A., 1932, 1150).—Adenylic acid (but not adenine nucleotide) forms complex, alkali-sol. compounds with Co (pink, then violet, then bluish-green), Fe (pale yellow), and Bi. Ni, Hg, and Mg do not react characteristically. W. McC.

Structure of proteins. XIII. Acropeptides obtained from gelatin by action of hot glycerol. Peptonised forms of these and their degradation by enzymes. A. Fodor and S. Kuk (Biochem. Z., 1933, **262**, 69—85; cf. A., 1932, 529; this vol., 621).—By fractional pptn. from aq. solution with $COMe_2$ the product *P* yields two *substances* $(C_{31}H_{48}O_{12}N_9)_2Ca$ having the same composition but different mol. wt. (1500, 741). Structures for these substances based on analyses and on the results of degradation experiments with enzymes are suggested. W. McC.

Union of biocolloids. XVIII. Synthetic nucleoproteins. S. J. von Przyłecki, S. Frajberger and W. Giedroyć (Biochem. Z., 1933, **262**, 224—236; cf. this vol., 463).—The properties of two- and three-component (two proteins, one acid) synthetic nucleoproteins containing the following components have been examined and possible modes of combination are suggested: serum-globulin, edestin, ovalbumin, gelatin, histone, peptone; guanylic and xanthylic acids, yeast-nucleic acid. W. McC.

Potentiometric analysis of pure animal proteins. J. Errera and Y. Hirshberg (Biochem. J., 1933, **27**, 764—770).—By plotting the changes in p_H of the solution of a protein, purified by electrodialysis, in acid or alkali, produced by the successive addition of given vols. of alkali or acid, against the corresponding final p_H of the solution, curves are obtained for ovalbumin, serum-albumin, hæmoglobin, and caseinogen from which are calc. the isoelectric points, the stoicheiometric relationships of the combination of the proteins with acid and base, the mean K_a and K_b of the CO_2H and NH_2 groups, and the no. of these groups per mol. of protein. H. D.

Phenylcarbimide–protein compounds. S. J. Hopkins and A. Wormall.—See this vol., 846.

Semi-micro-apparatus for the determination of carbon and hydrogen by the method of Orthner and Reichel. J. Lindner (Chem. Fabr., 1933, **6**, 277; cf. this vol., 731).—Errors introduced by using PbO_2 are described. E. S. H.

Causes of errors in determination of carbon, hydrogen, and nitrogen. E. Coffari (Gazzetta, 1933, **63**, 323—328).—The usual analytical methods are discussed. E. W. W.

Micro-determination of halogens in organic compounds. A. Elek and D. W. Hill (J. Amer. Chem. Soc., 1933, **55**, 2550—2554).—Halogen in 5 mg. of an org. substance is determined by fusion with Na_2O_2 in a micro-bomb, one analysis occupying 45 min. R. S. C.

Destruction of organic matter prior to determination of phosphorus and sulphur. E. Cherbuliez and F. Meyer (Helv. Chim. Acta, 1933, **16**, 613—614).—Details are given of an effective method (heating with $NaNO_3$–fuming HNO_3) for destruction of large amounts of org. matter prior to determination of P, Ca, and S (described) in org. compounds. J. W. B.

Identification of aldehydes and ketones by micro-melting point determination. R. Fischer (Mikrochem., 1933, **13**, 123—128).—The m.p. of semicarbazones, *p*-nitrophenylhydrazones, and *o*- and *p*-nitrobenzhydrazones, prepared by the method of Griebel and Weiss (A., 1928, 82), provides the best means of identification. J. S. A.

Determination of amino-acids by formol titration. N. Bulgakov (J. Appl. Chem. Russ., 1933, **6**, 375—379).—Borate is preferred to phosphate buffer

for the titration. CO_2 should be rigorously excluded from all solutions used. R. T.

Determination of glucose with ammoniacal silver nitrate solution. A. S. RUNDLE (Cuir tech., 1932, **20**, 258—262; Chem. Zentr., 1933, i, 978).—The solutions are boiled and acidified with AcOH; KCl is added, and the excess is titrated with $AgNO_3$. The quantity of $AgNO_3$ required is not directly proportional to the quantity of glucose; tables are required. Mixtures of glucose and lactose may be analysed analogously. A. A. E.

Determination of reducing sugars by titration of ferricyanide. S. W. COLE (Biochem. J., 1933, **27**, 723—726).—The determination of reducing sugars by titration of boiling ferricyanide, with a drop of methylene-blue as internal indicator, is described. Equivs. are given for glucose, maltose, and lactose, and the determination of lactose in milk and glucose in urine is described. H. G. R.

Analysis of organic liquids by the conductometric method. K. ŠANDERA (Chem. Obzor, 1932, **7**, 268—271).—The composition of binary mixtures (EtOH–H_2O, MeOH–H_2O, C_5H_{12}–MeOH, etc.) is determined by measuring the conductivity of a saturated solution of the liquid in a suitable electrolyte. CH. ABS.

Simple method for spectroscopic characterisation of organic dyes and other coloured substances. J. B. CHLOUPEK (Coll. Czech. Chem. Comm., 1933, **5**, 218—221).—The coloured material is allowed to diffuse from its conc. solution in glycerol or aq. sucrose into H_2O or suitable reagent, producing a layer with an exponential concn. gradient, the spectrum of which is observed. D. R. D.

Reaction of caffeine with iodine–potassium iodide solution. M. WAGENAAR (Mikrochem., 1933, **13**, 145—146).—Caffeine, but not theobromine or theophylline, gives with KI+I and CsCl well developed deep brown star-shaped clusters, sensitive to 0·002 mg. of caffeine. J. S. A.

Microchemical identification of coumarin. M. WAGENAAR (Mikrochem., 1933, **13**, 141—146).—0·02 mg. of coumarin may be detected by pptn. with AcOH from the warm NaOH solution. With KI+I or $ZnCl_2$+I solution, followed by dissolution in $COMe_2$ and evaporation, a network of characteristic bluish needles is obtained with 0·01 mg. Addition of $HgCl_2$ to an aq. chloral hydrate solution of coumarin gives on dilution with H_2O characteristic needles. J. S. A.

Identification of organic compounds. XIII. L. ROSENTHALER (Pharm. Ztg., 1933, **78**, 699—700).—The properties and reactions of atebrin (a dialkylaminoacridine), plasmoquin (an 8-amino-6-methoxydiethylamino*iso*amylquinoline), amatin [1 : 3 : 4-$C_6H_3Me(OAc)\cdot CO_2H$], butolan ($CH_2Ph\cdot C_6H_4\cdot O\cdot CO\cdot NH_2$), and per-abrodil (diethanolamine 3 : 5-di-iodo-4-pyridone-1-acetate) are described. H. A. P.

Biochemistry.

Synthetic atmospheric mixtures of carbon dioxide and oxygen in relation to animal life. J. W. HERSHEY (Trans. Kansas Acad. Sci., 1932, **35**, 141—143).—For mice and guinea-pigs O_2 95, CO_2 5% is optimal. CH. ABS.

Carbonic anhydrase and the state of carbon dioxide in blood. N. U. MELDRUM and F. J. W. ROUGHTON (Nature, 1933, **131**, 874—875).—Evidence in favour of the formation of compounds of a carbamate type (I) between proteins and CO_2 in blood is advanced. The formation of (I) is distinct from the H carbonate mechanism and does not appear to be catalysed by carbonic anhydrase. L. S. T.

Adaptations to hydrostatic pressure in whales. A. H. LAURIE (Nature, 1933, **132**, 135—136).—The blood of Blue whales contains organisms which absorb N_2 and account for the increased solubility of N_2 in the blood. In presence of O_2, N fixation apparently occurs and the excess N_2 resulting from compression of the lungs in deep diving is removed from the blood. L. S. T.

Heat of reaction of the oxygenation of hæmocyanin. R. K. BROWN (J. Cell. Comp. Physiol., 1932, **2**, 467—478).—Between 5° and 40° the equilibrium between O_2 and purified hæmocyanin (I) indicates a combination of 1 mol. O_2 with 1 mol. of hæmocyanin. The heat of oxygenation per mol. of O_2 was 14,800 and 16,000 g.-cal. for two samples of (I). A. G. P.

Solubility and dissociation tendency of carboxyhæmoglobin in ammonium sulphate solutions. S. P. L. SØRENSEN and M. SØRENSEN (Compt. rend. Trav. Lab. Carlsberg, 1933, **19**, No. 11, 1—34).—Suspensions of cryst. carboxyhæmoglobin (I) in conc. aq. $(NH_4)_2SO_4$ at 0° are stable for many months. (I) contains 35·3% H_2O when calc. on the anhyd. substance. The effect of the concn. of $(NH_4)_2SO_4$ on the solubility of (I) agrees with the relationship found by Cohn (A., 1932, 73). The p_H–solubility curve of (I) in presence of $(NH_4)_2SO_4$+NH_3 or H_2SO_4 has two min., one at p_H 6·6, the isoelectric point of (I), and the other at 5·4 corresponding with a sparingly sol. sulphate containing 12—13 mols. of H_2O per mol. of (I). Under similar conditions the ionisation curve is continuous, an inflexion occurring between p_H 5·5 and 6·3. The effect of the concn. of (I) on the equilibrium between the pptd. (I) and the medium containing $(NH_4)_2SO_4$ indicates that the dissociation is very small at high concns. but increases with increasing dilution, the vals. at all concns., however, being < those corresponding with serum-proteins. No fractionation of (I) could be effected. F. O. H.

Glutathione and changes in the spectrum of hæmoglobin. G. LITARCZEK and G. T. DINISCHIOTU (Compt. rend. Soc. Biol., 1933, **112**, 1014—1017).—The addition *in vitro* of glutathione (I) to rabbits' blood generally produces an increase of the "span" between the absorption bands of oxy- and

carboxy-hæmoglobin. As anæmia progresses, the increase is less marked, as if the blood became saturated with (I). (I) possibly exists in chemical combination with hæmoglobin. NUTR. ABS. (*m*)

[Detection of] small traces of blood. P. MEDINGER (Ann. Chim. Analyt., 1933, [ii], **15**, 241—251).—Modifications of known methods—development of colour with leucomalachite-green, formation of hæmatoporphyrin and observation of its fluorescence, formation of hæmochromogen and observation of its spectrum—are described. J. G.

Cell nuclei. II. O. FÜRTH. Bird's blood-corpuscle nuclei. T. LEIPERT and T. KUROKAWA (Biochem. Z., 1933, **261**, 425—432).—The nuclei (I) of hen's erythrocytes contain P 3·78, N 16·88, S 0·36, tryptophan 0·84, arginine 8·05, and purine-N 3·97%. The N is distributed as follows: NH_2-N, 13·5; melanin-N, 2·96; N of bases, 40·90; non-base-N, 41·66%. The histone fraction of (I) contains C, 51·88, H 8·02, N 18·19, S 0·88%. The N distribution is NH_3-N, 5·2; melanin-N, 0·61; non-base-N, 50·06 (of this 45·42% is NH_2-N and 4·64 non-NH_2-N), total N of bases 44·18 (of this 25·5% is arginine-N, 1·48% histidine, 17·2% lysine), and tyrosine 5·26%. The nucleic acid fraction of (I) is identical with thymus-nucleic acid. The P : N ratio is the same for both, both give the same colour reactions for their carbohydrate, and both contain adenine, guanine, cytosine, and thymine. P. W. C.

Tryptophan in blood development. R. S. ALCOCK (Biochem. J., 1933, 27, 754—758).—Rats kept on a diet deficient in tryptophan (I) failed to develop anæmia. Young rats suffering from milk anæmia recovered independently of the presence of (I) in the diet. H. D.

Protease and amylase in the blood of the silkworm (*Bombyx Mori*, L.). K. YAMAFUGI (Bull. Agric. Chem. Soc. Japan, 1933, **9**, 19—13).—The blood-protease (I) of silkworms shows optimum activity at p_H 2·3 and 8·8 and at 40°. The activity does not change with age, but in male is > in female larvæ. The blood-amylase (II) (p_H optimum 6·5, temp. optimum 35°) occurs to a greater degree in female than in male larvæ, and the amount increases with age. The (I) and (II) contents did not vary within the five species of silkworms examined. A. L.

Micro-determination of blood-fat. F. RAPPAPORT and H. ENGELBERG (Klin. Woch., 1932, **11**, 2080; Chem. Zentr., 1933, i, 979—980).—Blood is treated with a mixture of Et_2O and EtOH, an aliquot part of the filtrate being evaporated and the residue hydrolysed with NaOEt. The fatty acids are dissolved in $CHCl_3$ and light petroleum; an aliquot part of the solution is evaporated, and the residue oxidised with a mixture of $K_2Cr_2O_7$, $Ce(SO_4)_2$, and H_2SO_4. The excess of CrO_3 is determined iodometrically. A. A. E.

Differential lipin analysis of blood-plasma in normal young women. E. M. BOYD (J. Biol. Chem., 1933, **101**, 323—336).—The total lipin, neutral fat, phospholipin, cholesteryl ester, and neutral fat fatty acids, the free and combined cholesterol, and the phospholipins of normal young women have been determined by an oxidative technique. H. D.

Collection and preservation of small blood samples for glucose determinations. M. E. EWING (J. Lab. Clin. Med., 1933, **18**, 500—502).—The samples are collected and kept in capillary pipettes lined with NaF and $HgCl_2$ and sealed with rubber bands. The change in glucose concn. is < 5% in 14 days. CH. ABS.

Determination of lactose in blood. R. MORACCHINI and B. COSSU (Diagnost. Tecn. Labor., 1932, **3**, 140—148; Chem. Zentr., 1933, i, 979).—In Folin and Malmros' micro-method fermentation with brewer's yeast gives good results in differentiating blood-glucose and lactose. A. A. E.

Blood-sugar during fasting. Determination of blood-sugar with the Pulfrich photometer. B. J. KRIJGSMAN (Arch. néerl. Physiol., 1933, **18**, 173—192).—The quantity of blood required is 0·025 c.c. The blood-sugar of fasting rats decreases somewhat during the first 24—50 hr. and then varies about a const. mean during the next 5 days, vals. by day being > by night. This last effect is probably due to ultra-violet irradiation by day. W. O. K.

Physiological variations in the glucose ratio of blood and cerebrospinal fluid. D. J. COHN, A. LEVINSON, and F. MCCARTHY (Amer. J. Physiol., 1933, **103**, 613—619).—The average fasting val. for true glucose in blood is 85 mg. and in cerebrospinal fluid (I) 55 mg. per 100 c.c. (I) contains 8—17 mg. of non-glucose reducing substances per 100 c.c. The average ratio of glucose in (I) to blood-glucose in 10 cases was 71·5 (Folin–Wu method) and 87·6% (Somogyi method). NUTR. ABS. (*m*)

Determination of uric acid in unlaked blood and in urine. O. FOLIN (J. Biol. Chem., 1933, **101**, 111—125).—A complete revision of the colorimetric methods for determination of uric acid. H. G. R.

Theoretical CO_2 error of the Winterstein micro-electrode for determination of blood-p_H measurements. W. LAUBENDER (Arch. exp. Path. Pharm., 1933, **171**, 105—110).—The calc. CO_2 error is so considerable that, apart from previously noted drawbacks (see A., 1932, 635), the electrode is not suitable for determining blood-p_H. R. N. C.

Acid–base balance of new-born infants. III. Influence of cow's milk on the acid–base balance of the blood of new-born infants. E. MARPLES and V. W. LIPPARD (Amer. J. Dis. Child., 1933, **45**, 294—306).—In infants receiving whole cow's milk the serum-CO_2 is < in those receiving breast milk. Similar results are obtained when the CO_2 is determined during breast feeding and cow's milk periods in the same infants. The fall in CO_2 is associated with decrease in p_H and increase in undetermined acid. The acid–base balance of the blood of the newborn is more labile than that of older infants. NUTR. ABS. (*m*)

Determination of iron content of blood in children. I. P. SOBEL and I. J. DREKTER (Amer. J. Dis. Child., 1933, **45**, 486—497).—Venous blood-Fe is normally 40—52 mg. per 100 c.c.; in patho-

logical conditions it is 18·2—74 mg. Hæmoglobin concns. determined by the Newcomer method are usually > those calc. from the Fe content.
CH. ABS.

Blood-phosphate. M. SAHYUN (J. Biol. Chem., 1933, **101**, 295—299).—Higher vals. for blood-inorg. PO_4''' (I) in determinations on filtrates made 24 hr. after pptn. with $CCl_3{\cdot}CO_2H$ were observed than in those made immediately. Rabbits fasted for 24 hr. exhibited higher (I) vals. than those fed. The rate of hydrolysis of a phosphoric ester in the $CCl_3{\cdot}CO_2H$ filtrate of rabbit's blood was determined. H. D.

Bromine content of human blood. F. EWER (Z. klin. Med., 1932, **122**, 244—252; Chem. Zentr., 1933, i, 1152).—Blood-Br varies about 1 mg. per 100 c.c., even during administration of I′ or NaCl. After intravenous injection of thyroxine the blood-I increases rapidly, becoming normal after 48 hr. Cl also increases, but Br falls, although to < 0·7 mg. per 100 c.c. Increased urinary Br was not observed.
A. A. E.

Magnesium thiosulphate and blood coagulation. A. LUMIERE and S. SONNERY (Compt. rend. Soc. Biol., 1932, **111**, 391—392; Chem. Zentr., 1933, i, 1152).—MgS_2O_3 retards blood coagulation *in vitro*, and, like Na citrate, increases it *in vivo*. Mg citrate is not more active than Na citrate, and $Na_2S_2O_3$ is much less active. A. A. E.

Effect of intraperitoneal blood transfusion on various characteristics of blood. F. OOI (Tohoku J. Exp. Med., 1933, **20**, 300—319).—The effect on cell fragility and coagulation time is described. There is a slight relative increase in serum-albumin after about 8 hr. CH. ABS.

Precipitin reaction. II. Effect of certain electrolytes on the formation of precipitates. C. M. DOWNS and S. GOTTLIEB (J. Infect. Dis., 1932, **51**, 460—468).—Certain (*M*-)salts inhibit pptn. from horse serum and anti-horse rabbit serum; all the salts examined inhibited the formation of a ppt. from cryst. ovalbumin and its antiserum. Solubilities of washed sp. ppts. in acids and alkalis are independent of the salt present at formation of the ppts.
CH. ABS.

Phenylcarbimide–protein compounds and their immunological properties. S. J. HOPKINS and A. WORMALL (Biochem. J., 1933, **27**, 740—753).—*Compounds* of PhNCO (I) with caseinogen, gelatin (II), and horse serum-globulin (III) were prepared by treating the proteins with (I) at const. (8·0) and pptn. with AcOH. Similar *compounds* with *p*-$C_6H_4Br{\cdot}NCO$ (IV) were prepared in Et_2O solution. The decrease in free NH_2-N of the protein was approx. equal to the (IV) which reacted. Treatment of (III) with (I) produces no significant loss of its antigenic power, whilst a marked loss of specificity occurs. Compounds of zein [which has no lysine (V) groups] with (IV) could not be formed. The pptn. reaction between phenylureido-proteins and anti-bodies is most effectively inhibited by the corresponding compound of (V). The possibility that (V) is of significance in determining species-specificity is stressed. Compounds of (I) and (IV) with (II) readily give ppts. with antisera to compounds of (I) and (IV) with (III). H. D.

Relationship between structure of antigen and specificity of anti-body. V. H. ERLENMEYER and E. BERGER (Biochem. Z., 1933, **262**, 196—202; cf. this vol., 175).—Experiments with antigens obtained from cryst. ovalbumin and diazotised aromatic aminoarsinic acids, tested with sera immunised with such antigens, show that the specificity of the anti-bodies produced does not depend on the degree of purity of the protein used. As regards the quant. relation between the structure and specificity of the non-protein component of the complex antigens, aromatic sulphonic acids differ *in vivo*, but not appreciably *in vitro*. Anti-bodies produced by the action of a sulphanilic acid-azoprotein bind $PhSO_3H$ and $PhSeO_3H$, but not $PhSO_2H$. W. McC.

Standardisation of biological stains. I. General. II. Fluoran derivatives. A. R. PETERSON, H. J. CONN, and C. G. MELIN (Stain Tech., 1933, **8**, 87—94, 95—99).—I. The relative merits of analytical methods are discussed. In addition to chemical and physical examination, biological tests are essential.

II. Methods for testing fluorescein, eosin-yellowish, ethyleosin, eosin-bluish, erythrosin, phloxine-B, and rose-bengal are described. H. W. D.

Masson trichrome staining methods. N. C. FOOT (Stain Tech., 1933, **8**, 101—110).—Detailed directions for Masson's methods are given. The "light-green" procedure is favoured. Sections are prestained in Fe-hæmatoxylin, followed by a mixture of ponceau-xylidine and acid fuchsin. After mordanting in phosphomolybdic acid the sections are stained in light-green. H. W. D.

Iron hæmatoxylin [stability of staining solutions]. R. T. HANCE (Stain Tech., 1933, **8**, 117).—Stock solutions of Fe-hæmatoxylin (10% EtOH solutions) should be renewed yearly. A trace of $NaHCO_3$ added to a new 0·5% solution enables it to be used immediately. H. W. D.

Gingival tissue lipins. H. C. HODGE (J. Biol. Chem., 1933, **101**, 55—61).—The lipin content (I) of gum lies between that of skin (II) and intestinal mucosa (III), the phospholipins being nearer to those of (III), the total lipins and cholesterol more nearly like the vals. for (II). H. G. R.

Lipins of mammalian liver. III. Polydiaminophosphatide of pig's liver. E. FRÄNKEL, F. BIELSCHOWSKY, and S. I. THANNHAUSER (Z. physiol. Chem., 1933, **218**, 1—11; cf. this vol., 176).—The constituents of a sphingomyelin from pig's liver were choline, sphingosine, and H_3PO_4. The fatty acids consist of palmitic, lignoceric, and stearic acids in mol. proportions. The substance is probably a polydiaminophosphatide. J. H. B.

Phosphatides. VI. Fatty acids of the liver phosphatides and of the liver oil of *Etmopterus spinax*. E. KLENK (Z. physiol. Chem., 1933, **217**, 228—236; cf. A., 1932, 958).—The phosphatides consist of a mixture of lecithin and cephalin, the fatty acids of which contain only small amounts of saturated

acids (palmitic) and considerable amounts of highly unsaturated acids, principally C_{20} and C_{22}. Glycerides account for only a small fraction of the fatty acids of the liver oil, which are mostly combined with higher alcohols. Highly unsaturated C_{20} and C_{22} acids are present. J. H. B.

Egg- and plant-lecithin. Physiological dissimilarity. K. DRAGENDORFF (Chem.-Ztg., 1933, **57**, 493—494).—Apart from differences in chemical structure, egg- and plant-lecithin may differ physiologically owing to the presence or absence of associated compounds (*e.g.*, lutein in the former) and to differences in physical properties (*e.g.*, emulsifying power). In general the latter cannot replace the former physiologically. J. G.

Muscle-adenylic acid from yeast and yeast-adenylic acid from pancreas. Nomenclature of the adenylic acids. F. LINDNER (Z. physiol. Chem., 1933, **218**, 12—16).—So-called yeast-adenylic acid was obtained from pancreas (A., 1925, i, 182) and muscle-adenylic acid from yeast. The names syn- and erga-adenylic acid are suggested for the yeast- and muscle-product, respectively. J. H. B.

Nitrogenous extractives of ovaries. D. TRUBIZIN (Z. physiol. Chem., 1933, **217**, 105—108).—An aq. extract of cow's ovaries contained no carnosine, contrary to Heyl and Hart (A., 1928, 83). Guanine, NH_2Me, and choline were identified. J. H. B.

Distribution of sulphur in goat hair. D. J. LLOYD and R. H. MARRIOTT (Biochem. J., 1933, **27**, 911—914).—On treatment of the hair with 4*N*-NaOH, the cortex (I) (86·5% by wt.) is dissolved, leaving the medulla (II) (13·5%) intact. (I) contains 3·6% and (II) 0·23% S, indicating that (II) is substantially free from S. Keratin probably contains one cysteine residue to five other NH_2-acid residues. F. O. H.

Occurrence of amylase, invertase, and protease in the hen, *Hydrochelidon nigra*, L., and *Vanellus vanellus*, L. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1933, **262**, 175—180; cf. this vol., 736).—Invertase (I), amylase (II), and protease are found in glycerol extracts of the breast, intestine, and pancreas of *V. vanellus*. (I) and (II) are also found in such extracts of the blood and the thigh muscle, and (I) occurs also in the keratin. W. McC.

Reversible oxidation–reduction system in mammalian tissue. R. BIERICH, A. LANG, and A. ROSENBOHM (Naturwiss., 1933, **21**, 496—497).—By pptn. of tissue extract with Ag lactate, three reducing substances were obtained: (i) a substance from the supernatant liquid, not yet completely investigated, (ii) glutathione, and (iii) a small quantity of a yellow substance (I), colourless when reduced. The oxidation–reduction potential of (I) was lower than that of any similar system previously investigated. There is close relationship, and perhaps complete identity, between (I) and the yellow oxidation enzyme and its pigment constituent (Warburg and Christian, A., 1932, 1285). A. J. M.

New group of animal pigments (lyochromes). II. P. ELLINGER and W. KOSCHARA (Ber., 1933, **66**, [*B*], 808—813; cf. this vol., 298).—In agreement with Kuhn, the name "lyochrome" is assigned to the group of pigments, whereas the individual members are termed "flavins." The isolation of *lactoflavin* C (I) in addition to lactoflavins *A* (II) and *B* (III) (formerly lyochrome *A* and *B*) is described. The substances have no well-defined m.p. and are identified by cryst. form and analysis. (I) and (III) have nearly identical composition corresponding approx. with $(C_{19}H_{18}O_{12}N_{14})_x$, whereas (II) has a much lower N content (21·6%). (I) and (III) approximate in composition to uric acid, but are distinguished from it by colour and greater solubility in H_2O, from which they are not pptd. by NH_4Cl. (I) and (II) are immediately sol. in NH_3, (III) in *N*-NaOH. In the murexide test, (I) and (III) yield red solutions on addition of NH_3 which become lemon-yellow in presence of much HCl. The amorphous lactoflavin residues do not afford the red colour unless HNO_3 is replaced by HCl–$KClO_3$. Aq. solutions of lactoflavins are readily bleached on exposure to light if $COMe_2$, MeOH, or EtOH is present; solutions in C_5H_5N or EtOAc are stable. H. W.

Lactoflavin, the pigment of milk. R. KUHN, P. GYORGY, and T. WAGNER-JAUREGG (Ber., 1933, **66**, [*B*], 1034—1038).—Details are given for the isolation of *lactoflavin* (I), decomp. 271° (corr.; sealed capillary) after darkening at 240°, from milk, initial adsorption being effected by fuller's earth in strongly acid solution. Preliminary analyses indicate the formula $C_{17}H_{20}O_6N_4$. (I) resembles ovoflavin very closely, but identity cannot yet be assumed. Its absorption spectrum is recorded. (I) has an intense green fluorescence in H_2O. It is sensitive towards alkali, stable towards acid, and resistant to oxidation. It is the most active vitamin-B_2 prep. hitherto obtained. H. W.

Dialysis of milk. Distribution of phosphorus. L. H. LAMPITT and J. H. BUSHILL (Biochem. J., 1933, **27**, 711—722).—Apparatus is described whereby dialysis is carried out at a low temp. and the dialysate conc. Ultra-filtration is combined with dialysis by applying a vac. to the outside of the membrane. The serum obtained by "static" dialysis of a solution of spray-dried, separated milk has approx. the same total and inorg. P as an ultra-filtrate from the same solution. Continuous dialysis of fresh separated milk yields more inorg. P than static, the org. P remaining the same. Support is given to the statement that heat treatment reduces the inorg. P obtainable by dialysis or ultra-filtration. H. G. R.

Factors in the milk of individual cows which modify growth of lactic streptococci. H. R. WHITEHEAD and G. A. COX (Biochem. J., 1933, **27**, 951—959).—The formation of lactic acid in rennet curds inoculated with lactic streptococci is inhibited when the milk contains an abnormally high no. of leucocytes (I) (> 5,000,000 per c.c.). Previous heating of the milk at 49—52° for 30 sec. destroys the inhibiting action, which is probably due to phagocytosis of the bacteria by (I). In milk containing normal nos. of (I) (up to 1,000,000 per c.c.) a direct though not exact relation exists between the no. of (I) and the rate of formation of lactic acid; probably

some substance associated with the presence of (I) promotes the growth of the bacteria. This substance remains active after pasteurisation of the milk at 63° for 30 min. W. O. K.

Separation and determination of the proteins of carabao milk as compared with those of Filipino mother's milk in the early period of lactation. M. Ocampo (Univ. Philippines Nat. Appl. Sci. Bull., 1932, **2**, 357—382).—The milk of *Buffelus bubalus* contains 5·71% of total protein. Of the total N, 79·4% is as caseinogen, 10·3% as lactalbumin, and 3·4% as lactoglobulin. Corresponding vals. for human (Filipino) milk are: 1·58, 14·9, 44·8, and 16·9%. Ch. Abs.

Production of caseinogen in the breast during pregnancy. O. I. Cutler and J. H. Lewis (Amer. J. Physiol., 1933, **103**, 634—646).—Caseinogen is present in the udders of cows after the 24th week of pregnancy but not in those of heifers pregnant < 20 weeks Nutr. Abs. (*m*)

Influence of artificially dried grass in the winter ration of the dairy cow on the colour and vitamin-*A* and -*D* contents of butter. S. J. Watson, J. C. Drummond, I. M. Heilbron, and R. A. Morton (Empire J. Exp. Agric., 1933, **1**, 68—81).—The low vitamin-*A* content (I) of butter from cows on customary winter feeds was not increased by inclusion of grass silage in the ration. Artificially dried grass which had received N fertiliser raised the (I) of the butter to the summer grazing level. Artificially dried unmanured grass improved the (I) to an intermediate extent. Changes in yield and composition of milk due to the above grass diets were small, and the vitamin-*D* content remained unaffected until the grazing season began. A. G. P.

Variations in the quality of butter and the vitamin-*A*, carotene, and xanthophyll content as influenced by feeding artificially dried grass to stall-fed cattle. A. E. Gillam, I. M. Heilbron, R. A. Morton, G. Bishop, and J. C. Drummond (Biochem. J., 1933, **27**, 878—888).—With cows fed on hay and concentrates, the carotene (I), xanthophyll (II), and vitamin-*A* contents of the butter fall steadily during the winter and remain at a low level until the spring, when natural grazing produces a rapid rise in all three substances. Increases are also produced by replacement of the control diet by artificially dried non-N-treated grass and, to a greater extent, by dried N-treated grass, but not by grass silage of moderate quality. Ergosterol occurs in the unsaponifiable matter of grass, the spectroscopic $SbCl_3$ test for which gives higher vals. for (I) and (II) than does the direct absorption method. F. O. H.

Factors influencing the component fatty acids of butter. H. K. Dean and T. P. Hilditch (Biochem. J., 1933, **27**, 889—897).—An extension of previous investigations (A., 1930, 1308) indicates a seasonal abrupt increase (approx. 4 mols.-%) in the proportion of oleic and linoleic acids, together with a parallel decrease in butyric and stearic acids, these changes occurring in spring when the cows return to pasture. With increasing age of the cow, the unsaturated acids increase mainly at the expense of palmitic acid. The range of variation in palmitic and C_{18} acid contents of beef tallows (A., 1931, 1178) may also be related to the age of the animal. F. O. H.

Fatty acids and glycerides of the milk-fats of Indian goats and sheep. D. R. Dhingra (Biochem. J., 1933, **27**, 851—859).—Goat's milk contains 3·2—3·6% of fat, and sheep's milk 4·0—4·2%. The Polenske vals. are 8·2 and 8·0, respectively. There is a marked increase in the decoic + octoic acid content (10—12 mols.-%), and to a smaller extent in the hexoic acid content, chiefly at the expense of the oleic–linoleic acid fraction (11—12 mols.-%) as compared with cow's milk-fat. The palmitic acid content (26·9—31·6 mols.-%) is also reduced in the fully saturated glycerides as compared with approx. 39—43% for the corresponding components of cow's milk-fat. P. G. M.

Approximation of certain components of the ash of the milk of cow and sheep to those of blood. F. E. Nottbohm and K. Philippi (Z. Unters. Lebensm., 1933, **65**, 551—561).—With increasing Cl content, Na in cow's milk regularly increases, K remains const., and the alkali no. diminishes until a crit. Cl content of approx. 0·2% is reached, when Na becomes irregular, K and the alkali no. fall to the val. for blood, whilst the initial Cl>Na becomes, as in blood, Na>Cl. In sheep's blood with high Cl the approximation of the ash constituents to those of the ash of blood is still more marked. The crit. Cl content marks the breakdown of the selective secretory activity of the alveolar cells with respect to blood constituents. E. C. S.

Changes in bile chemistry and bile secretion under the influence of certain hormones and vegetable poisons. S. Leites and R. Isabolinskaja (Arch. exp. Path. Pharm., 1933, **170**, 592—608).—In dogs with a bile fistula the rate of secretion of bile is reduced during the 2 hr. following administration of adrenaline (I), thyroxine (II), parathyroid hormone, and atropine (III), and increased by histamine (IV) and large doses of insulin, whilst pituitary preps. (V) and ergotamine have no effect. None of the above compounds definitely alters the Ca, K, or cholesterol content of the bile with the exception of (II), which after subcutaneous or oral administration causes an increase in cholesterol concn. The concn. of the bile acids is sometimes reduced by (III) and (IV) and sometimes increased by (I) and (V). W. O. K.

Splenectomy in bile-fistula dogs. Bile-pigment over-production, anæmia, and intoxication. F. B. Queen, W. B. Hawkins, and G. H. Whipple (J. Exp. Med., 1933, **57**, 399—418).—The spleen and bile together are essential for normal metabolism of pigment; the bile salts probably play an obscure role. It is suggested that the body can synthesise the pyrrole aggregate. There is some evidence that the liver can directly synthesise bile-pigment. Ch. Abs.

Chemical composition of lymph from subcutaneous vessels. J. W. Heim (Amer. J. Physiol., 1933, **103**, 553—558).—The non-protein-N, urea, creatinine, sugar, and NH_2-acid contents of the

cervical lymph of dogs are similar to those of blood-plasma. The following constituents show differences from plasma: protein 3·32 g., Cl′ 711, inorg. P 5·9, Ca 9·8 mg. per 100 c.c. NUTR. ABS. (*m*)

Composition of aqueous humour, cerebrospinal fluid, lymph, and blood from frogs, higher animals, and man. A. M. WALKER (J. Biol. Chem., 1933, **101**, 269—287).—Reducing substances (I), inorg. PO_4''' (II), uric acid (III), and urea (IV) were determined in the plasma (V), lymph (VI), cerebrospinal fluid (VII), and aq. humour (VIII). For frogs the mean concns. of (I) and (II) in (VI) were respectively 97 and 94% of the corresponding (V) vals.; the mean (VII) concns. of (I) and (II) were 63 and 37% of the (V) vals.; the mean concns. of (I) and (II) in (VIII) were 69 and 41% of the (V) vals. For fowls, rabbits, dogs, and cats the mean concns. of (I), (II), (III), and (IV) in (VIII) were respectively 85, 37, 63, and 70% of the (V) vals. In depancreatised dogs the mean concns. of (I) and (II) in (VIII) were 88 and 44% of those of (V). In man the mean concn. of (I) in (VIII) was 60 mg. per 100 c.c., whilst that of (V) was 108 mg. It is concluded that the choroidal and ciliary epithelia exhibit selective qualities not possessed by capillary endothelium or by glomerular membrane. H. D.

Osmotic pressure and membranes. I. S. HIRONAKA (Japan. J. Med. Sci., IV, Pharmacol., 1932, **6**, 157—201).—The osmotic behaviour of true body-fluids towards collodion membranes has been studied by new methods. The actual vals. are small compared with the theoretical vals. Anomalous vals. for graduated concns. of electrolytes can have no biological significance. Urea (I), Et urethane, and $HCO{\cdot}NH_2$ exhibit negative osmotic pressure in higher concns. Addition of (I) lowers the osmotic pressure of solutions of sugar or NaCl. Curves showing the rate of flow of the solution through the membrane are more complex than the osmotic pressure curves, and there is no direct relationship between them. CH. ABS.

Nitrogenous constituents of gastric juice. I. Ammonia. H. STEINITZ (Arch. Verdauungskrankh., 1932, **52**, 31—37; Chem. Zentr., 1933, i, 1152—1153).—Blood-urea is regarded as the source of NH_3 (2—9 mg. per 100 c.c.) in gastric juice. A. A. E.

Acidimetry of gastric juice. II. Determination of free hydrochloric acid in human gastric juice. III. Error of titrated total acidity of human gastric juice. M. HORI (Japan J. Gastroenterol., 1933, **5**, 1—13, 14—18).—II. Determinations of the free HCl in human acidic gastric juice by Sahli's method agree closely with the correct vals. calc. from p_H determinations by the H electrode. Direct titration with 0·1*N*-alkali using one of the following indicators: *p*-dimethylaminoazobenzene (I), tropæolin-*OO*, 2 : 6-dinitrophenol (II), Gunzberg's reagent, Congo-red, Me-violet (III), and Me-orange (IV) give errors varying linearly with the protein content of the juice. (I) is not satisfactory; the error may exceed 100%. Approx. correct results are obtained with (II) (0·95), (III) (1·10), or (IV) (0·91) when the results are multiplied by the factors given. No relation exists between free HCl and protein content of various samples of gastric juice.

III. Titration of gastric juices by 0·1*N*-NaOH with phenolphthalein as indicator gives results which differ from the true total acidity obtained with bromothymol-blue (Inoue, A., 1930, 1204) by an amount proportional to the protein content. When the phenolphthalein titrations are multiplied by 0·91, the results are correct within 8%. Titrations with alizarin-red give approx. correct readings if multiplied by 1·01. W. O. K.

Use of maté tea for determination of the acidity of gastric juice. J. ORGAZ, R. V. DE IPOLA, and R. F. BUA (Semana méd., 1933, i, 547—558). CH. ABS.

Gastric secretion. T. G. KLUMPP and M. A. BOWIE (J. Clin. Invest., 1933, **12**, 1—12).—The histamine meal gives higher vals. for total and free acid than the Ewald and EtOH tests. Atropine tends to prolong the high acidity val. after histamine. $CaCl_2$ (intravenous) increases gastric secretion. CH. ABS.

Histamine test meals. W. S. POLLAND (Arch. Int. Med., 1933, **51**, 903—919).—Analysis of 988 consecutive histamine test meals shows mean total acidity for males from 101 units at age of 25 to 67 units at age of 65; mean total acidity for females from 82 units at age of 25 to 66 units at age of 65. S. H. M.

Fine structure of silk. I—IV. K. OHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 104—127).—The structure of silk has been investigated by *X*-ray methods. A. J. M.

Composition of glomerular urine. VII. Manipulative technique of capillary tube colorimetry. A. N. RICHARDS, J. BORDLEY, and A. M. WALKER. **VIII. Uric acid in glomerular urine of snakes and frogs.** J. BORDLEY and A. N. RICHARDS. **IX. Reducing substances in glomerular urine from frogs and necturi. Action of phloridzin.** A. M. WALKER and J. A. REISINGER. **X. Inorganic phosphate in glomerular urine from frogs and necturi.** A. M. WALKER. **XI. Creatinine in glomerular urine from frogs.** J. BORDLEY, J. P. HENDRIX, and A. N. RICHARDS (J. Biol. Chem., 1933, **101**, 179—191, 193—221, 223—237, 239—254, 255—267).—VII. The experimental details for the colorimetric analysis of urine obtained from single glomeruli and for the prep. of protein-free plasma filtrates and the determination of protein in minute amounts of fluid are described.

VIII. The Folin method for uric acid (I) determinations is adapted to capillary technique, whereby amounts of (I) down to 3×10^{-8} mg. are determined with an average error of approx. 5%. Perfusion of the kidneys of frogs with Clark–Ringer or a mixture of Clark's solution and horse serum to which (I) had been added, and analysis of the (I) content of the glomerular urine (II), showed no significant difference between the concns. of (I) in the perfusion liquid and (II). In thirteen experiments on living frogs and six on living snakes the concns. of (I) in serum and (II) were equal within the experimental error. Determination of the concn. ratios of (I) in bladder- and glomerular-urine gives a

filtration rate of 0·45 c.mm. for snakes, vals. which are sufficient to account for the excretion of (I) by glomerular filtration alone.

IX. Sumner's method of determining sugars (A., 1925, i, 1491) was adapted to capillary technique, and gave a max. error of 5%. Simultaneous determinations by the Hagedorn–Jensen method gave a max. discrepancy between the two methods of 5%. All the reducing substances of frog's plasma are filterable through cellophane. From determinations of the concns. of glucose (III) in a perfusing liquid and in (II) it is concluded that no significant difference between the two exists. In living frogs and necturi there is no difference in the concns. of (III) in serum and (II). Phloridzinised frogs do not differ from normal animals with regard to the reducing power of (II) and plasma, so that the glycosuria produced is ascribed to a decrease in the reabsorption of (III) from the tubule.

X. The Kuttner modification of the Bell–Doisy method for inorg. PO_4''' determination (A., 1930, 725) was adapted to capillary technique, giving results on $CCl_3{\cdot}CO_2H$ plasma filtrates with a max. error of 5%. Recovery experiments on the addition of PO_4''' to P-free filtrates showed that only 91—95% of the plasma-PO_4''' is determined by this method. All the PO_4''' which can be determined by this method in a serum $CCl_3{\cdot}CO_2H$ filtrate is filterable through a cellophane membrane. From a comparison of the serum- and (II)-PO_4''' in frogs and necturi it is concluded that all the PO_4''' is filterable through the glomerular membrane. Violent exercise and inhalation of CO_2 produce an increase in plasma- and lymph-PO_4''' in frogs.

XI. The Folin method for creatinine (IV) determination was adapted to capillary technique, whereby $1—3\times10^{-5}$ mg. of (IV) were determined with a mean error of 5%; the error due to the spontaneous change in colour of the (IV) reagent on keeping in capillaries was avoided by keeping the constituents separate until the instant of mixing with the solution of (IV). Frogs injected with a 0·2% solution of (IV) in Ringer solution showed the same concns. of (IV) in plasma and (II). The concn. ratio of (IV) in bladder-urine and plasma varied from 2·3 to 12·4. H. D.

New triol from the urine of pregnant mares. E. R. Smith, D. Hughes, G. F. Marrian, and G. A. D. Haslewood (Nature, 1933, **132**, 102).—The neutral fraction of an extract of the ketohydroxyœstrin-free urine of pregnant mares yielded a new *substance* $C_{21}H_{36}O_3$, m.p. 300° (decomp.), $[\alpha]_{5461}$ −44° (*triacetate*, m.p. 169°). It is probably closely related to pregnandiol, which could not be isolated from the extract. L. S. T.

Influence of diet on the urinary excretion of oxalic acid and protective colloids in man. K. Eimer and H. Bartels (Z. klin. Med., 1932, **122**, 1—22; Chem. Zentr., 1933, i, 961).—Normal daily urinary excretion of $H_2C_2O_4$ in man is 12—20 mg.; it is independent of the vol. of urine and under the same dietary conditions is nearly const. in individuals. Raw vegetable diets increase the quantity 2—3 times; spinach and tomatoes have a particularly marked effect, although the $H_2C_2O_4$ content of tomatoes is small compared with that of spinach. A raw vegetable diet diminishes, and a protein diet increases, the amount of protective colloids in the urine. Cooking of food has no influence on the effects. A. A. E.

Determination of oxalic acid in urine. S. Maugeri (Z. physiol. Chem., 1933, **217**, 138—140).—After deproteinisation with $CCl_3{\cdot}CO_2H$, the $H_2C_2O_4$ is pptd. as Ca salt and oxidised with $KMnO_4$ in presence of $MnSO_4$, the excess of $KMnO_4$ being determined iodometrically. J. H. B.

Excretion of iron in human urine under physiological and pathological conditions. F. Lanyar, H. Lieb, and A. Verdino (Z. physiol. Chem., 1933, **217**, 160—166).—Normal human urine contains $<$ 0·01 mg. of Fe per litre. Intravenous injection of 1·5—2 mg. of Fe^{III} NH_4 citrate or of 4 mg. of colloidal $Fe(OH)_3$ gave rise to a detectable amount of Fe in the urine. In no pathological condition examined did the kidneys excrete Fe. J. H. B.

Ethyl sulphide formation. Fractionation of the neutral sulphur of urine. A. A. Christomanos (Z. physiol. Chem., 1933, **217**, 177—185).—The Et_2S excreted by dogs in the urine is not increased by parenteral or peroral doses of cystine. The endogenous degradation of tissue-cystine or a related substance is held to be responsible for Et_2S production. The S-containing urine fraction pptd. by phosphotungstic acid, but not the Et_2S, is increased by a protein-rich diet. J. H. B.

Is methylglyoxal excreted in urine? R. Muller (Z. physiol. Chem., 1933, **217**, 253—254).—AcCHO could not be detected in urine (cf. Pi-Suner and Farran, this vol., 300). J. H. B.

Detection and determination of *l*-xyloketose in urine. M. Lasker and M. Enklewitz (J. Biol. Chem., 1933, **101**, 289—294).—Benedict's reagent is reduced by the urine of patients suffering from pentosuria at room temp. in 3 hr. or at 60° in 2—5 min., whereas it is not reduced at all by diabetic urine at room temp. and is reduced in 25—70 min. at 60°, thus providing a simple test for the presence of *l*-xyloketose (I) in urine. A formula is given for deriving the % (I) from the least amount of urine sufficient for complete reduction of the reagent. H. D.

Colorimetric determination of urobilinogen in urine and fæces. L. D. Scott (J. Lab. Clin. Med., 1933, **18**, 399—405).—Urine or fæcal emulsion is treated with p-$NMe_2{\cdot}C_6H_4{\cdot}CHO$, the red substance being extracted with amyl or butyl alcohol and the extracts being compared colorimetrically with a standard solution of $Fe(CNS)_3$. Normal urine gives no colour; in pernicious anæmia and in hæmolytic and latent jaundice large, whilst in partial or complete obstruction of the liver small, amounts are present. A. A. E.

Spectrophotometric investigation of urobilin. H. Rudert and L. Heilmeyer (Biochem. Z., 1933, **261**, 336—352).—The absorption curves for apparently pure samples of " acid " urobilin show no const. curve form, the absorption ratio varying from $8·2\times10^{-6}$ to $5·16\times10^{-5}$. Samples obtained from fæces

always give a lower val. than the purest samples of mesobilirubinogen. The optical properties of urobilin are greatly affected by oxidational processes, and accurate determination is not possible spectrophotometrically. The fluorescing power of the Zn salt varies inversely with the absorption ratio, and this also cannot be used for the determination. "Acid" urobilin has an absorption max. at 490 mμ and is converted by traces of aq. NH_3 and alkali into the "alkaline" form with a max. of 510 mμ, the conversion in all cases passing through an intermediate form with a max. at 450 mμ. Irradiation or the presence of traces of Na_2CO_3 or heavy metals accelerates the process. P. W. C.

Spectrographic analysis of the metallic content of meconium. J. H. Sheldon and H. Ramage (Biochem. J., 1933, **27**, 674—677).—Na, K, Ca, Mg, Cu (0·006—0·02%), Mn (0·002—0·008%), and Fe were detected. The Fe content was abnormally low and in some cases could only just be detected, probably owing to the avidity of the fœtal tissues for Fe. The reason for the unusually high Mn content is obscure. P. G. M.

Chemical composition of the urinary protein in albuminuria. K. Lang (Arch. exp. Path. Pharm., 1933, **171**, 73—78).—The tyrosine, tryptophan, cystine (I), and arginine (II) contents of the serum- and excreted proteins in albuminuria are identical. The kidney proteins show distinct differences, principally in low (I) content, and in high (II) content, of the globulin fraction. The protein excreted in albuminuria is principally serum-protein. R. N. C.

Changes in hæmoglobin spectrum in experimental anæmia in the rabbit. G. Litarczek and G. T. Dinischiotu (Compt. rend. Soc. Biol., 1933, **112**, 1011—1014).—In experimental anæmia (I) in rabbits the absorption band of oxyhæmoglobin is displaced towards red, whereas the band of carboxyhæmoglobin is displaced towards violet. The extent of such displacement varies with the degree of (I), and, accordingly, the "span" between the bands increases gradually as (I) develops. The glutathione content of the blood presents a striking parallelism with this "span." The hæmoglobin of anæmic blood may differ chemically from that of normal blood. Nutr. Abs. (*m*)

Consumption of oxygen by anæmic blood. K. Simidu (Japan. J. Med. Sci., II, Biochem., 1932, **1**, 267—281).—Red corpuscles at 32° consume O_2; this tendency increases as anæmia proceeds. Hæmolysed corpuscles behave similarly. The corpuscle-cystine and -cysteine vary with age, and are increased in chronic hæmorrhagic anæmia. Ch. Abs.

Quantitative aspects of iron deficiency in hypochromic anæmia. Parenteral administration of iron. C. W. Heath, M. B. Strauss, and W. B. Castle (J. Clin. Invest., 1932, **11**, 1293—1312).—1 g. of Fe as Fe NH_4 citrate given orally is equiv. in blood-building power to 32 mg. given parenterally, but the latter mode is impracticable owing to toxicity. Ch. Abs.

Gastric juice in pernicious anæmia. O. M. Helmer, P. J. Fouts, and L. G. Zerfas (J. Clin. Invest., 1932, **11**, 1129—1153).—There is anacidity or alkalinity, absence of rennin and pepsin, low Cl, high N and P, and no relation between acid, p_H, Cl, N, and P. Ch. Abs.

Gall-bladder function. IX. Anion-cation content of bile from normal and infected gall-bladder. C. G. Johnston, I. S. Ravdin, C. Riegel, and C. L. Allison (J. Clin. Invest., 1933, **12**, 67—75).—The more severe is the injury the lower is the bile salt and the higher is the Cl′ concn. After release from obstruction of the bile duct, bile salt fails to appear for several days. Ch. Abs.

Metabolism of normal and tumour tissue. VIII. Respiration in fructose and in sugar-free media. F. Dickens and G. D. Greville (Biochem. J., 1933, **27**, 832—841).—In phosphate or H carbonate buffers, the respiration of surviving nervous tissue of fed animals (R.Q. approx. 1·0) suffers a marked fall when deprived of glucose (I). Kidney and spleen are less affected, whilst testis is intermediate. The respiration of embryonic tissues (rat yolk-sac, chick and mammalian embryo) falls very little when they are deprived of (I). The respiration of Jensen rat sarcoma is not decreased, but the R.Q. falls slightly. Brain and retina oxidise fructose (II) readily with R.Q.=1·0 probably without intermediate formation of lactic acid. The R.Q. of testis, kidney, and liver is higher in presence of (II) than in the absence of sugar. Rat embryo and yolk-sac have a R.Q. of approx. 1·0 in its presence. Jensen rat sarcoma has the same R.Q. in (I) and in (II), and with this tissue in (II) as in (I) strong acid production persists in presence of O_2. W. O. K.

Influence of cations on the fermenting power of tumour cells. II. Potassium. A. Lasnitzki and O. Rosenthal (Biochem. Z., 1933, **262**, 203—223; cf. A., 1929, 718).—The anaerobic fermentation of glucose in tumour [Flexner–Jobling carcinoma, Jensen sarcoma (I)] cells from the rat in a medium free from K and Ca increases when KCl is added, but the increase is not proportional to [K·]. In the case of (I) an inhibitory action of K· can also be detected subsequently. K· has no effect on the fermentation when the medium contains no glucose. W. McC.

Relation between the growth vigour of tumours and their vitamin-*A* content. E. Vogt (Med. Klinik, 1932, **28**, 1344—1345; Chem. Zentr., 1933, i, 962).—Vitamin-*A* is present in benign and malignant tumours; in myoma little or no vitamin-*A* is present. In two cases sarcomatous neoplasms contained small quantities, and in carcinoma the largest quantities are present in rapidly developing growths. E

Glutathione and vitamin-*C* in tumour tissue. E. Boyland (Biochem. J., 1933, **27**, 802—805).—Colorimetric determination of glutathione in tumour tissue (sarcoma of rat, mouse, and fowl, carcinoma of mouse) gives results only about ⅓ of those obtained by the I titration method. The difference is accounted for by ascorbic acid, which has been determined independently. W. O. K.

Reducing bodies, and fumarase, in tumours. J. H. Quastel (Nature, 1933, **132**, 101).—Tumours

show powerful fumarase activity usually > that of the surrounding host tissue. Reducing agents also appear to be present. L. S. T.

Tissue metabolism. II. Inhibition of lactic dehydrogenase by derivatives of carcinogenic compounds. E. BOYLAND (Biochem. J., 1933, 27, 791—801).—Yeast lactic dehydrogenase is inhibited by the products obtained when various polycyclic hydrocarbons are exposed to ultra-violet irradiation, preferably in a non-aq. solvent. The solvent has considerable effect on the activity of the product. The inhibiting substance appears to be an acidic oxidation product. The carcinogenic hydrocarbons give rise to highly active products, but the latter are also obtained from inactive compounds such as cholesterol and anthracene. W. O. K.

Gonadotropic hormones and cancer. B. P. WIESNER and A. HADDOW (Nature, 1933, 132, 97).—Rats treated with gonadotropic hormones from urine showed a marked increase in the growth rate of implants of Jensen sarcoma. Treatment with bovine anterior pituitary extract had no significant effect. L. S. T.

Occurrence of heterophyl antigen. L. DE KROMME and J. R. DE B. GROENEVELDT (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 463—467).—Cancer cells contain heterophyl antigen, so that heterogenetic anti-bodies and heterophyl antigens are simultaneously present in the bodies of cancer patients. This appears to be sp. for cancer in human beings. H. D.

Nature of dental caries. ANON. (Nature, 1933, 131, 918).—Caries is directly due to the growth of lactobacilli in the mouth; the acid produced decalcifies the enamel. L. S. T.

Possible relation of aciduric and acidogenic micro-organisms to dental caries. W. H. TUCKER (J. Infect. Dis., 1932, 51, 444—459).—*L. acidophilus* was frequently present. CH. ABS.

Blood-sugar metabolism in certain dermatoses. Acne vulgaris. A. STRICKLER and P. D. ADAMS (Arch. Dermatol. Syph., 1932, 26, 1—10).—Acne vulgaris is not characterised by hyperglycæmia, which is probably not associated with seborrhœa, psoriasis, or vegetable parasitic infections. CH. ABS.

Cholesterol metabolism in certain dermatoses. A. STRICKLER and P. D. ADAMS (Arch. Dermatol. Syph., 1932, 26, 11—20).—Hypercholesterolæmia is not characteristic of acne vulgaris; seborrhœa, psoriasis, and vegetable parasitic diseases are probably not related to the blood-cholesterol. CH. ABS.

Phenolphthalein eruption. Causation. F. G. NOVY, jun. (Arch. Dermatol. Syph., 1932, 26, 125—130).—The dermatitis was due to the phenolphthalein mol., and not to any of its known cleavage products. CH. ABS.

Intermediate carbohydrate metabolism in muscle in diabetes mellitus. K. ADACHI and S. KASAI (Tohoku J. Exp. Med., 1933, 20, 320—330).—In normal subjects the blood-glucose decreases from 94 to 88·2 mg. per 100 c.c. in passing through the arm muscles; the lactic acid increases from 11·36 to 13·55 mg. per 100 c.c. In mild diabetes both glucose consumption and lactic acid production decrease; vals. return towards normal as glycosuria disappears under a dietary régime. CH. ABS.

Serum electrolytes. VIII. Concentration of serum-electrolytes and non-electrolytes following insulin administration in diabetic patients. F. W. SUNDERMAN, J. H. AUSTIN, and P. WILLIAMS (J. Clin. Invest., 1932, 11, 1261—1271).—Serum-inorg. PO_4''' and -cholesterol decreased, whilst total base, Na, Cl, and sp. conductivity increased. Increased electrolytes did not compensate for loss of sugar. CH. ABS.

Glycine treatment of progressive muscular dystrophy. Origin of creatine. S. KOSTAKOV and A. SLAUCK (Deut. Arch. klin. Med., 1933, 175, 25—37).—In seven cases of progressive muscular dystrophy glycine (I), in doses of 15 g. daily, produced an increase of the original creatinuria; parallel with this there was a decline in the abs. excretion of preformed creatinine. After about 4 weeks of continued administration of (I) the creatine excretion returned to its original val., or was abolished. Muscular dystrophy arises from a disturbance of creatine utilisation in the muscle, a defect remedied to some extent by (I). NUTR. ABS. (*m*)

Blood-plasma-lipins in epilepsy. I. I. MCQUARRIE, W. R. BLOOR, C. HUSTED, and H. A. PATTERSON. **II.** I. MCQUARRIE, C. HUSTED, and W. R. BLOOR (J. Clin. Invest., 1933, 12, 247—254, 255—265).—I. Blood-plasma-cholesterol (I) is normal in epilepsy; -lecithin (II) is low and -total fatty acid (III) high.

II. No const. relationship was found between (I), (II), and (III) in epileptic children and the occurrence of seizures. The (II) : (I) ratio is in general high near the time of seizure. CH. ABS.

Mitogenetic radiation of blood in experimental hyperthyreosis and in exophthalmic goitre. W. N. SAMARAEEV (Endokrinol., 1932, 11, 335—343; Chem. Zentr., 1933, i, 949).—Feeding thyreoidin to pigeons produces an increase in the mitogenetic radiation (I) of the blood. In exophthalmic goitre increased (I) is also observed. A. A. E.

Calcium and phosphorus metabolism. XX. High calcium excretion in exophthalmic goitre is not due to vitamin-*D* deficiency. D. M. TIBBETTS, R. MCLEAN, and J. C. AUB (J. Clin. Invest., 1932, 11, 1273—1279).—Addition to the diet of large amounts of irradiated ergosterol has no effect on the high Ca excretion in exophthalmic goitre, on basal metabolism, or on urinary excretion of NH_3 and titratable acids. CH. ABS.

Pathological physiology of infarct. I. The content of infarct tissue in reduced glutathione and other thiol groups. G. BORGER, T. PETERS, and M. KURZ (Z. physiol. Chem., 1933, 217, 255—273).—In infarct tissue cut off from O_2 supply, the SH-glutathione (I) does not increase (cf. Waldschmidt-Leitz *et al.*, A., 1930, 1217), but diminishes rapidly, reaching zero in 2—3 days. The (I) is first converted

chiefly into the ·S·S· form, which then gives rise to irreversible oxidation products. J. H. B.

Mineral metabolism in inflammatory conditions of the ear, nose, and throat. I. Content of fluids and total mineral content. R. MITTERMAIER (Arch. Ohren-, Nasen-, u. Kehlkopf-heilk., 1933, **134**, 147—159).—In acute and chronic inflammatory conditions of the nose and antra the highest mineral content (I) of the dried substance of the mucosæ and nasal secretions accompanies acute rhinitis. Secretion which remains for a long period in the antrum occasionally has a high (I). A change from an inflammatory to a mucous secretion increases (I). The parallel increases of H_2O and (I) in mucosæ and secretions suggest osmotic regulation.

NUTR. ABS. (*m*)

Protein and mineral metabolism in leucorrhœa. M. A. BRUCKNER (Arch. Gynakol., 1933, **153**, 89—96).—In the serum of women suffering from leucorrhœa the total proteins and Mg fall within normal limits, but there is an increase in globulin and a diminished Ca content (average 8·9 mg. per 100 c.c.). The variations in Mg are > normal. NUTR. ABS. (*m*)

Liver injury and blood-lactic acid. P. F. HAHN (J. Biol. Chem., 1933, **101**, 29—34).—Na lactate and lactic acid (I) given intravenously in large amounts cause a rapid disappearance of (I) from the blood. This is not affected by severe injury to the liver.

H. G. R.

Excretion of nitrogen by obese patients. R. W. KEETON and D. DICKSON (Arch. Int. Med., 1933, **51**, 890—902).—The excretion of N, especially as creatinine, by obese patients shows that the majority of them maintained a positive N balance when given 90 g. of protein per day and a diet 40—50% < their energy requirements. S. H. M.

Œdema of renal type. W. B. MCCLURE, C. B. DE TAKATS, and W. F. HINMAN (Arch. Int. Med., 1933, **51**, 819—865).—Low concn. of proteins in blood-plasma is probably not the cause of renal œdema.

S. H. M.

Relation between plasma-protein content, plasma-sp.-gr., and œdema in dogs maintained on a protein-inadequate diet and in dogs rendered œdematous by plasmapheresis. A. A. WELCH, C. E. SNELLING, and E. GOETTSCH (J. Clin. Invest., 1933, **12**, 193—216).—Below an albumin concn. of 1 g. per 100 c.c. œdema is always present; above 2 g. it is nearly always absent. The albumin levels are not always identical in the two cases.

CH. ABS.

Effect of serum transfusion on the plasma-protein depletion associated with nutritional œdema in dogs. A. A. WELCH, E. GOETTSCH, and E. B. REEVES (J. Clin. Invest., 1933, **12**, 217—227).—When normal serum is transfused into dogs with low serum-albumin resulting from a diet low in protein, the albumin immediately rises and the globulin falls.

CH. ABS.

Chemical changes in the blood of the dog in experimental acute pancreatitis. A. G. CLASEN, T. G. ORR, P. N. JOHNSTONE, and B. RICE (J. Lab. Clin. Med., 1933, **18**, 457—462).—Experimental pancreatitis in dogs is usually followed by increase in blood-urea-N and -non-protein-N, a slight decrease in -Cl, and slight variations in -creatinine, and -CO_2-combining power. The sugar content appears to be decreased at first and later reaches concns. > normal.

CH. ABS.

Glycogen and fat content of liver in pregnant albino rats. Carbohydrate metabolism in pregnancy. O. BOKELMANN and W. SCHERINGER (Arch. Gynakol., 1933, **152**, 562—572).—In pregnancy the abs. val. for the liver-glycogen (I) is > and the relative val. < in the normal animal. The abs. liver-fat (II) is also on the average higher in pregnancy, but the distribution is about the same as in the non-gravid (III) animal. Generally, there is evidence of glycogen–fat antagonism in the livers of pregnant animals, but not in (III). (I) varies widely in different animals, but is related inversely, whilst (II) is related directly, to the duration of pregnancy. Increased consumption of carbohydrate occurs in pregnancy.

NUTR. ABS. (*m*)

Urinary quotients during pregnancy and after parturition. M. KOJIMA (Arch. Gynakol., 1933, **152**, 573—578).—In rats and rabbits during the latter part of pregnancy there is an increase of the C : N ratio in the urine and later an abs. increase of the excretion of poorly oxidised C which may be continued during the day following parturition.

NUTR. ABS. (*m*)

Role of calcium, phosphorus, and vitamin-*D* in pregnancy. H. O. NICHOLAS and E. M. KUHN (J. Clin. Invest., 1932, **11**, 1313—1319).—When pregnant rats were fed with high- and low-Ca and -P diets to which were added large doses of viosterol, the young contained more ash, Ca, and P than those from mothers which had not had viosterol. Only when the diets of the mothers were deficient in Ca and P was there a drain on the maternal supplies of these elements. Viosterol possibly interferes with the course of the pregnancy. CH. ABS.

Excretion of xylose as a measure of renal function in children. E. H. FISHBERG and L. FRIEDFELD (Amer. J. Dis. Children, 1933, **45**, 271—278; cf. this vol., 86).—Approx. 25% of the ingested xylose (I) (1 g. per 3 lb., orally) is normally excreted in the urine within 24 hr. The blood-(I) is max. in 3 hr., and practically normal within 5 hr. In renal impairment only 5% of the ingested (I) is excreted in the urine in 24 hr. CH. ABS.

Behaviour of the lipins of the suprarenal capsules of splenectomised animals. S. MARINO (Arch. Farm. sperim., 1933, **55**, 243—254).—The lipin contents of the suprarenal capsules of splenectomised dogs varied considerably in the period following splenectomy. Total cholesterol and total fatty acids rose to max. in 2 months, falling to normal in 1 year; phosphatide- and lipin-P fell to min. in 30 days, rose to max. in 270 days, but at the end of 1 year had fallen to extremely low vals. compared with the normal. R. N. C.

Calcium and phosphorus metabolism in rhizomelic spondylosis. J. MORELLE and J. STEENHOUDT (Rev. belge Sci. méd., 1932, **4**, 623—639).—In three males suffering from spondylosis and receiving

diets containing < 0·15 g. of Ca daily, but otherwise adequate, the serum-Ca was 15·1, 11·6, and 10·5 mg. per 100 c.c., respectively. Plasma-inorg. P was normal in all and there was a negative Ca balance up to 0·7 g. in three-day periods, whilst a virtual equilibrium in P existed. In one case the hypercalcæmia was controlled by low Ca. Irradiation of the spine caused no difference in mineral balance. Amelioration was produced in two cases, but activity of the disease recurred. NUTR. ABS. (*m*)

Physico-chemical changes in the plasma of thyroidectomised dogs. J. ROSSIGNOLI, EL. DI BENEDETTO, I. GUERRERO, and EN. DI BENEDETTO (Rev. sud-amer. endocrinol., 1933, **16**, 188—189).—The viscosity, total protein, globulin, and non-protein-N are increased; the ratio albumin : globulin is decreased. CH. ABS.

Calcium and potassium content of dog tissues and the influence of thyroparathyroidectomy. F. P. UNDERHILL and T. C. JALESKI (J. Biol. Chem., 1933, **101**, 11—14).—Thyroparathyroidectomy has no effect on Ca and K content of tissue. In tetania parathyreopriva, serum-Ca is reduced, blood-K is unaffected. H. G. R.

Viscosity and protein equilibrium in human hyperthyroidism. EN. DI BENEDETTO (Rev. sud-amer. endocrinol., 1933, **16**, 189).—The albumin is increased and the globulin decreased; the viscosity is usually reduced. CH. ABS.

Pigment in the cerebrospinal fluid of a child with tubercular meningitis. P. GYORGY and R. KUHN (Naturwiss., 1933, **21**, 405—406).—The cerebrospinal fluid was yellow with a marked green fluorescence and the reaction and absorption spectrum indicated the presence of a pigment similar to but not identical with ovoflavin or the cryst. pigment of the yeast oxidation-enzyme (Warburg and Christian, this vol., 313). W. O. K.

Treatment of tuberculosis by copper salts. S. ANSBACHER (Diss., Geneva, 1933, 88 pp.).—The effect of Cu salts, insol. in H_2O but sol. in oil, *e.g.*, olive oil, on tuberculosis in guinea-pigs has been studied. The Cu salt of $CH_2Ac{\cdot}CO_2H$ is beneficial; the Cu salts of BzOH and $OH{\cdot}C_6H_2I_2{\cdot}CHO$ have little effect. S. H. M.

Blood determinations of ammonia and sulphur as factors in the uræmia of urinary obstructions. C. G. BANDLER and J. A. KILLIAN (J. Urol., 1933, **29**, 337—351).—In rabbits urinary obstruction or removal of renal function increases the inorg. and org. fractions of the blood-non-protein-S. In man the increase is much less marked, and occurs largely in the inorg. fraction. The blood-NH_3 is not appreciably changed. CH. ABS.

Excretion of non-protein-nitrogen by the intestine. J. L. WILLIAMS and G. F. DICK (J. Amer. Med. Assoc., 1933, **100**, 484—487).—In patients suffering from uræmia, chronic nephritis without uræmia, chronic myocarditis, and diabetes, 70% of the non-protein-N of the fæces (I) is present as NH_4 salts. The concn. of urea in (I) is always < that in the blood, whilst the converse holds for creatinine. The following are the max. vals. found in a uræmic case: urea-N 18; creatinine-N 22·5; uric acid-N 7·0 mg. per 100 c.c. of liquid (I). 0·025% of glucose was also found. NUTR. ABS. (*m*)

Effect of methylene-blue on phytotoxic reaction of normal and pathological blood. D. I. MACHT (Proc. Nat. Acad. Sci., 1933, **19**, 486—491).—Methylene-blue lowers the toxic effect of normal serum, CO-blood, and the sera of patients suffering from anæmia, leprosy, and pemphigus on the growth of *Lupinus albus* seedlings. H. D.

Comparison of the most important duodenal enzymes. C. D'IGNAZIO, L. G. MONTANI, and G. SOTGIU (Diagn. Tecn. Labor., 1932, **3**, 114—127; Chem. Zentr., 1933, i, 952).—Determinations of crepsin, diastase, trypsin, and lipase have little diagnostic val. A. A. E.

Growth and development. XVII. Relation between resting energy metabolism and body-weight in domestic mammals. XVIII. Relation between basal metabolism, resting metabolism, heat increments of feeding, and body-weight in farm mammals. S. BRODY, W. C. HALL, A. C. RAGSDALE, and E. A. TROWBRIDGE. **XIX. Relation between basal metabolism and body-weight in the growing domestic fowl.** S. BRODY, E. M. FUNK, and H. L. KEMPSTER. **XX. Relation between basal metabolism and body-weight in the growing rat.** U. S. ASHWORTH, S. BRODY, and A. G. HOGAN. **XXI. Relation between basal metabolism and body-weight in man. XXII. Relation between basal metabolism and body-weight in laboratory animals. XXIII. Relation between basal metabolism and mature body-weight in different species of mammals and birds.** S. BRODY and R. C. PROCTER. **XXIV. Decline in energy metabolism per unit weight with increasing age in farm animals, laboratory animals, and man.** S. BRODY, A. C. RAGSDALE, E. A. TROWBRIDGE, and W. C. HALL. **XXV. Course of energy and nitrogen metabolism in the domestic fowl during 48-day fasts, with special reference to temperament and training of the birds. Notes on 60-day fasts in swine.** V. W. PHILLIPS, U. S. ASHWORTH, and S. BRODY (Missouri Agric. Exp. Sta. Res. Bull., 1932, No. 166, 101 pp., No. 176, 59 pp., No. 179, 30 pp.).—XVII. Differences between resting and basal metabolism are established for cattle, sheep, horses, and pigs. Surface area is an unsuitable basis of comparison of metabolic rates, and mathematical representation of metabolism on a wt. basis is given. Differences due to sex and habits of the animals are examined.

XVIII. Experimental data show that basal metabolism vals. are 25—30% < corresponding resting metabolism vals., the difference being represented by the heat increment of feeding.

XIX—XXIV. Experimental data are presented and discussed with special reference to the influence of age and sex.

XXV. The survival period of individual hens varied widely with temperament and training to experimental conditions. Fasting hens survived longer than those receiving a N-free diet; the latter were more sensitive to polyneuritis. The excretion of total

creatinine (I) and total N followed nearly the same course throughout the fast. Although the energy metabolism declines steadily during fasting, the N and (I) excretion increases with time. The shape of the time curves of energy metabolism for hens closely resembles that for dogs and man, but the course of N and (I) excretion differs considerably. The latter is not controlled by the % of these substances in the body. A. G. P.

Associative effects of foods in relation to the utilisation of food energy. E. B. FORBES, W. W. BRAMAN, M. KRISS, and R. W. SWIFT [with A. BLACK, D. E. FREAR, O. J. KAHLENBERG, F. J. MCCLURE, and L. VORIS] (J. Agric. Res., 1933, **46**, 753—770).—Calorimetric tests with steers receiving rations of varied nutrient balance indicate that the net energy val. of feeding-stuffs is influenced by the nature of the other components of the complete ration. In practice, the energy val. of the ration as a whole is of prime importance, the vals. for individual constituents giving only superficial information. A. G. P.

Respiratory metabolism of *Fundulus heteroclitus* during embryonic development. W. R. AMBERSON and P. B. ARMSTRONG (J. Cell. Comp. Physiol., 1933, **2**, 381—397).—Changes in the R.Q. during the first 12 days of development are recorded; they support the theory of the successive utilisation of carbohydrate, protein, and fat during this period. The carbohydrate phase is limited to the first day. Fat metabolism becomes dominant with the establishment of circulation. A. G. P.

Distribution and changes in the inorganic salts during embryonic development of the chick. E. S. HORNING and G. H. SCOTT (Anat. Rec., 1932, **52**, 351—366).—During brain growth Ca salts gradually increase, but Fe salts decrease. The bronchi of the lungs (7 days) contain appreciable quantities of Fe; the other tissues contain chiefly Ca salts. CH. ABS.

Effect of temperature on the growth, fat and calcium metabolism, and mortality of the chick embryo during the latter part of incubation. A. L. ROMANOFF and H. A. FABER (J. Cell. Comp. Physiol., 1933, **2**, 466).—The fat and Ca metabolism was but little affected by temp. A. G. P.

Carbohydrate metabolism of the chick embryo. C. DONHOFFER (Biochem. J., 1933, **27**, 806—817).—The fermentable and Cu–CaO-precipitable reducing substances of the following fractions of the hen's egg: (*a*) EtOH-sol., (*b*) H_2O-sol. fraction of the EtOH ppt., and (*c*) H_2O-insol. fraction of the EtOH ppt., as well as glycogen of whole egg, have been determined during incubation. Free sugar reaches a min. on the tenth day and subsequently rises. Reducing power of (*b*) decreases in the first and increases in the second half of incubation; that of (*c*) tends to decrease from beginning to end of incubation. (*c*) is the chief source of glycogen formed during incubation. Total carbohydrate decreases to the ninth day and then remains const. W. O. K.

Glycogen formation in the fowl. A. R. G. EMSLIE and K. M. HENRY (Biochem. J., 1933, **27**, 705—710).—The relative rates of adsorption after ingestion were as follows: glucose (I) > galactose (II) >lactose (III). The rate of liver-glycogen formation in two series was (I)=dihydroxyactone>alanine> glycerol>Na lactate>$AcCO_2Na$, and (I)>(II)>(III) =starch>egg-white. Muscle-glycogen was increased by ingestion of (I), but not by that of any other substance. H. G. R.

Glycogen formation from succinic acid. R. STOHR (Z. physiol. Chem., 1933, **217**, 153—155).—Succinic acid (as Na salt) fed to rats produces a considerable increase in liver-glycogen. J. H. B.

Glycogen mobilisation by sodium hydrogen carbonate. R. STOHR (Z. physiol. Chem., 1933, **217**, 156—159).—0·2—0·5 g. of $NaHCO_3$ fed to fasting male rats produced a decrease in liver-glycogen; muscle-glycogen was practically unchanged. The mobilisation of liver-glycogen (with formation of lactic acid) is regarded as a defence reaction against alkalosis. J. H. B.

Glycogen formation from lower fatty acids with an even number of carbon atoms. I. Glycogen formation from acetic acid. R. STOHR (Z. physiol. Chem., 1933, **217**, 141—152).—When NaOAc and glucose were fed to female rats a definite increase in liver-glycogen was apparent over controls receiving only glucose. This indicates the probability of the conversion of AcOH into carbohydrate in the animal body. J. H. B.

Storage of carbohydrate in the liver of fat-fed rats. O. FURTH and E. H. MAJER (Pflüger's Archiv, 1932, **230**, 475—488; Chem. Zentr., 1933, i, 1157).—Feeding rats with lard does not lead to considerably increased liver-glycogen (I); beet freed from sugar and other extractives causes an increase. Pure cellulose does not lead to accumulation of (I); pectin takes part in sugar synthesis only under special conditions (intestinal flora). Fermentation lactic acid, but not AcOH, butyric, succinic, or valeric acid, takes part in the formation of (I). A. A. E.

Glycogen metabolism of animal "organisators." M. W. WOERDEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 423—426).—The glycogen content of the optical region of the Mexican axolotl at different stages of development is examined. H. D.

Ketosis. III. Comparative glycogen formation and retention after administration of glucose, galactose, and lactose. H. J. DEUEL, jun., E. M. MACKAY, P. W. JEWEL, M. GULICK, and C. F. GRUNEWALD (J. Biol. Chem., 1933, **101**, 301—322).—The glycogen (I) in the livers of dogs fed with 65 g. of galactose (II) per sq. cm. body-surface after a 6 days' fast is > that in dogs fed with a quantity of glucose (III) equal to the (II) retained by the first lot. The max. level for the dogs fed with (III) was obtained 12 hr. after feeding. The muscle-(I) was generally higher in the dogs fed with (III). In rats fed with (III) or (II) after a fast of 48 hr. the liver-(I) was higher in the animals fed with (III). The muscle-(I) in both cases was > that of controls given H_2O, the rise occurring more slowly in the rats fed with (II). Rats previously fed on a diet high in (III), (II), or lactose (IV), and killed after a

fast of from 0 to 72 hr. in every case had an average muscle-(I) highest in the case of the (II) or (IV) diet and lowest in that of the (III) diet. In animals killed without any intermediate fasting period the liver-(I) was highest with the rats fed with (III), and in most of the experiments in which a 24—48 hr. fast occurred the liver-(I) was highest in the animals fed with (II), intermediate in those fed with (IV), and least in those fed with (III). Rats killed after administration of (II) following a 48-hr. fast subsequent to being fed on a standard diet containing (III), (II), or (IV) had a liver-(I) highest in the case of those fed on a (II)-regime. Long-continued administration of (II) does not increase the tolerance for this sugar. H. D.

Alimentary hyperglycæmia. G. MARTINO (Compt. rend. Soc. Biol., 1933, **112**, 1002—1004).—Alimentary hyperglycæmia may be due to a blood-sugar-raising substance secreted by the pancreas, because it is produced in dogs by ingestion of peptone or HCl whether the liver-glycogen had previously been raised by a rich carbohydrate diet or lowered by fasting and phloridzinisation. NUTR. ABS. (*m*)

Glycolytic mechanisms of brain. C. A. ASHFORD (Biochem. J., 1933, **27**, 903—910; cf. this vol., 307).—The finding that rabbit's brain contains two mechanisms for the production of lactic acid (I) is confirmed (A., 1929, 1194; 1932, 188). The limited ability of brain tissue to produce (I) from glycogen (II) is probably due to its relative inability to synthesise active phosphoric esters which are converted into (I) much more readily than is (II). The formation of (I) from glucose is not inhibited by (II). The mechanisms responsible for the degradation of hexose mono- (III) and di-phosphoric esters (IV) follow slightly different paths, but on the whole involve a common enzyme system. (IV) is more readily hydrolysed than (III). When glucose and mannose are present together, the same enzyme is responsible for their degradation. Data are given for the production of (I) from glucose, mannose, fructose, galactose, (III), and (IV) by brain tissue. F. O. H.

Fructose solutions for parenteral injection. F. HOLTZ and R. STEINBRUCK (Arch. Pharm., 1933, **271**, 321—323).—Details are given for the prep. (from "dextropur"), sterilisation, and use of these solutions. R. S. C.

Volume change of muscle in relation to the chemistry of contraction. III. Changes of volume with chemical processes in muscle. O. MEYERHOF and W. MOHLE (Biochem. Z., 1933, **261**, 252—266).—The vals. for the change of mol. vol. in the formation of lactic acid from glycogen, hexose-phosphoric acid, and AcCHO, in the separation of H_3PO_4 from inorg. pyro-, creatine-, adenylpyro-, inosinepyro-, hexose-di-, and -mono-phosphoric acids, and in the separation of NH_3 from adenylic and adenylpyrophosphoric acids and urea are determined and correlated with the changes of muscular vol. The contraction in the vol. of muscle during activity is due to the changes of mol. vol. during the accompanying chemical processes of hydrolysis. P. W. C.

Muscle training. W. SEITZ (Z. physiol. Chem., 1933, **218**, 17—29).—Minced muscle from rabbits "trained" by electrical stimulation shows much slower changes in the solubility of the proteins, in synthetic power, and in NH_3 elimination on keeping than "untrained" muscle. By prolonged stimulation for many hr. daily, "over-training" was attained with reversal of the effects of training. J. H. B.

Influence of unphysiological nutrition on the composition of the organs and on metabolism. III. Diet rich in protein and its hydrolytic products. E. BONG, L. HILGENBERG, and P. JUNKERSDORF (Arch. exp. Path. Pharm., 1933, **171**, 16—37).—Fasting dogs were fed on a diet (I) consisting largely of protein and peptone. While the body-wt. increased, the blood-sugar decreased. The vol. of urine excreted rose, the N excreted varying inversely with the blood-N. After 3—4 days the liver-glycogen was > starvation val., but < the val. obtained with a diet of protein only; the liver-fat was normal, but the H_2O and N were both > normal. Muscle-glycogen, -fat, and -H_2O were all > normal vals.; heart- and kidney-glycogen had decreased. A second series of experiments, in which a diet of glycogen was administered for 7—8 days before (I), yielded mostly similar results, but the liver-, heart-, and muscle-glycogen had all fallen, especially the first-named, which, however, recovered after 7 days' administration of (I). R. N. C.

Manner of removal of proteins from normal joints. W. BAUER, C. L. SHORT, and G. A. BENNETT (J. Exp. Med., 1933, **57**, 419—433).—Following injection into the knee-joints of normal dogs, ovalbumin is removed only by way of the lymphatics. Horse serum-albumin is readily removed, whilst -globulin escapes with great difficulty, if at all. CH. ABS.

Amino-acid metabolism in the animal body. H. A. KREBS (Z. physiol. Chem., 1933, **217**, 191—227).—NH_2-acids (I) are deaminated more rapidly in the kidney than in the liver of the rat and other animals. The velocity of the reaction usually increases with increasing concn. of (I) up to about 0·05*M*. A series of optical antipodes of naturally occurring (I) are deaminated more rapidly (10—20 times) in rat's kidney than the natural acids. Of the natural acids the α-NH_2-dicarboxylic are the most readily attacked. The deamination of the α-NH_2-acids by the kidney is an oxidation with almost quant. production of the corresponding keto-acid. The deamination of NH_2-dicarboxylic acids, $(NH_2)_2$-acids, and glycine is likewise dependent on the presence of O_2. (I) are the principal source of the urine-NH_3 which is necessary for the regulation of the acid–base equilibrium. Acidosis is a consequence of inefficient deamination of (I) by the kidney. J. H. B.

Urinary excretion of creatine and creatinine on diets with and without meat. U. ZICKELBEIN (Z. ges. exp. Med., 1933, **87**, 112—125).—The daily human urinary output of creatine (I) and creatinine (II) was determined on a mixed diet and when the food was free from (I) and (II). On several occasions during the latter period meat extract or weighed amounts

of (I) were given. The (I) output was greater on the mixed diet due to the (II) ingested. Ingestion of 1·5 g. of (I) did not increase the output of (II) or lead to the appearance of (I); when > 1·5 g. was given, about 10% was excreted in the urine as (I) within a few hr. Administration of (II) was followed by increase of (II) (50—75% of extra intake) in the urine. NUTR. ABS. (*b*)

Relation between the excretion of creatinine-nitrogen and several body measurements. H. H. BEARD (Human Biol., 1932, **4**, 351—362).—An attempt to find correlation coeffs. between the amount of creatinine (I) eliminated and body-wt., 2/3 body-wt., height, or surface area failed to show any significant relationships. Creatine and (I) are the end-products of exogenous rather than of endogenous metabolism. NUTR. ABS. (*m*)

Effect of ingested creatine on the blood-sugar and -phosphate. R. S. STACEY (Biochem. J., 1933, **27**, 690—692).—Ingestion of creatine (I) has no effect on blood-sugar. The slight fall in plasma-inorg. P runs qualitatively but not quantitatively parallel with the rise in plasma-(I). There is no difference between normal and diabetic subjects. P. G. M.

Degradation of cholesterol by the animal organism. II. Balance experiments with carnivora on a diet rich in cholesterol. W. MENSCHICK and I. H. PAGE (Z. physiol. Chem., 1933, **218**, 95—103; cf. A., 1932, 1058).—Cats do not excrete or store the whole of the cholesterol (I) given, indicating a breakdown of (I) to about the same extent as in rabbits. Storage of (I) occurs in all organs except the brain; the storage in the liver was much >, in other organs <, in the rabbit.
J. H. B.

Nutritive values of fats. V. J. OZAKI (J. Agric. Chem. Soc. Japan, 1932, **8**, 1286—1303).—Acids and esters are classified according to nutritive val. (I) and toxicity (II). (I) of unsaturated acids decreases with increase in the no. of double linkings. (II) is fairly high for acids having a triple linking. Me or Et esters of unsaturated acids have (I).
CH. ABS.

Metabolism of fats in the caterpillar of *Galleria mellonella*. C. MANUNTA (Atti R. Accad. Lincei, 1933, [vi], **17**, 309—312).—The dry matter of the chrysalis contains about 52% of an oil containing 94·59% of fixed fatty acids and 11% of glyceryl: sap. val. 196, I val. 57·22, acid val. 10·2, ester val. 185·8. The fatty acids, m.p. 46—48°, have sap. val. 202·4, neutralisation val. 199, ester val. 3·4, and lactones (as stearolactone) 1·71%. The oil consists almost entirely of triglycerides of saturated and unsaturated acids, and is formed, probably in the larva, from the wax taken as food. A mechanism is suggested for the various stages in this transformation.
T. H. P.

Deposition and utilisation of *iso*oleic acid in the animal body. A. D. BARBOUR (J. Biol. Chem., 1933, **101**, 63—72).—A diet containing partly hydrogenated cottonseed oil causes *iso*oleic acid, derived from the oil, to appear in the body-fat. This disappears on fasting as readilv as any other fatty acid.
H. G. R.

Alimentary lipæmia after administration of fats to splenectomised animals. S. MARINO (Arch. Farm. sperim., 1933, **55**, 289—310).—After administration of olive oil or milk to dogs all fractions of the blood-lipins rise after 3—6 hr., and after 24 hr. fall below normal, but in splenectomised animals no hypoglycæmia is observed. The spleen is believed to play a part in the removal of excess lipins from the blood. R. K. C.

Central regulation of fat metabolism. I. BERLIN (Z. ges. exp. Med., 1933, **87**, 151—160).—Puncture of the floor of the fourth ventricle in rabbits led to a marked reduction in liver-glycogen (I) and an increase in liver-fat (II). Section of both splanchnic nerves, injections of adrenaline, denervation of the adrenals, and phloridzinisation all produced a reduction in (I), but little alteration in (II). The antagonism between (I) and (II) depends on intact splanchnic nerves and adrenals. NUTR. ABS. (*b*)

Relative merits of high- and low-silage feeding to cows in milk. K. GUPTA and R. S. GUPTA (Agric. Livestock India, 1933, **3**, 116—124).—Cows receiving low-silage rations ate more straw than those on high-silage rations (I). The total food consumption was thus equalised and the yield and quality of milk showed no appreciable difference. Live-wt. increases were greater in cows receiving (I).
A. G. P.

Nutritive deficiency of milk with specific reference to manganese, energy, and pituitary relations. E. C. VAN DONK, H. STEENBOCK, and E. B. HART (Amer. J. Physiol., 1933, **103**, 468—479).—Although the addition of Mn to a milk–Cu–Fe diet (I) facilitates the occurrence of œstrus (II) in rats and high vitamin-*D* inhibits it, pituitary transplants from rats on such diets have no effect on the wt. of the ovaries. There is abundant evidence, however, regarding the effect of various diets on œstrous rhythm. Subnormal (II) in rats on a stock ration is improved by inclusion of whole-milk powder, cod-liver oil, yeast, egg-yolk, dried beef liver, and wheat-germ oil, and this is also the most effective supplement to (I). Addition of sucrose facilitates (II), but not lactation. Diets low in vitamin-*B* or protein inhibit (II). On low vitamin-*A* diet œstrous changes are obscured. Desiccated thyroid (25 mg. daily) does not increase the frequency of (II). NUTR. ABS. (*m*)

Calcium and phosphorus metabolism of sheep. I. J. CUNNINGHAM (New Zealand J. Sci. Tech., 1933, **14**, 281—287).—With a ration of low nutrient val. and deficient in P and N the N and P balances of young sheep were negative and the Ca balance was positive. Addition of KH_2PO_4 depressed the Ca balance to a negative one without affecting the P and N balances. Addition of N (dried blood, gelatin), however, increased the retention of Ca, P, and N. Further addition of ground Nauru phosphate depressed P retention without improving the Ca retention. A. G. P.

Effect of ingestion of sodium, potassium, and ammonium chlorides and sodium hydrogen carbonate on the metabolism of inorganic salts and water. F. H. WILEY, L. L. WILEY, and D. S.

WALLER (J. Biol. Chem., 1933, **101**, 73—82).—On a salt-poor diet, NaCl causes retention of Na and Cl and increased excretion of Ca. KCl caused an increased excretion of inorg. SO_4, Na, and K, and a decrease in inorg. PO_4. NH_4Cl caused an increased excretion of Na, K (marked), Ca and Mg (slight), and an increased NH_3 formation and titratable acidity. $NaHCO_3$ caused increased excretion of Na, decreased excretion of K and Cl, and a marked decrease in NH_3 formation. Body-wt. declined only in NH.Cl ingestion, due to loss of body-H_2O.
H. G. R.

Inorganic salt balance during dehydration and recovery. F. H. WILEY and L. L. WILEY (J. Biol. Chem., 1933, **101**, 83—92).—Dehydration to the extent of 1·5% of the body-wt. causes no disturbance of the salt balance. Further dehydration causes loss of Na, K, and Cl, blood-serum being the first to respond, but there is also an accompanying loss of cellular H_2O. When further depletion of endogenous H_2O was avoided, there was a loss of K and inorg. PO_4 and retention of Na, indicating a shift of H_2O from cells to blood-serum and interstitial fluids. Subsequent administration of H_2O causes a loss of Na and retention of K, H_2O being stored in the cells. H_2O lost during dehydration was drawn from the cells.
H. G. R.

Selective accumulation of ions in cavities incompletely surrounded by protoplasm. S. C. BROOKS (Biol. Bull., 1933, **64**, 67—69).—Some accumulation of ions may occur in fluids which are only partly separated from the surrounding medium by living protoplasm.
H. G. R.

Biological action of strongly positive oxidation-reduction systems. E. H. FISHBERG and B. T. DOLIN (J. Biol. Chem., 1933, **101**, 159—171).—The system homogentisic acid–benzoquinone–AcOH, which fulfils all criteria of a reversible oxidation system, has been studied.
H. G. R.

Simultaneous measurement of cell permeability to water and to dissolved substances. M. H. JACOBS (J. Cell. Comp. Physiol., 1933, **2**, 427—444).—Mathematical expressions of penetration rates are derived and applied to experimental results obtained in the case of a marine egg exposed to a solution of non-electrolyte in sea-H_2O.
A. G. P.

Effect on the organism of the administration of large amounts of water. KUNSTMANN (Arch. exp. Path. Pharm., 1933, **170**, 701—718).—The drinking of large quantities of H_2O (average of 10 litres daily) by a man for several months led to a loss of NaCl from the organism (about 200 g.), whilst the NaCl concn. and osmotic pressure of the blood increased. Subjective symptoms included a craving for H_2O.
W. O. K.

Effect of ingestion of water and urea on cholesterol content of plasma. M. BRUGER and C. A. POINDEXTER (J. Biol. Chem., 1933, **101**, 21—28).—After ingestion of 500—1000 c.c. of H_2O, a decrease in blood-cholesterol was observed in only one case. An increase in blood-urea associated with a decrease in plasma-cholesterol was observed after ingestion of urea. This was not due to variation in H_2O content.
H. G. R.

Heat regulation and water exchange. XIV. Liver œdema in the mechanism of fever produced by tetrahydro-β-naphthylamine and by anaphylaxis. H. T. MARSHALL and H. G. BARBOUR. XV. Water content of the rat liver in Shiga vaccine fever and amidopyrine antipyresis. M. K. HORWITT, H. SHERMAN, and H. G. BARBOUR (J. Pharm. Exp. Ther., 1933, **48**, 209—215, 217—222).—XIV. The fevers produced in rabbits by injection of tetrahydro-β-naphthylamine and by anaphylaxis with horse-serum are attended by definite hydration of the liver, which takes place less rapidly than for cocaine fever. Results suggest that liver hydration facilitates the onset of febrile temp.

XV. Rats injected with Shiga vaccine developed fever with liver hydration; in some cases hypopyrexia occurred, with a still greater degree of hydration. Amidopyrine in large doses had no effect on the H_2O content of the liver in either normal or febrile rats.
R. N. C.

Comparative physiological actions of *dl*-β-phenyl*iso*propylamines. II. Bronchial effect. G. A. ALLES and M. PRINZMETAL (J. Pharm. Exp. Ther., 1933, **48**, 161—174).—β-Phenyl-ethyl- (I) and -*iso*propyl-amine (II), injected intravenously, dilated bronchi that exhibited natural or induced tone, but were less effective than adrenaline (III); the dilator effect was more prolonged in the case of (II) than (I). The corresponding 4-OH- and 3 : 4-$(OH)_2$-derivatives (IV) compared similarly with one another and with (III) in their bronchodilator effects. Perfusion experiments with isolated lungs gave negative results except with (IV).
R. N. C.

[Pharmacology of] some new alkamines in the tetrahydronaphthalene series. G. G. WOODS and N. B. EDDY (J. Pharm. Exp. Ther., 1933, **48**, 175—181).—The hydrochloride of 2-hydroxy-2-piperidino- (I), -2-dimethylamino- (II), and -2-diethylamino-tetrahydronaphthalene (III) (cf. A., 1931, 1052) resemble one another in their toxic and other effects on mice, rabbits, and cats. In mice the lethal doses were, respectively, (I) 435·25, (II) 574·37, and (III) 432·40; in rabbits, (I) 239·38, (II) 299·18, and (III) 281·06 mg. per kg. All three were emetic but not analgesic to cats. Respiration and O_2 consumption in rabbits were stimulated by doses of (I) 100, (II) 150, and (III) 50 mg. per kg., respectively. (I) suppressed intestinal evacuation in rabbits in doses of 30 mg. per kg.; (II) and (III) were inactive. All three exhibited local anæsthetic action which was definitely < that of procaine.
R. N. C.

[Pharmacology of] phenanthrene derivatives. I. Comparison of phenanthrene and some 2-, 3-, and 9-monosubstitution products. N. B. EDDY (J. Pharm. Exp. Ther., 1933, **48**, 183—198).—Phenanthrene (I) and four series of mono-substituted derivatives, comprising the 2-, 3-, and 9-Ac, -OH-, and -NH_2-derivatives and -carboxylic acids, were administered orally to cats. Absorption in the gastro-intestinal tract began almost at once, notwithstanding the general insolubility of the drugs, and proceeded

slowly, peak effects being observed after 2—5 hr., (I) produced mild general depression without analgesia, similar to the effect of small doses of barbiturates. In all four series, substitution in the 3-position produced the most active product. The 3-substitution derivatives in order of depressant activity were $R{\cdot}NH_2 > R{\cdot}CO_2H > R{\cdot}OH > R{\cdot}COMe$. All except the Ac derivatives were definitely analgesic; $2\text{-}C_{14}H_9{\cdot}NH_2$ was also analgesic in approx. fatal dose, but no analgesia was observed with the other derivatives. $9\text{-}C_{14}H_9{\cdot}CO_2H$ produced an unusual type of muscular disturbance. R. N. C.

Absorption and elimination of sodium α-pyrroleazo-*p*-phenylarsinate. P. FABIOLA (Arch. Farm. sperim., 1933, **55**, 255—266).—Na 2-pyrroleazo-*p*-phenylarsinate (I), when injected intravenously, is to a great extent eliminated in the urine unchanged. The % of As eliminated decreases as the dose is increased; a retention of 45% is found with the max. sublethal dose. When injected subcutaneously, (I) is absorbed very slowly (not complete for 5 days). R. N. C.

Chemotherapy of quinoline compounds. IV. Action of certain quinoline compounds on *Paramecia*. P. BRAHMACHARI, R. BANERJEA, and U. BRAHMACHARI (J. Pharm. Exp. Ther., 1933, **48**, 149—150).—Hydrochlorides of allyl- and allylthiocarbamido-8-aminoquinoline, and of certain Pr^{α} and Pr^{β} derivatives of 8-aminoquinoline were toxic to *Paramecia* in concn. of 1 : 2000. 8-β-Diethylamino*iso*propylamino-6-methoxy-2-methylquinoline dihydrochloride was toxic in concn. of 1—10,000, lactyl-8-aminoquinoline hydrochloride in 1 : 40,000, and 8-β-piperidino*iso*propylaminoquinoline dihydrochloride in 1 : 100,000. R. N. C.

Chemotherapy of derivatives of harmine and harmaline. I. C. E. COULTHARD, H. H. L. LEVENE, and F. L. PYMAN (Biochem. J., 1933, **27**, 727—738).—The prep. of harmol and harmalol is described. The peak of bactericidal activity is *n*-butyl- for *B. typhosus* (I) and *n*-amyl- for *S. aureus*, whilst the peak of amœbicidal activity is *n*-nonylharmol. In the ω-diethylaminoalkyl series the peak for (I) is ω-diethylaminononylharmol. No members of these series have antimalarial or trypanocidal activity. H. G. R.

Frohde's test for morphine. C. F. POE and P. S. STEHLEY (J. Lab. Clin. Med., 1933, **18**, 375—381).—The colour reaction is not sp. for any class of compounds or grouping, although alkaloids give the most positive results. CH. ABS.

Spectrographic pharmacology and toxicology. I. Spectrographic detection of poisons. II. Spectrographic detection of alkaloids. Tropine alkaloids. H. FISCHER (Arch. exp. Path. Pharm., 1933, **170**, 610—622, 623—634).—I. Apparatus for quant. visible and ultra-violet spectrographic analysis, especially appropriate for biological material, is described.

II. The ultra-violet absorption spectra of tropic acid and the tropine alkaloids have been investigated. The method has been applied to the detection and identification of atropine. W. O. K.

Action of pilocarpine and physostigmine on blood-sugar in normal, splanchnicotomised, and adrenalectomised rabbits. H. TADA (Tohoku J. Exp. Med., 1933, **20**, 275—299).—Bilateral splanchnicotomy or adrenalectomy diminishes, but does not prevent, hyperglycæmia (I) following subcutaneous injection of pilocarpine and physostigmine into rabbits. (I) is attributed chiefly to adrenaline secretion. Ergotamine (subcutaneously) decreases pilocarpine (I), but does not significantly affect the blood-sugar of normal or splanchnicotomised rabbits. CH. ABS.

Action of acetylcholine on respiratory exchange. M. LABBE and M. RUBINSTEIN (Compt. rend. Soc. Biol., 1933, **112**, 1040—1042).—In patients with various diseases, injection of acetylcholine (I) lowered the basal metabolic rate. The most marked reactions were obtained in those patients whose metabolism increased least on adrenaline (II) injection, thus supporting the view that (I) is antagonistic to (II). NUTR. ABS. (*b*)

Detection of an acetylcholine-like substance by reflector vasodilatation. K. GOLLWITZER-MEIER and M. L. OTTE (Arch. exp. Path. Pharm., 1933, **171**, 1—15).—During (but not before or after) vasodilatation of the major blood-vessels by stimulation of the sinus nerves, a substance with acetylcholine-like action was detected in the outflowing liquid. It was also detected in the walls of the normal vessel, stimulation increasing the concn. In the vessel walls it was associated with histamine; in the vessel contents it was often associated with histamine- and adenosine-like substances. The production of the substance by antidromic stimulation of the posterior roots has not been demonstrated with certainty. R. N. C.

Phloridzin glycosuria in pigs. O. FURTH and E. H. MAJER (Pflüger's Archiv, 1932, **230**, 489—498; Chem. Zentr., 1933, i, 1157).—The assimilation limit for glucose was 2—3 g. per kg. Large oral doses of phloridzin were given. Only half of the ingested glucose or starch appeared in the urine as "extra sugar." Apparently crude fibre is employed in the synthesis of fat from fermentation products rather than in the formation of sugar. A. A. E.

Effect on blood-sugar of some organic compounds with labile sulphur. II. A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1932, **20**, 181—189; cf. A., 1932, 1163).—Injection of Na *N*-ethyl-, *NN*-diethyl-, and *N*-propyl-dithiocarbamate causes hyperglycæmia in rabbits, whilst NH_4 dithiocarbamate and *N*-*p*-aminophenyldithiocarbamate and *piperidinium N-phenyldithiocarbamate* are inactive. R. K. C.

Hyperglycæmia in the cat following stimulation of the peripheral ends of sympathetic nerves. Z. M. BACQ (Compt. rend. Soc. Biol., 1933, **112**, 701—702).—In cats electrical stimulation (I) of the peripheral end of a cut purely sympathetic nerve caused an increase of 9—21 mg., whilst (I) of the sciatic caused an increase of 9—58 mg. of glucose per 100 c.c. of blood. In a chloralosed dog (I) had no effect on the blood-sugar level. NUTR. ABS. (*m*)

Mechanism of peptone hyperglycæmia. T. KATWA (Tohoku J. Exp. Med., 1933, 20, 365—388).—The hyperglycæmia in dogs is largely peripheral in origin. CH. ABS.

Influence of carbon dioxide on resorption through the skin in baths. K. EIMER and K. HEINZ (Arch. exp. Path. Pharm., 1933, 170, 683—700).—The absorption by the skin of the white mouse of EtOH, salicylic acid, salol, or salipyrin from H_2O at 32° in which the animal is immersed is accelerated by CO_2. In the case of antipyrine and also of compounds such as Li_2SO_4, which in the absence of CO_2 permeate the skin very slightly, CO_2 has no accelerating effect. W. O. K.

Effect of alcohol on [biological] oxidation. I. KANAI (Biochem. Z., 1933, 262, 41—56; cf. this vol., 182).—Repeated oral administration (I) of EtOH to rabbits leads, when the doses are small, to diminution of the ratios C : N and O : N in the urine and to unchanged or increased O : C; and when they are large to diminished C : N, but increased O : N and O : C ratios. Single small doses (II) of EtOH temporarily reduce the sugar content of the blood, whilst large single doses increase it. The hyperglycæmia produced by (I) of single doses of glucose or NH_2-acids is usually diminished and its duration reduced by simultaneous (I) of small doses of EtOH. (II) of EtOH given orally temporarily increase the glycogen content of the liver and temporarily reduce the R.Q. They often increase the basal metabolism, sometimes after temporarily reducing it. It follows from these results that oral administration of small amounts of EtOH causes qual. and often also quant. increase in biological oxidations, frequently after temporarily preventing destruction of sugar and promoting its conversion into glycogen. Large intoxicating doses, however, inhibit the oxidations. W. McC.

Distribution of avertin in the organism during narcosis. FISCHER and HUPPMANN (Pharm. Ztg., 1933, 78, 644—645).—The distribution in the various organs of rabbits during narcosis is inconst. W. O. K.

Mechanism of the action of narcotics. H. SULLMANN (Protoplasma, 1933, 18, 321—344).—Emulsions of olive oil in H_2O containing soap or gelatin are rendered unstable by the addition of narcotics. The latter accelerate phase inversion by $BaCl_2$. Urea and sugar have the reverse effect. The action of narcotics results from its disturbing effect on the emulsifier. Narcotic effects are discussed in relation to the physico-chemical condition of living cells. A. G. P.

Pharmacognosy of *Tanacetum vulgare*, L. R. JARETZKY and F. KUHNE (Arch. Pharm., 1933, 271, 353—358).—This drug contains *tanacetin* 2 (I), amorphous, hygroscopic. Only the essential oil has anthelmintic action, for which thujone is mostly responsible. Colour reactions for (I) allow its detection in various parts of *T. vulgare* and some other varieties, indicate the presence of another substance in certain varieties, and allow differentiation of the commoner varieties. R. S. C.

Expectoration and expectorants. T. GORDONOFF (Arch. Pharm., 1933, 271, 382—387).—A review. R. S. C.

Effect of blocking the reticulo-endothelial system, with or without simultaneous reduction of atmospheric pressure, on the metabolism of the liver and spleen. G. CRONHEIM (Biochem. Z., 1933, 262, 86—98; cf. this vol., 423).—In guinea-pigs blocking (I) of the reticulo-endothelial system by injection of Fe saccharate results in loss of body-wt., and this loss increases when the animals live in atm. of 330 mm. At the same time the wt. of the liver (II) decreases, whilst that of the spleen (III) increases. Changes equal to those produced in (II) by (I) cannot be produced by reduction (IV) of atm. pressure, and they closely resemble the effects of fasting. The body-wt. of rats decreases following (I), and the decrease grows following (IV), but the wt. of (II) and (III) remains unchanged. Chemical examination of (II) shows that in both animals (I) prevents the visual effects of (IV), but causes symptoms similar to those of fasting. W. McC.

Cytotoxin. I. Influence of hepatotoxin on liver-function. B. FUJIMOTO (Japan. J. Med. Sci., VII, Soc. Med. Hyg., 1932, 1, 279—388).—Dog's blood-sugar is 0·089—0·116 (average 0·103) g. per 100 c.c.; it is increased by injection of hepatotoxin (I) and other organotoxins. (I) prevents hyperglycæmia after injection of adrenaline. The liver-glycogen of treated dogs is practically normal. Iso-(I) produces greater functional disturbance of the liver than hetero- or auto-(I). CH. ABS.

Physical chemistry of inflammation and astringent action. Physico-chemical analysis of the biological effects of soaps and of tannin. W. BUCKENDAHL (Kolloid-Beih., 1933, 38, 57—98).—Experiments on the macroscopical and ultramicroscopical structure, [H·], surface tension, foaming power, and ultra-filtration of solutions of Na and K linoleates are described, as well as the influence of physiological salt solution and of tannin (I). Soaps have a strong toxic action on cells, in which the fatty acid plays the active part; the fatty acid forms a compound with hæmoglobin, which leads to hæmolysis. Whilst soap causes inflammation, the effect is neutralised by (I). In general, inflammatory and astringent action are considered to be antagonistic. (I) combines preferentially with proteins and protects the latter from the action of the soap. Whilst the toxic effect of soap is irreversible, that of small quantities of (I) is reversible; (I) cannot be washed out completely, however, when present in higher concns. E. S. H.

Effect of vinegar on circulating blood-cells. S. L. CRAWFORD and J. M. WARD (Fruit Products J., 1933, 12, 266—269).—In three generations of albino rats the feeding of cider vinegar produced no detectable effect. E. B. H.

Fate of glyceryl trinitrate in the tolerant and non-tolerant animal. L. A. CRANDALL, jun. (J. Pharm. Exp. Ther., 1933, 48, 127—140).—Tolerance, produced in the dog by administration of amyl nitrite, glyceryl trinitrate (I), or ethylene glycol

dinitrate, was accompanied by a cross-tolerance towards inorg. and org. nitrites. Perfusion of organs with solutions of (I) resulted in a partial destruction of (I), a varying % of the destroyed (I) being recovered as NO_2'. No conclusive difference was found between the results of perfusion of (I) in normal and tolerant dogs. Fresh blood destroyed (I), with production of NO_2', the activity being due to the erythrocytes. After discontinuance of tolerance doses, the rate of increase of destruction of (I) by blood was in general parallel to the rate of increase of response to a standard dose of $NaNO_2$, both becoming normal in about the same time interval. The mechanism of the tolerance is discussed. R. N. C.

Action of *X*-rays on cholesterol metabolism and counteraction by administration of lipins *per os*. M. KIESEL (Strahlenther., 1933, **46**, 311—342).—In rabbits *X*-ray irradiation was usually followed by fall in plasma-cholesterol (I). When "colsil" (a proprietary cholesterol–lecithin prep.) was administered shortly before irradiation the (I) rose in all cases. With human patients in 13 out of 20 cases there was a fall in (I), in the remaining 7 cases a rise. With administration of "colsil" before and after irradiation, 11 cases out of the 13 which previously registered a fall in (I) showed a marked rise (216% in 24 hr. in the extreme case). No difference in (I) was shown, as between carcinomatous and non-carcinomatous patients. NUTR. ABS. (*b*)

Acid poisoning of the organism by *X*-rays. K. ADLER (Klin. Woch., 1933, **16**, 300—302).—*X*-Irradiation of rabbits for 3 hr. leads to a fall in the concn. of serum-Ca, -K, and -Na and the skin content of Ca and K, and an increase in the output of Ca on the first day, in the output of K on the third day, and in the output of P on the second and eleventh days. When dogs are used, there is little change in mineral concn. or excretion, but a rise in the NH_3 coeff. of the urine. Irradiation of rabbits on a high-protein diet gave results similar to those in dogs. *X*-Irradiation leads to excessive acid production, and it is suggested that high-protein diet is advisable prior to *X*-ray therapy in order to prevent loss of minerals. NUTR. ABS. (*m*)

Mitogenetic radiation of nerve. A. GURWITSCH (Nature, 1933, **131**, 912).—A reply to criticism (this vol., 527). L. S. T.

The Hofmeister series [of anions] in heart-muscle. E. GELLHORN (Protoplasma, 1933, **18**, 411—419).—The automaticity of heart-muscle is restored by Na salts, the activity of which varies in the order of the Hofmeister series, citrate$>SO_4'' \ldots > CNS'$. A. G. P.

Effect of drugs causing deposition of fat in the organs on composition of body-fat. S. HOTTA (Tohoku J. Exp. Med., 1933, **20**, 211—228).—The same changes occur in the fat of the organs of animals poisoned with P, $CHCl_3$, and $NHPh{\cdot}NH_2$ as in the liver-fat of depancreatised animals, fat rich in saturated components being accumulated. When insulin (I) is given together with these toxic substances, the same changes are obtained, but when the administration is accompanied by infusion of sugar, the infiltration of saturated fat does not occur in animals poisoned with $CHCl_3$ or $NHPh{\cdot}NH_2$, but still occurs in P poisoning. The characteristic changes in the fat of the organs on administration of olive oil also are prevented by simultaneous administration of sugar, but occur when (I) also is given. The action of (I) on the distribution of fat in organs is obtained only in animals having pancreatic diabetes. NUTR. ABS. (*m*)

Effect of methylene-blue on hydrogen cyanide and carbon monoxide poisoning. M. M. BROOKS (Amer. J. Physiol., 1932, **102**, 139—141, 145—147; Proc. Soc. Exp. Biol. Med., 1932, **29**, 1228—1229; 1933, **30**, 493—494).—The rate of recovery after poisoning by HCN or CO is considerably accelerated by intraperitoneal injections of methylene-blue. H. G. R.

Nickel carbonyl poisoning. K. KOTZING (Arch. Gewerbepath. Gewerbehyg., 1933, **4**, 500—507).—$Ni(CO)_4$ has a sp. toxic action and does not produce the same effects as CO. A. G. P.

Storage of an antisyphilitic drug (tellurium) in the brain substance. F. JAHNEL, I. H. PAGE, and E. MÜLLER (Naturwiss., 1933, **21**, 416).—The grey but not the white matter of the central nervous system of rabbits which have been intramuscularly injected with suspensions of Te in oil contained relatively high concns. of Te. W. O. K.

Toxic action of certain chemicals on aquatic Oligochætes. C. HARUKAWA (Ber. Ohara Inst. landw. Forsch., 1932, **5**, 447—456).—The high toxicity of $Ca(OH)_2$ and KOH towards *Limnodrilus gotoi*, Hatai, is associated in part with the OH'. In comparative tests the order of toxicity was $Ca(OH)_2>KOH>KNO_3$. Very slight toxicity was shown by Na_2CO_3. A. G. P.

Iodine content of the blood after inunction of iodine ointment. P. KOHLER and R. JURGENS (Arch. exp. Path. Pharm., 1933, **171**, 38—45).—Application of I to the skin as a fat-sol. ointment was followed by a rise in blood-I, which was proportional to the amount of salve, the concn. of the I, and the area of skin surface treated. On repeated application of ointment, the blood-I remained at approx. the high val.; at a single application it reached a max. after 1 hr., subsequently falling slowly, but not reaching its initial val. It is concluded that storage of I occurs in the skin. R. N. C.

Pharmacology of iodine. II. Absorption of iodine by the buccal mucosa and its distribution in the organism. C. TIEDCKE (Klin. Woch., 1933, **12**, 383—386).—The buccal mucosa of dogs, rabbits, and guinea-pigs absorbs a considerable amount of I from a 1% solution or emulsion of KI. The I content of the thyroid showed only a small increase in comparison with other tissues. NUTR. ABS.

Effect of the level of calcium intake on the calcification of bones and teeth during fluorine toxicosis. H. M. HAUCK, H. STEENBOCK, and H. T. PARSONS (Amer. J. Physiol., 1933, **103**, 489—493).—Administration of NaF (0·15% of diet) to rats causes decreases in the abs. and % amounts of

bone-ash. On low-Ca diet the decrease is even greater, but on high-Ca diet there is a large increase in ash content, and F′ has a calcifying effect when incorporated in such diets. The ash content of the incisor teeth, on the other hand, decreases consistently with F′ feeding, even on high-Ca diet. The results could not be correlated with any consistent change in serum-Ca or -P. NUTR. ABS. (*m*)

Spectroscopic detection of the oxygen-carrying enzyme in acetic bacteria. O. WARBURG and E. NEGELEIN (Biochem. Z., 1933, **262**, 237—238; cf. Kubowitz and Haas, this vol., 188).—In suspensions (I) of *B. Pasteurianum* under anaerobic conditions the band (II) in the yellow becomes darker and sharper on passing in CO. At saturation the middle of the band is at 593 mμ. Saturation of (I) with O_2 causes disappearance of (II) and also of the two cytochrome bands (III) in the green, but if HCN is first added, (II) disappears, being replaced by a band (IV) at 640 mμ, whilst (III) remain. It follows that (II) is due to the O_2-carrying enzyme (V). (IV) is due to the oxidised form of (V) and contains $Fe^{\cdots}$. W. McC.

Catalase. VI. Size of particle and mol. wt. K. G. STERN (Z. physiol. Chem., 1933, **217**, 237—248; cf. this vol., 533).—From the rate of diffusion at p_H 7·2—7·3 of purified catalase solutions of different origin, the calc. mean radius of the particle is 2·73 mμ and the mol. wt. 68,900; the dimensions are thus similar to those of the hæmoglobin particle. J. H. B.

Intermediate compounds in enzymic reactions, illustrated by means of the catalase–H_2O_2 decomposition. H. ALBERS (Z. physiol. Chem., 1933, **218**, 113—128).—On the basis of the mass action law, general equations are developed for activity–p_S curves of enzymic systems which hold for the linking of any definite no. of substrate mols. to the enzyme mol. Applied to the decomp. of H_2O_2 by catalase, they show that H_2O_2 forms two compounds with the enzyme, a labile intermediate, catalase–$(H_2O_2)_2$, and in presence of excess of substrate a stable compound, probably catalase–$(H_2O_2)_6$. J. H. B.

Action of peroxidase. III. F. REUTER, H. WILLSTAEDT, and K. L. ZIRM (Biochem. Z., 1933, **261**, 353—365; cf. this vol., 154).—The importance of the Fe content and the manner of its occurrence for peroxidase (I) activity are investigated using a no. of synthetic Fe complex salts from different sources. Using chloro-, bromo-, and iodo-hæmins, the halogen did not affect the H_2O_2 optimum. The less closely related is the Fe-porphyrin to chlorophyll (II), the higher is the H_2O_2 optimum. (I) therefore belongs to the type of porphyrin obtained in hæmin and not to that in (II). P. W. C.

Gasometric method for determining oxidase activity. R. N. JEFFREY and W. V. CRUESS (Plant Physiol., 1933, **8**, 327—331). A. G. P.

Cozymase activation of some dehydrogenases. B. ANDERSSON (Z. physiol. Chem., 1933, **217**, 186—190).—The enzymic dehydrogenation of malic, lactic, citric, and glutamic acids, and of EtOH in presence of methylene-blue is activated by cozymase. J. H. B.

Tissue metabolism. I. Vitamin-B_1 and the co-enzyme of lactic dehydrogenase. E. BOYLAND (Biochem. J., 1933, **27**, 786—790).—Washed heart-muscle alone or with added lactate will not reduce methylene-blue, but addition of crude vitamin-B_1 preps. effects reduction. The co-enzyme (I) is not identical with vitamin-B_1. The respiration of Jensen rat sarcoma is not increased by addition of (I). Washed heart-muscle does not require the presence of (I) to effect oxidation of succinate or pyruvate. P. G. M.

Donator action of adenosinetriphosphoric acid and cozymase. C. G. HOLMBERG (Skand. Arch. Physiol., 1932, **64**, 177—183; Chem. Zentr., 1933, i, 949).—The activating effects of adenosinetriphosphoric acid and of cozymase on the action of seed extracts on methylene-blue are qualitatively similar. A. A. E.

Enzymic activity of fumarase preparations. K. P. JACOBSOHN and A. DA CRUZ (Biochem. Z., 1933, **261**, 267—274).—The velocity coeffs. for the action of fumarase preps. of ox-, pig-, and cod-liver, rabbit's liver, muscle, and kidney, and of the maceration extract of peas are tabulated. P. W. C.

Micro-determination of pyrocatechol and its use in the determination of phenolase. S. BLAZSÓ (Magyar Orvosi Arch., 1932, **33**, 376—382; Chem. Zentr., 1933, i, 952—953).—The pyrocatechol (I) is oxidised with 0·01*N*-alkaline $K_3Fe(CN)_6$, the excess of which is reduced with KI in presence of AcOH and $ZnSO_4$, the I being titrated with 0·01*N*-$Na_2S_2O_3$. The method is applicable to the exact determination of phenolase in blood and skin. The oxidation of (I) by $K_3Fe(CN)_6$ is not stoicheiometric; an empirical table is given. A. A. E.

Enzymic decomposition of cellulose and its fission products. W. GRASSMANN, L. ZECHMEISTER, G. TÓTH, and R. STADLER (Annalen, 1933, **503**, 167—179).—The enzyme of *Aspergillus oryzæ* (I) (cf. this vol., 748) ferments tunisin of animal origin at the same rate as vegetable cellulose; a similar behaviour is shown with dextrins from these sources. A prep. of (I) shows much greater activity towards cellulosic materials of high mol. wt. than does emulsin of a strength equiv. for a substrate such as cellobiose or salicin. Diaspore and bauxite, in addition to Al_2O_3,H_2O, have a marked selective affinity for cellobiase (II) and may be used to separate this from cellulase (III) in preps. of (I). In the series cello-biose, -triose, -tetraose, -hexaose, cellodextrin (mol. wt. approx. 1500), and cellulose, (II) shows enzymic action from cello-biose to -hexaose only, and is an oligosaccharase, and (III) has marked fermenting action only on the three highest members, and is therefore a polysaccharase. H. A. P.

Purification of plant-amylases. I. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1933, **83**, 505—515).—The amylase is pptd. with tannin and the ppt. treated first with $COMe_2$, which dissolves most of the tannin, and then with H_2O, which redissolves the amylase, leaving most of the remaining tannin-ppt. undissolved. This solution has 50—60 times the activity of the original. E. C. S.

Fractionation of myrosinase. C. NEUBERG and O. VON SCHOENEBECK (Naturwiss., 1933, **21**, 404—405).—Myrosinase (cf. A., 1926, 1060) may be fractionated by means of $Hg(OAc)_2$ into a sulphatase and a thioglucosidase. W. O. K.

Poisoning with iodoacetic acid of the lactic acid enzyme and methylglyoxalase. K. LOHMANN (Biochem. Z., 1933, **262**, 152—156).—$CH_2I{\cdot}CO_2H$ inhibits the production of lactic acid from glycogen in extracts of frog muscle freed from glutathione by dialysis. The action of methylglyoxalase is not inhibited by 0·01*N*-$CH_2I{\cdot}CO_2H$ or KF, although these attack the co-enzyme, reduced glutathione. W. McC.

Origin of glyceromonophosphoric acid and its role in glycolysis. R. NILSSON (Svensk Kem. Tidskr., 1933, **45**, 129—132).—The significance of the acid in yeast fermentation, in lactic acid formation, and in glycolysis is discussed (cf. this vol., 425). F. O. H.

Phosphatase. I. G. EHRENSVARD (Z. physiol, Chem., 1933, **217**, 274—280).—Treatment of a dried kidney prep. with trypsin and pptn. of inactive material with 20% aq. $COMe_2$ followed by adsorption of the enzyme on stearic acid yielded a phosphatase more active than a prep. from bones. J. H. B.

Phosphatase. II. Determination of serum-phosphatase. A. BODANSKY (J. Biol. Chem., 1933, **101**, 93—104). H. G. R.

Behaviour of phosphatase in presence of glutathione and iodoacetic acid. K. LOHMANN (Biochem. Z., 1933, **262**, 157—160; cf. Waldschmidt-Leitz *et al.*, this vol., 315).—At p_H 7·4 in presence or absence of $FeSO_4$ neither glutathione nor 0·002*N*-$CH_2I{\cdot}CO_2H$ has an inhibitory effect on the action of phosphatase (from kidney) on α- or β-glycerophosphoric acid, Embden's hexose monophosphate, or inorg. $H_4P_2O_7$ from muscle. With dialysed extracts the result is the same. Cysteine has a slight inhibitory effect. These and previous findings contradict the views of Waldschmidt-Leitz regarding the carbohydrate and phosphate metabolism of cells. W. McC.

Cozymase and phosphatase. K. MYRBACK (Z. physiol. Chem., 1933, **217**, 249—252).—At p_H 9, H_3PO_4 is eliminated from cozymase by phosphatase, inactivation of the co-enzyme occurring at the same rate. This indicates that the nucleotide isolated from yeast is actually cozymase (not merely its adsorbent) and that the H_3PO_4 is linked with the carbohydrate in the normal manner. J. H. B.

Phosphorylation and dephosphorylation. Production of natural hexose monophosphates from their components. K. LOHMANN (Biochem. Z., 1933, **262**, 137—151).—Glycogen added to dialysed muscle extract (I) is phosphorylated only when the complete co-enzyme system is present. Hexose diphosphate loses no phosphate (II) in (I), but after addition of Mg 1 mol. of (II) is eliminated, leaving Embden's ester (III), which is not dephosphorylated in presence of adenyl pyrophosphate. (III) is produced in a few sec. at 20° from either the keto- or aldo-hexose monophosphate in extracts (muscle, liver, brain, kidney) by the action of washed dried yeast. Inorg. pyrophosphate (IV) is produced in muscle and liver extracts only when Mg is present, the max. effect being obtained when the ratio $2Mg^{\cdot\cdot} : P_2O_7$ is $\not< 1$. The velocity of this reaction decreases as the acidity of the extracts increases. Under conditions where (IV) is eliminated HPO_3 is not hydrolysed. W. McC.

Enzymic hydrolysis of lecithins and lysocithins. A. CONTARDI and A. ERCOLI (Biochem. Z., 1933, **261**, 275—302).—Lecithin is hydrolysed by a system of enzymes consisting of lecithase *A* which removes 1 mol. of fatty acid, yielding lysocithin (the enzyme is present in snake and bee venom), lecithase-*B* which can remove both mols. of fatty acid, thus converting either lecithin or lysocithin into the choline ester of glycerophosphoric acid, a cholinephosphatase (I) which then removes choline, and a glycerophosphatase which finally hydrolyses glycerophosphoric acid. Absence of (I) appears to be a characteristic of plant seeds before ripening is complete. Certain enzyme extracts containing either large amounts or little or no (I) have not, whilst extracts having a moderate amount of enzyme have, a protective action against beriberi in pigeons. P. W. C.

Protein nature of enzymes. Pancreatic lipase. D. GLICK and C. G. KING (J. Amer. Chem. Soc., 1933, **55**, 2445—2448).—The prep. of lipase (I) from pancreas is modified to give a 894-fold purification. (I) is considered to be a globulin, since it is best extracted by 10% aq. NaCl, is pptd. by half-saturated aq. $(NH_4)_2SO_4$ or saturated aq. $MgSO_4$, and somewhat by saturated aq. NaCl, and is pptd. by dialysis of the purest solutions, and since (before dialysis) it gives the ninhydrin, biuret, and xanthoproteic reactions. The validity of the so-called "lipase val." is criticised. R. S. C.

Esterase character of pectase (pectin-demethoxylase). Z. I. KERTESZ (J. Amer. Chem. Soc., 1933, **55**, 2605).—Typical esterases (*e.g.*, from castor beans or from pancreas) form gels from apple or lemon pectin at p_H 5 or 8, but not at p_H 3, thus confirming the esterase character of pectase, for which the name "pectin-demethoxylase" is proposed. R. S. C.

Determination of activity of pepsin and rennin in stomach contents. B. ANDERSEN (Biochem. Z., 1933, **262**, 99—118).—Methods for the determination of the activity of the pepsin (I) and rennin (II) (Holter's method, this vol., 94) in gastric fluids (III) (particularly those of infants) are described, and an arbitrary method of expressing this activity is worked out. In the (III) of infants the ratio (IV) of the activities of (I) and (II) is const., and equals that found for adults. (IV) differs from the ratio obtained when pepsin other than that in (III) is used. W. McC.

Dilatometric investigation of the hydrolysis of proteins and their degradation products. II. Hydrolysis of ovalbumin and caseinogen. P. RONA and H. FISCHGOLD (Biochem. Z., 1933, **261**, 366—373).—With ovalbumin, the formation of 1 millimol. of NH_2 groups during peptic hydrolysis corre-

sponds with a vol. decrease of 17·5—18 cu. mm., and during alkaline hydrolysis with a vol. increase of 14·5 cu. mm. With caseinogen, there exists during peptic hydrolysis no proportionality between vol. changes and production of NH_2 groups, but with alkaline hydrolysis the vol. increases about 20 cu. mm. for the formation of 1 millimol. of NH_2 groups. P. W. C.

Histochemistry of enzymes. IV. Peptidase content of some marine invertebrates. K. LINDERSTRØM-LANG. **V. Micro-determination of sugars.** K. LINDERSTRØM-LANG and H. HOLTER (Compt. rend. Lab. Carlsberg, 1933, **19**, No. 13, 1—13; No. 14, 1—12).—IV. The micro-method (A., 1932, 427; this vol., 426) shows the unfertilised eggs of *Urechis caupo* (I) and of *Dendraster excentricus* (II) to have a const. peptidase activity when taken from the same animal. Low concns. of sea-H_2O accelerate and high concns. inhibit the enzyme action. Fertilisation of the eggs of (I) produces a decrease in the activity followed by an increase after 3—6 hr., whilst after 20—30 hr. the activity again decreases. The nucleus of the unfertilised eggs of (II) appears to be more active than the cytoplasm. The spermatozoa are inactive.

V. The iodometric method (A., 1929, 858) and the necessary apparatus (cf. A., 1931, 1455) are modified, so that with 7 cu. mm. of 0—1·5% aq. sugar an accuracy of approx. $2·5\times10^{-4}$ mg. of glucose is obtained. F. O. H.

Intracellular enzymes of tissues and glands. II. Pancreatic desmotrypsin. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1933, **218**, 77—94; cf. A., 1932, 881).—About 30% of the total enzyme content of pancreas consists of desmotrypsin (I) insol. in glycerol. Although completely inactive, it does not lack kinase, which is present as a complex, since, on keeping with aq. glycerol, (I) slowly becomes completely activated and gradually dissolves. (I) is not homogeneous; it contains di- and poly- but not tri-peptidase; it is mostly sol. in neutral electrolytes, the residual portion being sol. in dil. NaOH or HCl. (I) gives typical protein reactions, which, however, are shown only weakly by the lyotrypsin obtained on autolysis. J. H. B.

Influence of bile on tryptic digestion *in vitro*. H. J. VONK, P. A. ROELOFSEN, and C. ROMIJN (Z. physiol. Chem., 1933, **218**, 33—51).—At slightly acid reaction, tryptic digestion of fibrin, ox- and pike-flesh is favoured by bile and $K_4Fe(CN)_6$, but inhibited at p_H 8—8·7. At p_H 7·2—7·5, there is no effect. Similar concns. of the reagents show a somewhat parallel increase or inhibition of swelling of the substrate at the corresponding p_H vals. The effect is attributed to the strengthening of the negative charge on the acid side exercised by the activators, supplemented in the case of bile by a sp. action on the enzyme. J. H. B.

Influence of oxygen tension on the reversal of proteolysis (protein synthesis) in certain malignant tumours and normal tissues. C. VOEGTLIN, M. E. MAYER, and J. M. JOHNSON (J. Pharm. Exp. Ther., 1933, **48**, 241—265).—Oxygenation of digests of voluntary muscles of rats and rabbits resulted in a rapid reversal of proteolysis (I) [to protein synthesis (II)]. Similar results were obtained with digests of the Jensen rat sarcoma, Walker rat carcinoma 256, and a digest of papain, blood fibrin, and reduced glutathione (III). The conditions for (II) by proteolytic enzymes of tissue were: (1) a relatively high O_2 tension, (2) a p_H near neutrality, (3) a relatively high concn. of SH groups attached to proteins or (III) which could give rise to a relatively high concn. of disulphide, and (4) a sufficient concn. of protein degradation products. (II) was accompanied by a fall in total SH and reduced (III) concn. On reverting from oxygenation to anaerobic digestion, (I) was resumed, but the total SH and reduced (III) did not recover their original vals. Addition of small amounts of Cu immediately before oxygenation resulted in a temporary acceleration of (II), followed by resumption of (I). Results are discussed in relation to physiological and pathological problems connected with tissue-(II). R. N. C.

Arginase. IX. Control of arginase action by oxygen. S. EDLBACHER, J. KRAUS, and F. LEUTHARDT (Z. physiol. Chem., 1933, **217**, 89—104; cf. A., 1932, 650).—In organ extracts and suspensions arginase action is irreversibly inhibited by O_2. Glycerol protects the enzyme; N_2, H_2, CO_2, cysteine, glutathione, and Fe^{II} salts apparently activate it, owing to displacement of or combination with O_2. The activity–p_H curve of tumour-arginase from mouse carcinoma shows a max. at p_H 7; under anaerobic conditions the optimum is the same as for normal arginase, viz., 9·2. The activity of the tumour-enzyme is increased by 400—600%, normal arginase at most by 50%. Histidase does not show this characteristic anaerobic activation. The inhibition of arginase by heavy metals is detectable in $10^{-4}M$ solution. The O_2 acceptors (thiols?) probably control arginine hydrolysis in the living cell. J. H. B.

Uricolysis. I. Occurrence and properties of uricase. II. Preparation and investigation of purified uricase solutions. H. KLEINMANN and H. BORK (Biochem. Z., 1933, **261**, 303—323, 324—335).—I. Pig's liver, spleen, kidney, pancreas, and bile and to a smaller extent horse leucocytes contain uricase (I). Insulin and human organs and tissues are free from (I). Oxidation of uric acid (II) does not occur in absence of O_2, and is accelerated by perfusion with O_2. The p_H optimum curve has optima at p_H 8·85 and 10. The kinetics of (I)-action are investigated. (I) forms a compound with (II), which is precipitable by acid. (I)-action is inhibited by H_2S, and is completely lost on centrifuging off the H_2S-ppt. and on adding NaCN, the action thus resembling a heavy metal catalysis. Uricolysis is not inhibited by the products of the reaction. Oxidation of (II) is catalysed by $Cu^{\cdot\cdot}$, but this reaction is not accelerated by O_2.

II. Adsorption of (I) from aq. extracts of pig's liver at p_H 4 is quant. on treatment twice with kaolin and $Al(OH)_3$, but only partial with kieselguhr and animal C. Elution of (I) from the kaolin adsorbate occurs with acids (0·1*N*-HCl, 0·1*N*- and 0·01*N*-AcOH), bases (0·1*N*- and 0·01*N*-

NaOH, 0·01*N*-NH_3), and salt solutions (1% NaH_2PO_4 and Na_2HPO_4) and from the $Al(OH)_3$ adsorbate by 0·01*N*-NH_3 and 1% NaH_2PO_4 and Na_2HPO_4. The prep. of eluates which quantitatively degrade (II) and in which (I) is greatly purified is described, and the properties are investigated. (I) is pptd. from the eluates by $COMe_2$. P. W. C.

Uricolysis. III. Products of the enzymic decomposition of uric acid. H. Kleinmann and H. Bork (Biochem. Z., 1933, 262, 20—40; cf. A., 1932, 882).—The sole products of the complete enzymic degradation of uric acid are CO_2 and allantoin (I) (in mol. proportions 1 : 1) on the one hand and CO_2, $H_2C_2O_4$, and urea (1 : 1 : 2) on the other. These proportions are not appreciably altered by change in p_H (7·0, 8·85, 10·03), although the amounts of $H_2C_2O_4$ and urea decrease, whilst that of (I) increases with increasing p_H. (I) is an end-product, and is not further degraded. Urea forms loose EtOH-insol. compounds with $H_2C_2O_4$ (mol. proportions 1 : 1) and NaCl. The degradation closely resembles that which occurs during chemical oxidation (not with H_2O_2) in neutral or feebly alkaline medium (cf. Biltz and Schauder, A., 1924, i, 569). A method for the isolation and determination of the degradation products is described. W. McC.

Uricase. VI. Distribution in various animals. R. Truszkowski and C. Goldmanówna (Biochem. J., 1933, 27, 612—614).—2 g. of fresh tissue were ground and shaken for 60 min. with 20 c.c. of 0·025—0·5% uric acid (Li salt) and the latter was determined colorimetrically. Uricase is present in the liver of all animals examined and in the kidneys of some (ox, pig, dog, rat, frog), but is absent from other tissues. P. G. M.

Action of metals on enzymes. II. M. Jacoby (Biochem. Z., 1933, 262, 181—184; cf. this vol., 535).—The reversibility (I) of the action of Cu decreases gradually with time and is greatly reduced after 24 hr. (I) also decreases as temp. increases (—5° to 37°). As regards the effect of reaction, for Cu (I) is least at alkaline reaction (max. between p_H 7 and 8), but for Hg and Ag it is least at acid reaction. With Hg (I) also decreases in proportion as the amount of metal increases. W. McC.

Action of cyanides on the development of yeasts. M. N. Meisel (Bull. Acad. Sci. U.R.S.S., 1932, 1337—1344).—As regards toxicity towards yeast, HgCN>NaCN>KCN>NH_4CNS. *Saccharomyces cerevisiæ* is more resistant than *S. Ludwigii*, and old cultures than young. Separate yeast cells withstand treatment with 5% aq. KCN for 24 hr. The protoplasm changes in appearance, the vacuoles develop alkalinity, and colonies differ greatly from the normal form. By treatment with KCN, 40 strains of *S. cerevisiæ*, differing in morphological and physiological properties, have been isolated. These peculiarities have persisted over a year and have withstood 30-fold sub-culturing. Some of the "saltants" accumulate much and others little fat, and some liquefy gelatin. T. H. P.

Mechanism of oxidation processes. XXXIV. Anaerobic fermentation of citric acid by yeast. H. Wieland and R. Sonderhoff. **XXXV. Aerobic dehydrogenation of alcohol by yeast.** H. Wieland and F. Wille (Annalen, 1933, 503, 61—70, 70—84).—XXXIV. Fermentation of citric acid (I) with "impoverished" yeast gives 1·6—1·7 mols. AcOH, 0·1—0·33 mol. HCO_2H, and < 2 mols. CO_2 per mol. of (I), and in addition small amounts of succinic acid, EtOH, and MeCHO. The CO_2 is too much (allowing for self-fermentation) and the HCO_2H correspondingly too little for the equation: $OH{\cdot}C(CO_2H)(CH_2{\cdot}CO_2H)_2 \rightarrow CO(CH_2{\cdot}CO_2H)_2 + HCO_2H \longrightarrow 2AcOH + CO_2 + HCO_2H$, and dehydrogenation must be assumed to occur: $HCO_2H - 2H \longrightarrow CO_2$. H_2 is not evolved and air-oxidation is excluded, and it is concluded that the H_2 is absorbed by the yeast. Succinic acid is probably formed by a similar process from AcOH, and the intermediate formation of oxalacetic acid (II) is improbable. Formation of (I) is not observed in the fermentation of (II) and AcOH or Me·CHO by yeast.

XXXV (cf. A., 1932, 302). The quotient CO_2 evolved/O_2 absorbed is determined kinetically for the oxidation of EtOH by impoverished yeast in a buffered solution at p_H 6·8. Yeast itself takes up CO_2 during the reaction, the absorption being incomplete at the end of 1 hr., and more marked in pure H_2O than at p_H 6·8; the absorbed CO_2 is almost completely removed by acidification and passage of a stream of inert gas. The corr. val. of CO_2/O_2 is approx. const. (0·48 at end of 1 hr., 0·55 after 2 hr.) and independent of EtOH concn. The oxidation of EtOH to AcOH is therefore accompanied from the earliest stages by further oxidation to CO_2 and H_2O, the two reactions occurring to approx. equal extents, as is confirmed by determination of AcOH produced. Rather more EtOH is consumed than is accounted for by the above mechanism and is explained by the formation among other products of succinic acid (equiv. to 13% EtOH after 25 hr.). H. A. P.

Relation of thiol to inhibition of yeast fermentation by iodoacetic acid. E. F. Schroeder, G. E. Woodward, and M. E. Platt (J. Biol. Chem., 1933, 101, 133—144).—Inhibition of fermentation by $CH_2I{\cdot}CO_2H$ runs parallel with a decrease in the glutathione (I) content of the yeast and is complete when 30% of (I) is lost. This also occurs with α- but not with β-iodopropionic acid or I. With I (I) may be reduced by 70% before complete inhibition. H. G. R.

Rôle of phosphate in alcoholic fermentation and in the respiration of yeast. A. M. Malkov (Biochem. Z., 1933, 262, 185—195; cf. A., 1932, 577).—Biological oxidations which occur during alcoholic fermentation (I) are inhibited by pyro- and still more by ortho-phosphate, both of which promote (I) by producing Fe–P compounds. The phosphates also promote the more economic propagation of yeast. W. McC.

Simultaneous demonstration of starch and fat in protozoa. W. L. Doyle (Stain Tech., 1933, 8, 117).—Equal parts of a 0·3% solution of I in 60% EtOH and a saturated solution of Sudan III or scarlet-R in 60% EtOH+10% $COMe_2$ are mixed just before use. Applied to *Chilomonas paramecium*, this

fluid successfully stained the starch and fat simultaneously. H. W. D.

Nutrition of *Euglena*. II. *E. stellata*, *klebsii*, *anabæna*, *deses*, and *pisciformis*. H. Dusi (Ann. Inst. Pasteur, 1933, **50**, 840—890).—*E. stellata* is very sensitive to the reaction of the medium, p_H 5·5 being the optimum for growth. A significant amount of Ca must be present in the medium for cultivation to occur, and in this respect *E. stellata* differs from all the other *Euglena* studied. Lysine exerts a most favourable influence on the growth of these cultures. *E. klebsii* shows optimum growth at p_H 6—7, and gives very poor growth with mineral salts (NO_3' and NH_4 salts) as the source of N, but good growth with certain NH_2-acids (I) and with peptones (II). *E. anabæna* is difficult to cultivate in mineral media, NH_4 phosphate alone of the salts tested being satisfactory as a source of N; (I) are not very satisfactory, but (II) are very favourable to growth. Culture is possible over the range p_H 5·5—8·5 and best at 6·0—8·0. *E. deses* does not multiply in a purely mineral medium containing NO_3' or NH_4 salts, but requires org. N in the form of (I) or (II). No culture of *E. pisciformis* was possible with NO_3', NH_4 salts, (I), or with hydrolysed silk as the source of N, but (II) mixtures from muscle-proteins gave good growth. In a general summary, the results of the experiments with these *Euglena* and with *E. gracilis* are tabulated and the findings discussed in relation to the function of chlorophyll and light. A. W.

Sap stains of wood in Japan. I. *Ceratostomella sp.*, Rumbold, the cause of a blue stain of pine trees in Western Japan. Y. Nisikado and K. Yamauti (Ber. Ohara Inst. landw. Forsch., 1933, **5**, 501—539).—The growth and activity of the organism is described. O_2 is necessary for its growth. A. G. P.

Kinetics of intracellular carbohydrate oxidation of *Sarcina lutea*. II. B. B. Rubenstein (J. Cell. Comp. Physiol., 1933, **2**, 445—455; cf. this vol., 753).—The cell-free filtrate from *S. lutea* contained the enzymes necessary for the oxidation of sugar to AcOH. A scheme of intracellular carbohydrate oxidation is suggested in which the key (or slowest) reaction is the activation of glucose. A. G. P.

Growth of *Clostridium botulinum* on casein hydrolysate and hydrolysate preparations. W. Burrows (J. Infect. Dis., 1932, **51**, 298—308).—Arginine is not an important factor; traces of flavianic acid are not detrimental. No cultural differences between types *A* and *B* were detected. Ch. Abs.

Botulinus toxin; destruction by heat. H. Sommer and E. W. Sommer (J. Infect. Dis., 1932, **51**, 243—254).—Toxins prepared by adsorption on $Al(OH)_3$ and by separation of *Cl. botulinum* are most stable to heat at p_H 5; purified preps. (acid pptn.) are equally resistant at p_H 4·4 and 5. A sharp optimum at p_H 5 is a criterion of the purity of toxin preps. Aminoids and milk do not retard destruction at p_H 5; buffer solutions containing tervalent anions enhance thermal inactivation at p_H 5 and 7, but bivalent anions are without influence. The velocity of thermal destruction varies greatly in different fruit and vegetable juices of the same p_H val. After 4 hr. at 68°, type *A* toxins are destroyed at approx. a bimol. rate, whilst type *C* toxins are destroyed at a unimol. rate. The rate of destruction is increased 10 times on raising the temp. by 10°. Ch. Abs.

Cultural requirements of bacteria. III. Diphtheria bacillus. J. H. Mueller, K. S. Kleise, E. F. Porter, and A. Graybiel (J. Bact., 1933, **25**, 509—519).—Cystine, tryptophan, and certain unidentified substances are essential to the growth of the organism. A. G. P.

Staining of diphtheria bacilli. J. Siegler (Magyar Orvosi Arch., 1932, **33**, 401—403; Chem. Zentr., 1933, i, 980).

Fixation of dyes by microbes as a function of p_H. P. Lasseur, A. Dupaix, and L. Georges (Compt. rend., 1933, **196**, 1749—1751).—Curves are given showing the variation with p_H of (*a*) the surface tension of and (*b*) fixation of safranine, methylene-blue, diamine-blue, Congo-red, and acid fuchsin by aq. suspensions of *B. caryocyaneus*. Their irregularities are not completely accounted for by the change of the sign of the plastid charge from positive to negative above p_H 3. A. C.

Metabolism of the *Brucella* group. VIII. Nutrient requirements in synthetic media. IX. Physicochemical requirements in synthetic media. C. E. Zobell and K. F. Meyer (J. Infect. Dis., 1932, **51**, 344—360, 361—381).—VIII. Lactates, citrates, and asparagine supply C; $NH_4^{\cdot}$ and certain NH_2-acids supply N. Sulphates and thioamino-acids supply S; phosphates supply P. Mg and either Na or K are essential; Fe is beneficial.

IX. The influence of osmotic pressure and surface tension is described. The optimal p_H is 6·6—7·4. The organisms are sensitive to O_2, and all require CO_2 or carbonates. Ch. Abs.

Electrophoresis of *Brucella*. Lisbonne and Seigneurin (Compt. rend., 1933, **196**, 1747—1748).—The mobilities of *B. melitensis* and *B. abortus* are independent of their species, but depend on the nature of the host. A. C.

Anaerobic decomposition of *l*-cystine by *Proteus vulgaris*. H. L. A. Tarr (Biochem. J., 1933, **27**, 759—763).—A strain of *P. vulgaris* was washed in SO_4'' solution and incubated with cystine (I) in PO_4''' buffer at p_H 7·8; each mol. of (I) gave 2 mols. of H_2S, NH_3, AcOH, and HCO_2H. H. D.

Sulphur-oxidising bacteria. D. I. Aquino (Univ. Philippines Nat. Appl. Sci. Bull., 1932, **2**, 309—338).—Soil-S composts afforded *Thiobacillus thio-oxidans* (I), a *T. sp.* (II), and *Thiophysa sp.* (III); all oxidised S or $Na_2S_2O_3$ and (I) liquefied gelatin. The rate of oxidation was proportional to the concn. of $Na_2S_2O_3$ up to 0·2*M*, and fell sharply at higher concns. Addition of glucose increased (II, III) or decreased (I) the oxidation of $Na_2S_2O_3$. Addition of $Ca(NO_3)_2$ decreased the oxidation of $Na_2S_2O_3$ by (II) except in presence of $CaCO_3$. In general, $CaCO_3$ increased the amount of oxidation. Ch. Abs.

Fermentation studies on *Lactobacillus acidophilus* and *L. bulgaricus*. R. H. WEAVER (J. Infect. Dis., 1932, **51**, 273—279).—In a suitable medium, all strains ferment maltose, sucrose, and fructose with the production of acid. CH. ABS.

Lactobacteria. C. A. SAGASTUME (Semana med., 1933, I, 1022—1031).—The growth of *B. acidophilus* from human intestinal mucosa is stimulated by peptone and NH_2-acids. CH. ABS.

Cheese-ripening studies. Nitrogen requirements of the lactic acid bacteria: effect on the sugar-fermenting abilities of enriching peptic caseinogen digest broth with yeast extract. W. SADLER and B. A. EAGLES (Biochem. J., 1933, **27**, 771—777).—For all the bacteria used the stimulating effect on the lactic fermentation of mannitol, glucose, fructose, lactose, etc. of a 5% addition of yeast extract (I) (0·33% total N) to the nutrient peptic digest (II) (0·5% total N) can be reproduced by doubling the total N of the (II) without addition of (I). P. G. M.

Oxidations and reductions determined by *Acetobacter xylinum*. M. COZIC (Compt. rend., 1933, **196**, 1740—1741).—The oxidation by *Acetobacter xylinum* of primary and *sec.* alcohols at p_H 7 may be effected in the absence of O_2 by adding a dye having an oxidation–reduction potential > -150 mv., *e.g.*, indigodisulphonate and Nile-blue. Free energy calculations agree with thermochemical data for the alcohol and its oxidation product. The rate of oxidation by O_2 is 50 times that in the presence of dyes. 0·01*N*-KCN increases O_2 consumption 5—10 times without affecting dye reduction. The respiratory power of cultures is decreased by 75% by washing with H_2O, whilst the reducing power is unchanged. Cultures are poisoned by bromoacetic acid esters. A. C.

Acetone and butyl alcohol fermentation of cane molasses. I. *Bacillus butyligenus*. K. MUTA (J. Agric. Chem. Soc. Japan, 1933, **9**, 19—44).—The organism, from Formosan soil, produces $COMe_2$ and BuOH from cane molasses. Fermentation should be commenced in vac. Molasses (90 kg.) gave an oil (17 kg.) containing $COMe_2$ 27·38, BuOH 55·01, EtOH 4·71, H_2O 8·03%, together with CO_2 and H_2. CH. ABS.

Butyl–acetone group of bacteria. I. Gelatinolysis. C. H. WERKMAN and G. L. STAHLY (Iowa State Coll. J. Sci., 1933, **7**, 93—109).—The gelatinolytic properties of 22 cultures have been determined by (*a*) max. temp. of gelation, (*b*) Hg–protein pptn., and (*c*) viscosity measurements. CH. ABS.

Intermediary compounds in the acetone–butyl alcohol fermentation. M. J. JOHNSON, W. H. PETERSON, and E. B. FRED (J. Biol. Chem., 1933, **101**, 145—157).—$COMe_2$ (I) is formed rapidly by fermentation of $CH_2Ac{\cdot}CO_2H$ by *Clostridium acetobutylicum*, reaching a max. at the time of most rapid (I) production. This appears to be an intracellular effect. $AcCO_2H$ (II) was readily fermented and is transformed mainly into AcOH, (I), and $CHAcMe{\cdot}OH$. A new method for the determination of (II) is given. β-Hydroxybutyric acid had no effect on the fermentation, but AcCHO and aldol were toxic. H. G. R.

Mechanism of decarboxylation. M. G. SEVAG (Naturwiss., 1933, **21**, 466).—The O_2 consumption of solutions of glucose and lactic acid incubated with type I pneumococcus shows that the reaction energy of the latter is increased (350%) by addition of $AcCO_2H$ (I), which reacts with the H_2O_2 liberated in the decarboxylation reaction. Even when 5100 c.c. of O_2 are consumed no trace of H_2O_2 is found in the reaction products, whilst without the addition of (I), 50% of the theoretical amount of H_2O_2 is found. H. D.

Differentiation of virulent and non-virulent pneumococci (type I). M. G. SEVAG (Naturwiss., 1933, **21**, 466).—Virulent and non-virulent pneumococci are differentiated by their comparative fermentation rates of lactic acid and glucose; the O_2 consumption in the presence of $AcCO_2H$; decomp. of EtOH and PrOH; the effect of KCN on their activity, and the increased O_2 consumption on addition of $AcCO_2H$ to the glucose or lactic acid substrate. H. D.

Correlation of protective value with titres of other antibodies in type I antipneumococcus serum. L. D. FELTON (J. Immunol., 1931, **21**, 341—356). CH. ABS.

Precipitin reaction. Precipitating haptenes; species differences in antibodies. M. HEIDELBERGER and F. E. KENDALL (J. Exp. Med., 1933, **57**, 373—379).—Partial hydrolysis products of the sp. polysaccharide of type III pneumococcus ranging from 550 to 1800 in formula wt. can be quantitatively freed from unhydrolysed polysaccharide. The fractions yield sp. ppts. with type III antipneumococcus horse serum, but fail to ppt. homologous rabbit antisera. The aldobionic acid does not ppt. antisera. CH. ABS.

Biology of the tubercle bacillus. III. Does the so-called fatty capsule serve to protect the tubercle bacillus? J. WEINZIRL (J. Bact., 1933, **25**, 447—459).—Addition of glycerol to culture media increased the production of lipins by *M. tuberculosis*, and such organisms had increased resistance to bactericides. A. G. P.

Lipins of tubercle bacilli. XXXII. Isolation of trehalose from the timothy-grass bacillus. M. C. PANGBORN and R. J. ANDERSON (J. Biol. Chem., 1933, **101**, 105—109).—After acetylation of crude polysaccharides from EtOH–Et_2O extract of timothy-grass bacilli, 40% was isolated as cryst. trehalose octa-acetate. H. G. R.

Lipins of bacillus Calmette–Guerin (BCG). E. CHARGAFF (Z. physiol. Chem., 1933, **217**, 115—137).—BCG is richer in lipins than human (I) and bovine tubercle bacilli grown under similar conditions. The compositions of the fat and phosphatide differ but little from that of the virulent organisms. Saturated liquid fatty acids are also present. The only noteworthy difference is in the wax fraction, the "unsaponifiable fraction" of which has a mol. wt. by titration of 770 as compared with 1380 for that of (I). J. H. B.

Composition of the active principle of tuberculin. XVI. Local cutaneous sensitisation produced in normal rabbits and guinea-pigs by the protein of tuberculin. F. B. SEIBERT (J. Infect. Dis., 1932, **51**, 383—406).—The protein used is purified by means of $(NH_4)_2SO_4$, $CCl_3{\cdot}CO_2H$, or concn. and washing (ultra-filtration). CH. ABS.

Production of antityphoid substance by irradiation of the skin with ultra-violet rays and the role of the spleen hormone therein. M. MATSUSHITA (J. Chosen Med. Assoc., 1932, **22**, 787—805).—The sera of normal or immunised rabbits contain a small amount of antityphoid substance (I); on ultra-violet irradiation of the skin in the presence of spleen, (I) increases. Irradiation produces a histamine-like substance which causes the spleen to produce a hormone which controls the production of (I). CH. ABS.

Behaviour of bacteriophage in body-fluids and exudates. M. G. COLVIN (J. Infect. Dis., 1932, **51**, 527—541).—Body-fluids inhibit bacteriophage. Repeated contact of organisms with serum makes them lysis-resistant; in serum the protein fraction is the main factor in lysis inhibition, whilst in urine the crystalloid fraction inhibits. CH. ABS.

Substance, from organ extracts, which affects the circulatory system. K. FELIX and A. VON PUTZER-REYBEGG (Klin. Woch., 1932, **11**, 1838—1839; Chem. Zentr., 1933, i, 1152).—The arginine fraction of mesenteric extracts affords a *substance* $C_4H_{12}N_6$ (*flavianate*, $C_4H_{12}N_6(C_{10}H_6O_8N_2S)_2$, m.p. 226—227°; *picrate*, m.p. 196—197°; *chloroaurate*, m.p. 204°), which reduces the blood-pressure of cats and rabbits; it gives Sakaguchi's reaction, but not a diazo-reaction. A. A. E.

Comparison of adrenaline, sympatol, and ephetonal. E. SCHILLING and G. KOPP (Deut. med. Woch., 1932, **58**, 1399—1401; Chem. Zentr., 1933, i, 959).—Intramuscular injection of adrenaline (0·7—1·0 mg.) has a considerable effect on human blood-pressure and -sugar; sympatol (180—240 mg.) has only a slight effect. Ephetonal (100 mg., oral) has a weaker, but longer continued, effect than 1 mg. of adrenaline. A. A. E.

Splenic hormone and its influence on thrombocytogenesis after ultra-violet ray radiation. G. TOYODA (J. Chosen Med. Assoc., 1932, **22**, 673—691).—Thrombocytosis (I) following ultra-violet irradiation does not occur with splenectomised rabbits. The rays stimulate the skin and produce a histamine-like substance (II) which gives Pauly's reaction; (II) causes the spleen to secrete a hormone (III) which controls (I). If the skin is removed before irradiation there is no (I), and (II) is not present in the blood. (III) is not destroyed by heating at 100° for 2 hr.; it is insol. in Et_2O, but sol. in H_2O. CH. ABS.

Secretion of insulin during irradiation of the pancreatic region. J. LA BARRE and P. LORTHIOIR (Compt. rend. Soc. Biol., 1933, **112**, 722—724).—Dogs (chloralosed) after laparotomy and fixation of the pancreas to the anterior abdominal wall were exposed to X-rays for 15—18 min. and 10 min. later the pancreatic vein was anastomosed with the jugular vein of a receptor dog under chloralose and previously decapsulated. A fall of the blood-sugar level reaching its max. in about 12 hr. was produced in the receptor. Since this irradiation hypoglycæmia could not be produced if all secretion of adrenaline from the donor were prevented, it follows that irradiation hypoglycæmia is due primarily to a hypersecretion of adrenaline in the donor, which in turn stimulates the output of insulin from the pancreas of the receptor. NUTR. ABS. (*m*)

Effect of insulin on the calcium content of the blood and the aqueous humour of the eye. C. E. RAITHA (Skand. Arch. Physiol., 1932, **64**, 184—194; Chem. Zentr., 1933, i, 960).—With rabbits injection of insulin caused irregular variations in serum-Ca. In hypoglycæmic convulsions serum-Ca is often increased. Insulin increases the Ca in the aq. humour, but small doses cause a slight decrease at first owing to the increased excretion of adrenaline. A. A. E.

Action of hormones on yeasts, moulds, and bacteria. A. A. IMSCHENETZKI (Bull. Acad. Sci. U.R.S.S., 1932, 1559—1577).—The action seems to be sp. The germination of yeast- and mould-spores and the vegetative growth are accelerated by thyreoidin, which also quickens alcoholic fermentation. Thyreoidin has little stimulating action on bacterial spores and none on cell-multiplication. Under the influence of adrenaline, yeast (*S. Ludwigii*) cells become elongated and mycelial, the vacuolisation, accumulation of fat, and granularity of the protoplasm also becoming more marked. Insulin causes disappearance of glycogen from the cells of *S. cerevisiæ*. T. H. P.

Parathyroid hormone and its occurrence in other organs. G. PERITZ (Deut. med. Woch., 1932, **58**, 1354—1356; Chem. Zentr., 1933, i, 1151).—Injection into dogs of parathyroid hormone is followed by a fall, a rise, and sometimes then a further fall in serum-Ca. The parathyroid extract contains two (separable) hormones; the fraction which depresses serum-Ca gives Pauly's diazo-reaction, but is not identical with (is in fact antagonistic to) histamine. The (colloidal) factor which raises serum-Ca does not give Pauly's reaction. Both factors are present in the placenta. A. A. E.

Effect of thyroid on secretion and cholesterol content of bile. V. P. BESUGLOV and L. M. TUTKEVITSCH (Z. ges. exp. Med., 1933, **87**, 52—57).—A single subcutaneous injection of thyroxine (1—2 mg.) into dogs with a bile fistula led to a reduction in the vol. of bile secreted and a marked fall in its cholesterol (I) content; thyroidectomy was followed by an increase in the output of bile and in its (I) content. Injection of tetrahydro-β-naphthylamine also led to a moderate and transient fall in the vol. and (I) content; gynergen had no effect. It is concluded that the thyroid secretion regulates not only the secretory activity of the liver, possibly through the sympathetic, but also total (I) metabolism. NUTR. ABS. (*b*)

Effect of "antithyreoidin-Mobius" on glycogen metabolism. A. WITTGENSTEIN (Arch. exp. Path. Pharm., 1933, **171**, 46—53).—While normal

sheep serum was without effect, antithyreoidin-Mobius depressed or prevented the removal of glycogen from the liver by thyroxine. The effect was the same whether the antithyreoidin was injected before, after, or simultaneously with the thyroxine. Commercial antithyreoidin, preserved with PhOH, was more effective than the freshly-prepared product, but this was not due to the PhOH. R. N. C.

Determination of the functional activity of the thyroid by means of urine or serum. II. Influence of alkaline earths on the function of the thyroid. M. Koh (J. Chosen Med. Assoc., 1932, **22**, 907—913).—When injected as chloride, Ca and Na accelerate, whilst K and Mg retard, the thyroid function. Ch. Abs.

Influence of prepituitary extract on the weight of the thyroid. B. A. Houssay, P. Mazzocco, and A. Biasotti (Soc. Argentina Biol., 1932, May 12).—Prepituitary extract causes an increase in wt., hypertrophy, and decrease in the I content of the thyroid gland. Ch. Abs.

Activity of the thyreotropic hormone of the anterior lobe of the pituitary, and Reid Hunt reaction. C. Oehme, H. Paal, and O. Kleine Arch. exp. Path. Pharm., 1933, **171**, 54—64).—The hormone is not identical with the secretion of the gland responsible for the positive Reid Hunt reaction (I), since (*a*) the hormone is destroyed by boiling under any conditions, the (I) only by boiling in presence of O_2, (*b*) protein-free ultra-filtrates of extracts of the gland have lost considerably their thyreotropic and metabolic effects, whilst the (I) is unchanged, and (*c*) oral administration of gland extract produces only the (I). R. N. C.

Reid Hunt reaction and liver-glycogen. I. Knaab (Arch. exp. Path. Pharm., 1933, **171**, 65—72).—The resistance to MeCN poisoning (I) in mice bears no relationship to the liver-glycogen (II). There is no parallelism between the fall in (II) produced by injection of thyroxine and the increased resistance to (I) (the Reid Hunt reaction), (II) reaching a min. and beginning to recover before the MeCN-resistive power has reached its max. In the case of mice fed on oats, the resistance to (I) is prolonged by insulin, but there is no corresponding depression of (II). R. N. C.

Action of prolan, prahormon, and anterior pituitary extracts on the thyroid gland. H. O. Kleine (Arch. Gynakol., 1932, **152**, 34—41; Chem. Zentr., 1933, i, 958).

Anterior pituitary hormone, which regulates fat metabolism, in "Inkretan." F. Boenheim and F. Heimann (Z. ges. exp. Med., 1932, **83**, 637—640; Chem. Zentr., 1933, i, 957).—Of the commercial preps. examined only "praphyson" and a prep. from the glandular part of the pituitary contained the anterior pituitary hormone which regulates fat metabolism. "Praphyson" is present in "Inkretan." A. A. E.

Effects of anterior pituitary extracts on nitrogen metabolism, water balance, and energy metabolism. O. H. Gaebler (J. Exp. Med., 1933, **57**, 349—363).—Intraperitoneal or subcutaneous administration of the globulin fraction greatly increases the N balance of dogs; urinary N and blood-non-protein-N decrease, whilst fæcal N is unchanged. The N gained may be converted into reserve protein. The effect of the extracts on protein catabolism is greatest when this is high. H_2O intake and urine vol. are increased; an increase in heat production is effected by oxidation of fat. Ch. Abs.

Melanophore hormone. I. F. G. Dietel (Klin. Woch., 1932, **11**, 2075—2078; Chem. Zentr., 1933, i, 957).—The melanophore hormone (I) only expands the pigment cells; the frog's pituitary gland secretes also a diuretic hormone, whilst that of warm-blooded animals secretes (I) and an antidiuretic hormone. A. A. E.

Pituitary control of skin pigment in elasmobranch fish. H. M. Lundstrom and P. Bard (Biol. Bull., 1932, **62**, 1—9; Chem. Zentr., 1933, i, 956).—Removal of the posterior pituitary lobe leads in *Mustelis canis* to fading of the skin owing to contraction of the melanophores (I); the effect is not produced by removal of the anterior lobe or destruction of the hypothalamus. Extracts of the posterior lobe cause expansion of (I) and darkening of the skin of hypophysectomised fish; pitocin does not produce this effect. A. A. E.

Separation of the anterior pituitary-like hormone from the urine of pregnant women. C. A. Elden (J. Biol. Chem., 1933, **101**, 1—9).—The hormone is separated by adsorption on willow C or kaolin at p_H 4·2 and extraction with 0·1*N*-NaOH. The active material is very sensitive and is partly destroyed, but not pptd. by EtOH, $COMe_2$, and $(NH_4)_2SO_4$. H. G. R.

Endocrine factors concerned in the control of the ovarian cycle. I. *Xenopus lævis* as a test animal. C. W. Bellerby (Biochem. J., 1933, **27**, 615—620).—AcOH extracts of bovine anterior pituitary can be standardised by their effect on ovulation in *X. lævis*, which occurs in 18—48 hr. after administration of an active extract, but never spontaneously. The results are more nearly proportional to dosage than with mice, and the same animals may be used repeatedly. P. G. M.

Action of prolan. A. Wehner (Deut. tierärztl. Woch., 1933, **41**, 24—25; Chem. Zentr., 1933, i, 957).—The effect on egg-production of hens is described. A. A. E.

Effect of the ovarian hormones, theelin and corporin, on the growth of the mammary gland of the rabbit. C. W. Turner and A. H. Frank (Missouri Agric. Exp. Sta. Res. Bull., 1932, No. 174, 28 pp.).—Injection of theelin caused growth of the duct system and slight lobule proliferation (I). Injection of corporin into gonadectomised rabbits had no effect on (I), but simultaneous injection of corporin and theelin caused hyperplasia of gland lobules after 15 days. Stimulation of lactation did not occur. A. G. P.

Relationship between ovarian function and calcium metabolism. Effect of œstrin. O. Bockelmann (Arch. Gynakol., 1933, **152**, 492—500).—In female white rats subcutaneous injection

for 3 weeks of œstrin (3—8 mouse units daily) causes loss of wt. and of total Ca (expressed as % of body-wt. or of the ash of the animals). NUTR. ABS. (*m*)

Gonadotropic hormones (ϱ-factors). IV. Preparation of extracts for clinical use, with observations on stability in solution and standardisation processes. P. G. MARSHALL (Biochem. J., 1933, **27**, 621—627).—The prep. is described of clinical extracts which are stable at 0° for at least 10 days, but lose 50% of their activity in 17 days at room temp. Further purification of protein-free specimens cannot be effected by the use of $PdCl_2$ or by BzOH adsorption at p_H 5·0. Aq. NH_3 (*d* 0·880) has no effect on the activity in 24 hr. at 0°. P. G. M.

Occurrence of œstrogenic substances in bitumen. S. ASCHHEIM and W. HOHLWEG (Deut. med. Woch., 1933, **59**, 12—14; Chem. Zentr., 1933, i, 954).—Bituminous materials afford extracts having a biological action corresponding with that of the follicular hormone. Brown coal contained 400, bituminous coal 1000, petroleum 1000—2000, and asphalt 10,000 mouse units per kg. A. A. E.

Female sexual hormone. X. Preparation of a crystalline plant tokokinin (thelykinin) and its identification with α-follicular hormone. A. BUTENANDT and H. JACOBI (Z. physiol. Chem., 1933, **218**, 104—112; cf. this vol., 643).—From palm-kernel residues (50 kg.) the principle active in the Allen–Doisy test (tokokinin, thelykinin) was isolated in cryst. form (18 mg.) and identified with α-follicular hormone from pregnancy or mare's urine. J. H. B.

Detection of the luteohormone (specific hormone of the corpus luteum) in human tissue and body-fluids. C. CLAUBERG, H. W. THIEL, and R. ZIECKER (Arch. Gynäkol., 1932, **152**, 61—81; Chem. Zentr., 1933, i, 955).—The hormone was not found in urine, blood, placenta, or corpus luteum cysts. Tests for the hormone, which is sensitive to alkali, are discussed. The hormone is regarded as a labile derivative of the follicular hormone, into which it is converted during its passage through the body. A. A. E.

Assay and absorption of testicular hormone dissolved in oil. V. KORENCHEVSKY, M. DENNISON, and A. KOHN-SPEYER (Biochem. J., 1933, **27**, 778—782).—The increase in wt. of the prostate+seminal vesicles and of the penis of castrated rats was 3—4 times as large after 7 days' injections as after 4 days', the animals being killed on the eighth day in each case. A change in the involution of the thymus and a decrease in the size of the adrenals also occurred. The rat and capon units are nearly equal. P. G. M.

Influence of testicular hormone on cryptorchid rats. V. KORENCHEVSKY, M. DENNISON, and A. KOHN-SPEYER (Biochem. J., 1933, **27**, 783—785).—Contrary to its effect on castrated rats, testicular hormone has a slightly depressing effect on the prostate and seminal vesicles, and also on the testes. P. G. M.

Chemistry of sexual hormones. A. GIRARD (Bull. Soc. Chim. biol., 1933, **15**, 562—606).—A lecture.

International standard and unit of vitamin-*A*. L. RANDOIN (Bull. Soc. Chim. biol., 1933, **15**, 637—641).—It is proposed that α- and β-carotene, together with vitamin-*A* (renamed auxemasterol), are designated as vitamins-*A*. The standard carotene prep. of the Health Committee of the League of Nations is described. F. O. H.

Need for a standard of reference in vitamin-*A* testing. K. H. COWARD, K. M. KEY, and B. G. E. MORGAN (Biochem. J., 1933, **27**, 873—877).—Equal doses of a vitamin-*A* prep. can induce very different responses in groups of rats at different times. Hence for a correct assay a simultaneous test on a reference standard is essential. F. O. H.

Avitaminosis and intoxication. III. Experimental syndrome from avitaminosis-*A* and chemical intoxication by metals and metalloids. M. MITOLO (Atti R. Accad. Lincei, 1933, [vi], **17**, 739—744).—Ingestion by rats suffering from avitaminosis-*A* of a mixture of salts of metals and metalloids (cf. this vol., 443) in doses non-toxic to normal animals has no accelerating action on the effects of the avitaminosis, nor does the latter increase the toxicity of the mixture. R. N. C.

Vitamin-*A* concentration of cod-liver oil correlated with age of cod. N. L. MACPHERSON (Nature, 1933, **132**, 26—27).—Young cod give liver oils of pale colour and low vitamin content, whilst old cod give highly pigmented oils rich in vitamin. Feeding conditions and oil content of livers are minor factors compared with age. L. S. T.

Formation of vitamin-*A* in maize sprouts by light, and the transfer of the vitamin from the sprout to the grain. G. P. GOODE (Bull. Basic Sci. Res., 1932, **4**, 55—58).—Irradiation of the sprouts increased their vitamin-*A* content, and part of the vitamin was transferred to the grain during the process. CH. ABS.

Effect of light on the vitamin-*A* activity and the carotenoid content of fruits. L. L. W. SMITH and A. F. MORGAN (J. Biol. Chem., 1933, **101**, 43—54).—Chlorophyll is not a necessary intermediary for the formation of pro-vitamin-*A*. Carotene (I) and vitamin-*A* (II) are formed in the dark, but in slightly smaller amounts than in the light. Lycopene is probably not a precursor of (II). The relation between the daily intake of (I) on a (II)-free diet and the growth per unit of total (I) ingested is const. H. G. R.

Decrease in vitamin-*A* produced by heat treatment of milk. S. SCHMIDT-NIELSEN, A. FLOOD, and J. STENE (K. Norske Vidensk. Selsk. Forh., 1932, **5**, 110—113; Chem. Zentr., 1933, i, 1214).—Pasteurisation (63°, 15 min.) and, less markedly, stassanisation (73°, 15 sec.) diminish the vitamin-*A* content of the fat. A. A. E.

Relations between carotene (vitamin-*A*) and thyroxine. I. ABELIN (Z. physiol. Chem., 1933, **217**, 109—114).—The liver of hyperthyreoidised animals is less able to store certain vital substances such as glycogen, fats, lipins, H_2O, and creatine–creatinine. The deposition or conversion into vitamin-*A* of carotene is likewise inhibited, thus ex-

plaining inhibition of growth by thyroxine. Carotene–thyroxine solutions show a decrease in thyroxine on keeping, suggesting chemical interaction. J. H. B.

Ultra-violet absorption spectra of carotene and vitamin-*A*. J. W. Woodrow and J. B. Philipson (Proc. Iowa Acad. Sci., 1931, **38**, 218).—Carotene from carrots has an absorption band at 335—330 mμ; a band in this region is characteristic of vitamin-*A* in animal fats. Ch. Abs.

Vitamin-*A* and carotene. X. Relative minimum doses of vitamin-*A* and carotene. T. Moore (Biochem. J., 1933, **27**, 898—902).—Comparison was made in rats of the biological activities of β-carotene (I) (2000 yellow and 350 blue units per mg.) and of a vitamin-*A* (II) concentrate [3500 blue units per mg. and 328 mμ=950 indicating a content of approx. 60% of (II) (this vol., 323)]. The rates of growth indicate that (I) is utilised in the body as efficiently as preformed (II) at levels approaching the min. dose. F. O. H.

Vitamin-*A* and -*D* in tuna meal. R. W. Truesdail and L. Shahinian (Ind. Eng. Chem., 1933, **25**, 661—662).—Tuna meal contains 14 (Sherman) units of vitamin-*A* and 62 units of vitamin-*D* per g. A. G. P.

(*a*) Calcium and phosphorus metabolism. (*b*) Fundamental nature of vitamin-*D* action. J. P. McGowan (Biochem. J., 1933, **27**, 934—941, 943—950).—(*a*) In rabbits on diets varying in CaO/P_2O_5 ratio, the retention of Ca decreased as the ratio fell. When much $CaCO_3$ was present the Ca balance was strongly positive, whilst the P balance was low and a high % of the P_2O_5 excreted was found in the fæces. When steamed bone-flour and $CaHPO_4$ were added to the stock ration, which itself gave a positive P balance, the latter became negative. A large positive balance of P occurred even when there was little Ca in the diet, indicating that P can be stored otherwise than as a Ca salt.

(*b*) Administration of very large toxic doses of irradiated ergosterol resulted in the shift of the excretion of P from the fæces to the urine. The blood-P_2O_5 increased, but the -Ca underwent no consistent change. The main effect of vitamin-*D* is probably to produce P_2O_5 in the body from endogenous sources (*e.g.*, lipins). W. O. K.

Antirachitic factor in preserved eggs. E. Lesne and R. Clement (Compt. rend. Soc. Biol., 1932, **107**, 1533—1534; Chem. Zentr., 1933, i, 1155).—The vitamin-*D* content of eggs, which is not high, is not appreciably diminished by hard-boiling or by keeping the eggs for 8 months in $Ca(OH)_2$ or Na silicate solution. A. E. E.

Vitamin-*D* content of vegetable oils. T. Berzaczy and K. Rupilius (Wien. klin. Woch., 1932, **45**, 1156—1158; Chem. Zentr., 1933, i, 962).—Olive oil and a vegetable table oil contained prophylactic quantities of vitamin-*D* for rats; they had also some therapeutic effect. A. A. E.

Role of vitamin-*D* in the nutrition of the pig. R. D. Sinclair (Sci. Agric., 1933, **13**, 489—504).—The growth response of pigs to solar or artificial irradiation and to the feeding of cod-liver oil was inversely proportional to the Ca content of the basal ration. Addition of ground limestone to the ration alleviated a condition of stiffness, suggestive of rickets, in the animals, improved growth, lowered the food requirement for growth, and increased the ash content of the bones and the Ca content of the serum. The rachitic syndrome which developed was characterised by a diminution in the level of blood-Ca without change in that of -org. P. The antirachitic factor increased the blood-Ca and the Ca × P product. A. G. P.

Calcium content of cow's blood. I. Effect of feeding cod-liver oil. W. L. Little and E. C. V. Mattick (Vet. Rec., 1933, **13**, 238—245).—Although it leads to slight increase in the average val. for total and diffusible Ca and P in the serum, administration of cod-liver oil (I) (4 oz. per day for 11—51 days ante partum) has no effect on the fall in the Ca content of the blood which occurs at calving. This fall is relatively greater in the diffusible fraction. Low vals. persist during 2—3 days post partum, (I) has also no effect on the fall in the P content of the blood which occurs at calving. Again the fall is relatively greater in the diffusible fraction. The return to normal val. of P is almost always complete in the first 2 or 3 days. A simple technique for the determination of diffusible Ca and P is given. Nutr. Abs. (*m*)

Growth and cell replacement in vitamin investigation. VIII. The unspecific basis of rickets and similar diseases; bones. IX. Cartilage. W. Kollath (Arch. exp. Path. Pharm., 1933, **170**, 635—665, 666—682).—An extensive study, chiefly histological, of the effect of various deficiencies in the diet on the formation of bone and cartilage. In the production of rickets and allied conditions, not only vitamin-*D* but also a no. of other unidentified factors are concerned, whilst the mineral metabolism is also important. W. O. K.

Vitamin-*B* content of rice. S. Ghosh and A. Dutt (Indian J. Med. Res., 1933, **20**, 863—868).—The colour of the grain is not necessarily an index to its vitamin-*B* content or to its colour index by Spruyt's method. The most important factor is the degree of polishing. Ch. Abs.

Deductions as to the constitution of vitamin-B_1 from the absorption spectra of B_1 concentrates. F. F. Heyroth and J. R. Loofbourow (Bull. Basic Sci. Res., 1932, **4**, 35—54).—Biologically inactive purine or pyrimidine derivatives account for a large part of the absorption of the less active concentrates. Vitamin-B_1 is characterised by an absorption max. at 2600 Å., and probably contains a pyrimidine ring or is a compound of the same type as ergothioneine. Ch. Abs.

Catatorulin. Method of comparing the oxidative factor in vitamin-B_1 concentrates. R. Passmore, R. A. Peters, and H. M. Sinclair (Biochem. J., 1933, **27**, 842—850).—The co-enzyme activities of various preps. on the O_2 uptake in presence of lactate of brain tissue of avitaminous rabbits (catatorulin activity) correspond approx. with their vitamin-B_1 activity. Samples of cryst. vitamin-B_1

show high catatorulin activity. Catatorulin may be identical with vitamin-B_1. W. O. K.

Mineral content of the skin of rats suffering from beriberi: formation of vitamin-B_1 by moulds. H. T. FAWNS and A. JUNG (Biochem. J., 1933, **27**, 918—933).—*Aspergillus niger* grown on a substrate free from vitamin-*B* (I) contains (I), especially in the conidia. In rats on a diet deficient in (I) the skin after Et_2O extraction contained more K and usually more Ca than normally. The ratio of Ca+Mg to K+Na remains approx. const. Et_2O-insol. PO_4''' tends to fall and Cl to rise in the skins of the (I)-deficient animals. W. O. K.

Chemistry of the vitamins. T. WAGNER-JAUREGG (Arch. Pharm., 1933, **271**, 369—382).—A lecture. Lactoflavin, the colouring matter of milk, has been crystallised and possesses vitamin-B_2 activity. R. S. C.

Effect of ultra-violet rays on the dermatitis-preventing vitamin. A. G. HOGAN and L. R. RICHARDSON (Missouri Agric. Exp. Sta. Res. Bull., 1932, No. 178, 18 pp.).—Irradiation of yeast with a quartz–Hg arc resulted in the destruction of vitamin-B_2. A. G. P.

Influence of the constitution of lipins on the evolution of total *B*-avitaminosis, and generality of the need of vitamin-*B* in the utilisation of lipins by the organism of the pigeon. R. LECOQ and J. SAVARE (Compt. rend., 1933, **196**, 1693—1695).—Experiments with several different lipins show that a lipin content of 50% in a sugar-free diet does not prevent polyneuritis in pigeons deprived of vitamin-*B* complex. Avitaminosis ensues the more rapidly the higher is the unsaturated acid content of the lipin. A daily dose of 0·75 g. of dried brewer's yeast is prophylactic and curative on all the diets except that containing castor oil. A. C.

Evolution of total *B*-avitaminosis in relation to digestibility and nature of dietary protein. R. LECOQ (Compt. rend., 1933, **196**, 2033—2035; cf. A., 1932, 657; this vol., 99).—The appearance of avitaminosis in pigeons fed on a mainly protein diet is more rapid if the protein is rendered more digestible by peptonisation. Natural proteins exert an economy of vitamin-*B*, and extend the survival period. Brewer's yeast relieves or prevents avitaminosis in all cases. A. C.

Vitamin-*B* complex and high-protein diets. F. T. G. PRUNTY and M. H. ROSCOE (Biochem. J., 1933, **27**, 699—704).—No relation has been found between the protein (I) intake and the vitamin-B_2 (II) requirement. Excess (I) causes a reduced food intake and, hence, a depressing effect on growth, whilst (II) has an effect on the growth, independent of the appetite. Excess (I) did not affect the incidence of the dermatitis characteristic of deficiency of (II). H. G. R.

Similarity between avitaminosis-*B* and -*C* and certain alimentary disequilibria (carbohydrate and mineral). R. LECOQ (J. Pharm. Chim., 1933, [viii], **18**, 11—24).—In pigeons, the presence in the diet of a large excess of lactose or galactose may lead to the development of polyneuritic symptoms even when large quantities of vitamin-*B* (brewer's yeast) are also administered. Similar but less striking results were obtained with rats. In guinea-pigs, deficiency of P together with excess of Ca in the diet leads to disorders which closely resemble scurvy. This result is obtained even in presence of vitamins-*C* and -*D*. W. O. K.

Vitamin-*C*. A. LUTTRINGHAUS (Chem.-Ztg., 1933, **57**, 513—514).—A summary. F. O. H.

Chemical test for vitamin-*C*, and the reducing substances present in tumour and other tissues. L. J. HARRIS (Nature, 1933, **132**, 27—28).—Substances which may invalidate the chemical test for vitamin-*C* (this vol., 433) are recorded and discussed. L. S. T.

Colour reactions of vitamin-*C*. N. BEZSSONOFF and A. DELIRE (Compt. rend., 1933, **196**, 2036—2038).—In addition to lemon juice (I), quinol (II) and pyrocatechol (III) may be titrated with 2 : 6-dichlorophenol-indophenol (IV). The vals. of (IV) equiv. to a given quantity of (I), (II), and (III), and E_H for (I), (II), and (III) decrease as the concn. of the reducing substance increases. As in the case of Bezssonoff's reagent for vitamin-*C* (A., 1926, 722) the non-specificity of (IV) is indicated by its decolorisation by certain wines and sauerkraut juice which are devoid of antiscorbutic activity. A. C.

Vitamin-*C* in the adrenal gland. G. BOURNE (Nature, 1933, **131**, 874).—Cytological preps. of vitamin-*C* in the adrenal have been obtained by fixing the gland tissue with CH_2O vapour and impregnation with dil. $AgNO_3$. L. S. T.

Ascorbic acid content of the adrenals and livers of different animals. J. L. SVIRBELY (Biochem. J., 1933, **27**, 960—963).—By the use of the 2 : 6-dibromophenol-indophenol method the following average vals. have been obtained for ascorbic acid content (in mg. per g. tissue): pig adrenal 1·15; liver 0·12; ox adrenal 0·76; liver 0·31; calf adrenal 0·99; liver 0·33; sheep adrenal 1·33; liver 0·46; dog adrenal 1·46; liver 0·16; cat adrenal 1·22; liver 0·18; rabbit adrenal 2·16, 1·83; liver 0·11, 0·08; white-mouse adrenal 2·40; liver 0·45; rat adrenal 5·20; liver 0·21. In scorbutic guinea-pigs the vals. were much reduced both in adrenals and in liver. W. O. K.

Antiscorbutic activity of apples. T. WALLACE and S. S. ZILVA (Biochem. J., 1933, **27**, 693—698).—The N content is inversely related to the antiscorbutic activity, but there is no strict proportionality. Acidity, sugar, and ash are not correlated with the vitamin-*C* content, but total sugar is increased with lower N. H. G. R.

Antiscorbutic vitamin. E. B. VEDDER (Milit. Surg., 1932, **71**, 505—575).—Physiologically active needles, m.p. 180—182°, were obtained from lemon juice. Vitamin-*C* is regarded as an isomeride of glycuronic acid, and its chief function is considered to be that of building up cartilage and connective tissue. CH. ABS.

Vitamin-*C*. VI, VII. Effect of light on production of vitamin-*C* during germination of

seeds. T. MATSUOKA (Mem. Coll. Agric. Kyoto, 1932, No. 24, 37—47; J. Agric. Chem. Soc. Japan, 1933, 9, 81—89).—Vitamin-*C* production in rice seeds germinated in sunlight, under a 1000-watt lamp, and in absence of light is the same by the third day; thereafter the quantity formed in light increases with time, but the amount formed in the dark is very small. CH. ABS.

Physiological experiments on vitamin-*C* (ascorbic acid) and reductone (enol-tartronaldehyde). H. VON EULER and E. KLUSSMANN (Z. physiol. Chem., 1933, **217**, 167—176).—Apart from the adrenals, the organ with the highest reducing power as measured by the phenol-indophenol indicator is the thymus gland of young animals (rabbits). In the scorbutic guinea-pig, ascorbic acid (I) is low in the adrenals, but is restored to a high concn. after injection of (I). Adrenaline or methylene-blue injection lowers the (I) content. (I), reductone (II), and dihydroxyacetone reduce methylene-blue directly, but (II) cannot replace (I) in the organism. J. H. B.

Vitamin-*C* (ascorbic acid) as an activator of catheptic enzymes. I. P. KARRER and F. ZEHENDER (Helv. Chim. Acta, 1933, **16**, 701—703).—Vitamin-*C*, like H_2S and other SH compounds, activates proteases of the cathepsin type (prep. from pig's liver, Waldschmidt-Leitz, A., 1927, 794) from which the natural activators have been removed by washing with $COMe_2$. It is not an activator for papain. J. W. B.

Effect of metals on the vitamin-*C* content of milk. F. SCHLEMMER and H. CAHNMANN (Deut. Nahrungsm. Rund., 1932, 182—183; Chem. Zentr., 1933, i, 1214).—The vitamin-*C* is destroyed by Cu, and less markedly by Sn; Ni, Cr, and Al are least destructive. A. A. E.

Narcotine and vitamin-*C*. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 93—98).—The methylnornarcotine prep. and glycuronic acid used by Rygh and Rygh (A., 1932, 1294) do not show antiscorbutic properties in guinea-pigs. β-d-*Glycuronolactone*, m.p. 172—174°, obtained from β-(l-*menthyl*)-d-*glycuronic acid* m.p. 92—93°, was also used in place of the free acid with similar results. F. R. S.

Two vitamin-*E* fractions. H. VON EULER, H. HELLSTROM, and E. KLUSSMANN (Svensk Kem. Tidskr., 1933, **45**, 132—134).—The unsaponifiable fractions of the Et_2O-extracts of dried wheat embryo (I) and lettuce (II) (A., 1931, 1341) were freed from sterols by cold MeOH. The ultra-violet absorption spectra of the two MeOH solutions were determined, and the carotenoid nature of vitamin-*E* is discussed. The $SbCl_3$ reaction is much more marked with the fraction from (II) than with that from (I), a xanthophyll content of 0·0286% being indicated for (II). F. O. H.

Method and instrument for the determination of chlorophyll. R. E. OLTMAN (Plant Physiol., 1933, **8**, 321—326).—A photo-electric cell is utilised to determine the intensity of light transmitted by an aq. solution of K chlorophyllin. A. G. P.

"Maturity" of sugar cane. I. Introduction. II. Chemical life-history of "Hayaue"-plant canes. III. Significance of sucrose accumulation. IV. Significance of water. V. Utilisation of solar energy. VI. Changes in chemical composition of cane stalks deprived of leaves. S. KOMATSU, S. OZAWA, and Y. MAKINO (Mem. Coll. Sci. Kyoto, 1933, **A**, **16**, 1—125).—I. General remarks on the photo-synthesis of sugars.

II. The chlorophyll content reaches a max. at the beginning of June (0·27 mg. per sq. cm.), at which time the H_2O content (76%) is also a max., and runs approx. parallel with the latter. The sugar content of the lower portions of stalk shows a min. in June and increases thereafter. The non-reducing sugars show a max. when reducing sugars are at a min. The fibre content runs parallel with that of the non-reducing sugar.

III. Sucrose accumulates in the stalk in cool weather when not required as nourishment. The sugar content is reduced during the flowering period.

IV. Drought increases the fibre content through increased transpiration.

V. A mathematical treatment of the utilisation of solar energy in both photosynthesis and transpiration.

VI. Photosynthesis ceases on denudation of the stalks and the sucrose content decreases until a new leaf-system is formed. The optical rotation of the stalk-juice falls at first and then rises as fresh growth occurs; there is less difference in the reducing-sugar content owing to the altered chemical composition of the sugars. P. G. M.

Changes during vernal activity of *Gingko biloba*. R. SCHOLZ (J. Elisha Mitchell Sci. Soc., 1932, **48**, 133—137).—Fatty and essential oils, resins, and BzOH are stored in ducts formed in the primordia of the leaf buds. Starch is formed photosynthetically as the first product and converted into glucose and NH_2-acids without storage. The chief storage product is tyrosine. CH. ABS.

Bases for calculations in measuring changes in leaves during the night. F. E. DENNY (Contr. Boyce Thompson Inst., 1933, **5**, 181—194).—The N content of leaves did not change during the 12-hr. period (night) of experiment. Carbohydrate changes, whether observed by comparison of twin leaves, or calc. on the basis of residual dry wt. (*i.e.*, total dry wt. less carbohydrates) or on the total N, were the same. Comparisons made on the total dry wt. basis gave results which were not quantitatively and, in some cases, not even qualitatively correct. A. G. P.

Influence of phosphorus and of day length on physiological functions in plants. Z. M. EIDELMAN (Nauch. Agron. Zhur., 1930, 7, 387—402).—At average day length and relatively high temp., but not otherwise, the max. photosynthetic activity is coincident with max. P content and dry wt. Respiration energy usually changes little with alteration in the amount of P. The chlorophyll content varies approx. inversely with P content. P absorption increases with the percentage of P present and with increase in light-duration period during each 24 hr. CH. ABS.

Absorption and accumulation of solutes by living plant cells. V. Effects of time, oxygen and salt concentration on the absorption and respiration of storage tissue. F. C. STEWARD (Protoplasma, 1933, **18**, 208—242; cf. this vol., 436).—The intake of $K^{\cdot}$ and Br' by potato tissue from KBr solutions is controlled by the $[O_2]$, which becomes a limiting factor at partial pressures $<$ atm. The effect of O_2 on respiration is of a similar character. In solutions containing $<0{\cdot}0468$ g.-equiv. of KBr per litre, respiration is independent of the external [KBr]. The ratio of Br' absorbed to HCO_3' produced varies with the [KBr] and $[O_2]$, but with fixed rates of HBr intake the respiration remains const. over long periods. No indication of an approaching equilibrium was observed. A. G. P.

Absorption of salts by plants. III. Quantitative relations between respiration and absorption of anions. H. LUNDEGARDH and H. BURSTROM (Biochem. Z., 1933, **261**, 235—251).—Using wheat plants in a special type of H_2O culture, the anions and cations of the solution, the absorption of anions and cations by the roots, and the formation of HCO_3' and CO_2 by respiration are determined. The total respiration increases and falls with absorption of anions, but is independent of absorption of cations. P. W. C.

Ion intake in *Valonia* as affected by hydrochloric acid and carbon dioxide. S. C. BROOKS (Proc. Soc. Exp. Biol. Med., 1932, **29**, 933—934).—The sap of living cells of *V. ventricosa* in sea-H_2O, acidulated to 5·2 with CO_2 or HCl, shows an increase in Na and a decrease in K with CO_2, whilst HCl has the opposite effect. H. G. R.

Nutrient intake of submerged plants. F. GESSNER (Ber. deut. bot. Ges., 1933, **51**, 216—228).—Plants examined were able to take up P and N from extremely dil. solutions. The intake of P in darkness was $>$ in light. The intake of NO_3' was independent of the proportion of PO_4''' in the nutrient and *vice versa*. Among the cations tested, only Mg had a slight retarding action on the PO_4''' intake. The latter was increased in the presence of SO_4''. A. G. P.

Assimilation of sugars by pollen tubes. H. COUPIN (Compt. rend., 1933, **196**, 1529—1530).—Germination of pollen grains of *Narcissus pseudonarcissus* on isotonic solutions of salts (small amount) and a sugar occurs readily with sucrose and (better) dextrin. H. B.

Response of plants to water deprivation or to insufficient water supply. P. M. TIKHONOV (Nauch. Agron. Zhur., 1930, **7**, 99—122).—Tests on oats and wheat are recorded. Varieties having the higher drying capacity showed also a higher content of sol. carbohydrates at the beginning of the process. CH. ABS.

Variability of the amount and composition of the ash of the Wagener apple under Nova Scotian conditions. W. A. DE LONG (Sci. Agric., 1933, **13**, 505—511).—Continuous use of $NaNO_3$ alone produces fruit of relatively low total ash, K, and P contents as compared with those of unmanured trees. Repeated use of KCl increased the ash and K contents of fruit. Acid phosphates and basic slag had much smaller effects, the increased P content of the apples being slight. A. G. P.

Functional relations between phosphorus compounds and organic acids in plants. T. DEMIDENKO (Nauch. Agron. Zhur., 1930, **7**, 123—133).—Results for legumes, buckwheat, mustard, and cereals are recorded. CH. ABS.

Phosphorus compounds of plants. VII. Solubility of phosphorus compounds of hempseed. E. PISCHINGER (Bull. Acad. Polonaise, 1932, **B**, 37—50).—The proportion of P extracted by NaOH, HCl, and AcOH of varying concn. is in conformity with the presence of nucleic, phytic, and mineral P compounds. Relationships between the ratio total : mineral P and the p_H of the extract, irrespective of the nature of the extracting medium, resemble those previously recorded for barley, oats, maize, and beans (cf. A., 1932, 1181). A. G. P.

Comparative composition of the dry material of the homologous leaves of fructiferous and sterile branches of a vine. H. LAGATU and L. MAUME (Compt. rend., 1933, **196**, 1445—1447).—The dry material from the fructiferous source contains less N and more H_3PO_4 than that from the sterile source. H. B.

Role of calcium in the life of the cell. Experiments with *Micrasterias*. H. WAREN (Planta [Z. wiss. Biol.], 1933, **19**, 1—45).—Brief exposure to nutrients containing a heavy excess of Ca causes less injury to *Micrasterias* than to those having a smaller excess of Ca. Cell division is entirely prevented in the former case, but proceeds normally in the second. An antagonism exists between Ca and Mn in this respect. In nutrients of low Ca content Mn tends to inhibit, and in those of high Ca content to accelerate, cell division. No division occurs under conditions of Ca deficiency. In Mn-free nutrients Ca deficiency produces irreversible injury within a few days, but in the presence of Mn injury is retarded and is to some extent reversible. In its effect on cell division Ca may be replaced to a certain extent by Sr, but daughter cells are reduced in size. Partial substitution of Ca by Ba leads to the production of abnormal and short-lived daughter cells. Addition of $Ce(NO_3)_3$ to nutrients containing $Sr(NO_3)_2$ not only prevents cell division, but also causes direct injury. A. G. P.

Possible effect of hydrogen-ion concentration on the absorption of potassium and phosphorus by wheat plants under field conditions. J. DAVIDSON (J. Agric. Res., 1933, **46**, 449—453; cf. B., 1927, 950).—In entire wheat plants during the early stages of growth and in stems at a later period, the K content was greater and the P content less on plots receiving $NaNO_3$ than on unmanured controls. The effect is ascribed to changes in soil-p_H due to application of $NaNO_3$. A. G. P.

Relationship between the formation of calcium oxalate crystals in certain conifers and leaf-fall. T. DOMINIK (Bull. Acad. Polonaise, 1932, **B**, 9—17).—Formation of crystals of CaC_2O_4 in the leaves of certain conifers increases with age and is accentuated

in the intracellular substance of the separation membrane with approaching leaf-fall. The crystals induce a lowering of the cohesiveness of tissues at this point. A. G. P.

Action of injected nutrient substances on plants. A. MAZZARON (Boll. Soc. Eustach., 1931, **29**, 61—69; Chem. Zentr., 1933, i, 953).—NH_4 salts and NO_3' are equally effective whether injected or absorbed by the root. A. A. E.

Injection of certain salts into the protoplasm and vacuoles of the root hairs of *Limnobium spongia*. T. KERR (Protoplasma, 1933, **18**, 420—440).—Root hairs develop in 0·015—0·002*M* solutions of $CaCl_2$ but not in NaCl, KCl, or $MgCl_2$. When injected into the protoplasm, NaCl and KCl are relatively non-toxic. In high concns. (0·1—2·0*M*), these salts and also glucose and sucrose increase the fluidity of protoplasm. In lower concns. (<0·1*M*) injection causes a temporary retardation of protoplasmic movement, but no other visible effect. Injection of $CaCl_2$ of > 0·04*M* causes local and persistent coagulation. More dil. solutions (0·04—0·005*M*) produce local solidification which is later incorporated. Solutions of $MgCl_2$ > 0·1*M* produce general reversible coagulation. $MgCl_2$, NaCl, and KCl injected into the vacuole have no effect except in concns. sufficient to bring about osmotic changes. $CaCl_2$ causes a pptn. of CaC_2O_4. Injection of high concns. of NaCl or KCl into the cytoplasm causes the root hair to burst at the tip without rupture of the vacuolar membrane. $CaCl_2$ breaks the internal membrane without bursting the cell. NaCl and KCl retard and $CaCl_2$ accelerates the formation of a protoplasmic plug at the site of puncture. A. G. P.

Sap hydraulics. E. D. WOODHOUSE (Plant Physiol., 1933, **8**, 177—202).—The mechanism of movement of sap through plant tissues is examined and discussed. A. G. P.

Action of saponin on plant cells. O. B. MUNTHIU (Protoplasma, 1933, **18**, 441—472).—Saponin increases the permeability of plant cells to plasmolytic agents, the extent of the change varying with the nature of the agent used. A. G. P.

Determination of arsenic in plant materials. R. B. DEEMER and J. A. SCHRICKER (J. Assoc. Off. Agric. Chem., 1933, **16**, 226—232).—As is evolved by the Gutzeit procedure as AsH_3, which is absorbed by Br–HNO_3 in a Winkler spiral and determined colorimetrically, after driving off HNO_3, by the oxidation of Zinzadze's Mo-blue reagent (A., 1931, 1021). Low results are obtained with solutions prepared by the wet ashing process, so the As is distilled as $AsCl_3$ by the process of Taber, using 2 g. of Cu_2Cl_2 instead of $FeSO_4$. The determination is then completed as before. T. McL.

Rapid determination of potassium in plant tissues. V. H. MORRIS and R. W. GERDEL (Plant Physiol., 1933, **8**, 315—319).—The method of Jacobs and Hoffman (A., 1932, 102) is adapted for the examination of sap, green tissue, and ash of maize. The customary cobaltinitrite ppt. is treated with a 1% solution of choline hydrochloride and a 2% solution of $K_4Fe(CN)_6$. The green colour developed is proportional to the amount of Co present. Results compare favourably with those of the chloroplatinate method. A. G. P.

Manganese content of some Australian timbers. W. E. COHEN and A. B. JAMIESON (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 116—119).—Differences are recorded in the Mn content of sap and intermediate wood and true wood of individual trees of *Northofagus cunninghamii* and *Eucalyptus salmonophloia*. These differences are not const. for the species and are inapplicable for diagnostic purposes. A. G. P.

Determination of rubidium in certain plants. E. S. BURKSER, V. L. MILGEVSKAYA, and A. S. BENDERSKAYA (Trav. Lab. biogeochim. Acad. Sci. U.S.S.R., 1932, **2**, 85—90).—Rb contents are: bean seeds 0·00034, barley kernels 0·00057, *Salicornia herbacea* 0·00192%, *Suaeda maritima*, trace. CH. ABS.

Concentration of radium in various organisms. B. BRUNOVSKI (Trav. lab. biogéochim. acad. sci. U.S.S.R., 1932, **2**, 9—24).—Ra in *Lemna minor* and *L. polyrrhyza*, L., was determined; it was detected in *L. trisulca*, L. Vals. are max. in spring and min. in autumn. CH. ABS.

Acids of the cranberry [*Vaccinium oxycoccus*]. A. LEBEDEV and E. LINQUIST (Z. Unters. Lebensm., 1933, **65**, 476—477).—Nearly one half the acidity of the cranberry is due to quinic acid. E. C. S.

Two species of prickly-pear growing in New South Wales. I. E. J. WHITELOCK and F. R. MORRISON (J. Proc. Sydney Tech. Coll. Chem. Soc., 1933, **5**, 46—50).—Glucose is present in the EtOH–H_2O extracts of *Opuntia Ficus-Indica*, Mill, and *O. inermis*, P DC. var. The former also contains KNO_3, whilst the latter contains an org. Mg compound. A. A. L.

Raffinose in cereals. H. COLIN and H. BELVAL (Compt. rend., 1933, **196**, 1825—1827).—Raffinose is present in the embryos of rye, barley, and oats, whilst fructosan is present in the protein. Neither is present in maize or sorghum. A. A. L.

Soluble carbohydrates of unripe pumpkin (*Cucurbita pepo*), and the hydrolysis of its cellulose. M. G. TICHMENEV (J. Appl. Chem. Russ., 1933, **6**, 320—325).—The air-dry, unripe fruit (without peel and seeds) contains H_2O 6·15, Et_2O-sol. substances 2·26, pentosans 5·95, cellulose 11·71, N 1·19, and ash 6·62%. The sol. carbohydrates include starch, *d*-fructose, and glucose. The cellulose yields exclusively glucose on hydrolysis. R. T.

Determination of uronic acids and methoxyl in certain plants and plant materials. M. PHILLIPS, M. J. GOSS, and C. A. BROWNE (J. Assoc. Off. Agric. Chem., 1933, **16**, 289—292).—Uronic acids are determined by distillation with 12% HCl and collection and titration of the CO_2 liberated, carbonate-CO_2 being first removed by heating the reaction mixture at 70° for 30 min. and passing a current of CO_2-free air. OMe was determined by the method of Phillips (B., 1932, 618). Results are given for 23 plant materials; they show that there is no relation between the amount of OMe and uronic acid in plant

materials. The amount of uronic acid is appreciable, and varies from 4·0% in melon to 17·72% in orange peel, calc. on the dry material. T. McL.

Chemistry of higher fungi. XXII. *Ganoderma lucidum*, Leiss, *Hydnum imbricatum*, L., and *Cantharellus clavatus*, Pers. L. Leukacs and J. Zellner (Monatsh., 1933, **62**, 214—219).—The Et_2O extract of *G. lucidum* gives on hydrolysis ergosterol (I) and fatty and resin acids. EtOH extracts mannitol (II) and a resin of phlobaphen type (III), and H_2O extracts a polysaccharide which on hydrolysis gives both pentoses and hexoses. The residue after extraction with inert solvents is sol. in cold dil. aq. alkali to a solution which gives a ppt. resembling the humic acids with dil. mineral acids. The light petroleum extract of *H. imbricatum* similarly gives (I) and a sterol of lower m.p. (? fungisterol) (IV), stearic (?) and oleic acids, and NMe_3. (II), (III), a brown amorphous dye, and choline (V) are extracted by EtOH, and the H_2O-sol. polysaccharide gives only pentoses on hydrolysis. From *C. clavatus* (I), (IV), (II), (V), stearic and oleic acids, and glucose are isolated in a similar manner. The EtOH extract contains pale reddish-violet and greenish-yellow dyes, and the H_2O-sol. polysaccharide gives pentoses and glucose (free from mannose and galactose) on hydrolysis. H. A. P.

Lichen chemistry. II. *Alectoria ochroleuca*, Ehrh. J. Klima (Monatsh., 1933, **62**, 209—213).—In addition to barbatic and *l*-usnic acids, the lichen contains a saturated *hydrocarbon*, $C_{30}H_{62}$, m.p. 65°, a sterol (not isolated pure), a *compound*, $C_4H_{10}O_4$, m.p. 103° (Ac_4 derivative, m.p. 75°), glucose, choline, and lichenin; the acids of the saponifiable fraction are oleic and linoleic and a small amount of saturated fatty acid. H. A. P.

Comparative plant chemistry. XXIV. *Heracleum spondylium*, L. E. Fraenkel and J. Zellner (Monatsh., 1933, **62**, 206—208).—The petrol-insol. fraction of the C_6H_6 extract of the root contains *substances*, m.p. $<100°$, 112° ($C_{2\cdot73}H_{2\cdot43}O$), and 217° ($C_{2\cdot83}H_{2\cdot01}O$); the last two are non-phenolic, and give a negative cholesterol reaction. The resin sol. in light petroleum gives on hydrolysis a *sterol*, m.p. 132° (*Ac* derivative, m.p. 118°), and resin acids. The EtOH extract contains glucose and bases of the choline group. Starch is also present. H. A. P.

Antioxidant of lettuce. H. S. Olcovich and H. A. Mattill (Proc. Iowa Acad. Sci., 1931, **38**, 172—173).—The antioxidant, $C_{13}H_{14}O_5$, m.p. 142°, containing <1 phenolic group, was obtained by extracting a solution of lipins in light petroleum with 92% MeOH, distilling in vac., and crystallising from the 160—180° fraction. Ch. Abs.

Proteolytic enzymes in plants. Juice of *Calotropis gigantia* (Akanda). K. P. Basu and M. C. Nath (J. Indian Chem. Soc., 1933, Ray No., 107—117).—The juice contains an enzyme (I) capable of hydrolysing (optimum p_H is 4·95 and optimum temp. of 50°) gelatin, caseinogen, egg-albumin, and fibrin, but not peptone, which is activated by HCN, H_2S, and cysteine (not by cystine). $Na_4P_2O_7$ inhibits the action of (I) but not in presence of H_2S. The juice contains a S compound. H. B.

Algæ which excrete soluble organic pigmented matter in the sea. G. Ranson (Compt. rend., 1933, **196**, 1927—1930).—The pigmented substance excreted by *Navicula ostrearia*, Bory, is probably a phosphatide. J. W. B.

Contents of the rhizomes of *Curcuma domestica* (Temoe Lawak). II. H. Dieterle and P. Kaiser (Arch. Pharm., 1933, **271**, 337—342; cf. A., 1932, 1178).—The essential oil from these rhizomes contains *d*- [not *l*- (*loc. cit.*)] -camphor 1, *cyclo*isoprenemyrcene (I) 85, α-p-*tolylethyl alcohol* (II) 5, and decomp. products 9%. (II) and the larger (cf. *loc. cit.*) amount of (I) are contained in the fraction, b.p. 140—150°/11 mm., which is resolved by distillation at 1 mm. (II), b.p. 120—122°/0·08 mm. (*phenylurethane*, m.p. 97·5°), is oxidised by $KMnO_4$ in $COMe_2$ to *p*-tolyl Me ketone, b.p. 109°/11 mm. (*semicarbazone*, m.p. 204—205°), *p*-$C_6H_4Ac\cdot CO_2H$, and *p*-$C_6H_4(CO_2H)_2$. R. S. C.

Coccids produced in Japan. I. Waxy substances of *Ceroplastes rubens*, Mask. M. Kono (J. Agric. Chem. Soc. Japan, 1932, **8**, 1150—1160).—The wax, sol. in C_6H_6, $CHCl_3$, and CCl_4, has d^{15} 1·03, m.p. 55—58°, acid val. 63·4, sap. val. 139·0, ester val. 75·5, I val. 90·3, Ac val. 23·8, neutral fat 36·5%, unsaponifiable matter 19·98%. Melissic acid, ceryl alcohol, a cyclic alcohol, $C_{11}H_{18}O$, b.p. about 120°, $[\alpha]_D^{20}$ +47·3°, ceryl melissate, m.p. 86°, melissic ester, $C_{11}H_{18}O$, m.p. 68°, a red colloidal substance, abietic acid, m.p. 163°, $[\alpha]_D^{0}$ +69·2°, and an unsaponifiable substance (? a resinol), $C_{16}H_{26}O$, b.p. 190°/2 mm., $[\alpha]_D^{22}$ −27·75°, were isolated. Ch. Abs.

Nigaki oil. M. Tsujimoto and H. Koyanagi (Bull. Chem. Soc. Japan, 1933, **8**, 161—167).—The consts. of the oil from the whole fruit, shell, and kernel of *Picrasma quassioides*, Benn, are recorded. Petroselic, palmitic, and probably oleic, linoleic, linolenic, and lauric, but not tariric, acids are present. R. S. C.

Alteration of castor oil by heat. M. Roy (Compt. rend., 1933, **196**, 1423—1424).—When castor oil is heated at 140° in vac. or N_2, little change in *d*, viscosity, *n*, acid val., and I val. occurs; in air, and more so in O_2, the I val. decreases whilst the other vals. increase. H. B.

Ginseng root (*Panax ginseng*, Song-Sam). I. Sun (Arch. exp. Path. Pharm., 1933, **170**, 443—457).—The main roots of *P. ginseng* contain more vitamin-B_1 than the finer secondary roots, whilst the opposite is true of vitamin-B_2. The MeOH extract contains a substance stimulating the growth of *Paramecium caudatum*. Toxic and hæmolytic substances are also present. W. O. K.

Chemical constituents of rice embryo. R. H. Kimm aad T. Noguchi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 1—14).—Recrystallisation of the brown ppt. settling out of an Et_2O extract of rice embryo (I) gives phytosterolin. Myristic, palmitic, cerotic, and behenic acids were obtained from the solid acids, separated from the EtOH extract of (I). Linoleic acid tetrabromide was obtained by

bromination of the unsaturated acids. The unsaponifiable matter (II) in the C_6H_6 extract of (I) contains 0·5% of ergosterol. Recrystallisation of (II) from EtOH gives melissyl alcohol; from the mother-liquors dihydrositosterol and, after acetylation and bromination stigmasterol acetate tetrabromide and γ-sitosterol were separated. The hydrolysed acetates were fractionally pptd. from C_6H_{14}. The last fraction was recryst. from EtOH, $COMe_2$, and MeOH, giving a *sitosterol*, m.p. 156°, $[\alpha]_D$ −14·5° (*acetate*, m.p. 111°, $[\alpha]_D^{23}$ −9·87°; *propionate*, m.p. 106°, $[\alpha]_D^{23}$ −6·78°; *benzoate*, m.p. 129°, $[\alpha]_D^{20}$ +14·48°). Melissyl cerotate was obtained from (I). H. D.

Chemistry of the roots of *Thevetia neriifolia* (Juss). N. Ghatak and G. P. Pendse (Bull. Acad. Sci. U.P. Allahabad, 1933, **2**, 259—262).—Extraction of the roots with EtOH gave *thevetene*, $C_{43}H_{86}$, m.p. 79—80° (Br_2-derivative, m.p. 87—88°), thevetin, *neriifolin* (which with Zn–Ac_2O forms a *substance*, m.p. 93°), and a small amount of oil. F. R. S.

Philyrin and its hydrolysis by emulsin. A. Kramer (Bull. Soc. Chim. biol., 1933, **15**, 665—684).—The stems of *Philyrea* are extracted with EtOH, the extract is treated with Et_2O, followed by MgO, and the mixture is evaporated to dryness. Aq. extraction etc. of the residue yields philyrin, $C_{27}H_{34}O_{11}$ (I) (A., 1886, 1040), m.p. 162° (Maquenne block), $[\alpha]_D$ +46·71° in EtOH, +46·25° in Ac_2O. (I) is hydrolysed by H_2SO_4, emulsin, and *Aspergillus niger* (but not by *B. Delbrücki* or dried bottom yeast), yielding glucose and philygenol, $C_{21}H_{24}O_6$, m.p. 134·5° (block), $[\alpha]_D$ +95·35° in AcOH, which has one OH and three OMe groups and on fusion with KOH yields protocatechuic acid. F. O. H.

Composition of alder buckthorn bark. I. Enzyme hydrolysing water-soluble anthraquinone glucosides. II. Precipitate obtained by enzymic action. Emodin and frangulin. M. Bridel and C. Charaux (Bull. Soc. Chim. biol., 1933, **15**, 642—647, 648—664).—I. The bark contains one or more H_2O-sol. hydroxymethylanthraquinone glucosides, together with enzymes capable of hydrolysing them. Thus aq. extraction under conditions by which the enzymes are not destroyed yields a solution which slowly deposits a ppt., a reducing sugar being liberated.

II. An aq. digest of the bark is allowed to autolyse and the residue extracted with Et_2O, affording a crude prep. which on purification with $CHCl_3$ and 95% EtOH yields frangulin (I) (2·5% of the bark). The low yields of other investigators (cf. J.C.S., 1892, **61**, 1) are due to incomplete enzymic hydrolysis of a complex (glucoside ?) of (I) before extraction. Cryst. (I), m.p. 249°, $[\alpha]_D$ −134·4° in 80% AcOH, yields emodin and rhamnose on hydrolysis. F. O. H.

***Buddleia* and buddleoflavonoside.** H. Yu (Bull. Soc. Chim. biol., 1933, **15**, 482—497).—The leaves, flowers, and seeds of *B. variabilis*, Hemsl, extracted with hot aq. 80% EtOH yield an anthocyanin *buddleoflavonoside* (I), anhyd., m.p. 274—276° (block), $[\alpha]_D$ −97·35° in $COMe_2$. After removal of this, a lævorotatory glucoside, hydrolysable by emulsin with production of a black compound, remains in the extract. The leaf extract contains in addition a lævorotatory reducing glucoside, *buddleoside*, hydrolysable by dil. aq. H_2SO_4, but not by emulsin. (I) occurs especially in the buds, and the leaves yield 0·2—0·67% according to the time of year. When hydrolysed with 6% aq. H_2SO_4 or AcOH and aq. H_2SO_4 it yields *buddleoflavone* (II), m.p. 265° (block), optically inactive, and a mixture of glucose and rhamnose. When fused with alkali (II) yields phloroglucinol, anisic acid, and $COMe_2$, and is therefore 1 : 3-*dihydroxy*-4′-*methoxy*-α-*acetoflavone*. A. L.

Chemistry of Buddleia. II. H. Yu (Bull. Soc. Chim. biol., 1933, **15**, 616—622).—Hydrolysis of buddleoside, $C_{15}H_{20}O_8$, $[\alpha]_H$ −52° (preceding abstract), yields a uronic acid (osazone, m.p. 174°) and propylpyrocatechol. A melanogenic glucoside, hydrolysed by H_2SO_4 or emulsin, is also present. F. O. H.

Floridoside of *Lemanea*. E. de Wildeman (Bull. Acad. roy. Belg., 1933, [v], **19**, 599—601).—The discovery of floridoside in *L. nodosa*, Kütz (this vol., 652), is correlated with earlier work on the carbohydrate of *L. annulata*, Kütz. The occurrence of glycogen and simpler carbohydrates in *Ascomycetes* is discussed. F. O. H.

Initial digitalis glucosides. A. Stoll and W. Kreis (Compt. rend., 1933, **196**, 1742—1744).—By eliminating enzyme action, extraction of *Digitalis lanata* affords *lanata-glucosides A*, *B*, and *C*, each isomorphous with the natural mixture. Hydrolysis yields 1 mol. of digitoxigenin, gitoxigenin, and digoxigenin, respectively, and (in each case) AcOH (1 mol.), glucose (1 mol.), and digitoxose (3 mols.). The glucosides differ from the *purpurea* analogues by an extra COMe group. They undergo hydrolysis by an enzyme, termed *digilanidase*, present in *lanata* leaves, and yield acetyl-digitoxin, -gitoxin, and -digoxin. A. C.

Glucosides of *Digitalis lanata*, Ehrh. P. Mohs (Arch. Pharm., 1933, **271**, 393—399).—Partly contrary to the lit. (A., 1930, 1561, etc.), lanadigin is $C_{47}H_{73}O_{19}Ac$, and gives, when hydrolysed, a reducing *disaccharide*, m.p. 220°, $[\alpha]_D$ +29·2° to 29·8° in H_2O (Ac_6 derivative, m.p. 196°), glucose, and digitoxose; the Ac group is attached to a sugar residue. Lanata-glucoside II is a mixture (mixed crystals) of an acetylated glucoside (possibly Scholl's digilanid *A*) (giving only digitoxigenin, when hydrolysed) and another glucoside. Lanata-glucoside III (Ac_6 derivative, $[\alpha]_D$ −17·0° in $CHCl_3$) is $C_{46}H_{55}O_{14}\cdot Ac$. R. S. C.

Detection of saponins in the seeds of *Gramineæ*. T. Solacolu and E. Welles (Compt. rend. Soc. Biol., 1933, **112**, 1007—1009).—The presence of saponins (I) has been demonstrated in the seeds of nine families of plants. (I) are most prevalent in *Gramineæ*. Nutr. Abs. (*m*)

Indole derivatives from two chlorophyll mutants of barley strains. H. von Euler and H. Hellstrom (Z. physiol. Chem., 1933, **217**, 23—27).—A cryst. methylated indolyl *base*, $C_{11}H_{14}N_2$, m.p. 130·5°, was isolated from the chlorophyll-defective mutant Albina 1. It was present in Albina 3, but was not found in other Albina types or in green plants. This is the first chemical differentiation observed

between the genetically different chlorophyll-defective mutants of the Albina type. J. H. B.

Raponticin, and anthraquinone derivatives from *Rheum emodi*, Wall. (Indian or Himalayan rhubarb). M. G. MODIUDDIN and M. C. T. KATTI (J. Indian Inst. Sci., 1933, **16 A**, 1—9).—91% EtOH extracts from the powdered rhizomes most of the anthraquinone derivatives found so far in *R. palmatum*, Linn., or *R. officinale*, Baill., in addition to raponticin (> 0·7%). J. L. D.

Agar-agar. III. E. TAKAHASHI and K. SHIRAHAMA (J. Agric. Chem. Soc. Japan, 1932, **8**, 1259—1266).—Hydrato-kanten λ is the Ca salt of λ-acid ("kanten-acid"), $[\alpha]_D$ −31° (galactose 39·47, pentose 8·17, SO_4 8%, a ketose and a hexose; no uronic acid or methylpentose), unstable, which has been prepared from the electrodialysed material. CH. ABS.

Identity of asebotoxin with phloridzin. M. BRIDEL and A. KRAMER (Bull. Soc. Chim. biol., 1933, **15**, 531—551).—Asebotoxin isolated from the leaves of *Kalmia latifolia*, L., is identical with phloridzin. A. L.

Nitrogenous constituents of Florida Valencia orange-juice. E. K. NELSON, H. M. MOTTERN, and C. W. EDDY (Fruit Products J., 1933, **12**, 231—235, 250).—Distribution of the sol. N in orange juice (half in the NH_2-form) has been studied. Pptg. agents for the removal of N are tabulated. Stachydrine, arginine, choline, asparagine, aspartic acid, and probably histidine are present. No changes in the bases were detected in deteriorated juice. E. B. H.

Presence of an oxygen-free alkaloid in *Gelsemium sempervirens*. V. HASENFRATZ (Compt. rend., 1933, **196**, 1530—1532).—Sempervirine (Stevenson and Sayre, A., 1915, i, 85) [hydrochloride (+$2H_2O$); nitrate (+$2H_2O$), which is almost insol. in H_2O; picrate; chloroplatinate], which appears to be identical with the sempervine of Chou (A., 1931, 1172), is $C_{19}H_{16}N_2$(+H_2O), m.p. 258—260° (Maquenne block), α—0° (in $CHCl_3$). H. B.

Alkaloids of *Mahonia philippinensis*, Takeda. E. R. CASTRO, A. C. SANTOS, and P. VALENZUELA (Univ. Philippines Nat. Appl. Sci. Bull., 1932, **2**, 401—405).—Tetrahydro-berberine, -shobakunine, and -jatrorrhizine were isolated. CH. ABS.

Origin and function of berberine in *Berberis Darwinii*. B. T. CROMWELL (Biochem. J., 1933, **27**, 860—872).—The highest concn. of berberine (I) occurs in the roots. There is little seasonal variation from October to March, but it tends to rise during the summer months. A progressive increase occurs with age, the root-bark of a 30-year-old plant containing 11% of the dry wt. Ringing the stem produces a concn. of (I) above the point of ringing, thus proving that synthesis takes place from products normally translocated from leaves to root. Lack of Ca does not interfere with synthesis of (I). Asparagine fertilisation produces an increase in (I) content, whilst with NH_4 salts and NO_3' an addition of glucose is necessary. (I) is a product of protein metabolism. P. G. M.

Nitrogen metabolism of alkaloidal plants. K. T. SUCHORUKOV and N. A. BORODULINA (Bull. Acad. Sci. U.R.S.S., 1932, 1517—1530).—Alkaloids exert a dynamic action in the plant cell, acting as an internal buffer towards nitrogenous nutriment and as an external buffer towards changes in the reaction of the medium. Soil is rendered favourable to the accumulation of alkaloids in the plant by increasing its content of NH_4 salts and by lowering its nitrifying properties; its reaction should be either neutral or alkaline. T. H. P.

Presence of proteins in the pecto-cellulose membrane. A. DAUPHINÉ (Compt. rend., 1933, **196**, 1738—1739).—Although usual chemical tests do not show the presence of protein in the pecto-cellulose membranes of several plant groups, this is demonstrated by adsorption of tannin. Removal of protein prevents this adsorption. The protein appears to be linked to the pectose. A. C.

Composition of mulberry leaves. I. Cystine and cysteine. Y. KISHI (J. Agric. Chem. Soc. Japan, 1933, **9**, 49—54).—The quantities of cystine and cysteine, determined by Okuda's method, are small in the buds and young leaves and increase in older leaves, reaching a max. and declining with age. The quantities vary with the variety of tree. The "hish-age" (unsound) stem contains > a normal stem, but the leaves contain < normal leaves. CH. ABS.

Application of cryolysis to biological problems. F. F. NORD [with O. M. VON RANKE-ABONYI and G. WEISS] (J. Indian Chem. Soc., 1933, Rây No., 251—283).—See A., 1932, 337, 1203. H. B.

Micro-determination of lipin-phosphorus. FLATTER (Bull. Soc. Chim. biol., 1933, **15**, 607—615).—The method of Mâchebœuf (A., 1926, 1067) allows 0·2—0·6 mg. of lipin-P to be accurately determined. F. O. H.

Determination of phosphoric acid by oxine. K. SCHARRER (Biochem. Z., 1933, **261**, 444—449).—Gravimetric determination of H_3PO_4 using oxine (5-hydroxyquinoline) and $(NH_4)_2MoO_4$ as precipitants is described and applied to a variety of org. substances. P. W. C.

Determination of traces of iodine in organic material. T. LEIPERT (Biochem. Z., 1933, **261**, 436—443).—A method is described which is suitable both for elementary micro-analysis and also for determination in biological material. The org. substance is treated with CrO_3–H_2SO_4 and $Ce(SO_4)_2$ as catalyst, whereby the I is converted into HIO_3 which is reduced to I and determined. P. W. C.

Determination of iodine. P. KUHN and A. LOESER (Arch. exp. Path. Pharm., 1933, **170**, 609).—A reply to criticism (this vol., 106). W. O. K.

Micro-determination of iron in biological material. W. LINTZEL (Z. ges. exp. Med., 1933, **86**, 269—274).—The material is wet ashed, boiled with Na_2SO_3, made alkaline with NH_3, treated with 2 : 2-dipyridyl–quinol solution, and compared in the colorimeter with standard $FeCl_3$ solution. NUTR. ABS.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1933.

General, Physical, and Inorganic Chemistry.

Blue and violet spectra of hydrogen molecule. D. Chalonge and E. Vassy (Compt. rend., 1933, **196**, 1979—1981; cf. A., 1931, 991).—By a method similar to that of Freeman (cf. A., 1927, 81) with p.d. of 80 and 82 volts, respectively, the blue and violet spectra of H_2 were obtained. The blue spectrum is continuous; the violet shows, superposed on a continuous spectrum, the lines of the secondary spectrum and faint first lines of the Balmer spectrum. C. A. S.

Doppler effect in hydrogen at high voltages. K. Lion (Z. Physik, 1933, **83**, 442—443).—Discharge potentials above 100 kv. produced no limit of line displacement. A. B. D. C.

Wave-mechanical calculation of the Rydberg correction for helium terms. E. A. Hylleraas (Z. Physik, 1933, **83**, 739—764). A. B. D. C.

Zeeman effect for perturbed N_2^+ terms. A. E. Parker (Physical Rev., 1933, [ii], **44**, 84—89).—Data and explanations of the Zeeman patterns at field strengths up to 27,000 gauss are given. N. M. B.

Rotational analysis of the perturbed (13, 15) $^2\Sigma$—$^2\Sigma$ N_2^+ band. A. E. Parker (Physical Rev., 1933, [ii], **44**, 90—91; cf. preceding abstract). N. M. B.

Multiplets in the spectra of O III, O IV, O V, and C III. P. G. Kruger and W. E. Shoupp (Physical Rev., 1933, [ii], **44**, 105—108).—New and revised multiplet data are given from photographs of spectra in the region 100—650 Å. N. M. B.

Lowest excited state of neon according to Slater's method. S. Rozental (Z. Physik, 1933, **83**, 534—542).—Theoretical. A. B. D. C.

Pressure effects of foreign gases on the sodium *D* lines. H. Margenau and W. W. Watson (Physical Rev., 1933, [ii], **44**, 92—98).—True line contours were photographed and photometrically evaluated for the effect on the Na *D* lines, at low pressure of Na vapour, of A, N_2, and H_2 at 0—17 atm. pressure. The red shift of the absorption max. varies linearly with the density of the perturbing gas; asymmetries to the red for A and N_2, and slightly to the blue for H_2, are found; both *D* lines show the same broadening and shift; results can be accounted for by assuming a distance of closest approach of about 9 Å. between excited Na and the foreign gas mols. N. M. B.

Measurements of the intensity distribution and width of predissociation lines of the AlH molecule. L. Farkas and S. Levy (Z. Physik, 1933, **84**, 195—207).—Width and intensity distribution of the rotation lines of AlH, investigated with a Fabry–Perot étalon, agree with Kronig's theory of predissociation. A. B. D. C.

Arc spectrum of chlorine. C. C. Kiess (Bur. Stand. J. Res., 1933, **10**, 827—839).—Using new type plates for the long and short wave-length regions, the no. of lines previously known has been approx. doubled. Data for 441 lines are tabulated; the analysis of Cl I is revised, new terms are given, and previous classifications are corr. N. M. B.

High-frequency discharges in argon. II. Spectral properties. S. P. McCallum, L. Klatzow, and J. E. Keyston (Phil. Mag., 1933, [vii], **16**, 193—197; cf. this vol., 439).—The high-frequency discharge in A gives rise to a continuous spectrum from 6100 to 2200 Å. in addition to line spectra. Similar continuous spectra are observed with He and Ne. The distribution of energies of the electrons in A about the mean energy is much narrower than in He. An explanation is offered. A. J. M.

Spectrum of the A^{++} ion, A III. V. von Keussler (Z. Physik, 1933, **84**, 42—55).—The energy of ionisation of A^{++} is 4·7 volts. A. B. D. C.

Series of alkaline atoms in an electric field. E. Segrê and G. C. Wick (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 534—542).—The intensities of K lines of both permitted and forbidden series are calc. for the spectrum excited in an electric field, the results agreeing with experiment (cf. following abstract). J. W. S.

Influence of electric fields on the absorption spectrum of potassium. C. J. Bakker (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 589—594).—With increasing field strength the absorption limit is moved to longer wave-lengths. New absorption lines which appear are interpreted as "forbidden" lines. J. W. S.

Arc spectra of chromium, manganese, cobalt, and nickel. H. Slevogt (Z. Physik, 1933, **84**, 136).—A correction (cf. this vol., 547). A. B. D. C.

Spark spectrum of copper between 400 and 240 Å. L. Bloch and E. Bloch (Compt. rend., 1933, **197**, 132—134; cf. this vol., 2).—86 lines have been measured between λ 383·33 and 322·85 Å., and 57 more (311·99—240·40) determined by extrapolation. C. A. S.

Band spectrum of copper hydride. A. HEIMER and T. HEIMER (Z. Physik, 1933, **84**, 222—235).—Dissociation energies for CuH are 3·2 for $^1\Sigma$, 1·8 for $^1\Sigma^*$, and 0·8 volts for $^1\Sigma^{**}$. A. B. D. C.

First spark spectrum of arsenic. A. S. RAO (Indian J. Physics, 1933, **7**, 561—584; cf. A., 1932, 668).—The spectrum of As has been studied under varying conditions of excitation in the region 8400—4000 Å.; 280 lines have been ascribed to As II, many of them being classified. Higher members of the mp^3P terms have been identified and combinations involving the transition of one of the inner group of s^2p^2 electrons have been detected. Cases of interpenetration of different sub-levels indicating a strong tendency towards JJ coupling are pointed out. The largest term is $4p^3P_0$ (ν=162,788 cm.$^{-1}$), *i.e.*, ionisation potential about 20·1 volts for the singly-ionised As atom. J. W. S.

Nuclear spin of arsenic. A. S. RAO (Z. Physik, 1933, **84**, 236—247).—Nuclear moment is 3/2. A. B. D. C.

Nuclear moment of krypton. H. KOPFERMANN and N. WIETH-KNUDSEN (Naturwiss., 1933, **21**, 547—548).—The $1s$—mp lines of Kr under high dispersion show a strong central component and several weak ones. The central line is due to the sum of the components of the even isotopes of Kr; the weak components are due to Kr^{83}. The lines previously discovered now fall into a simple hyperfine structure term scheme, giving for the mechanical moment of Kr^{83} the val. $I \leqslant 7/2$. A. J. M.

Intensity measurements with the members of the principal series of rubidium and cæsium. H. J. HÜBNER (Ann. Physik, 1933, [v], **17**, 781—815).—The determinations were made by introducing salts of Rb and Cs into O_2–H_2 (I) or coal gas–compressed air (II) flames, temp. being 2850° and 2176° abs., respectively. The intensities were determined by a photographic–photometric method. The intensity ratio of the components of the second and third members of the principal series of Cs for an "infinitely thin" thickness of the light source was determined. For the second Rb member the val. for (I) was 2·55, and for (II) 2·58. In (II) the ratio for the third Rb member was 3·25 and for the third Cs member 8·0. A. J. M.

Hyperfine structure and nuclear moment of rubidium. H. KOPFERMANN (Z. Physik, 1933, **83**, 417—430).—The mechanical moment of Rb^{87} is 3/2, and of Rb^{85} 5/2, whilst the magnetic moment of 87 is nearly double that of 85. A. B. D. C.

Absence of fine structure in the arc spectrum of silver. S. TOLANSKY (Proc. Physical Soc., 1933, **45**, 559—564).—No fine structure in the region 8300—4000 Å. was detected. Its absence is attributed to electron configuration rather than to smallness of nuclear magnetic moment. N. M. B.

Mean life of cadmium atom in state 2^3P_1. P. SOLEILLET (Compt. rend., 1933, **196**, 1991—1993; cf. A., 1932, 439).—Direct measurement of the mean life of the Cd atom in state 2^3P_1 by means of radiation of λ 3261 Å. gives $2{\cdot}45\times10^{-6}$ sec. C. A. S.

New resonance series in antimony vapour. R. SIKSNA (Compt. rend., 1933, **196**, 1986—1987).—Mg II λ 2929 and 2937 Å. give rise each to a resonance series in Sb vapour at 950°; one anti-Stokes and 15 positive terms of both series were observed (cf. this vol., 200). C. A. S.

Atomic fluorescence of antimony. R. SIKSNA (Compt. rend., 1933, **197**, 134—136; cf. A., 1926, 776).—In the fluorescence spectrum of Sb excited by strongly condensed sparks of Cd and Zn, 2 and 11 at. lines, respectively, were observed. C. A. S.

Width of absorption lines of I_2. I. I. AGARBICEANU (Compt. rend., 1933, **197**, 38—39).—Examination of the absorption spectrum of I_2 alone and in presence of O_2 indicates that the enlargement of the lines is due to the mutual interaction of mols. during collision and to the instability of the two levels by the passing of the mols. between which the line is produced. The O_2 depolarises the fluorescence light of I_2 (cf. this vol., 201). C. A. S.

Recombination radiation in the cæsium positive column. F. L. MOHLER (Bur. Stand. J. Res., 1933, **10**, 771—780).—Radiation emitted along the axis of the positive column was measured spectrophotometrically, and electrical measurements were made with small probe surfaces. Data for at. consts. determining the rate of interaction of electrons, ions, and atoms in a discharge are obtained. N. M. B.

Arc spectrum in air at normal pressure of neodymium for λλ 2400—3100 Å. S. PINA DE RUBIES (Compt. rend., 1933, **197**, 33—35).—184 new lines are tabulated (cf. A., 1931, 890). C. A. S.

Polarisation phenomena in the stepwise excitation of mercury fluorescence. E. F. RICHTER (Ann. Physik, 1933, [v], **17**, 463—464).—A correction (cf. A., 1931, 8). W. R. A.

Non-Ritzian nature of the ^3S terms of mercury. I. WALERSTEIN (Nature, 1933, **132**, 139). L. S. T.

Variation in intensity in radiation emitted by a mercury vapour arc during lighting. L. GRILLET (Compt. rend., 1933, **197**, 311—313).—The ratios of the intensities of various lines in the spectrum of a Hg-vapour lamp with a.c. to those for a similar lamp with d.c. vary from about 4·5 for λ 5461, 4358, and 4046 to 11 for λ 4077, and 12·5—13 for λ 5791—5770; the ratios increase in all cases to about unity in 1·5—2·5 min., and attain the above approx. steady vals. in about 5 min. C. A. S.

Determination of the excitation function for some mercury terms. R. SEILER (Z. Physik, 1933, **83**, 789—805).—Excitation functions were determined from the energy lost by an electron beam exciting the Hg vapour. A. B. D. C.

Optical potentials of the mercury atom. So-called ultra-ionisation potentials. R. G. LOYARTE and M. H. DE BOSE (Physikal. Z., 1933, **34**, 589—592).—Priority is claimed in the determination of ultra-ionisation potentials of the Hg atom. A table of potentials is given and analysed. A. J. M.

Continuous gas spectra. II. W. FINKELNBURG (Physikal. Z., 1933, **34**, 529—560).—A summary. A. J. M.

Gas breakdown at normal pressure. J. J. SAMMER (Z. Physik, 1933, **83**, 814—831).—Theoretical, showing why the discharge is conc. in a narrow column. A. B. D. C.

Calculation of extent of polarisation of resonance radiation. P. SOLEILLET (Compt. rend., 1933, **197**, 316—318; cf. A., 1929, 120; 1932, 891).—Mathematical. C. A. S.

Hyperfine structure of perturbed series. E. G. JONES (Proc. Physical Soc., 1933, **45**, 501—506).—Theoretical. N. M. B.

Forbidden lines in astrophysical sources. J. C. BOYCE, D. H. MENZEL, and (MISS) C. H. PAYNE (Proc. Nat. Acad. Sci., 1933, **19**, 581—591).—From a survey, based on the analysis of spectra, of the metastable states of the atoms from H to A, tables are given of calc. and observed forbidden transitions, wave-lengths of lines and their sources, and relative intensities of nebular pairs, and of auroral and nebular lines. The newly observed line λ 4725 is attributed to Ne IV. N. M. B.

Night light and Northern lights. L. A. SOMMER (Z. Physik, 1933, **84**, 268—270).—Vegard's measurements of wave-lengths of Northern lights (A., 1932, 1187) are in good agreement with those of the night sky (cf. this vol., 332). A. B. D. C.

Spontaneous absorption of radiation and deviation of spectral lines of nebulæ. E. SEVIN (Compt. rend., 1933, **197**, 26—28). C. A. S.

Excitation of *X*-rays by collision of high-velocity positive ions. K. LION (Z. Physik, 1933, **83**, 431—441).—Soft *X*-rays with wave-lengths > 6 A. are excited by positive rays of 150 kv. A. B. D. C.

Crystalline diffraction spectrography of γ- and *X*-rays of the radium family. M. VALADARES (Compt. rend., 1933, **197**, 144—145; cf. this vol., 443).—The strong lines 138·9, 143·0, 160·7, and 165·8 X of Ra-*B*+*C* agree well with the *K* lines of Bi experimentally determined, and with those calc. from the energies of the electronic levels of element 83. They are therefore lines of fluorescence, as also are probably the weak lines of this region. The line 232·7 X may be identical with Ellis and Skinner's line 53·6 kv. of Ra-*B*+*C* (cf. A., 1924, ii, 137; 1932, 556). C. A. S.

Wave-length determinations in the very soft *X*-ray region. F. C. CHALKLIN and L. P. CHALKLIN (Phil. Mag., 1933, [vii], **16**, 363—389).—A grating *X*-ray spectrograph is described. Measurements for soft radiation from C, N, O, Mo, Rh, Pd, Ag, Ta, W, Pt, and oxidised W and Ta are recorded, and the origin of the lines is discussed. H. J. E.

Quadrupole and other weak lines in the *K*-spectra of the elements 37 Rb to 42 Mo. II. E. CARLSSON (Z. Physik, 1933, **84**, 119—130; cf this vol., 332). A. B. D. C.

Natural widths of the *Kα* *X*-ray doublet from Fe (26) to Ag (47). S. K. ALLISON (Physical Rev., 1933, [ii], **44**, 63—72).—Data are given for the full widths at half max. of the $K\alpha_1$ and $K\alpha_2$ lines of Fe, Co, Ni, Cu, Zn, Ge, Sr, Zr, Nb, Mo, Ru, Rh, Pd, and Ag. N. M. B.

Precision measurements of the *L* series of molybdenum and silver. P. HAGLUND (Z. Physik, 1933, **84**, 248—259).—A new vacuum tube spectrometer is described. A. B. D. C.

***L*-, *M*-, and *N*-absorption in the ultra-soft *X*-ray region.** J. A. PRINS and A. J. TAKENS (Z. Physik, 1933, **84**, 65—74).—Measurements are in agreement with energy levels deduced from the harder region, except for the $M_{IV,V}$-level of 52 Sn, 48 Cd, and 47 Ag, and the deviations are similar to those observed for 74 W to 90 Th. A. B. D. C.

Absorption effect in the *M*-series [of tungsten and tantalum]. V. KUNZL (Nature, 1933, **132**, 139). L. S. T.

***M*-level of magnetised iron.** PRIVAULT (Compt. rend., 1933, **197**, 140—142; cf. this vol., 441).—Application of a field of 15,500 gauss to an Fe cathode had no effect on λ of $K\beta_1$ and $K\beta_2$, > 0·03 and 0·06 X, or on the energies of levels M_3 and M_5 > 0·2 and 0·4 ev., respectively. C. A. S.

Determination of the *J*-discontinuity by a condition of matter. *J*-Phenomena. X. C. G. BARKLA and J. S. KAY (Phil. Mag., 1933, [vii], **16**, 457—472).—Only certain specimens of a given substance show *J*-phenomena. There are also optimum working conditions of the *X*-ray tube for its appearance. H. J. E.

Electron configuration in metallic phases. U. DEHLINGER (Z. physikal. Chem., 1933, **B**, **22**, 45—59).—From the colours of Ag, Cu, and Au and their disappearance when these metals are alloyed with metals of the Fe and Pt groups, and from the miscibility relations in such alloys, it is concluded that in the body-centred cubic phase CuPd there is in the electron gas one electron per atom and a further electron oscillates between every two atoms, so that in Hume-Rothery's body-centred phases (A., 1926, 356) there are 3/2 electrons per atom involved in the linking. The nos. of electrons in Hume-Rothery's β, γ, and ε phases seem to be a consequence of a principle according to which those phases are especially stable, at least at high temp., in which only those terms necessary for the lattice construction are each occupied by a single electron in so far as they are not equiv. in respect of energy. R. C.

Electron microscope images of surfaces exposed to electrons. E. RUSKA (Z. Physik, 1933, **83**, 492—497). A. B. D. C.

Electron microscope observations of the barium evaporation cathode. E. BRÜCHE and H. JOHANNSON (Z. Physik, 1933, **84**, 56—58).—The grains of Ba on the surface of a Ni cathode are conveniently photographed by the electron microscope. A. B. D. C.

Scattering of electrons by heavy atoms. W. HENNEBERG (Z. Physik, 1933, **83**, 555—580).—Theoretical treatment of elastic scattering, particularly by Hg, Kr, and A at 100—800 volts. A. B. D. C.

Inelastic electron scattering by helium atoms. A. L. HUGHES and J. H. MCMILLEN (Physical Rev.,

1933, [ii], **44**, 20—24).—Data and angular distribution curves, for the primary electron energy range 27·5—400 volts and angular range 6—150°, are given for electrons scattered by He atoms when the electrons have lost 21·12 volts energy, thereby exciting the atom to the 2^1P state. Results agree with theory. N. M. B.

Small-angle inelastic scattering of electrons in helium. R. WHIDDINGTON, T. EMMERSON, and J. E. TAYLOR (Nature, 1933, **132**, 65). L. S. T.

Electron diffraction by liquids. L. R. MAXWELL (Physical Rev., 1933, [ii], **44**, 73—76).—Diffraction patterns were obtained for interference by the transmission of 14—30 kv. electrons through thin films of phytol and three oils. N. M. B.

Arrangement for producing rapid ions. H. KALLMANN (Sitzungsber. Preuss. Akad. Wiss., Phys. Math. Klasse, 1933, **12**, 1—12).—H^+, Li^+, Li^{++}, and Li^{+++} ions were accelerated by successive passage through a series of oppositely directed fields, part of the charge being removed before the ion passed into the reverse field. The apparatus is described. A max. kinetic energy of $1·65 \times 10^6$ volts was obtained. H. J. E.

Effect of neutral gas molecules on slow protons (total action, scattering, charging). C. RAMSAUER and R. KOLLATH (Ann. Physik, 1933, [v], **17**, 755—780).—The effective cross-sections of Kr, Xe, and CH_4 with respect to protons were determined, and scattering measurements were carried out with Kr and Xe. In the scattering process positively-charged gas mols. are produced. With respect to their charging capacity, the inert gases form a series from He to Ne in the order of the periodic table, and CH_4 also falls into the series. A connexion between charge and ionisation potential can be traced only in the inert gas series. From the behaviour of protons scattered elastically, the velocity and directional distribution of the gas mols. collided with are calc. A. J. M.

Influence of magnetic field on stream of cadmium atoms. Lande factor, g, for state 2^3P_1. P. SOLEILLET (Compt. rend., 1933, **197**, 46—47).—A horizontal beam of light of λ 3261 Å. was passed through a vertical stream of Cd atoms at 600° abs. A magnetic field of 0·025 gauss was applied perpendicularly to both beam and jet and the effect on the polarisation of the fluorescence light observed in the same direction. From the result the Larmor rotation, ω_0, being $3·67 \times 10^5$, the Lande factor, g, was deduced as 1·75, *i.e.*, nearly the theoretical 1·50. C. A. S.

Formation of negative ions in mercury vapour. U. STILLE (Ann. Physik, 1933, [v], **17**, 635—653).—Negative ions are not produced when the discharge is passed through pure Hg vapour. Negative ions with e/m of the order of that of Hg ions are produced when a trace of H_2 is admitted to the discharge tube, and these are probably HgH^- ions. A. J. M.

Production and behaviour of negatively-charged metallic particles in electrical discharges. K. SOMMERMEYER (Physikal. Z., 1933, **34**, 582—589).—The conditions under which a transport of negatively-charged metallic particles formed by vaporisation or sputtering in the neighbourhood of the cathode in a discharge tube containing the inert gases takes place towards the anode are investigated. Where the vaporisation or sputtering was rapid, the metal followed the lines of force. The explanation of this is discussed. Ions of at. or mol. size may be formed, but probably the particles are larger. A. J. M.

Radiation from canal-ray impact. F. L. VERWIEBE (Physical Rev., 1933, [ii], **44**, 15—19).—The beam from a metal target on which H canal rays impinged contained at. H, neutral particles, and protons. A radiation of wave-length 1216 Å., agreeing with that of the first Lyman line, was detected. N. M. B.

Conditions for the occurrence of the Ramsauer effect. W. Voss (Z. Physik, 1933, **83**, 581—618).—Theoretical. A. B. D. C.

Determinations of effective cross-sections of gas molecules. H. L. BROSE (Ann. Physik, 1933, [v], **17**, 816—820).—The principal differences between the methods of Townsend and Ramsauer for determining the effective cross-section of gas mols. are discussed. A. J. M.

Quantum mechanical cross-section for ionisation of helium by electron impact. W. W. WETZEL (Physical Rev., 1933, [ii], **44**, 25—30).—Mathematical. Results indicate that the max. probability of ionisation occurs when the energy transfer is about 3·5 volts > the ionisation potential. N. M. B.

Revision of the at. wt. of thallium. Analysis of thallous chloride. G. P. BAXTER and J. S. THOMAS (J. Amer. Chem. Soc., 1933, **55**, 2384—2387).—From determinations of the ratio TlCl : Ag, the at. wt. of Tl is 204·40. J. G. A. G.

At. wt. of lead from Katanga pitchblende. G. P. BAXTER and C. M. ALTER (J. Amer. Chem. Soc., 1933, **55**, 2785—2792).—Full details are given of work previously reported (cf. this vol., 659). J. G. A. G.

Isotopes. F. W. ASTON (Science, 1933, **78**, 5—6).—A lecture. L. S. T.

Arrangement of at. nuclei and the prediction of isotopes. S. B. L. MATHER (J. Amer. Chem. Soc., 1933, **55**, 3053—3056).—The existence of a no. of isotopes is predicted by means of Gamow's classification of at. nuclei. J. G. A. G.

Radioactivity of some rare-earth elements. W. YEH (Compt. rend., 1933, **197**, 142—143; cf. this vol., 4, 442).—Examination of the oxalates of La, Nd, and Sm by means of a Geiger–Müller counter indicated slight emission (1/15th that of Sm) of α-particles by Nd, but complete absence of activity in La. C. A. S.

Radium solutions. A. BECKER (Z. Physik, 1933, **83**, 701—710).—Ra in solution gives a const. emission of its emanation over 18 years (cf. A., 1922, ii, 810); the effect of sulphates and carbonates on this emission has been determined. A. B. D. C.

Investigation of wave radiation from radium-*D* by the Wilson chamber method. G. F. VON D. ZU VISCHERING (Z. Physik, 1933, **84**, 17—41).—Secondary electrons due to γ-rays were investigated in a Wilson chamber, and the ranges of these electrons were used to determine the energy of the rays. A. B. D. C.

Diminution of velocity of α-particles in hydrogen. G. MANO (Compt. rend., 1933, **197**, 47—49; cf. A., 1932, 671).—The velocities of slower α-particles from Th-*C*+*C*′ after passage through lengths varying up to 12 cm. of H_2 at n.t.p. have been determined. The results agree with those deduced from Bethe's formula as corrected by Bloch (cf. A., 1930, 972; Ann. Physik, 1933, **16**, 285), if the mean energy of excitation be taken as 16·0 volts. C. A. S.

Retardation of α-particles. G. MANO (Compt. rend., 1933, **197**, 319—322; cf. A., 1928, 104; 1930, 659; also above).—Experimental results regarding retardation and the vals. of *E*, the mean energy of excitation of the atom, deduced therefrom, are compared with the results of Bethe's and Bloch's theories (cf. A., 1932, 789; this vol., 443). Bethe's theory applies to elements of low, Bloch's to those of high, at. wt. C. A. S.

Proton emission by excitation of the boron nucleus by α-rays. H. POSE and F. HEIDENREICH (Naturwiss., 1933, **21**, 516—517).—The determinations of Bothe and Franz, who investigated the no. of H particles liberated from B with a Geiger–Müller tube, were repeated using an electrometer. Absorption curves for protons released by α-rays of range 3·72, 2·67, and 2·32 cm., respectively, agree with those of Bothe and Franz. A. J. M.

Collisions of α-particles with fluorine nuclei. N. FEATHER (Proc. Roy. Soc., 1933, **A**, **141**, 194—209).—Stereoscopic photographs have been taken of the tracks of nearly $0{\cdot}5\times10^6$ α-particles in a CF_4–He mixture. No proton disintegration was obtained. The range–velocity curve for F recoil atoms has been constructed, and less complete data establishing the range–velocity relation for C recoil atoms have been obtained. L. L. B.

Photographic method of determining absorption of β-rays. (MLLE.) R. MACAIGNE (Compt. rend., 1933, **196**, 1993—1995).—The absorption by Al of β-rays from Ra-*D*+*E* determined photographically agrees with that determined by an ionisation chamber and supports the val. 16·9 for μ/ρ of Al for β-rays from Ra-*E* (cf. A., 1927, 915). C. A. S.

β-Ray magnetic spectrum of Ac-*B*+*C*+*C*′+ T. GRAF (Compt. rend., 1933, **197**, 238—241; cf. this vol., 4).—The *HR* (referred to that of Th-*B* as 1382·6) energies, origins, intensities, and energies of the γ-radiation have been determined for eight new lines with *HR* and origins: 767·10, L_2; 857·60, M_1; 879·55, N_1; 2245·3, *K*; 2301·3, N_1; 2548·1, L_1; 2597·0, M_1, and 3796·0, *K*. The max. *HR* for the β-rays of Ac-*C*″ is 6000 (cf. A., 1930, 8). C. A. S.

Emission of positive electrons by γ-rays of Ra-*B*+*C*. GRINBERG (Compt. rend., 1933, **197**, 318—319).—γ-Rays from Ra, filtered through 3·5 cm. Pb, falling on 2 mm. thick Pb gave rise to four positive electrons (energies 0·089, 0·38, 0·38, and 0·62 $\times10^6$ ev.) for 129 negative electrons (max. energy 1·7 $\times10^6$ ev.). These results agree with those of Curie and Joliot (cf. this vol., 658). C. A. S.

Scattering of short-wave γ-rays. L. MEITNER and H. KOSTERS (Z. Physik, 1933, **84**, 137—144).—A study of the undisplaced component of radiation of wave-length 4·7 X scattered by the nuclei of Fe and Pb. A. B. D. C.

Transmutation of elements by protons. M. L. E. OLIPHANT and (LORD) RUTHERFORD (Proc. Roy. Soc., 1933, **A**, **141**, 259—281).—An apparatus is described by means of which the disintegration of such active elements as Li and B may be examined at low voltages (20,000—200,000 volts) and in the form of very thin films. Li gave particles at 30 kv. with protons bombarding the target, whilst the effect from B was negligible below 60 kv. Very thin films of Li and B were studied, as well as thick films. Mol. H_2 ions gave particles at about twice the energy required for protons, and the yield increased at twice the rate as the energy increased. Fe, O, Na, Al, N, Au, Pb, Bi, Tl, U, and Th gave no observable effect when bombarded with protons or mol. ions at energies up to 200 kv. Be and F gave small effects. The disintegration of the B^{11} nucleus by proton capture is discussed. L. L. B.

Complexity of the proton and mass of the neutron. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1933, **197**, 237—238; cf. this vol., 762).—It is suggested that the emission by Al and B under the influence of α-particles of protons, neutrons, and positive electrons may be simultaneous, and that the proton, $^-$, may consist of a neutron, ω, and a positive electron, ε^+, associated together with condensation of mass. The transmutation of $B^{10}+\alpha$ would then be to $C^{13}+\omega+\varepsilon^+$ and to $C^{13}+^-$ simultaneously; whence is deduced the val. 1·011 (He=4) as the mass of ω, instead of 1·0065 (cf. A., 1932, 790). This val. agrees better with 9·011 for Be^9 (cf. this vol., 442), indicating that Be^9 consists of $2\alpha+\omega$; also with 8×10^6 ev. as the energy of the neutron from Po+Be, and with the emission of low-energy neutrons by Po+Al and Po+Na, although not on the present val. of the mass of Li^7, with that of those from Po+Li. C. A. S.

Emission of neutrons. (MME.) I. CURIE and F. JOLIOT (J. Phys. Radium, 1933, [vii], **4**, 278—286).—Under bombardment by Po α-radiation, F, Na, and Al emitted neutrons and probably γ-radiation; the emission of neutrons by these nuclei, which are known to emit protons also, shows that a nucleus can undergo two types of transmutation by α-rays. For H, C, O_2, N_2, P, and Ca no penetrating radiation was detected. Resonance energies of the α-radiation corresponding with the emission of neutrons are: Be $2{\cdot}6\times10^6$, and B $2{\cdot}2\times10^6$ ev.; emission of neutrons from Li begins at 5×10^6 and of γ-rays at 3×10^6 ev. N. M. B.

Positrons and atomic nuclei. G. W. TODD (Nature, 1933, **132**, 65).—Evidence against the view (this vol., 658) that the proton consists of a neutron and positron is advanced. L. S. T.

Cosmic radiation measurements with a new tube-counter. L. TUWIM (Compt. rend., 1933, **197**, 79—81; cf. *ibid.*, **196**, 350).—The advantage of the new tube-counter is that it distinguishes between the actions of cosmic rays on different elements, and facilitates counting collisions. The nos. of collisions per c.c. per sec. for air and H_2 are, respectively, 3·3 and 0·42 unprotected, and 2·4 and 0·33 behind 10 cm. of Pb. The ratio of the nos. for air and H_2 indicates that the action of cosmic rays on matter consists of two distinct effects: ionisation affecting the extra-nuclear electrons, and absorption affecting the nucleus. Of 10^8 collisions between cosmic particles and mols. of air only 1 is nuclear (cf. this vol., 551). C. A. S.

Very soft radiation from insulators. G. REBOUL (Compt. rend., 1933, **196**, 1987—1989; cf. A., 1932, 672).—The loss of electrification by insulating material, *e.g.*, resin, paraffin, etc., electrified by friction is accompanied by emission of very soft radiation capable of affecting a photographic plate after prolonged exposure, due perhaps to electric discharges at the surface, or to re-establishment of the electronic equilibrium of the insulating material. C. A. S.

Electricity released from matter. K. K. DARROW (Science, 1933, **77**, 591—595).—A lecture. L. S. T.

Electron theory of metallic conduction. J. C. SLATER (Science, 1933, **77**, 595—597).—A lecture. L. S. T.

Most probable values of e, e/m, and h. II. K. SHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 128—137; cf. A., 1932, 1187).—The most probable vals. of these consts. are recalc. taking into account the most recent determinations, including the determination of abs. wave-length of X-rays (Witmer and Cork), e/m by Dunnington, and experiments with photo-electrons by Kretschmar. The most probable vals. are: $e=(4{\cdot}804\pm0{\cdot}003)\times10^{-10}$ e.s.u., $e/m=(1{\cdot}7602\pm0{\cdot}0005)\times10^{7}$ c.g.s./e.m.u., $h=(6{\cdot}626\pm0{\cdot}006)\times10^{-27}$ erg/sec. A. J. M.

Wave equation of electrons in the general relativity theory. L. INFELD and B. L. VAN DER WAERDEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1933, No. 9, 25 pp.). A. J. M.

Comparison of the nuclear theories of Heisenberg and Wigner. I. C. ECKART (Physical Rev., 1933, [ii], **44**, 109—111; cf. this vol., 334).—Mathematical. N. M. B.

Magnetic interaction of a valency electron with inner shells. M. H. JOHNSON, jun., and G. BREIT (Physical Rev., 1933, [ii], **44**, 77—83).—Mathematical. N. M. B.

Passage of photons through atoms. V. TRKAL and F. ZAVISKA (J. Phys. Radium, 1933, [vii], **4**, 269—277; cf. Posejpal, A., 1932, 1187).—Polemical. N. M. B.

Does the negative energy spectrum influence nuclear phenomena? G. BECK (Z. Physik, 1933, **83**, 498—511).—Dirac's wave equation and the resulting negative energy levels are applied qualitatively to Klein's paradox, collisions, and the continuous β-ray spectrum. A. B. D. C.

Statistics of diatomic gases. K. SZELL (Z. Physik, 1933, **84**, 112—119).—Fermi–Dirac and Bose–Einstein statistics are applied to the rotation of a rigid diat. mol. A. B. D. C.

Spectrographic examination of radiation from resistance cells. G. DECHENE (Compt. rend., 1933, **196**, 1989—1991).—The radiation emitted at an electrode when a high-tension current is passed through a semi-conducting substance, *e.g.*, yellow HgO or effloresced Na_2CO_3 (cf. A., 1926, 1072), consists usually of a band at 50—170 Å. sometimes extending to 10—200 Å., and occasionally a narrow band at about 20 Å., with a diffuse one at 250—700 Å. C. A. S.

Absorption of metallic and colloidal silver. P. MARECHAL (Compt. rend., 1933, **196**, 1984—1985).—The absorptions for λ 2600—3730 Å. of metallic Ag cathodically sputtered and of colloidal Ag are identical for equal thicknesses of metal. The light traversing the colloidal solution therefore passes through and not between the metallic particles. C. A. S.

Structure and Zeeman effect of the CO_2 emission doublet band at 2900 A. R. SCHMID (Z. Physik, 1933, **83**, 711—738). A. B. D. C.

Position of absorption bands of coloured alkali halide crystals. J. H. DE BOER and W. DE GROOT (Z. Physik, 1933, **83**, 517—520).—Frohlich's theoretically deduced relation of frequency of absorption max. and grating const. (this vol., 446) applies to excited states of the coloured lattice, whereas Mollwo's apparently equiv. empirical relation (A., 1932, 673) applies to absorption by alkali atoms bound to vacant spaces within the crystal. A. B. D. C.

Intensity distribution in the spectrum of beryllium oxide. R. C. JOHNSON and E. G. DUNSTAN (Phil. Mag., 1933, [vii], **16**, 472—478).—Microphotometer peak intensity measurements were made for the $'\Sigma \longrightarrow {}'\Sigma$ system of BeO, and the transition probabilities were calc. H. J. E.

Infra-red arc spectra of manganese and rhenium. W. F. MEGGERS (Bur. Stand. J. Res., 1933, **10**, 757—769).—Using new type ultra-sensitive plates for the region 7200—11,000 Å. data are recorded for about 200 lines of Mn and 300 lines of Re. New lines disclose new spectral terms or at. energy levels. Lines of both spectra show hyperfine structure. N. M. B.

Absorption spectrum of sulphur dioxide in ultra-violet. A. JONESCU (Compt. rend., 1933, **197**, 35—37).—Some 500 absorption bands of SO_2 to about 2500 Å. have been examined and a formula for their frequencies is deduced. Their relation to the states of activation of the mol. and its predissociation and dissociation, and the heats thereof, are discussed (cf. A., 1932, 1075; this vol., 660). C. A. S.

Example of the influence of the nature of chemical linkings on absorption of light. J. P. MATHIEU (Bull. Soc. chim., 1933, [iv], **53**, 426—429).—The absorption spectrum of a tartaric acid

solution of $Cr(OH)_3$ shows a change from the normal heteropolar compound to a complex homopolar compound. This view is confirmed by comparison of the absorption curves of the heteropolar $CrCl_3,6H_2O$ and the homopolar $H_3Cr(C_2O_4)_3$. E. S. H.

Ultra-violet absorption of binary liquid mixtures. II. System allylthiocarbimide–piperidine in ethyl alcohol. R. KREMANN and R. RIEBL (Z. physikal. Chem., 1933, **165**, 372—378; cf. this vol., 207).—The extinction at the max. of the ultra-violet absorption band of allylthiocarbimide, at which wave-length the absorption of $C_5H_{10}N$ is negligible, is a max. for an equimol. mixture, which is ascribed to the formation of an equimol. compound. R. C.

[Ultra-violet] absorption of certain classes of organic molecules. D. BIQUARD (Ann. Chim., 1933, [x], **20**, 97—151).—Absorption has been measured from 2780 to 2300 Å. The absorptions of inactive diphenylsuccinic acid and of its Et ester are > those of the stereoisomeric racemic compounds. There is no definite difference between the absorptions of the racemic and active forms of phenyl- and benzyl-lactic acids and their Me esters. The absorption spectra of the H sulphite and cyanohydrin of $CH_2Ph{\cdot}CHO$ and of $Ph{\cdot}[CH_2]_2{\cdot}CHO$ are the same as that of PhMe, the ·CHO band being absent. The spectra of the acids $Ph{\cdot}[CH_2]_n{\cdot}CH(OH){\cdot}CO_2H$ become progressively closer to that of PhMe as n increases from 0 to 2. *α-Hydroxy-β-phenylbutyric acid*, m.p. 121—122°, is formed by treatment of $CHPhMe{\cdot}CH(OH){\cdot}SO_3Na$ with KCN followed by hydrolysis with HCl. A. G.

Absorption and fluorescence spectra of the acid sulphates of quinine and ten of its derivatives in water and aq. sulphuric acid solution. L. J. HEIDT and G. A. FORBES (J. Amer. Chem. Soc., 1933, **55**, 2701—2709; cf. this vol., 792).—Absorption spectra are recorded for the range 480—220 mμ. As the size of the group attached to position 6 of the quinoline nucleus of cinchonidine, cinchonine, hydrocupreine, optochin, eucupine, and vuzin increases, the absorption max. are broadened and shifted towards the red. A similar effect occurs when the *sec.*-OH at position 4 of quinine is replaced by CO (quinicine) or by CO_2H (quininic acid). The fluorescence spectra excited by λ 366 mμ in aq. or 0·9*M*-H_2SO_4 solutions have no fine structure and are substantially identical. The results are correlated with the photochemical reduction of chromate in the presence of these alkaloids. J. G. A. G.

Change of light absorption and refraction in the formation of artificial resin masses. J. H. DE BOER, R. HOUWINK, and J. F. H. CUSTERS (Rec. trav. chim., 1933, **52**, 709—718).—Polystyrene (I) absorbs less light than monostyrene and the bands are displaced in the direction of shorter wave-length. The absorption curve of (I) is in accordance with an alkylbenzene structure. The absorption curve of CH_2O–PhOH resin is typical of a phenol; on condensation the whole curve is displaced towards the red end to an extent agreeing with a substitution of Me in PhOH. Polymerisation of styrene is accompanied by a decrease in mol. refraction, but mol. refraction increases during the condensation of CH_2O with PhOH or $C_6H_4Me{\cdot}OH$. The increase of refraction and the displacement towards the red are related quantitatively. E. S. H.

Photographic-photometric method of measuring absorption by solutions in the visible. F. W. BEYER (Z. Physik, 1933, **83**, 806—813).—The method described was used to determine the absorption spectra of $[Co(NH_3)_6]Cl_3$ and $[Co\,3\,en]Cl_3$. A. B. D. C.

Absorption in the ultra-violet of some β-arylacrylic acids and their derivatives. (MLLE.) R. M. DA COSTA.—See this vol., 822.

Absorption spectra of *m*-bromophenol-indophenol, 2 : 6-dibromophenol-indophenol, and guaiacol-indophenol. M. M. BROOKS (J. Amer. Chem. Soc., 1933, **55**, 2434—2435).—Extinction coeffs. for 0·0001*M* solutions at p_H 11·7 are recorded for the range 510—680 mμ. J. G. A. G.

Infra-red spectrum of carbon dioxide. II. A. ADEL and D. M. DENNISON (Physical Rev., 1933, [ii], **44**, 99—104; cf. this vol., 661).—Mathematical. Consideration of the interaction between the vibration and rotation of the CO_2 mol. leads to the complete potential function for CO_2. N. M. B.

Infra-red absorption spectrum of pyridine and of some of its derivatives. I. Spectrum from about 0·80 to about 2·5 μ of pyridine and of some of its homologues. L. PASSERINI (Gazzetta, 1933, **63**, 305—319).—The absorption spectra of C_5H_5N, α- and β-picoline, αα′-lutidine, and collidine have been determined for λ 0·80—2·5 μ. The principal bands of C_5H_5N are also given by its homologues, with similar intensity, but the positions of the max. differ slightly. O. J. W.

Infra-red absorption spectra of organic compounds containing two chromophores. P. LAMBERT and J. LECOMTE (Compt. rend., 1933, **197**, 234—235; cf. A., 1932, 55).—The absorption spectra between λ=6 and 16 μ have been examined of 17 compounds $A{\cdot}[CH_2]_n{\cdot}B$, where A is Ph and B is Ph or CO_2Et, or A=B=OPh, and n=0—10. The spectra when n=0 differ entirely from those when n=1, and both from those for n > 1. These last show substantial but smaller progressive differences, and the spectrum of $Ph{\cdot}[CH_2]_3{\cdot}CO_2Et$ only distantly resembles that of an equimol. mixture of PhEt and EtOAc. These differences from the results in the ultra-violet are due to absorption in the infra-red of the CH_2 group and of C chains. C. A. S.

Intensity relations in the Raman spectrum of hydrogen. II. S. BHAGAVANTUM (Indian J. Physics, 1933, **7**, 549—559; cf. this vol., 548).—All the rotation lines in the Raman spectrum of H_2 gas are depolarised to the same extent, $\rho=0{\cdot}85\pm0{\cdot}05$. The relative intensities are in agreement with theory. The discrepancy with theory in the relative intensities of the *Q* and *R* branches of the vibration scattering is confirmed, and also, contrary to theory, it is found that the line arising from mols. in zero rotation state in the *Q* branch is depolarised to some extent. J. W. S.

Two new Raman lines of water. M. MAGAT (Compt. rend., 1933, **196**, 1981—1983).—Using Hg

light filtered through a solution of Victoria-blue, the following observations of a band which would include Ellis' hypothetical 510 cm.$^{-1}$ (cf. A., 1931, 1211) were made: in H_2O 396—796 (with 4358 Å.), and 465—766 (with 2537 Å.), in aq. $Ca(NO_3)_2$+LiCl 350—740, and in aq. $MgCl_2$ 350—785 (cf. A., 1932, 983). This band is perhaps due to a forbidden frequency of the H_2O mol. On this basis a revised interpretation of these bands is given (cf. this vol., 445). A new band was found at 152—225 cm.$^{-1}$, corresponding with 600 g.-cal. per mol. C. A. S.

Comparative intensity measurements on Raman lines of inorganic complexes. I. HANSEN-DAMASCHUN (Z. physikal. Chem., 1933, **B**, **22**, 97—113).—The results show that the linking is very similar in SO_4'', ClO_4', CO_3'', and NO_3' and approximates to the homopolar type, whilst the complexes $[Zn,6NH_3]''$ and $[Cd,6NH_3]''$ are far removed from the homopolar type of linking. R. C.

Raman spectrum of calcium nitrate. E. BAUER, M. MAGAT, and A. DA SILVEIRA (Compt. rend., 1933, **197**, 313—315; cf. A., 1932, 983).—The ratios of the intensities of the Raman lines 720 and 740 cm.$^{-1}$ of NO_3' have been determined for various concns. of $Ca(NO_3)_2$ without and with addition of LiCl. The results do not support Grassmann's theory (cf. A., 1932, 1075). C. A. S.

Raman effect of some complex cyanides. R. SAMUEL and M. J. KAHN (Z. Physik, 1933, **84**, 87—91).—Raman effect due to complex cyanides of Cr, Co, Ni, Ru, and Rh was observed. Those with co-ordination no. 6 gave two frequencies, corresponding with the C–N vibration and with the vibration of this group and the central atom; the second was absent from complexes with other co-ordination nos. The C–N frequency appears to increase with the homopolarity of the linking. A. B. D. C.

Raman spectra of iodides. II. Ethyl, propyl, and *iso*butyl iodides. N. G. PAI (Indian J. Physics, 1933, **7**, 519—529; cf. A., 1932, 1189).—A no. of new Raman frequencies are reported for these compounds and are compared with infra-red absorption data. J. W. S.

Raman spectrum of some heterocyclic organic compounds. I. M. MILONE and G. MULLER (Gazzetta, 1933, **63**, 334—338).—The Raman spectra of dimethyl- and methylethyl-furazan and of dimethyl-oxdiazole have been determined. They show lines characteristic of the groups CH, CH_2, C·C, C:N, and N·N. O. J. W.

Raman spectra of pinene, thiophen, salol, and thymol. S. VENKATESWARAN and S. BHAGAVANTAM (Indian J. Physics, 1933, **7**, 585—593).—The frequencies observed and the extent of their depolarisation are given in tabular form, and are discussed in relation to the results with analogous compounds. J. W. S.

Raman spectrum of pyrrole and some derivatives. G. B. BONINO, R. MANZONI-ANSIDEI, and P. PRATESI (Z. physikal. Chem., 1933, **B**, **22**, 21—44).—The Raman spectra of pyrrole, *N*-acetylpyrrole, 2-methylpyrrole, opsopyrrole, kryptopyrrole, 2 : 4-dimethyl-3-propylpyrrole, and 2-methylpyrrolidine have been examined. A model of the pyrrole mol. is discussed. R. C.

[Raman effect and] acetylenic linking: Δ^β-acetylenes. (MLLE.) B. GREDY (Compt. rend., 1933, **197**, 327—328; cf. this vol., 553).—The Raman spectra of CMe:CR (R=Me, Et, Pr$^\alpha$, and Bu$^\alpha$) all show the pair of lines near 2236 and 2304 cm.$^{-1}$ (2238 and 2316 for R=Me, 2235—2238 and 2303—2304 for the others), and the two lines near 376 (373—380) and 1381 (1380—1383). *Δ^β-Heptinene*, b.p. 111·5—112·5°, is obtained in 70% yield by the action of Me_2SO_4 on Na-hexinene (cf. A., 1888, 929). C. A. S.

Raman spectra of oximes. G. B. BONINO and R. MANZONI-ANSIDEI (Z. physikal. Chem., 1933, **B**, **22**, 169—180).—The frequency 1630 cm.$^{-1}$ is assigned to the C:N linking. The results support the usual structural formula for the oximes and the formula with the semipolar double linking for the Na salts of the aromatic oximes. R. C.

Fluorescence of sulphur dioxide. W. LOTMAR (Z. Physik, 1933, **83**, 765—785).—Powerful fluorescence is produced by Zn 2100 Å. line. Quenching and the effect of foreign gases indicate that the life period of the mol. thus excited is shortened by the presence of a predissociation limit. Observed bands are given in a term scheme. A. B. D. C.

Extinction of fluorescence in solutions by organic substances. J. EISENBRAND (Z. physikal. Chem., 1933, **B**, **22**, 145—168; cf. A., 1932, 1188, 1189).—The extinction of the fluorescence of quinine sulphate in MeOH solutions containing H_2SO_4 has been studied. Since the dihydric phenols have effectively the same extinguishing power as their ethers, theories of extinction depending on the reducing properties of the phenols (*ibid.*, 578) are untenable. Hydrocarbons containing incompletely saturated conjugated double linkings have extinguishing power; hydrocarbons with completely saturated conjugated double linkings, *e.g.*, C_6H_6, or with only a single double linking have none. Introduction into C_6H_6 of such substituents as impair the saturation of the conjugated system, *e.g.*, Me, OH, OMe, confers extinguishing power. There is no simple relation between extinguishing power and optical absorption, dipole moment, mol. refractivity, or ionic charge of the foreign substance, but in general a hydrocarbon exhibiting exaltation of mol. refraction has extinguishing power. The principal part in such extinctions as the above is probably played by the particularly loosely held electron associated with unsaturated conjugated double linkings. R. C.

Efficiency of the chemiluminescence accompanying oxidation of Grignard compounds. C. D. THOMAS and R. T. DUFFORD (J. Opt. Soc. Amer., 1933, **23**, 251—255).—Heats of oxidation for 11 aliphatic and 5 aromatic Grignard compounds, and total luminous efficiencies of chemiluminescence for MgPhBr, -C_6H_4Me·MgBr, *p*-C_6H_4Br·MgBr, and *p*-C_6H_4Cl·MgBr are given. N. M. B.

Phosphorescence of solid nitrogen and its relation to crystal structure. L. VEGARD (Science, 1933, **77**, 588—589).—A summary. L. S. T.

Bands in the thermoluminescence spectrum of fluorite from Obira, Japan. E. IWASE (Nature, 1933, **131**, 909—910). L. S. T.

Fluorescence of solutions and gases. A. BOUTARIC and J. BOUCHARD (J. Phys. Radium, 1933, [vii], **4**, 324—332).—Mathematical. N. M. B.

Emission from oxide-coated cathodes. II. M. BENJAMIN and H. P. ROOKSBY (Phil. Mag., 1933, [vii], **16**, 519—525; cf. this vol., 446).—Emission from a simple mixture of BaO and SrO is governed by that from each oxide separately. Solid solutions of the oxides give increased emission. The emission–composition curve has an optimum val. H. J. E.

Thermal and photo-electric emission of cæsium–cæsium oxide cathodes and the influence of cæsium atoms in the dielectric. J. H. DE BOER and M. C. TEVES (Z. Physik, 1933, **83**, 521—533).—Emission is increased by the presence of Cs atoms in the oxide layer, due to readier transmission of the electrons. A. B. D. C.

Theory of thermo-electric cells consisting of combinations of semi-conductors. C. WAGNER (Z. physikal. Chem., 1933, **B**, **22**, 195—198).—From the sign of the thermo-e.m.f. of a cell consisting of two pieces of the same material with different electronic conductivities, *e.g.*, Cu_2O at 1000° in equilibrium with different O_2 pressures, it can be decided whether electron excess or electronic deficiency conduction predominates (cf. this vol., 888). R. C.

Thermal and voltaic potential of cuprous oxide. G. MÖNCH and S. STECHHÖFER (Z. Physik, 1933, **84**, 59—64).—E.m.f. due to unequally tempered ends of Cu_2O amounted to 0·1 volt, and that due to a temp. difference of 100° to 0·4 volt. A. B. D. C.

Internal photo-electric absorption in halide crystals. R. W. GURNEY (Proc. Roy. Soc., 1933, **A**, **141**, 209—215).—Theoretical. In the quantum-mechanical model of an insulating crystal, bands of electron levels are separated by wide zones of disallowed energies. Throughout an imperfect crystal are distributed numerous submicroscopic cracks, on and near the surfaces of which are localised levels with energies lying in the disallowed zones. Various inter-related phenomena are discussed in terms of transitions between the allowed electron levels. L. L. B.

Crystal photo-effect with photo-electric conducting sodium chloride. S. PELZ (Naturwiss., 1933, **21**, 517).—If a crystal of NaCl coloured yellow by exposure to Ra is illuminated over half its surface, a current flows without the application of an external field, the phenomenon being similar to that observed with cuprite and galena. If the crystal is intensively illuminated a secondary effect occurs. The primary effect occurs also with coloured KCl, and although not previously observed, the possibility of its occurrence has been demonstrated theoretically by Fowler. A. J. M.

Photo-electric effects of crystals of argentite, proustite, and pyrargyrite. G. ATHANASIU (Compt. rend., 1933, **197**, 42—44).—On inserting a crystal of argentite in a circuit and illuminating the contact with one electrode a negative e.m.f. is observed with light of λ 0·5—1·4 μ, max. for 1·15 μ. Proustite and pyrargyrite with a Pt electrode give a positive current, max. for 0·58 and $< 0{\cdot}45\ \mu$, and 0·62—0·65 and $< 0{\cdot}45\ \mu$, respectively, but sometimes negative with a Cu electrode for red light; an auxiliary current of 0·6 volt is required to reverse the effect. In all cases the $\lambda\lambda$ of the light giving max. e.m.f. are those giving max. conductivity at low temp. (—110° to —137°) (cf. A., 1920, ii, 212; 1924, ii, 82). C. A. S.

Electrical conductivity of zinc and cadmium oxides. H. H. VON BAUMBACH and C. WAGNER (Z. physikal. Chem., 1933, **B**, **22**, 199—211).—The conductivity, κ, of a rod of ignited ZnO or CdO at about 450—650° decreases at any given temp. with increasing O_2 pressure, p, according to $\kappa = kp^{-1/n}$, where k and n are consts. For ZnO in H_2O–H_2 mixtures and CdO in Cd vapour κ is abnormally great. The suggested explanation of these observations is the presence in the oxide phase of an excess of metal, varying regularly with p and probably consisting of cations in lattice interstices and excess electrons. Thermo-e.m.f. measurements indicate that the conductivity of the ZnO is of the electron excess type. R. C.

Misplacement phenomena in cuprous oxide and their effect on electrical properties. H. DUNWALD and C. WAGNER (Z. physikal. Chem., 1933, **B**, **22**, 212—225; cf. A., 1931, 793).—The sp. conductivity of Cu_2O at 800—1000° is approx. proportional to $p^{1/7}$, where p is the O_2 pressure in the gas phase, which is qualitatively explained by the assumption that the transport of electrons occurs mainly by electron deficiency conduction (cf. Wagner, this vol., 888), a theory confirmed by thermo-e.m.f. measurements at various O_2 pressures. The share of $Cu^{\cdot}$ ions in the conduction at 1000° is about 4×10^{-4}. The variation of the excess of O in the Cu_2O above the stoicheiometric ratio with p and temp. has been measured. Assuming that in the Cu_2O lattice there are electron deficiency centres and empty places in the $Cu^{\cdot}$ partial lattice, the experimental observations at 800—1000° are explained. The diffusion coeff. for the formation of a film of Cu_2O on Cu in $O_2/<100$ mm. at 1000° has been calc. R. C.

Electrical conductivity of cupric oxide. H. H. VON BAUMBACH, H. DUNWALD, and C. WAGNER (Z. physikal. Chem., 1933, **B**, **22**, 226—230).—The conductivity of compact CuO at 600—1000° increases only very slightly with the partial pressure of O_2 in the gas atm., and is practically entirely electronic. The interpretation is that the misplacements in the lattice consist of equiv. nos. of $Cu^{\cdot\cdot\cdot}$ ions and electrons, $Cu^{\cdot\cdot} \rightleftharpoons Cu^{\cdot\cdot\cdot} + \ominus$. Burnt rods of finely-divided CuO behave anomalously in conductivity. R. C.

Electronic properties of conductors and insulators. R. H. FOWLER (Proc. Roy. Soc., 1933, **A**, **141**, 56—71).—A crit. survey of current views on the nature of cryst. insulators and their electronic properties. Tamm's theory of surface levels on an insulator is analysed, and the view that the existence of these surface levels in cryst. insulators is one fundamental reason for their insulating properties is abandoned. L. L. B.

Theory of ordered mixed phases. III. Misplacement phenomena in polar compounds as the basis of ionic and electronic conduction. C. WAGNER (Z. physikal. Chem., 1933, **B**, **22**, 181—194; cf. A., 1931, 1223).—Electronic conduction in semiconductors may depend either on the presence of effectively free electrons, corresponding with the classical electron gas theory ("electron excess conduction"), or on the presence of electron deficiency centres, *i.e.*, lattice constituents which have lost some of their normal complement of electrons and are therefore able to participate in exchange of bound electrons ("electron deficiency conduction"). The deviation from the stoicheiometric composition often gives the concn. of misplacements in the lattice, and therefore determines conduction. With predominant electronic conduction, the conductivity decreases with increasing partial pressure, p, of the electronegative lattice component if the conduction is of the electron excess type, and increases if it is of the electron deficiency type, whilst it is independent of p if free electron and electron deficiency centres are present in equiv. amounts. With cationic conduction predominating, the concn. of interstitial cations is equiv. to that of empty places in the cation partial lattice, and similarly for predominating anionic conduction. R. C.

Influence of surface charge on conductivity measurements of insulators. A. D. GOLDHAMMER (Z. Physik, 1933, 84, 212—217). A. B. D. C.

Dependence of dipole moment on solvent, infra-red terms, and linking moments. O. FUCHS and H. L. DONLE (Z. physikal. Chem., 1933, **B**, 22, 1—20).—The principal errors in the determination of dipole moment by the method of dil. solutions are the effect of the solvent and the uncertainty of the infra-red terms. The measured moment is always influenced by the solvent, particularly with mols. containing polar groups which can rotate towards each other, but by a suitable choice of solvent its effect may be rendered negligible. From an examination of data for the infra-red terms of the displacement polarisation of various dipole-free aromatic mols. it has been possible to calculate the vals. for various simple polar C_6H_6 derivatives more accurately than hitherto, and thus recalculate the dipole moments. A review of linking moments shows that exact data are still lacking. The dipole moments of various ketones have been redetermined. R. C.

Composition of electric moments of polyalcohols: moments of associated dipoles. P. GIRARD and P. ABADIE (Compt. rend., 1933, **197**, 146—148).—The statical dielectric const., ε_s, is proportional to c, the no. of dipoles per unit vol., d, and γ, the polarisability of the mol., *i.e.*$=Acd\gamma$, where A is a const.; $\gamma=\gamma+\gamma''$, where γ is the induced polarisability and negligible compared with $\gamma''(=\mu^2/3kT)$, the permanent polarisability (μ is the permanent moment of the dipole, k Boltzmann's const., and T the abs. temp.). As and d for the polyalcohols considered are practically const., $c\mu^2$ is so also if T is; or if μ_1 is the elementary moment due to one alcohol function ($=1{\cdot}6\times10^{-18}$ e.s.u.), n being the no. of alcohol functions, and c varies as n. These conclusions are verified for (figures are vals. of ε_s at the temp. noted): glycol 37·6, 20°; glycerol 40, 20°; 32·5, 80°, 26·6, 120°; 22, 170°; erythritol 28·2, 120°; xylitol 40, 20°; sorbitol 33·5, 80°; mannitol 24·6, 170°; glucoheptitol 27·4, 120°; and glucoheptulitol 27·1, 120°. C. A. S.

Relation between dipole moment and cohesion forces. II, III. A. E. VAN ARKEL and J. L. SNOEK (Rec. trav. chim., 1933, **52**, 719—732, 733—741; cf. A., 1932, 983).—II. Theoretical. The influence of Debye's attraction term on the relative b.p. of simple aliphatic halogen and nitro-derivatives is discussed. From the properties of CCl_3Me, CCl_2Me_2, $CClMe_3$, and $CCl_3{\cdot}NO_2$ a lower limit 3·2 Å. is deduced for the at. diameter of Cl, whilst the val. obtained from salts is 3·6 Å. Debye's formula does not lead to a satisfactory derivation of dipole moment from b.-p. data for mols. which deviate widely from the spherical form; better agreement is obtained by introducing a form factor. Qual. agreement is obtained in the isomeric groups cyanide–carbylamine and nitro–nitrite. With mols. showing association, such as alcohols, acids, and amines, the moments are probably peripheral, so that the dipoles of such mols. approach each other closely.

III. The former theoretical considerations are applied to numerous derivatives of C_2H_6, C_3H_8, C_5H_5N, diazine, thiophen, and $C_{10}H_8$. E. S. H.

Free rotation and the electrical moments of diacetyl, acetylacetone, acetic anhydride, and ethyl acetate. C. T. ZAHN (Physikal. Z., 1933, **34**, 570—574).—Ac_2 shows a much smaller moment (1·25—1·48) than it would have if there were complete rotation (3·2). Moreover, it is dependent on temp., which indicates either completely free rotation, or complete hindrance. The *trans*-position is taken up. With CH_2Ac_2 there was no temp. effect. The tautomerism of this compound is discussed, and vals. for the moments of the different forms are calc. The experimental val. (3·0) makes the compound a mixture of the diketone and the enol form. In the case of Ac_2O there was no dependence on temp. The mol. can be the ordinary free mol. or the linked form, there being little difference in the calc. vals. of the moments of the two forms. Similarly, EtOAc can also be either the free mol. or the linked form. It is clear that strong intermol. forces exist between groupings, and that this is not confined to mols. containing double linkings. The hindrance may be due simply to the electrostatic action of the polarised atoms. A. J. M.

Dipole moments of *p*-chloro- and *p*-bromophenol. M. A. G. RAU (Physikal. Z., 1933, **34**, 575).—The method used by Williams and by Donle (this vol., 448) in evaluating the dipole moments of these compounds is subject to error, giving rise to the differences between their vals. The method of Hedestrand (A., 1929, 647) applied to their data yields results agreeing with each other. The vals. of dielectric const. and density of both observers plotted against concn. give linear curves, showing the absence of association in the concn. range used. A. J. M.

Dielectric constants of some organic liquids. S. SUGDEN (J.C.S., 1933, 768—776).—A simple

resonance method of measuring dielectric consts. of liquids is described. Errors due to the form of the cell and consts. of the circuit are discussed and evaluated. The following vals. are obtained for the dielectric const. at 25°: C_6H_6, 2·272 ± 0·001; PhCl, 5·612 ± 0·006; $[CH_2Cl]_2$ 10·36 ± 0·02; COPhMe, 17·39 ± 0·02; PhCN, 25·19 ± 0·04, $PhNO_2$, 34·75 ± 0·07. No variation of the dielectric const. with frequency is found over the range 60—1500 kilocycles per sec. J. W. S.

Refractive power of some gaseous fluorides. W. Klemm and P. Henkel (Z. anorg. Chem., 1933, **213**, 115—125).—Vals. of n for BF_3, CF_4, SiF_4, GeF_4, SF_6, SeF_6, and TeF_6 were measured interferometrically for wave-lengths 5876 and 5461 Å. The mol. refractions for 5876 Å. were calc. The position of the absorption bands of each compound was calc. from its dispersion curve. All lie in the far ultraviolet. H. J. E.

Double refraction of oriented surface layers. A. M. Taylor and A. King (Nature, 1933, **132**, 64).—Evidence of the double refraction of the interfacial layer between melted normal fatty acids and glass has been obtained. The birefringence is small, usually $< 0·0001$, and exists for a few degrees of temp. just above the f.p. of the acid. The mols. of acid are thus oriented at a glass-liquid interface to a depth comparable with a wave-length of visible light. The sharpness with which birefringence disappears at a crit. temp. may indicate that the anisotropic layer is a new phase and that the fatty acid behaves as a liquid crystal immediately above its m.p. L. S. T.

Optical rotatory power. IV. Rotatory dispersion of bornyl and menthyl xanthates, especially in the region of absorption. T. M. Lowry and H. Hudson (Phil. Trans., 1933, **A, 232**, 117—154).—The series of xanthates studied show two absorption bands, one at about 3600 Å. being attributed to the ·CS·S· group, and a stronger about 2800 Å., to the :CS group. A new equation has been developed to which both conform closely. The circular dichroism is of opposite signs in the two bands, and in the first follows a similar course to the absorption. In the region of transparency the anomalous rotatory dispersion can be expressed with exactness by two terms of Drude's equation, and a new equation has been devised to represent that in the absorption region. F. L. U.

Rotatory power of active dilactamide. P. Vièles (Compt. rend., 1933, **197**, 40—42).—The rotatory dispersion of *l*-dilactamide (cf. A., 1932, 253) between λ 5893 and 4047 Å. (given by a single Drude term), and the variation of the power with temp. (linear between 10° and 32·75°) and concn. (parabolic), have been determined. The two latter are mutually independent. Measurements with mixtures of *d*- and *l*-dilactamide indicate non-existence of a racemic compound in solution. C. A. S.

Nature and space extension of scattering moments for optically active molecules. W. Kuhn and K. Bein (Naturwiss., 1933, **21**, 529).—Theoretical. A. J. M.

Optical and thermodynamic activity of camphorsulphonic acid in solutions of neutral salts. C. Drucker (Z. physikal. Chem., 1933, **165**, 411—419).—The effect of alkali salts, $BaCl_2$, and $La(NO_3)_3$ on the optical rotation, activity coeff., f, conductivity, and f.-p. depression of the acid in aq. solution has been examined. The mol. rotation is depressed by salts in varying degree, the decrease for NaCl alone being almost proportional to the salt concn., c. f increases with, but much more rapidly than, c. R. C.

Rotatory dispersion of organic compounds. XXI. Cyclic derivatives of tartaric and malic acids. B. Jones (J.C.S., 1933, 788—796).—The rotatory dispersions of *Me*, m.p. 74°, and Et benzylidenetartrate, dibenzylidenetartrate, *acetylmalic anhydride*, m.p. 58°, and Et β′β′β′-trichloro-α′-hydroxyethyl-α-anhydrotartrate have been studied for solutions in EtOH, $COMe_2$, and Ac_2O, and for the wave-length range 6708—4358 Å. Measurements with the first two compounds were extended to 3239 Å. It is concluded that although ring formation tends to simplify the dispersion, the anomalies disappear completelv only when free rotation is inhibited. J. W. S.

Magnetic-optic minima of organic compounds. J. L. McGhee and M. Lawrenz (J. Amer. Chem. Soc., 1933, **55**, 2614—2615; cf. A., 1930, 1541).—For each of the homologous series alkyl bromides, alkyl acetates, and alcohols, the scale readings for the min. increase with increasing wt. of alkyl. The scale readings decrease for the fatty acids. J. G. A. G.

Magnetic birefringence in liquid mixtures. S. W. Chinchalkar (Indian J. Physics, 1933, **7**, 491—518).—The deviation of the magnetic birefringence in liquid mixtures from theoretically calc. vals. has been investigated. The results are correlated with the existing data on the variation of magnetic birefringence with temp., the variation of mol. optical anisotropy with temp., and optical anisotropy in the vapour and liquid phases. It is suggested that the variation in the effective optical anisotropy of the mols. with dilution is at least one, and probably the main, cause of the deviations observed. J. W. S.

Abnormal electric and magnetic birefringence. R. Lucas and M. Schwob (J. Phys. Radium, 1933, [vii], **4**, 287—300).—Anomalies of change of sign of birefringence under the influence of solvents or of temp. effect contrary to theory were shown by camphor, fenchone, and Et phenylsuccinate. Results are explained by the theory of mol. polymorphism. N. M. B.

Electrical Kerr effect and association in liquids. I. Kerr effect in liquids and solutions and its dependence on temperature. II. Orientation in liquids and its influence on molecular refraction, molecular polarisation, degree of depolarisation due to molecular light scattering, and on the Kerr effect. H. A. Stuart and H. Volkmann (Z. Physik, 1933, **83**, 444—460, 461—482).—I. An abs. method was used to determine the temp. variation of the Kerr const. of C_6H_6, C_7H_{14}, and CCl_4, and the concn. variation of the molar Kerr const. of solutions of $PhNO_2$ in these liquids. The

results disagree with the Langevin–Born theory even for dil. solutions on account of orientation within the liquid.

II. The phenomena were investigated for non-dipole liquids, and show that deviations due to orientation of the mols. occur when the density of the mols. is so large that disordered orientation of the mol. axes is unlikely. A. B. D. C.

Molecular structure of polyalcohols deduced from their dispersion and absorption for radio frequencies : molecular association. P. GIRARD and P. ABADIE (Compt. rend., 1933, **196**, 1995—1997; cf. A., 1932, 899).—Absorption and dispersion curves for λ 20—5000 cm. for glycerol (at 25° and 37°) and sorbitol (at 80°) compared with the corresponding curves deduced from the vals. of the at. radius, a (depending on the expression for the time of relaxation), that give the nearest similar curves, indicate in glycerol two kinds of dipoles, simple and associated 2 and 2, united laterally, probably all becoming simple at 50°, and in sorbitol simple mols. and mols. associated 2 and 2, 3 and 3, and perhaps 4 and 4. $[CH_2{\cdot}OH]_2$ and xylitol at 20° show respectively slight and strong association. It is shown that the time of relaxation decreases proportionally to the no. of elementary dipoles in the mol. of a polyalcohol, which implies the probability of a cylindrical or an ellipsoidal shape for such a mol. C. A. S.

Structure of crystallised platinocyanides. H. BRASSEUR (Compt. rend., 1933, **196**, 2015—2017).—Pauling has shown that the CN groups (regarded as units) in the platinocyanides are in one plane with the Pt. From a comparison of the optical properties of the platinocyanides with those of cyanuric triazide (cf. this vol., 559) and Wooster's deductions as to the connexion between double refraction and structure (cf. A., 1932, 10) it is concluded that the line joining the C and N atoms in each CN group is perpendicular to the above plane. C. A. S.

Determination of molecular structure by means of electron diffraction. VI—VIII. Ethyl chloride, bromide, and iodide. L. BRU (Anal. Fís. Quím., 1933, **31**, 115—121).—The distances between the C and Cl, C and Br, and C and I atoms are $1{\cdot}81\pm0{\cdot}08$, $2{\cdot}02\pm0{\cdot}07$, and $2{\cdot}32\pm0{\cdot}04$ Å., respectively. H. F. G.

Constitutional factors controlling phototropic changes in carbonyl compounds. V. Relationship between the polar characters of substituent groups and the activation energies of proton addition. W. S. NATHAN and H. B. WATSON (J.C.S., 1933, 890—895; cf. this vol., 505).—A quant. relationship exists between the critical increment of the reaction of oxonium ion with $COMe{\cdot}C_6H_4X$ and the dipole moment of PhX. The relationship applies also to new data for the speed of phototropic change of substituted ω-chloroacetophenones. Almost identical connexion is observed between the dipole moment of MeX and the difference in the crit. increments of dissociation and association of the acid $CH_2X{\cdot}CO_2H$. These relationships indicate the absence of electromeric displacements in the cases considered. J. W. S.

Free radicals of organic radicals. Quantum-theoretical contributions to the problem of aromatic and unsaturated compounds. IV. E. HÜCKEL (Z. Physik, 1933, **83**, 632—668).—Free radicals with C^{III} and N^{II} occur only with aromatic and unsaturated substituents of these atoms; this is due to the four C valencies assuming the tetrahedral directions in the mol., and their assuming three directions oriented at 120° in a plane together with a free valency normal to the plane (*i.e.*, a single electron proper function with this plane as a node exists containing one electron, a $[p]_h$-electron) in the radical; the $[p]_h$-electron for these radicals can give resonance with similar electrons in the neighbouring C atoms, and the corresponding gain in energy gives a small resultant energy of dissociation. Transition from one structure to the dissociated structure is discussed from the point of view of energy of activation. Finally, the discrepancy between an equilibrium const. for the gas phase and that observed for solutions is shown to be due to change in phase vol. of the solvent due to dissociation of the solute (cf. A., 1931, 1000; Pauling and Wheland, J. Chem. Physics, 1933, **1**, 362). A. B. D. C.

Diamagnetic susceptibility of the hydrogen molecule. K. HONDA and T. HIRONE (Z. Physik, 1933, **84**, 208—211).—Paramagnetism of diat. mols. due to thermal rotation gives a susceptibility independent of temp., and the sum of this for H_2 and Van Vleck's diamagnetic susceptibility gives good agreement with the observed susceptibility. A. B. D. C.

Electric polarisability and diamagnetic susceptibility of molecules. S. BHAGAVANTAM (Indian J. Physics, 1933, **7**, 617—621).—Vinti's relation (A., 1932, 1191) is tentatively applied to simple mols., using Van Vleck's formula for diamagnetic susceptibility. The results are discussed. J. W. S.

Variation of the magnetic properties of barium with temperature. C. T. LANE (Physical Rev., 1933, [ii], **44**, 43—45).—The susceptibility–temp. curve for a range of 400° showed a discontinuity at 350°, similar to that occurring at the Curie point in ferromagnetics, and supporting evidence for α and β modifications as given by the resistivity–temp. curve. N. M. B.

Magnetic properties of artificially anisotropic substances. W. KÖNIG (Ann. Physik, 1933, [v], **17**, 736—746).—The susceptibilities of solutions of $MnCl_2$, $MnSO_4$, $CoSO_4$, $MgSO_4$, and $NiSO_4$ in gelatin, moulded into cylindrical form and under definite deformations, were determined. A. J. M.

Magnetic properties of celloidin, agar-agar, and celluloid under artificial anisotropy. K. WEISEL (Ann. Physik, 1933, [v], **17**, 747—754; cf. preceding abstract).—Celloidin and agar-agar were found unsuitable. The susceptibility of celluloid plates under various deformations was determined. A. J. M.

Paramagnetism and chemical linking. E. RABINOWITSCH (Z. Elektrochem., 1933, **39**, 702—715).—A review.

Photometric determination of *X*-ray quality. W. H. Love (J. Cancer Res. Comm. Sydney, 1933, **5**, 11—15).—The evaluation of the relative energy associated with the various wave-lengths, and the determination of the wave-length–energy curve, are described. N. M. B.

Determinations of the signs of the Fourier terms in complete crystal structure analysis. K. Banerjee (Proc. Roy. Soc., 1933, **A**, **141**, 188—193).—Mathematical. It is shown that the signs of the Fourier terms can be found with the help of the equations developed by Ott (A., 1928, 821). The method is used to find the signs of the terms S_{00l} of anthracene crystal, for the different vals. of l. L. L. B.

Quartz as a standard for accurate lattice-spacing measurements. A. J. Bradley and A. H. Jay (Proc. Physical Soc., 1933, **45**, 507—522).—With Cu $K\alpha$ radiation, sharp and accurately measurable $K\alpha$ doublets were obtained. Determination of the axial ratio from an *X*-ray powder photograph gave c/a 1·10002±0·00004, whence a—4902·9 and c=5393·3X. Data for quartz from different sources are given. N. M. B.

Origin, first appearance, and growth of crystal nuclei: influence of H. F. current. D. Samuracas (Z. Krist., 1933, **85**, 474—478; cf. A., 1932, 567).—An over-cooled molten (*e.g.*, salol) or a supersaturated solution of a substance [*e.g.*, aq. $Pb(NO_3)_2$] is cooled slowly from 0 to 0′ in time t, and then suddenly to 0″, the temp. being so adjusted that the sudden fall renders visible the nuclei formed by the slow cooling. With 0 and 0″ const. the no. of nuclei increases with 0—0′. Each nucleus is surrounded by a "crystallisation field" in which more nuclei tend to appear. With t, 0, 0″ const. the time before nuclei become visible increases with 0′. High-frequency current increases the no. but decreases the size of the nuclei, which arrange themselves along the lines of force. C. A. S.

The α β transformation of calcium. F. Ebert, H. Hartmann, and H. Peisker (Z. anorg. Chem., 1933, **213**, 126—128; cf. Rinck, A., 1931, 416).—*X*-Ray photographs show that face-centred cubic α-Ca is transformed reversibly at 450° into hexagonal β-Ca (a 3·98, c 6·52 Å.; $c:a$=1·639; 2 atoms of Ca in unit cell). This explains the observed change in reactivity of Ca with N_2 at this temp. H. J. E.

Structural peculiarities of bismuth and antimony. A. Schulze (Z. physikal. Chem., 1933, **165**, 188—194; cf. this vol., 116).—The electrical resistance–temp. curve of polycryst. Sb is discontinuous at 105—110°. This anomaly seems to be due, not to polymorphic transformation, of which *X*-ray examination gives no indication, but to mechanical deformation, for it is absent with single crystals of Sb or polycryst. Sb which has been heated at 600° and slowly cooled. Dilatometric measurements gave similar results. R. C.

Modifications of phosphorus pentoxide. K. Boratynski (Rocz. Chem., 1933, **13**, 340—345).—Commercial P_2O_5, d 2·288, consists of cryst. (I), d 2·284, amorphous (II), d 2·207, and vitreous, d 2·382—2·422, modifications. 50% yields of (I) are obtained by sublimation at 300°/760 mm., and 80% at 250°/15 mm. (I) readily dissolves in H_2O, whilst (II) imbibes H_2O and forms a gel, the velocity of dissolution of which is proportional to the temp. R. T.

***X*-Ray study of modifications of phosphorus pentoxide.** A. Nowakowski (Rocz. Chem., 1933, **13**, 346—350).—*X*-Ray spectra of commercial P_2O_5 indicate that this consists chiefly of the cryst. modification, part of which is converted into vitreous non-volatile P_2O_5 during sublimation, as is shown by the diminished anisotropy of the product. R. T.

Perfection of crystal laminæ. W. N. Bond (Phil. Mag., 1933, [vii], **16**, 410—422).—By examining the banded spectrum of white light reflected from mica laminæ 0·01 mm. thick, the latter were found to be uniform in thickness to 8×10^{-8} cm. H. J. E.

Crystallisation of ingots. R. G. Heggie (Trans. Faraday Soc., 1933, **29**, 707—721).—Experiments with stearic acid show that equiaxial crystallisation is promoted by slow cooling and by motion of the melt. Under still conditions, equiaxial crystallisation of solid solutions is possible only below a crit. rate of cooling dependent on the temp. of freezing range. For a pure substance (*e.g.*, Sn) this is zero, so that only columnar crystallisation can occur. Matuschka's theory of a dynamic heat balance (B., 1931, 1012) is upheld. J. S. A.

Evidence for the cybotactic group view of the interior of a liquid. G. W. Stewart (Indian J. Physics, 1933, **7**, 603—615).—Fifteen different experimental results are quoted which support the cybotactic view of liquids, in which the latter are regarded as consisting of aggregates which crudely simulate cryst. orderliness and of mols. approx. at random. J. W. S.

Diffraction of *X*-rays by liquid sulphur. A. H. Blatchford (Proc. Physical Soc., 1933, **45**, 493—500).—Data for the range 130—260° are given. Results indicate that the diffraction is due to an unstable grouping of S atoms becoming less pronounced with rise of temp. At 220° a sudden alteration corresponds with the change from the form S_λ to S_μ. N. M. B.

Crystal structure of borides of the type MB_6. F. Laves (Z. physikal. Chem., 1933, **B**, **22**, 114—116).—An error in Stackelberg and Neumann's paper (this vol., 116) is corrected. The lattice of these borides consists of a three-dimensional structure of B atoms in the interstices of which are the metal atoms. R. C.

Crystallography of some compounds of gadolinium and samarium. A. Pabst (Amer. J. Sci., 1933, [v], **26**, 72—79).—Crystals of $Gd(CO_2H)_3$, $Gd(OAc)_3,4H_2O$, $Gd(CO_2Et)_3,3H_2O$, $Gd(CO_2Pr^\alpha)_3,2H_2O$, $Sm(BrO_3)_3,9H_2O$, and $Gd(BrO_3)_3,9H_2O$ are described. C. W. G.

Correct setting of crystals. [Structure of methylammonium cuprichloride and dimethylammonium chlorostannate.] G. Greenwood (Z. Krist., 1933, **85**, 420—424).—The selection as unit

cell of that of which the angles are nearest right angles gives results in agreement with Fedorov's method. This is illustrated by *X*-ray examination of $(NH_3Me)_2CuCl_4$ d_4^{20} 1·719, unit cell *a* 7·30, *b* 7·535, *c* 18·55, containing 4 mols., and $(NH_2Me_2)_2SnCl_4$, with *a* 14·00, *b* 7·20, *c* 7·08, and 2 mols. (cf. A., 1902, i, 747). C. A. S.

Crystal structure of ammonium hydrogen fluoride. L. PAULING (Z. Krist., 1933, **85**, 380—391; cf. this vol., 13).—The unit cell of NH_4HF_2 has *a* 8·33, *b* 8·14, *c* 3·68 Å., and contains 4 mols., space-group V_h^7—*Pman*. Each N is attached to four F ions at a distance of 2·76 Å. by H linkings (cf. A., 1928, 690; 1932, 1191), the proton being probably nearer N than F; each F ion is attached to two N and one F ion, the F–H distance in the linear HF_2 group being 1·184 Å. C. A. S.

Crystal structure of cæsium, thallium, and rubidium perrhenates. F. M. JAEGER and J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 523—528).—$RbReO_4$, like $KReO_4$ and $AgReO_4$ (A., 1930, 20), is tetragonal-bipyramidal in structure, $a_0 : c_0 = 1 : 2·2707$, whereas $CsReO_4$ and $TlReO_4$ are orthorhombic with a definite pseudo-tetragonal character, $a_0 : b_0 : c_0 = 0·961 : 1 : 2·3901$ and $0·970 : 1 : 2·2985$, respectively. These results are compared with those for corresponding osmiamates (cf. this vol., 13). J. W. S.

Structure of sanidine and other felspars. W. H. TAYLOR (Z. Krist., 1933, **85**, 425—442; cf. A., 1929, 749).—Sanidine, *d* 2·57, *n* 1·52, $(KNa)AlSi_3O_8$, has *a* 8·4, *b* 12·9, *c* 7·1 Å., β 116°, with 4 mols. in the unit cell, space-group C_{2h}^3. A structure based on a framework of linked SiO_4 and AlO_4 tetrahedra is suggested, and the analogy to that of danburite illustrated (cf. A., 1931, 415). C. A. S.

***X*-Ray examination of garnet from the gorge of the Lieser near Spittal (Carinthia).** H. HERITSCH (Z. Krist., 1933, **85**, 392—403).—The garnet contains SiO_2 36·91, TiO_2 0·22, Al_2O_3 19·24, Fe_2O_3 5·04, FeO 19·58, MnO 0·42, MgO 1·93, CaO 16·61, corresponding with $(Ca,Mg,Fe^{II},Mn^{II})_3(Al,Fe^{III})_2Si_3O_{12}$; *d* 3·877, *n* 1·777. The unit cell has *a* 11·668 A., and contains 8 mols. The properties and structure agree with those calc. from Menzer's classification (cf. Z. Krist., 1928, **69**, 300), the garnet filling a gap between his grossular-andradite and almandine-pyrope. C. A. S.

***X*-Ray examination of bauxites and mullites.** M. E. NAHMIAS (Z. Krist., 1933, **85**, 355—369).—There is no stable cryst. compound of Al_2O_3 and SiO_2 between sillimanite (I) and mullite (II). For (II) the formula $3Al_2O_3,2SiO_2$ is proved by the fact that all excess of SiO_2 or Al_2O_3 beyond that formula appears as tridymite or corundum. Kaolinite at 450° passes into a mixture of γ-Al_2O_3 and amorphous SiO_2 (sometimes regarded as metakaolinite; cf. B., 1929, 172), which continues as such to 950°, when (II) begins to be formed, and is completely so at 1050°, with no formation of (I) at any stage. (I) and (II) are both rhombic with respectively *a* 7·52, *b* 7·65, *c* 5·78 Å., and *a* 7·52, *b* 7·65, *c* 2·89 Å., space-groups V_{16}^h and (perhaps) V_h^1, but the structure of (II) is doubtful; variations in (II) of different origins are perhaps due to the presence in solid solution of varying amounts of TiO_2 and Fe_2O_3. Eleven analyses of bauxites are given (cf. B., 1933, 147). C. A. S.

Crystal structure of nacrite. J. W. GRUNER (Z. Krist., 1933, **85**, 345—354).—Nacrite, $Al_2(OH)_2Si_2O_5$, is monoclinic hemihedral; the unit cell has *a* 5·16, *b* 8·93, *c* 28·60 Å., β 91° 43′, and contains 8 mols., $d_{calc.}$ 2·581, space-group C^4. The structure resembles that of dickite and kaolinite (cf. A., 1932, 987; this vol., 45), but each alternate layer is rotated through 180° relatively to its neighbours, thus explaining the different optical properties. Varying amounts of dickite were present in the specimens examined. C. A. S.

Crystal structure of the dihalides. J. M. BIJVOET [with NIEUWENKAMP] (Chem. Weekblad, 1933, **30**, 479—483).—Principally a review, with particular reference to the Cd and Hg halides. Sublimed $CdBr_2$ yields an *X*-ray diagram of similar type to that of $CdCl_2$, but when cryst. from aq. solutions and dehydrated at room temp. it yields a simpler diagram, which, however, reverts to the normal slowly at room temp. or more rapidly at 400°. H. F. G.

Crystal structure of hydrohalides of ephedrine and ψ-ephedrine. B. GOSSNER and H. NEFF (Z. Krist., 1933, **85**, 370—379).—The following are given for *d*, *a*, *b*, *c* (in A.), β, no. of mols. in unit cell: *r*-ephedrine hydrochloride 1·231, 13·27, 7·04, 13·44, 118° 24′, 4; hydrobromide 1·444, 13·15, 7·11, 14·00, 119° 25′, 4; hydriodide 1·586, 13·40, 7·23, 14·70, 120° 24′, 4; *r*-ψ-ephedrine hydrochloride (I) 1·186, 24·48, 9·97, 18·58, 90°, 16; hydrobromide 1·403, 13·87, 6·80, 14·04, 116° 51′, ?; hydriodide 1·550, 13·49, 6·97, 14·62, 114° 26′, ? (cf. A., 1930, 470). All are monoclinic prismatic, space-group C_{2h}, except (I), which is rhombic dipyramidal, V_h^5. The bearing of the foregoing on mol. and crystal structure of racemic compounds is discussed. C. A. S.

Crystal structure of sugar derivatives. E. G. COX and T. H. GOODWIN (Z. Krist., 1933, **85**, 462—473; cf. A., 1932, 1192).—The following data are given: for *d*, *a*, *b*, *c* (in Å.), and no. of mols. in the unit cell: α-methyl-*d*-glucoside (cf. A., 1922, i, 128), 1·48, 11·21, 14·57, 5·29, 4; β-methyl-*d*-glucoside hemihydrate (I), 1·49, 7·32, 7·32, 33·6, 8; α-methyl-*l*-arabinoside, 1·47, 9·32, 16·92, 4·68, 4; β-methyl-*l*-arabinoside (II), 1·44, 16·56, 7·74, 5·89, 4; β-*d*-glucosan, 1·64, 6·65, 13·14, 7·46, 4; γ-monoacetyl-methyl-*l*-rhamnoside (cf. A., 1932, 45), 1·41, 7·98, 18·25, 7·08, 4; *d*-chitosamine hydrochloride (III) (cf. A., 1932, 271), 1·55, 7·68, 9·18, 7·11, 2. Except (I), tetragonal trapezohedral, $P4_12_12$—D_4^4, and (III), monoclinic sphenoidal, $P2_1$—C_2^2, all are rhombic bisphenoidal, $P2_12_12_1$—Q^4. (II) also occurs in monoclinic crystals, $a : b : c = 1·154 : 1 :$ β 115·5° approx.; both forms crystallise together from EtOH. C. A. S.

Minute structure of cotton fibre. K. ATSUKI and M. ISHIWARA (J. Soc. Chem. Ind. Japan, 1933, **36**, 221B).—Microscopical examination of the swollen fibre and *X*-ray analysis show that the fibrils form right and left spirals at approx. 90° in the direction

of the principal axis, whilst the micelles lie with their main axes perpendicular to the fibril axis. A. A. L.

X-Ray investigation of proteins. II. Gelatin. K. Hess and C. Trogus (Biochem. Z., 1933, **262**, 131—136; cf. this vol., 731).—The fibres of unstretched sheet gelatin (I) have a high degree of orientation, the axis of the fibres being perpendicular to the plane of the sheet. (I) resembles cellophane and like products. An explanation of the change which occurs on stretching is given, and the *X*-ray diagram of (I) is compared with those of animal products (untwisted gut, isinglass, leather). The result of purification of the materials is considered. W. McC.

X-Ray spectrum of fibrin. J. R. Katz and A. de Rooy (Rec. trav. chim., 1933, **52**, 742—746).—Fibrin is shown to have a cryst. structure. In the stretched material the polypeptide chains lie in the direction of the fibre. E. S. H.

Electrical properties of thin platinum films obtained by cathodic sputtering. A. Fery (Ann. Physique, 1933, [x], **19**, 421—507).—Pt-black was deposited by a discharge in air freed from H_2O vapour, and the variation of resistivity as a function of thickness, determined optically and gravimetrically, was investigated between 10 and 1320 mμ. A crit. thickness is indicated at 240 mμ; beyond 285 mμ the resistivity passes to that of ordinary catalytic Pt. Divergent vals. in previous data appear to be due to heating of the Pt in the course of deposition. N. M. B.

Electrical properties of thin platinum films obtained by cathodic sputtering in elementary gases. A. Fery (J. Phys. Radium, 1933, [vii], **4**, 301—315; cf. preceding abstract).—For a discharge in He, O_2, N_2, and H_2, as opposed to air, the Pt films showed no uniform resistivity, and absorbed gas during their formation. On warming to any fixed temp., their resistance diminished isothermally; for higher temp. the surfaces are blistered by the emission of the absorbed gas. N. M. B.

Absence of a permeability anomaly for iron from the wave-length region between 84 and 1300 m. G. R. Wait (Z. Physik, 1933, **83**, 786—788).—Polemical against Malov (A., 1932, 449), and reasserting the absence of this anomaly. A. B. D. C.

Magnetic quadrupole field and energy in cubic and hexagonal crystals. L. W. McKeehan (Physical Rev., 1933, [ii], **44**, 38—42; cf. this vol., 766, 767).—Mathematical. N. M. B.

Superconductivity and the Hall effect. E. H. Hall (Proc. Nat. Acad. Sci., 1933, **19**, 619—623).—Evidence pointing to the non-existence of the Hall effect in the superconductive state of metals is critically reviewed. N. M. B.

Elastic constants of Rochelle salt by a dynamical method. R. M. Davies (Phil. Mag., 1933, [vii], **16**, 97—124).—The elastic limit is a linear function of temp. from 0° to 20°, but there are discontinuities at about 23° and — 40°, corresponding with similar discontinuities observed with other physical properties. The results indicate that the substance is unsuitable for piezo-electric resonators in accurate work, but may be used where only moderate accuracy is required. A. J. M.

Effect of mechanical stress on the disruptive strength of dielectrics. A. Gemant and T. Akahira (Nature, 1933, **132**, 99—100).—The increase of disruptive strength by compression and the decrease by dilatation obtained with various substances are described. L. S. T.

Plasticity of quartz. K. Zinserling and A. Schubnikov (Z. Krist., 1933, **75**, 454—461; cf. A., 1932, 1080).—The twinning produced by pressure on various faces of a quartz crystal is described and deduced from the crystal structure. The elastic limit of quartz at 573° is about 1/15th that at room temp., but the twinning produced is similar. There are three varieties of plasticity characteristic of rock-salt, calcite, and quartz produced, respectively, by translation, twin-gliding, and with no visible displacement of the crystal particles. C. A. S.

Temperature dependence of Young's modulus for nickel. J. Zacharias (Physical Rev., 1933, [ii], **44**, 116—122).—A new method of measurement between 30° and 400° is described, and applied to single crystals and hard-drawn, polycryst. commercial Ni. For annealed specimens up to 200° the decrease is 13%, followed by an increase of approx. 6% to the Curie point, and thence a linear decrease. For hard-drawn specimens and those quenched at 1100°, the min. is absent, the decrease being continuous to the Curie point, where the temp. coeff. changes abruptly. N. M. B.

Determination of mol. wt. of compounds dissolved in liquid ammonia at room temperature. A. I. Schattenstein and A. M. Monossohn (Z. physikal. Chem., 1933, **165**, 147—153).—By means of a new type of differential manometer for the determination of v.p. of solutions in liquefied gases the mol. wts. of $CO(NH_2)_2$, fructose, quinhydrone, NH_4Cl, and NH_4NO_3 in liquid NH_3 at 10° have been determined with an estimated precision of 3%. R. C.

Theory of anomalous magnetic and thermoelectric effects in metals. D. Blochinzev and L. Nordheim (Z. Physik, 1933, **84**, 168—194).

Electrical resistance of palladium wires charged with hydrogen. II. Up to 470° and 140 kg. per sq. cm. H. Hagen and A. Sieverts (Z. physikal. Chem., 1933, **165**, 1—10).—Results previously reported (this vol., 467) have been confirmed and amplified. With increase of the H_2 pressure at a given temp. Q passes through a max., Q', then through a very flat min., Q''. The pressures corresponding with both of these rise with the temp., and Q' and Q'' could not be located, with the pressures used, above 362° and 212°, respectively. Below 270° Q'' possibly corresponds with the upper concn. limit of the β-phase. R. C.

Thermal and electrical conductivities of several metals between —183° and 100°. W. G. Kannulink (Proc. Roy. Soc., 1933, **A**, **141**, 159—168).—The electrical method previously used (cf. *ibid.*, 1931,

A, **131**, 320) to determine the thermal and electrical conductivities of a metal wire has been extended to include observations between −183° and 100°. The wires studied were pure W (in monocrystal form), Mo, Ag, and Fe. L. L. B.

Determinations with the aid of liquid helium. XXII. Resistance of metals, alloys, and compounds. W. MEISSNER, H. FRANZ, and H. WESTERHOFF (Ann. Physik, 1933, [v], **17**, 593—619).—Pure Nb becomes superconducting (I) at 9·2° abs., a temp. > that at which any other pure metal reaches that state. Pb–As alloys existing as heterogeneous mixtures become (I) at the temp. at which Pb does, if there is a continuous Pb path through the sample. Mo–C alloys with 42—58 at.-% C have the same transition point (8·5° abs.). A large no. of compounds with uniform cryst. structure (ε and γ structure), and selenides and tellurides are not (I) above 1·3° abs. A no. of arsenides and W bronzes are not (I). The superconductivity of NbO and SnO is probably due to a small amount of Nb and Sn, respectively. Some other oxides were not (I). CuS is the only sulphide which is (I). A. J. M.

Absorption coefficients of liquids for ultrasonic waves. P. BIQUARD (Compt. rend., 1933, **197**, 309—311; cf. A., 1932, 900).—An improved method of determining the coeff. of absorption of ultrasonic waves is described. Applied to 8 org. liquids, it gives results from 6 to < 100 times experimental. The coeff. seems to vary as the square of the frequency. C. A. S.

Velocity of sound in gases in tubes. G. W. C. KAYE and G. G. SHERRATT (Proc. Roy. Soc., 1933, A, **141**, 123—143).—The velocity of sound at 18° and 100° has been measured by the resonating tube method, using air, H_2, CO_2, SO_2, NH_3, and EtCl contained in glass, Cu, and C tubes of various diameters. Frequencies from 500 to 27,000 cycles per sec. were provided from a valve-oscillator circuit. For all the gases, the Helmholtz–Kirchhoff formula is quantitatively correct as regards the variation of tube velocity with radius and frequency. The formula does not, however, take account of the influence of the wall surface. In smooth tubes there is a reduction of about 10% in the theoretical val. of c, and in rough-walled tubes an increase of about 30%. L. L. B.

Thermal expansion of boron. E. DUPUY and L. HACKSPILL (Compt. rend., 1933, **197**, 229—230).—The coeff. of linear expansion of cryst. B (99·5% pure) between 20° and 750° is $8·3 \times 10^{-6}$, without any anomalies. C. A. S.

Thermal expansion of zinc by the *X*-ray method. E. A. OWEN and J. IBALL (Phil. Mag., 1933, [vii], **16**, 479—488).—The mean coeff. of linear expansion parallel and perpendicular to the hexagonal axis was measured between 20° and 400°. In this temp. range Zn is hexagonal, no allotropic modifications existing. H. J. E.

F.p. of iridium. F. HENNING and H. T. WENSEL (Bur. Stand. J. Res., 1933, **10**, 809—821).—Direct and indirect measurements of the ratio of brightness for red light of a black body immersed in freezing Ir to that of a similar black body in freezing Au led to the val. 2454° for the f.p. of Ir. N. M. B.

Method of measuring the specific heats of poor conductors. W. G. MARLEY (Proc. Physical Soc., 1933, **45**, 591—601).—An improved form of the method of cooling is described and results for various substances are given. N. M. B.

Empirical molecular heat equations from spectroscopic data. W. D. M. BRYANT (Ind. Eng. Chem., 1933, **25**, 820—823).—The mol. heats of 18 gases and vapours, calc. from spectroscopic vibration frequencies, agree closely with experimental vals. A group of 16 empirical second-power equations has been derived to fit the theoretical mol. heat curves from 300° to 2000° abs. The deviation is generally < 3%. E. S. H.

Rotational specific heat of a polyatomic molecule for high temperatures. (MISS) E. VINEY (Proc. Camb. Phil. Soc., 1933, **29**, 407).—A correction (cf. this vol., 206). N. M. B.

Some properties of pure H^2H^2O. G. N. LEWIS and R. T. MACDONALD (J. Amer. Chem. Soc., 1933, **55**, 3057—3059).—H_2O containing 99·99% of H^2H^2O, m.p. 3·8°, b.p. 101·42°/760 mm., d^{25} 1·1056, has been prepared. The temp. of max. d is 11·6° (approx.). V.-p. data are recorded. J. G. A. G.

Isopycnals of liquid helium. W. H. KEESOM and (MISS) A. P. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 482—487).—Isopycnals of liquid He have been measured between the saturated v.p. and 25 atm. and between 1·15° and 4·2° abs. The isopycnals comprise two branches which correspond with He II and He I, respectively, and which meet the λ-curve acutely, *i.e.*, $(\partial p/\partial T)_v$ is discontinuous at this point. As $(\partial p/\partial T)_v$ for liquid He II is negative over the whole region investigated, isentropic as well as isenthalpic expansion is associated with a rise of temp. The phenomenon of the existence of a temp. of max. density is more evident the higher is the pressure. J. W. S.

Comparison of the densities of carbon monoxide and oxygen and the at. wt. of carbon. M. WOODHEAD and R. WHYTLAW-GRAY (J.C.S., 1933, 846—854).—The relative densities of O_2 and CO have been measured by the buoyancy balance method (A., 1931, 890). It is concluded that 12·011 is a close approximation to the at. wt. of C on the chemical scale, vals. accepted hitherto being too low. This indicates that the proportion of C^{13} is 1%. These results are in accord with recent observations. J. W. S.

Vapour pressures of fumigants. V. αβ-Propylene dichloride. O. A. NELSON and H. D. YOUNG (J. Amer. Chem. Soc., 1933, **55**, 2429—2431).—The v.p. in the range 15—100° is given by $\log P_{mm} = 7·7086 - 1782·8/T$ (b.p. 96·4°/760 mm., and d^{20} 1·1545). J. G. A. G.

Thermal properties of halides. VII. Formation of polymerised molecules by halide vapours. W. FISCHER. **VIII. Gas densities of BF_3, SiF_4, and GeF_4 at room temperature and near the b.p.** W. FISCHER and W. WEIDEMANN (Z. anorg. Chem., 1933, **213**, 97—105, 106—114; cf. this

vol., 560).—VII. Polymerised mol. formation is correlated with mol. structure, the valency and electron structure of the cation, and with the lattice type of the solid halide.

VIII. Vals. at 20°, at −34° (for GeF_4), and at −75° (for BF_3 and SiF_4) are recorded. Double mol. formation was not observed. The densities of liquid BF_3 and GeF_4 were measured. H. J. E.

Vapour–liquid equilibria of hydrocarbons at high pressures. W. K. Lewis and C. D. Luke (Ind. Eng. Chem., 1933, **25**, 725—727).—Curves for the correction factor, μ, to the gas laws, applicable to hydrocarbons above C_3, are modified in minor details, and corresponding corrections have been made on the fugacity chart. A method of determining the volatility of high-b.p. hydrocarbons at high pressures is based on the volatility of C_6H_6 in N_2 at similar pressures. The correction factor for the internal energy of hydrocarbon vapours at low vapour vols. has been determined by graphical integration from the isometrics of those hydrocarbons for which data are available. The resulting corrections are relatively independent of the temp. C. E. M.

Entropy in intermediate phases. A. Olander (Z. physikal. Chem., 1933, **165**, 65—78).—Theoretical. By comparison of the val. of the partial molal entropy of constituents of an intermediate phase, derived theoretically, with the val. deduced from data for temp. coeff. of e.m.f. it is possible to decide whether the lattice structure of the phase is ordered or not, and if it is ordered to determine the no. of "misplaced" atoms. Existing data are analysed in this way. R. C.

Van der Waals equation. H. M. Martin (Engineering, 1933, **136**, 1—2).—A criticism. The mol. forces are not gravitational, but are due to residual affinity. C. W. G.

Calculation of the second virial coefficient of gases. T. S. Wheeler (Indian J. Physics, 1933, **7**, 595—601).—Mathematical. J. W. S.

Hydrodynamics and kinetic theory of gases: theory of surface tension. Y. Rocard (Compt. rend., 1933, **197**, 122—124; cf. this vol., 113, 503).—The formula deduced is $H-7{\cdot}32\sqrt{\lambda\sigma(\rho_1-\rho_2)P_c(T_c-1{\cdot}03T)}/\rho_cT_c$, where H is the surface tension, λ a numerical factor but little >1, σ the diam. of the mol., ρ_1, ρ_2 the density of the liquid and gas, T_c, ρ_c the critical temp. and density, respectively, and T a temp. not far removed from T_c. It applies accurately to substances with at most a weak dipole and approx. spherical mols., *e.g.*, Hg, O_2, Cl_2, C_6H_6, but shows differences up to 40% for elongated mols., or such as have a strong permanent dipole, *e.g.*, H_2O, alcohols. C. A. S.

Ellipsoidal viscosity distribution. W. S. Kimball (Phil. Mag., 1933, [vii], **16**, 1—49).—Mathematical. A. J. M.

Measurement of the viscosity of a molten metal by means of an oscillating disc. V. H. Stott (Proc. Physical Soc., 1933, **45**, 530—544).—The theory, corrections, and application to molten Sn of the method using a disc of Al_2O_3 are described. N. M. B.

Structure viscosity of dilute amalgams. R. Kohler (Kolloid-Z., 1933, **64**, 200—205).—Structure viscosity has been observed in 0·3% Cu amalgam and in 0·5 and 1% Ag amalgams; the viscosity of the latter decreases with time. The results support the view that dil. amalgams are colloidally disperse systems. E. S. H.

***X*-Ray investigations of the gold–rhodium and silver–rhodium alloys.** R. W. Drier and H. L. Walker (Phil. Mag., 1933, [vii], **16**, 294—298).—The Au–Rh system shows two series of solutions. The contraction of the Au lattice and the expansion of the Rh lattice correspond with a solubility of Rh in Au of 4·1—8·9 at.-%, and a solubility of Au in Rh of 1·1—2·5 at.-%. Solubility of Ag in Rh, or vice versa, could not be detected, but theory suggests that they should be slightly sol. in one another. J. W. S.

***X*-Ray study on electrolytic nickel–iron alloys.** K. Iwase and N. Nasu (Sci. Rep. Tohoku, 1933, **22**, 328—337).—Fe–Ni alloys deposited from acid solutions of the mixed sulphates consist of solid solutions —pure α with up to 14% Ni, $\alpha+\gamma$ with 14—58% Ni, and pure γ with >58% Ni in the deposit. A. R. P.

Hall effect and other physical constants of alloys. I. Lead–bismuth alloys. W. R. Thomas and E. J. Evans (Phil. Mag., 1933, [vii], **16**, 329—353; cf. A., 1932, 330).—The electrical resistivities, temp. coeffs. of resistance, thermoelectric powers, densities, and Hall coeffs. have been measured, and the variation of these properties with composition is discussed. H. J. E.

Alloys of platinum with cobalt. V. A. Nemilov (Z. anorg. Chem., 1933, **213**, 283—291).—The system forms a continuous series of solid solutions with a minimum in the liquidus at 1468° and 25 at.-% Pt. The Brinell hardness curve of annealed alloys has maxima at 11·61 at.-% Pt (149) and 50·65 at.-% Pt (195) and a min. at 20·55 at.-% Pt (105); the hardness of alloys quenched from 1200° rises linearly from 111 with 5·15 at.-% Pt to 148 with 40·9 at.-% Pt. These differences are ascribed to a transformation in the nature of the solid solution and are accompanied by changes in the microstructure, the large polygonal grains of the high-temp. solid solution breaking up into smaller crystals on annealing at 900°. A. R. P.

Magnetostriction of nickel–cobalt alloys. Y. Masiyama (Sci. Rep. Tohoku, 1933, **22**, 338—353).—Alloys with 0—30% Co undergo a longitudinal contraction in a magnetic field which reaches a max. at about 200 gauss and is the less the higher is the Co content. Alloys with >30% Co contract in low-strength fields and then expand in stronger fields, the initial contraction being smaller and the secondary expansion greater the higher is the Co content; with 40—70% Co the secondary expansion exceeds the initial contraction in fields of >400 gauss. The transverse effect of magnetostriction is the converse of the longitudinal effect, and the vol. effect is the difference of these two effects, being an expansion in alloys with <75% Co and a contraction in alloys with >75% Co. A. R. P.

Ferrosilicons. H. DELOMENIE (Compt. rend., 1933, **197**, 249—252).—Comparison of Si–Fe alloys prepared from pure materials in a ZrO_2 crucible (I) with the industrial product (II) shows that SiFe in (I) occurs in dendrites or granulations, but in (II) in large cryst. masses, due to slower cooling. As the % of Si increases, SiFe disappears and the alloy becomes eutectiform, resembling pearlite. At 50·14—53·5% Si the structure is that of a pure compound ($FeSi_2$) or a solid solution of Si therein, crystals of Si appearing above 54·5% Si. Alloys (I) containing 50% Si do not, as the same alloys (II), crumble in moist air, nor do they do so with small additions of either P or Al, but do so rapidly with evolution of PH_3 if both (0·03—0·04% P and 2—3° Al) are present. C. A. S.

Transformation of solid metallic phases. V. Calculation of kinetic curves for the system Au–Cu. U. DEHLINGER (Z. Physik, 1933, **83**, 832—842).—The kinetic differential equation previously deduced (cf. A., 1932, 454) is integrated for the case of transition from disordered to ordered AuCu and $AuCu_3$. A. B. D. C.

M.p. of some binary and ternary copper-rich alloys containing phosphorus. W. E. LINDLIEF (Met. and Alloys, 1933, **4**, 85—88).—In the Cu–P system the eutectic occurs at 8·38% P and 714° and the liquidus of hypoeutectic alloys falls in a smooth curve very slightly concave to the composition axis. The eutectic temp. is raised by addition of 1% Si to 725°. In the Cu–Zn–P system a ternary eutectic is formed at 690° and 32·5% Zn and consists of α-solid solution, Cu_3P, and a Zn-rich phosphide of unknown composition. Tables and diagrams of the m.p. in the Cu–Zn–P and Cu–Si–P system are included. A. R. P.

Equilibrium diagram of copper–tin–phosphorus alloys. J. VERO (Z. anorg. Chem., 1933, **213**, 257—272).—The ternary system has been examined by thermal methods up to 20% Sn and 8·5% P; diagrams are given for const. P contents of 1, 2, and 3% and for const. Sn contents of 5, 10, 15, and 20%. With up to 5% Sn and 7% P the system is eutectiferous, the α-Cu_3P eutectic at 5% Sn containing about 6·5% P and melting at about 690°. With higher Sn contents a secondary peritectic reaction α+liq.$\rightleftharpoons$β is followed by the four-phase reaction α+liq.$\rightleftharpoons$β+Cu_3P at 637°; no evidence of the formation of a ternary eutectic has been found. The solid alloys contain, besides the usual Cu–Sn phases, only the Cu_3P phase, and the various transformation temp. in the Cu–Sn system remain unchanged on addition of P. On annealing eutectiferous alloys just below the eutectic temp., the Cu_3P constituent of the eutectic segregates as spheroidal particles evenly disseminated in the α-matrix. A. R. P.

Carbides of low tungsten and molybdenum steels. F. R. MORRAL, G. PHRAGMEN, and A. WESTGREN (Nature, 1933, **132**, 61—62).—*X*-Ray analysis of residues obtained from W magnet steels confirms the presence of WC and Fe_3W_3C (A., 1930, 1503) and reveals that of a third *carbide* (I), probably Fe_4C (with a small amount of Fe replaced by W), lattice parameter 10·51 Å. (I) is also present in small amounts in high-speed steels, whilst in Fe–W–C alloys (II) low in W (2%) it appears to be the only carbide present. In (II) containing 1·5% W, (I) is mixed with cementite. It also occurs in low-Mo steels. A more correct formula is probably $(Fe,W)_4C$ or $(Fe,Mo)_4C$. L. S. T.

***X*-Ray studies of very complex mixtures of long-chain compounds.** E. OTT and D. A. WILSON (Science, 1933, **78**, 16—17; cf. this vol., 342).—In general, long-chain compounds of varied length and type form solid solutions. This is the case with mixtures of the normal C_{10}—C_{18}, the C_{13}—C_{18} alcohols, and the normal paraffins C_{19}, C_{21}, C_{32}, and C_{36} and other substances. L. S. T.

Ternary azeotropic mixtures. II. The heteroazeotrope: acetone–water–carbon disulphide. W. SWIENTOSŁAWSKI and L. WAJCENBLIT (Rocz. Chem., 1933, **13**, 318—321).—The heteroazeotrope, b.p. 38·042°, contains CS_2 75·21, COMe$_2$ 23·98, and H_2O 0·81%. R. T.

Curve passing through azeo- and heteroazeotropic points. T. BYLEWSKI (Rocz. Chem., 1933, **13**, 322—333).—The composition of two-phase binary liquid mixtures can be determined with a mean error of $\geqslant$0·01% by Swientosławski's ebullioscopic method. The composition of the vapour phase of the system $Bu^{\beta}OH$–H_2O at the b.p. under various pressures has been determined. The curve connecting azeo- and heteroazeo-tropic points of this system has a break at the point of intersection with the miscibility curve. R. T.

Variations in composition of binary azeotropic mixtures with change in temperature. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1933, **13**, 334—339).—In the case of binary azeotropic mixtures of an associated (I) and unassociated liquid, the content of (I) increases with rise of temp., whilst where both are associated the content of the more associated one increases. This rule does not apply to mixtures of H_2O and alcohols. R. T.

Coefficient of volatility of hydrogen chloride in ether. T. MOUNAJED (Compt. rend., 1933, **197**, 324; cf. this vol., 784).—The coeff. of volatility (cf. this vol., 16) of HCl in Et_2O has been determined for concn. 0·32—7·07*M*; it increases at first slowly, then rapidly, and then again slowly, which seems to support the theory of complex formation. C. A. S.

Vapour pressure of low-boiling paraffin hydrocarbons in absorber oil. G. L. MATHESON and L. W. T. CUMMINGS (Ind. Eng. Chem., 1933, **25**, 723—725).—A modified Calingaert–Hitchcock apparatus (A., 1927, 417) for determining vapour–liquid equilibria is described. All the low-boiling paraffins show a positive deviation from Raoult's law. The pressure deviations of the normal paraffins are found to be approx. the same at a given molal concn. and temp. C. E. M.

High-pressure rectification. II. *n*-Pentane–*n*-heptane system. L. W. T. CUMMINGS, F. W. STONES, and M. A. VOLANTE (Ind. Eng. Chem., 1933, **25**, 728—732).—V.-p. data for the mixtures are recorded and their application to high-pressure rectification is pointed out. C. E. M.

Vapour–liquid equilibria for *n*-hexane–benzene mixtures. C. O. TONGBERG and F. JOHNSTON (Ind. Eng. Chem., 1933, **25**, 733—735; cf. B., 1932, 826).—Pure *n*-C_6H_{14} has been obtained from petroleum by distillation and removal of C_6H_6 by nitration or by distillation with Bu$^{\gamma}$OH. The two hydrocarbons do not form a const.-boiling mixture; enrichment of the vapour practically ceases at concns. $< 3{\cdot}5$ mols.-% C_6H_6. C. E. M.

Streaming double refraction of critical liquid mixtures. WO. OSTWALD and H. ERBRING (Kolloid-Z., 1933, **64**, 229—232).—Streaming double refraction has been observed in crit. liquid mixtures of (*a*) hexane–MeOH, (*b*) CS_2–MeOH, and (*c*) $PhNO_2$–hexane. The effect is traced to deformation during the flow of drops which have low interfacial tension. E. S. H.

Miscibility of aromatic halogen compounds in solid state. L. KLEMM, W. KLEMM, and G. SCHIEMANN (Z. physikal. Chem., 1933, **165**, 379—390).—Thermal diagrams for binary mixtures of hydrocarbons and their mono-chloro-, -bromo-, and -fluoro-compounds in several aromatic series have been determined in order to obtain information relative to the miscibilities in the solid state. Whilst in some cases the substitution products are all completely miscible with each other and with the parent hydrocarbon, the miscibility is sometimes only partial, and is markedly affected by the position of the halogen. According to the miscibility relations, there is less similarity between the hydrocarbon and its F-compound, and between the F- and Cl-compounds, than between the Cl- and Br-compounds, but the F-compounds appear to be typical halogen compounds in the series. R. C.

Solubility of lime in water and specific conductivities of its saturated solutions. A. D. GRIEVE, G. W. GURD, and O. MAASS (Canad. J. Res., 1933, **8**, 577—582).—Conductivity data (0—130°) and solubility data (determined conductimetrically) (0—25°) are recorded. The dissociation const. at various temp. is deduced. D. R. D.

Ammonium sulphite. I. Solubility and transition point. II. Equilibrium in the system ammonium sulphite–ammonium sulphate–water. III. Equilibrium in the system SO_2–NH_3–H_2O. IV. Heat of dissolution of ammonium sulphite and hydrogen sulphite. F. ISHIKAWA and T. MUROOKA. F. ISHIKAWA and H. HAGISAWA. F. ISHIKAWA and T. MUROOKA (Sci. Rep. Tôhoku, 1933, **22**, 201—219, 220—234, 235—243, 244—248).—I. The solubility of $(NH_4)_2SO_3$ rises from 38·21 g. per 100 c.c. of solution at 0° to 74·88 g. at the transition point (80·8°±0·2); below this the monohydrate is stable and above, the anhyd. salt. The cryohydric point is −12·96° (28·85 g. per 100 c.c.)

II. The solubility of $(NH_4)_2SO_4$ is $41{\cdot}22+0{\cdot}09t$ g. per 100 c.c. at $t°$; the salt forms no double salt or solid solution with $(NH_4)_2SO_3$. The composition of solutions in the univariant system $(NH_4)_2SO_4$–$(NH_4)_2SO_3$–H_2O has been determined between −21·5° (cryohydric point) and 100°.

III. The solubility of $(NH_4)_2SO_3$ in aq. NH_3 at 25° is given by $C_1=39{\cdot}45-1{\cdot}346C_2$, where C_1 and C_2 represent g. $(NH_4)_2SO_3$ and NH_3 per 100 c.c. In solutions containing an excess of SO_2 the solid phase is $(NH_4)_2S_2O_5$ and not NH_4HSO_3.

IV. The heat of dissolution of $(NH_4)_2SO_3,H_2O$ is 4·66 and of $(NH_4)_2S_2O_5$ 5·84 kg.-cal. per mol. A. R. P.

Hydrates of cerium sulphate and the inverse fusion points. N. H. J. M. VOOGD (Rec. trav. chim., 1933, **52**, 768—793).—The solubilities in H_2O of $Ce_2(SO_4)_3,8H_2O$ and $Ce_2(SO_4)_3,9H_2O$ between 0° and 45° have been determined. Koppel's observation (A., 1904, ii, 819), that the range of stability of the octahydrate is lower than that of the nonahydrate, is confirmed. E. S. H.

Solubilities of weak acids in salts of weak acids at very high concentrations. S. S. DOOSAJ and W. V. BHAGWAT (J. Indian Chem. Soc., 1933, **10**, 225—232).—The solubilities of benzoic, salicylic, cinnamic, and succinic acids in Na formate, acetate, salicylate, citrate, benzoate, and chloride have been determined over a wide range of concn. The solubility of the acid generally increases with its strength, but is influenced also by the basicity. E. S. H.

Solubility of calcium oxalate in salt solutions. K. L. MALJAROV and A. J. GLUSCHAKOV (Z. anal. Chem., 1933, **93**, 265—268).—Data for 0·3%—10% NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, NaCl, $MgCl_2$, and $MgSO_4$ solutions are recorded. H. J. E.

Solubility of thiocarbamide in water, methyl alcohol, and ethyl alcohol. L. SHNIDMAN (J. Physical Chem., 1933, **37**, 693—700).—Vals. are given for the interval 15—80° (H_2O) and 20—70° (MeOH and EtOH). F. L. U.

Hydrotropy. S. FORSSMAN (Biochem. Z., 1933, **263**, 135—143; cf. von Brücke, A., 1932, 1288).—The solubilities (at 16—18° and 100°) of *iso*amyl and octyl alcohols, citronellol (I), *cyclo*hexanol, PhMe, $CH_2Ph{\cdot}OH$, $PhNO_2$, NH_2Ph, $NHPh{\cdot}NH_2$, cinnamaldehyde, quinoline, borneol (II), *dl*-fenchyl alcohol, cholesterol, caseinogen, quinine, cinchonine, brucine, gelatin, and human blood-serum in aq. solutions of KPh_2 and K di-*o*-, *m*-, and *p*-tolyl phosphate have been examined. As regards dissolving power the isomerides form the series $o>m>p$. With (I) but not with (II) changes in $[\alpha]$ indicate the formation of loose additive compounds. W. McC.

Crystallisation. A. SCHWEIZER (Rec. trav. chim., 1933, **52**, 678—700).—Supersaturated solutions of sucrose or tartaric acid cannot be made to crystallise except by inoculating with crystals or crystal nuclei. *d*-Mannitol, pyrogallol, quinol, resorcinol, and pyrocatechol form unstable supersaturated solutions, which crystallise with time. The viscosity of the solution has a considerable influence. Crystallisation nuclei are considered as dissolved mol. complexes, arranged according to the crystal lattice. E. S. H.

Coprecipitation. VI. Internal structural changes on ageing of freshly prepared precipitates. I. M. KOLTHOFF and E. B. SANDELL (J. Physical Chem., 1933, **37**, 723—733; cf. this vol., 564).—Crystals of $KClO_4$ immersed in a saturated solution of $KClO_4$ in 0·1*N*-$KMnO_4$ become coloured

internally owing to penetration of $KMnO_4$ into submicroscopic cracks and faults in the crystals. Crystals of freshly pptd. CaC_2O_4 or $BaSO_4$ exhibit similar imperfections, in consequence of which the former has been shown to take up KIO_3 and the latter $KMnO_4$. Impurities thus occluded tend to escape by effusion on ageing, but are frequently retained by external blocking of the faults by lattice material. Impure crystals blocked in this way can be purified only by slow recrystallisation by way of the solution. Cryst. ppts. prepared at 100° are more homogeneous than those prepared at room temp. F. L. U.

Theory of Liesegang precipitates. H. BAUER (Kolloid-Z., 1933, 64, 181—184).—A mathematical treatment of the supersaturation theory. E. S. H.

Periodic Liesegang precipitation in non-colloidal media. R. FRICKE, J. LUKE, and K. MEYRING (Z. Elektrochem., 1933, 39, 629—641).—By diffusion of HNO_3 into aq. $Ba(NO_3)_2$ in a capillary a periodic pptn. of $Ba(NO_3)_2$ was obtained. The capillary was then cut into sections 0·6—0·9 cm. long, and micro-determinations of Ba and HNO_3 were made for each. Beyond the last $Ba(NO_3)_2$ ppt. the liquid was supersaturated with respect to $Ba(NO_3)_2$, a new crystal zone forming when a max. supersaturation was exceeded. The effect of ageing on the concn. distribution was studied. Results are discussed in terms of the diffusion of $Ba^{\cdot\cdot}$ and HNO_3. H. J. E.

Distribution of methylamine between water and chloroform and existence of methylamine complexes of the metal-ammine type. W. A. FELSING and S. E. BUCKLEY (J. Physical Chem., 1933, 37, 779—786).—The distribution ratio of NH_2Me between H_2O and $CHCl_3$ decreases with increasing concn., but is const. for very dil. solutions. A complex of the ammine type is formed with $Cu^{\cdot\cdot}$, the ratio $NH_2Me/Cu^{\cdot\cdot}$ approaching 6 as a max. F. L. U.

Experimental evidence for activated adsorption of hydrogen by charcoal. R. BURSTEIN, A. FRUMKIN, and N. FEDOTOV (J. Amer. Chem. Soc., 1933, 55, 3052—3053).—H_2 adsorbed at 20—100° by activated C does not exchange with $Na^{\cdot}$, whereas H adsorbed in the temp. region of activated adsorption (300—800°) is readily replaced by $Na^{\cdot}$ from NaOH at room temp. In the latter case, if the quantity of adsorbed H is small, the whole is quantitatively exchanged, whereas only part is exchanged if the quantities are larger. Thus, the H adsorbed at high temp. remains on the C surface (probably in an at. form) and does not diffuse into the interior of the solid. J. G. A. G.

Activated adsorption. L. J. BURRAGE (Trans. Faraday Soc., 1933, 29, 677—678).—The experimental basis of the theory is not upheld by recent work. J. S. A.

Adsorption of nitrogen by carbon at high pressures. A. VON ANTROPOFF [with F. STEINBERG] (Z. Elektrochem., 1933, 39, 616).—The adsorption isotherms have been studied from —160° to 150° and up to pressures of 200 kg. per sq. cm. At the higher pressures and lower temp. approx. saturation was observed. Results are represented by the Langmuir formula. H. J. E.

Adsorption. II. Comparison of the isothermals of carbon tetrachloride and carbon disulphide on charcoal. L. J. BURRAGE (Trans. Faraday Soc., 1933, 29, 673—676).—The isotherms for CS_2 and CCl_4 vapours at 25° have been compared with special reference to the displacement of tenaciously held O_2. Contrary to previous results (this vol., 457), CS_2 appears to be less effective than CCl_4 in breaking up the C_xO_y complex. CS_2 appears, like CO_2, to be attached quasichemically to the C_xO_y complex. J. S. A.

Chemisorption on charcoal. I. Acid constituent of charcoal. A. KING (J.C.S., 1933, 842—846).—When pure charcoal is exposed to air or O_2 and then extracted with H_2O, traces of $H_2C_2O_4$ are found in solution. When the O_2 is removed by heating in vac. at 850° and is replaced by N_2, CO_2, or N_2O no $H_2C_2O_4$ is formed, but when replaced by NO a trace is produced. When C exposed to air is shaken with dil. H_2SO_4 and the filtrate added to starch–KI solution a blue colour is produced. The results are interpreted on the supposition that a "peroxide" is formed on the surface of the C (cf. A., 1931, 316) which decomposes on heating into CO_2 and CO, under the action of H_2O into $H_2C_2O_4$, and on treatment with H_2SO_4 producing H_2O_2. J. W. S.

Adsorption and reduction processes on active charcoal. H. LENNIG (Kolloid-Z., 1933, 64, 143—153).—Experiments with Hg^{II} salts, Fe^{III} salts, $Na_2Cr_2O_7$, and $K_2Cr_2O_7$ are described. Adsorption and reduction are parallel. Increase in the concn. of the salt increases the amount of reduced metal after adsorption is complete. The abs. increase of metal adsorbed by the C diminishes the amount of reduced metal in the solution. Max. reduction is obtained at a definite adsorption val., which is sp. for the metal and independent of the nature of the anion. De-gassed C adsorbs salts of $Hg^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ more strongly than does ordinary C; no difference is observed with NaOH, but de-gassed C adsorbs HCl less strongly. E. S. H.

Specific heat of sorbed matter. J. L. PORTER and R. C. SWAIN (J. Amer. Chem. Soc., 1933, 55, 2792—2794).—The sp. heat of H_2O adsorbed by highly activated sugar C is nearly unity and therefore the H_2O is essentially in the ordinary liquid state (cf. this vol., 773). On the other hand, the heat capacities of H_2 and A adsorbed on C at $< 90°$ abs. are considerably $<$ those of H_2 and A in the free state. The distinction between the physical adsorption of the gases and the persorption of the H_2O is emphasised. J. G. A. G.

Evolution of gas from worked metals. O. WERNER (Z. Elektrochem., 1933, 39, 611—616).—The emanation from Ba–Zn alloys containing Th-*X* was removed by a CO_2 stream and measured electroscopically. Changes in the alloy on heat treatment, working, and recrystallisation were correlated with changes in the rate of escape of emanation. H. J. E.

Detection of adsorbed gas films on heated filaments. G. VAN PRAAGH (J.C.S., 1933, 798—800).—The presence of an adsorbed monat. film of I does not affect the emissivity of a Pt filament, but

increases the accommodation coeff. This method has been used to show that when Pt is heated in I vapour at 0·027 mm. an adsorbed film is formed below 1565° abs., but not above 1635° abs. This result is in agreement with kinetic measurements. J. W. S.

Adsorption of gases at virgin salt surfaces. F. DURAU and A. HORN (Naturwiss., 1933, **21**, 528).—A virgin salt surface can be prepared by evaporating a solution of the salt in vac., melting the product, and powdering it. A virgin surface of $CdCl_2$ has been used in the study of the adsorption of N_2. A. J. M.

Sorption of water vapour by mineral salts. K. V. FLEROV and O. I. GRUNBERG (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 183—190).—A classification of mineral salts, based on the nature of the process of H_2O absorption, is suggested. A. M.

Adsorption of iodine by potassium iodide. B. WHIPP (Proc. Roy. Soc., 1933, **A**, **141**, 217—232).—Evidence is presented for the existence of a bimol. layer of I on KI crystals at saturation pressure. An isotherm is suggested which fits the experimental results over the whole pressure range. This expression contains only the two consts. of Langmuir involving the extent of the adsorbing surface and the rate of evaporation of the mols. in the adsorbed phase. The surface mols. in the bimol. film have properties similar to those in the surface of crystals of pure I. The existence of KI_3 as a separate phase has been disproved. L. L. B.

Adsorption of oxides of nitrogen on silica gel. V. N. SCHULTZ, E. M. SCHTEIFON, and A. M. KUBAREVA [with J. V. KORZINKINA] (J. Chem. Ind. Russ., 1933, No. 3, 10—14).—The velocity of adsorption of NO_2 increases with rise of temp. Desorption of NO_2 is practically complete at 150°. Gel saturated with NO_2 can adsorb considerable quantities of H_2O. R. T.

Adsorption of thorium-*B* and -*C* from solution. I. J. F. KING and A. ROMER (J. Physical Chem., 1933, **37**, 663—673).—Technique of the measurements is described. Glass selectively adsorbs Th-*C* to an extent depending on the acidity. F. L. U.

Photographic method of study of phenomena of adsorption of radioactive elements. H. HERSZFINKIEL and M. BIRENBAUM (Rocz. Chem., 1933, **13**, 306—317).—A drop of AgCl, AgBr, $BaSO_4$, or SiO_2 hydrosol is placed on a cover-glass, and exposed to a Pt wire activated in radon. After the colloid has coagulated, the drop is covered with a thin sheet of mica, without displacing the centrally situated coagulate, and a photographic plate is exposed to the action of the system through the mica. The photographs obtained after 15 min. exposure indicate that Ra-*B* and -*C* are partly in solution and partly in adsorption; both mol. dispersion and aggregate formation are observed in each phase. After 45 min. the solution no longer exhibits activity, which is distributed uniformly in the coagulate. R. T.

Adsorption by charcoal of phenols and polyalcohols from aqueous solution. R. AMIOT (Compt. rend., 1933, **197**, 325—327).—Data for glycerol, erythritol, mannitol, sucrose, PhOH, *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}OH$, guaiacol, pyrocatechol, resorcinol, and orcinol are reproduced by an equation of the form $y=ax^n/(1+bx^n)$. C. A. S.

Adsorbent properties and specific surface of lead sulphate. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1933, **55**, 2656—2664; cf. this vol., 346).—The solubility and sp. surface of $PbSO_4$ in H_2O, dil. $Pb(NO_3)_2$, and dil. Na_2SO_4 have been determined. The data indicate that if any adsorption of $Pb^{"}$ and SO_4'' occurs, it is limited to the corners and edges of the crystals. J. G. A. G.

Adsorption of ponceau-4R (new-coccine) and methylene-blue by lead sulphate and the influence of adsorbed ponceau on the speed of kinetic exchange. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1933, **55**, 2664—2672; cf. this vol., 346).—The adsorption of methylene-blue by a suspension of $PbSO_4$ is much $<$ that of ponceau-4R, of which approx. 1 ponceau ion is adsorbed from a saturated solution per 6 mols. of $PbSO_4$ at the crystal surface. The adsorption of ponceau increases in the presence of excess of $Pb(NO_3)_2$ and decreases with excess of SO_4'' in the solution. These and other results are interpreted on the basis of a reversible exchange adsorption between ponceau ions and SO_4'' at the surface of the crystal lattice. Adsorbed ponceau ions retard the kinetic exchange of Th-*B* at the H_2O–$PbSO_4$ interface. J. G. A. G.

Adsorptive properties of Armenian volcanic rocks. S. M. VELLER and A. C. ARUTUNIAN (J. Appl. Chem. Russ., 1933, **6**, 571—573).—The decolorising properties of Armenian kieselguhrs and pumices have been determined. R. T.

Quantitative relationships in the phenomena of exchange adsorption. A. I. RABINERSON (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 151—182).—The data for Na- and H-kaolins, a solonetz, and a permutite show that the adsorption of Ca and Ba can be expressed by $x=km^{1/n}$, where x=quantity of ions adsorbed, m=wt. of adsorbent, and k and n are consts.; the equation is valid over a wide range. The anomalous rise in the curve x/m against m shown by the adsorption of $BaCl_2$ in the Na-kaolin is not observed with H-kaolin. The relation between adsorption and dilution is expressed by $x=kv^{1/n}$, where v=vol. A. M.

Photo-effect and adsorption at the water–air boundary. H. CASSEL (Z. Elektrochem., 1933, **39**, 571—572; cf. Zimmermann, A., 1926, 886).—The surface tension and photo-effect for aq. Et_2 dihydrocollidinedicarboxylate and for a film of NPh_3 on H_2O have been measured. The photo-effect is not due to the formation of a solid surface film. H. J. E.

Adsorption of sodium linoleate in preference to that of sodium oleate on the surface of nickel and copper. B. S. SRIKANTAU (J. Indian Chem. Soc., 1933, **10**, 233—235).—Preliminary results show that at concns. $>0{\cdot}2\%$ Na linoleate is adsorbed preferentially, suggesting that the adsorbed mols. lie horizontally, attached by the double linking. E. S. H.

Surface tension of mercury and water in contact with saturated vapours of organic liquids [at 25°]. F. E. BARTELL, L. O. CASE, and H. BROWN

(J. Amer. Chem. Soc., 1933, **55**, 2769—2776; cf. this vol., 775).—The surface tension (drop wt.) of Hg in contact with the saturated vapours of eleven org. liquids, the interfacial tension (capillary rise) of H_2O in contact with six org. liquids, and the surface tension of H_2O saturated with the org. liquids in contact with the saturated vapours have been determined. The deviations from previously accepted vals. are discussed. The data show that, contrary to the conclusions of others, when a film is spontaneously formed on the surface of a liquid (*e.g.*, Hg, H_2O) the sum of the interfacial tension of the liquid against the film liquid plus the surface tension of the film liquid is equal to the surface tension of the liquid supporting the film at saturation v.p. J. G. A. G.

Action of light on the surface tension of soap solutions. L. D. MAHAJAN (Nature, 1933, **132**, 67).—Light decreases the surface tension of soap solutions by an amount which varies with the type of soap and with concn. The effect is not confined to Boys' soap solutions. L. S. T.

Solvation of molecules and equation of state of adsorption film. S. E. BRESLER, J. B. CHARITON, B. A. TALMUD, and D. L. TALMUD (Z. physikal. Chem., 1933, **165**, 195—208).—Compression curves for films of cetyl alcohol and oleic acid on aq. solutions of glucose and Na and K salts have been obtained. All these solutes increase the surface pressure, and the order of effectiveness of either anions or cations is a lyotropic series. The effect of the sol. substance thus depends on its dehydrating action, which presumably influences the electrostatic interaction between polar groups in the surface film (cf. this vol., 674). A theoretical investigation of the effect of the dehydration of polar mols. on the equation of state of a surface film supports this interpretation. R. C.

Comparison of equation of state of unimolecular films with experiment. J. GUASTALLA (Compt. rend., 1933, **197**, 307—308).—The proposed equation of state (cf. this vol., 668) shows fair agreement with that obtained experimentally for oleic acid on 0·01*N*-HCl. The coeffs. seem to depend on the electric moment. C. A. S.

Strength of emulsifier films at liquid–liquid interfaces. J. A. SERRALLACH, G. JONES, and R. J. OWEN (Ind. Eng. Chem., 1933, **25**, 816—819; cf. A., 1931, 1229).—A modified du Noüy tensiometer has been adapted to determine the strength of coherent films at the interface between emulsifier solutions and various oils. Data are given for olive oil, cod-liver oil, castor oil, and mineral oil with several emulsifiers. The strength of the film varies with time in a way which is sp. for each system. The efficiency of an emulsifier does not appear to depend primarily on the strength of the films which are formed; the main factors are probably the preliminary lowering of interfacial tension and the rapidity of film formation. E. S. H.

Hydroxyl group and soap film structure. W. J. GREEN (Nature, 1933, **131**, 872).—NH_4 oleate (9%) is quickly changed to a thick but clear gel by small amounts of glycol, *cyclo*hexanol, propenol, and EtOH; further quantities of these alcohols produce a limpid, clear liquid. The resulting solutions, especially on dilution, give lasting films which thin to the "black" state through several grades. The reaction suggests that soap mol. aggregates are formed by means of OH groups rather than as ordinary hydrates, and indicates a mechanism by which layers of mols. are rooted in a H_2O surface, or linked in a stable soap film. L. S. T.

Wettability of insoluble substances and power of attraction at interface of immiscible liquids. H. DEVAUX (Compt. rend., 1933, **197**, 105—108).—For most insol. substances, and especially elementary substances, wettability is imperfect; hence such substances tend to accumulate at the surface of separation of two immiscible liquids, this being a region of specially powerful attraction. It may be exerted on a substance dissolved in one of the liquids, in which case the phenomenon is a special case of adsorption (cf. A., 1932, 1085). C. A. S.

Interaction between soot films and oil. S. C. BLACKTIN (Nature, 1933, **131**, 873—874).—Attention is directed to the difference in results obtained due to impact (this vol., 672) and those due to interaction (A., 1932, 464). L. S. T.

"Molecular solders" and their applications. D. L. TALMUD (Kolloid-Z., 1933, **64**, 227—229).—Theoretical. "Mol. solders" are adsorption layers between the surfaces of two solid phases. E. S. H.

Electrosmosis and anomalous osmosis. D. R. BRIGGS (Proc. Nat. Acad. Sci., 1933, **19**, 704—710).—The electrokinetic potential in the case of gum arabic is a function of the degree of ionisation of the primary salt valencies of the colloid and of the degree of oriented adsorption of foreign salt. C. W. G.

Stationary, checked, and other states of osmotic systems. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 516—523).—Theoretical. J. W. S.

Nature of alleged molecular sieve membranes. R. BEUTNER, M. CAPLAN, and W. M. LOEHR (J. Biol. Chem., 1933, **101**, 391—400).—The contact of collodion (I) with dil. aq. KCl, NaCl, LiCl, or $CaCl_2$ is followed by a chemical surface reaction, whereby base is removed by (I) and liberated HCl is detectable by titration or measurement of p_H. The reaction can be correlated with the surface boundary potentials of the systems if consideration is given to the effect of the liberated HCl (A., 1926, 120). The theory that p.d. following variation in concn. at surfaces of (I) are due to differential ionic mobilities in the pores (A., 1929, 87) is refuted. F. O. H.

Production of Merget's phenomenon by arsonvalisation with short waves. H. BORDIER (Compt. rend., 1933, **196**, 255—257).—Merget's phenomenon of thermodiffusion (cf. A., 1874, 380, 759) has been examined in a new way. A porous vessel filled with powdered brick and provided with a tube penetrating to the centre is closely encased with cardboard and heated. If the porous block is dry, no air escapes through the tube, but if it is moist, air escapes in increasing quantity and for a longer period the more moisture there is present. Similar results are

obtained if the block is moistened with MeOH, $COMe_2$, or Et_2O, the amount of air expelled increasing with the volatility of the liquid. C. A. S.

Continuity of Merget's phenomenon [thermodiffusion]. H. BORDIER (Compt. rend., 1933, **196**, 819—820; cf. preceding abstract).—Thermodiffusion takes place with Et_2O or EtCl as moistening liquid without heating, and continues until all the liquid has evaporated, the temp. of the porous block falling by 1—2°. C. A. S.

Merget's phenomenon may be produced by vaporisation of solids. H. BORDIER (Compt. rend., 1933, **196**, 1142—1144; cf. preceding abstracts).—A porous block is impregnated with an Et_2O solution of camphor or I. Evaporation of the Et_2O causes Merget's phenomenon. After complete removal of Et_2O, rise of temp. reproduces the effect when the enclosed solid volatilises. A. C.

Empirical equation for calculating osmotic pressures. (EARL OF) BERKELEY (Phil. Mag., 1933, [vii], **16**, 298—310).—An empirical equation is shown to fit closely the results obtained with a series of sugar-like compounds. The modifications required to render the equation applicable to salt solutions are also discussed. J. W. S.

Alkoxides and their molecular compounds. I. H. ULICH and W. NESPITAL (Z. physikal. Chem., 1933, **165**, 294—310).—F.-p. measurements with C_6H_6 solutions of Al ethoxide, *iso*propoxide, and benzyloxide show these solutes to be highly polymerised. The dipole moments are very small, indicating that the polymerised alkoxide mols. have such a structure that the individual group moments cancel themselves out almost completely. The most probable structure is a ring formed from three or four $Al(OR)_3$ mols., each Al atom being surrounded tetrahedrally by four OR groups. These alkoxides have no tendency to form co-ordinated compounds with org. mols. In C_6H_6 solution $Al(OEt)_3,AlCl_3$ is present largely as double mols., which, according to the dipole moment, have a ring structure. $Al(OPr^{\beta})_3$ and $AlCl_3$ react in C_6H_6 forming the *compound* $Al_3Cl_5(OPr^{\beta})_4$, apparently having a ring structure. R. C.

Compressibility of solutions. I. Apparent molal compressibility of strong electrolytes. F. T. GUCKER, jun. (J. Amer. Chem. Soc., 1933, **55**, 2709—2718).—With the exception of H_2SO_4 solutions at 18°, the apparent molal compressibility of electrolytes, $\phi = \beta_1 V_1$, is almost independent of temp. and is a linear function of the square root of the vol. concn. for all cases for which data are available, where β and β_1 are compressibility coeffs. for the solution and H_2O, respectively. The higher is the valency type of the salt, the more negative become the vals. of ϕ, but for all electrolytes, the vals. of ϕ become less negative as the concn. is increased. Vals. of ϕ at infinite dilution are additive properties of the ions. β is related to concn. by the equation $\beta=\beta_1+ c+Bc^{3/2}$, where A and B are sp. consts. J. G. A. G.

Dielectric constants of dilute solutions of strong electrolytes. M. JEZEWSKI and J. KAMECKI (Physikal. Z., 1933, **34**, 561—565).—The dielectric consts. of dil. solutions of HCl, NaCl, KCl, $MgSO_4$, and $CuSO_4$ have been determined by the resonance method. The results for bi-bivalent electrolytes are in agreement with the Debye–Falkenhagen theory, but for uni-univalent electrolytes there are large deviations. A. J. M.

Mechanical subdivision to colloidal dimensions. E. PODSZUS (Kolloid-Z., 1933, **64**, 129—143).—A review of milling processes. E. S. H.

Influence of convection on Brownian motion. K. SITTE (Z. Physik, 1933, **83**, 266—269).—Polemical, against Sato (this vol., 460). A. B. D. C.

Influence of convection on Brownian motion. II. M. SATÔ (Z. Physik, 1933, **83**, 412—416).—Convection increases Brownian motion due to condensation and re-evaporation of gas mols. A. B. D. C.

Mechanical properties of disperse systems. I. Deformation of subsoils by pressure. G. I. POKROWSKI and V. G. BULYTSCHEV (Kolloid-Z., 1933, **64**, 175—178).—Mathematical. E. S. H.

Thermal conductivity of colloid systems. S. BRESLER (Kolloid-Z., 1933, **64**, 178—181).—Theoretical. E. S. H.

Viscosimetry of colloids, especially solutions of cellulose esters. R. EISENSCHITZ (Kolloid-Z., 1933, **64**, 184—194).—Mainly theoretical. Some experiments on the viscosity of cellite solutions are described, which lead to the view that these solutions are elastic and relaxing. E. S. H.

Influence of particle form and specific volume on the viscosity of lyophilic colloids. I. SAKURADA (Kolloid-Z., 1933, **64**, 195—200).—The viscosity formula of Fikentscher and Mark (A., 1929, 1379) is valid for squalene, polystyrene, and cellulose nitrate and acetate solutions. Methods of determining the consts. are worked out. E. S. H.

Viscosity of disperse systems of different plasticity. D. DERJAGUIN and M. VOLAROVITSCH (Kolloid-Z., 1933, **64**, 233—234).—Polemical (cf. this vol., 460). E. S. H.

Ultra-filtration of soap solutions. J. W. MCBAIN, Y. KAWAKAMI, and H. P. LUCAS (J. Amer. Chem. Soc., 1933, **55**, 2762—2769).—By ultra-filtration with cellophane membranes, the degree of hydration of colloidal particles in sols is measured in terms of an added indifferent reference substance of which the concn. in the filtrate is $>$ in the original or the residue. Using KCl, the hydration of K laurate is 12 mols. of H_2O per equiv. of soap, but when the total ionic concn. is small, the effect of the Donnan equilibrium (cf. this vol., 567) is superimposed and higher vals. are obtained. Na palmitate, salted out by the NaCl, has 2 mols. of H_2O per equiv. of soap. J. G. A. G.

Phase equilibria of acid soaps. I. Anhydrous acid potassium laurate. J. W. MCBAIN and M. C. FIELD (J. Physical Chem., 1933, **37**, 675—684; cf. B., 1927, 18).—The equilibrium diagram for K laurate–lauric acid (KL–HL) is given. The acid salt KL,HL is not miscible in the solid state with either component. It is decomposed above 91·3° and forms a eutectic (40·0°) with HL. F. L. U.

Influence of hydrophilic colloids or adsorbent compounds on the solubility of sparingly soluble substances. I. Influence of gelatin on solubility. H. BRINTZINGER and H. G. BEIER (Kolloid-Z., 1933, **64**, 160—172).—Gelatin increases the solubility of the following substances in H_2O: BzOH, *o*- and *m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, anisic acid, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, *o*-, *m*-, and *p*-$C_6H_4Br{\cdot}CO_2H$, cinnamic, sulphanilic, anthranilic, hippuric, and camphoric acid, strychnine, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. The solubility of $NHPh_2$ is not affected by gelatin. Causes are discussed. E. S. H.

Dependence of the stability of carbon suspensions on the gas charge and composition of the solution. II. N. BACH (Kolloid-Z., 1933, **64**, 153—160; cf. A., 1928, 1321).—According to the behaviour in adsorption experiments, the stability of suspensions of platinised C charged with O_2 or H_2 is increased when the conditions favour the adsorption of ions, *i.e.*, the O_2-charged (I) particles are more stable in acid and the H_2-charged (II) particles in alkaline solutions. (I) behaves as a positive colloid, being sensitive to multivalent anions, whilst (II) behaves as a negative colloid. The sign of charge of (II) can be reversed by adding $ThCl_4$, but on further addition the positive particles are coagulated. C which has been oxidised superficially with O_3 has a min. stability in pure H_2O and is stabilised by multivalent anions and cations. Suspensions of platinised C containing H_2 show a min. stability when ion adsorption is least. E. S. H.

Protective action of colloids. I. Ionic adsorption in the coagulation of protected sols. II. S. S. JOSHI and A. J. RAO (J. Indian Chem. Soc., 1933, **10**, 237—246, 247—255).—I. Experiments with As_2S_3 sols, protected by gelatin, Na oleate, or starch, using aq. $FeCl_3$, $BaCl_2$, or HCl as coagulating agents, show that generally the adsorption of the coagulator increases when the amount of protective agent is increased. Certain exceptions are discussed.

II. The exceptional behaviour mentioned above is observed also in the viscosity, but not in the turbidity. E. S. H.

Kinetics of coagulation of titanium dioxide sol. S. M. MEHTA and (MISS) O. JOSEPH (J. Indian Chem. Soc., 1933, **10**, 177—188).—In the coagulation of TiO_2 sol by aq. NaCl or $MgCl_2$, Smoluchowski's equation is applicable only to a limited range of concn. of the electrolyte. The velocity curves are S-shaped for sols dialysed up to 18 days, but lose this form after more prolonged dialysis. E. S. H.

Highly polymerised compounds. LXXXIII. Streaming double refraction of dilute solutions of molecule colloids. R. SIGNER and H. GROSS (Z. physikal. Chem., 1933, **165**, 161—187).—Measurements have been made with a new apparatus capable of measuring the streaming double refraction, S, of very dil. solutions of highly polymerised substances. For the hemicolloidal polystyrenes in *cyclo*hexanone solution and the hemi- and eu-colloidal cellulose nitrates in BuOAc solution, S at a given concn. is proportional to the streaming gradient, G, and $S/G\eta c$—const., where c is the concn. and η the viscosity This equation is valid for Et oleate solutions at all concns. up to 100% of ester, whilst for the lower polystyrenes it holds only up to a certain limiting concn., which decreases with increasing mol. wt. and apparently represents the transition from sol to gel solutions. For eucolloidal polystyrenes S is not a linear function of G. These results for the cellulose nitrates and the lower polystyrenes agree with Boeder's theory (A., 1932, 571), showing that the dissolved mols. are straight threads. The vals. of the rotation diffusion consts. calc. by this theory are proportional to the reciprocals of the mol. wts. deduced from viscosity data. Kuhn's theory that the S of solutions of mol. colloids is due to extension of isotropic elongated structures (*ibid.*, 1201) is untenable. R. C.

Reversibility of equilibria in cellulose reactions. C. TROGUS (Z. physikal. Chem., 1933, **B**, **22**, 134—144).—In view of the micellar character of the reactions the final states do not represent reversible equilibria. In the reaction between cellulose and aq. N_2H_4 the N_2H_4 concn. necessary for the reaction within the micelles in the formation of hydrazinocellulose is about 20% > the concn. required to prevent the decomp. of the intramicellar system. This suggests that migration of the reagent in or out of the fibre is opposed by some kind of resistance. The apparent equilibrium encountered in the formation of Na cellulose I and Na cellulose II from hydrocellulose is due to the inadequate precision of the analytical methods; X-ray examination shows the absence of true equilibria. R. C.

Size of the micelle and colloidal particle of cellulose nitrate. K. ATSUKI and M. ISHIWARA (J. Soc. Chem. Ind. Japan, 1933, **36**, 220—221B).—The size is deduced from the no. of particles visible in the ultramicroscope when dil. $COMe_2$ solutions of known concn. are treated with H_2O. The result agrees with that calc. from the rate of diffusion of cellulose nitrate solutions in $COMe_2$. A. A. L.

Mechanical material constants of colloids. R. EISENSCHITZ and W. PHILIPPOFF (Naturwiss., 1933, **21**, 527—528).—Regarding solutions of the cellulose esters as elastic, relaxing bodies, an equation is given connecting amplitude of damped oscillations with the amount of damping and frictional resistance. The equation has been tested experimentally and qual. agreement found. A. J. M.

Lyotropic series in swelling and its extension to organic and non-ionising substances. IX. Influence of aliphatic and alicyclic compounds with two or more hydrophile groups on the swelling of potato starch. J. R. KATZ, A. WEDINGER, and F. J. F. MUSCHTER (Biochem. Z., 1933, **262**, 355—363).—The power of a series of aliphatic compounds having two hydrophile groups (OH, CO_2H, SO_3Na) to increase the swelling of starch is much < that of related compounds with one such group, due to a corresponding feebler adsorption. With the series of hydroxy-propionates and -butyrates the weakening effect is the greater the greater is the distance between OH and CO_2H. P. W. C.

Mechanism of deformation of thread-like substances. I. O. KRATKY (Kolloid-Z., 1933, **64**,

213—222).—A theoretical paper, discussing the relation between degree of stretching and orientation, and the calculation of double refraction. E. S. H.

Colloidal aluminium oxide–cupric chloride systems, prepared by the action of alcoholic cupric chloride solution on aluminium. A. KUTZELNIGG and W. WAGNER (Kolloid-Z., 1933, 64, 209—211).—When $CuCl_2$ in EtOH acts on Al foil in presence of a little H_2O, green jellies are formed, which dry to brown or green xerogels (I), containing $Al(OH)_3$, $CuCl_2$, and $AlCl_3$. The green (I) are less rich in Cu. Colourless gels, free from Cu, are obtained when displacement of $Cu^{\cdot\cdot}$ proceeds to completion. The (I) decrepitate on adding H_2O, then swell, and dissolve in part colloidally. E. S. H.

Formation of thixotropic ferric oxide gels. A. KUTZELNIGG and W. WAGNER (Kolloid-Z., 1933, 64, 212).—Thixotropic gels of $Fe(OH)_3$ (containing considerable amounts of $FeCl_3$ and $CuCl_2$) are obtained by acting on Cu with $FeCl_3$ in EtOH. E. S. H.

Paradoxical solubility phenomenon with gelatin. C. E. LARSON and D. M. GREENBERG (J. Amer. Chem. Soc., 1933, 55, 2798—2799).—Gelatin and AcOH are completely miscible above a certain temp. which decreases with increasing gelatin : AcOH ratio and varies with the sample of gelatin. Dilution of such a homogeneous mixture with AcOH causes pptn. of gelatin. J. G. A. G.

Complex coacervation. XVIII. Experiments on arabates in connexion with the origin of capillary-electrical charge. H. G. B. DE JONG and P. VAN DER LINDE (Biochem. Z., 1933, 262, 161—174).—The electrochemical equiv. wt. of the arabate ion is approx. 1200, when determined analytically. The change of charge brought about by hexol nitrate, however, indicates an apparent equiv. wt. of about 700. This effect varies with dilution and the consequent shift of p_H. At p_H 3 it gives practically the electrochemical val., whilst at p_H 4·3 it approximates to the val. which is characteristic for neutral arabates. It is suggested that this is in part due to the adsorption of OH' at neutral positions on the particles. H. W. D.

Complex coacervation. XIX. (*a*) Autocomplex coacervation with negative and positive hydrophile sols. (*b*) Correlation between the reciprocal hexol number and the tendency of negative hydrophile sols to form autocomplex coacervates. H. G. B. DE JONG and P. VAN DER LINDE (Biochem. Z., 1933, 262, 390—405).—New examples of autocomplex coacervation (I) both in pure aq. medium (Ba chondroitin sulphate, Na thymus-nucleate, agar, etc.) and with the help of desolvation substances, *e.g.*, $COMe_2$, EtOH (sol. starch, glycogen) are described and the reciprocal hexol no. (II) has been determined. The lower is the valency of the cations bringing about (I) in pure aq. medium the less is (II). P. W. C.

Complex coacervation. XX. Correlations. Systems with two co-existing complex or autocomplex coacervates. H. G. B. DE JONG and A. DE HAAN (Biochem. Z., 1933, 263, 33—49).—The origin of the capillary electric charge is considered, and the no. of ionogenic centres is found to be related to the no. of centres of negative capillary electric charge arising from simple contact with H_2O. The phenomena of mutual contacts of two co-existing complex or autocomplex coacervates are examined. Frequently the droplets of the one coacervate are completely enveloped by those of the other. H. W. D.

Union of biocolloids. XIX. Polyosoproteins (polysaccharoproteins). S. J. VON PRZYLECKI, E. MYSTKOWSKI, and B. NIKLEWSKI. **XX. Proteins and crystalloids.** M. D. GRYNBERG (Biochem. Z., 1933, 262, 260—271, 272—279).—XIX. The rotations of mixtures of proteins (ovalbumin, gelatin) and polysaccharides (dextrin, glycogen) do not correspond with the arithmetical sum of the rotations of the constituents, the deviations varying with the p_H. The turbidities of these substances and mixtures of them in H_2O also vary with the p_H. Union between these two groups of substances has now been detected by a variety of methods and occurs in all cases over a wide range of p_H.

XX. The union of proteins (caseinogen, gelatin, globulin, and albumin) with org. anions and its dependence on p_H and the ratio of the CO_2H/NH_2 groups of the protein are investigated, using H_3PO_4, guanidine, creatine, and creatinine. P. W. C.

Physical chemistry of starch and bread-making. XII. Transformation of starch preparations with the potato-starch (*B*) spectrum into preparations with the wheat-starch (*A*) spectrum and the reverse. J. R. KATZ and J. C. DERKSEN (Z. physikal. Chem., 1933, 165, 228—233; cf. this vol., 464).—On evaporation of an aq. solution of sol. starch at or above 60° a residue with an *A* spectrum results, whilst the product of evaporation at room temp. has a *B* spectrum. Either substance may be partly transformed into a substance having the other spectrum by keeping in contact with H_2O at an appropriate temp. R. C.

Solvo-systems of chemical compounds. L. F. AUDRIETH (Z. physikal. Chem., 1933, 165, 323—330).—The chemical relations of NH_3 and N_2H_4 to their allied compounds are set out so as to exhibit a parallelism with the relations of H_2O to acids, salts, and bases. R. C.

Relation between kinetics and chemical equilibrium. I. Isomerisation of the *iso*butyl bromides. II. Reversible transformation of Δ^{β}-hexachloro*cyclo*pentenone into Δ^{γ}-hexachloro-*cyclo*pentenone. A. BERTHOUD and D. PORRET (J. Chim. phys., 1933, 30, 396—413).—I. The authors' data support Brunel's views (A., 1917, i, 625).

II. Küster's val. (A., 1896, ii, 158) for the equilibrium const. is confirmed, but the observed velocity of transformation is much lower, especially if the materials used are very pure. The conversion of the Δ^{γ}- into the Δ^{β}-compound is accelerated by the formation of a catalyst during the reaction. Deviations from theory observed with these compounds and with $Bu^{\beta}Br$ are attributed to catalytic effects. D. R. D.

Ebullioscopic method for determining the equilibrium constant of esterification. W.

SWIENTOSLAWSKI (J. Physical Chem., 1933, **37**, 701—707; cf. A., 1929, 396).—Improved apparatus is described. The b.p. of equilibrium mixtures for different proportions of AcOH and EtOH are given. F. L. U.

Polyhalides. II. Formation and dissociation of chlorodibromides and tribromides of sodium, potassium, strontium, and barium. S. K. RAY (J. Indian Chem. Soc., 1933, **10**, 213—224; cf. A., 1932, 996).—For dil. solutions (0·5—0·06*N*) and moderate concns. of halogens, the formation of the compounds $NaClBr_2$, $KClBr_2$, $SrCl_2Br_4$, $BaCl_2Br_4$, $NaBr_3$, KBr_3, $SrBr_6$, and $BaBr_6$ has been established by the f.-p. method. Dissociation consts. and heats of formation are recorded. E. S. H.

Dissociation of water in strontium chloride solutions at 25°. J. E. VANCE (J. Amer. Chem. Soc., 1933, **55**, 2729—2733).—From the e.m.f. of the cells $H_2|0{\cdot}013M\text{-}Sr(OH)_2+0{\cdot}02—2{\cdot}5M\text{-}SrCl_2|AgCl|Ag$ and $H_2|0{\cdot}01M\text{-}HCl+0—0{\cdot}5M\text{-}SrCl_2|AgCl|Ag$ at 25°, the activity coeff. of 0·01*M*-HCl and the dissociation of H_2O in aq. $SrCl_2$ have been computed (cf. A., 1932, 997). J. G. A. G.

Ionisation of *dl*-alanine from 20° to 45°. L. F. NIMS and P. K. SMITH (J. Biol. Chem., 1933, **101**, 401—412).—The method of determining ionisation consts. of weak bases and acids from e.m.f. measurements of suitable cells without liquid junction (A., 1932, 695) has been modified. Vals. are given for $-\log K_{a_1}$, $-\log K_{a_2}$, and the heats of ionisation of *dl*-alanine at 20—45°. F. O. H.

Acidity of organic acids in methyl and ethyl alcohols. W. L. BRIGHT and H. T. BRISCOE (J. Physical Chem., 1933, **37**, 787—796).—Vals. of K_A (in Bronsted's equation) have been determined for aq. MeOH and aq. EtOH solutions of BzOH, its Me, NH_2-, OH-, Cl-, and NO_2-derivatives, and fatty acids C_3—C_6. The results are discussed in reference to the influence of the character and position of substituents and of the nature of the solvent. F. L. U.

Affinity constant of aniline in acetone–water mixtures. A. N. CAMPBELL and E. M. BROWN (Trans. Electrochem. Soc., 1933, **63**, 291—295).—The compositions of the two liquid layers formed by NH_2Ph–$COMe_2$–H_2O mixtures over the whole range of two-phase systems at 30° have been determined, and, using vals. of Pring (A., 1924, ii, 596) for K_w in $COMe_2$–H_2O mixtures, vals. of the affinity const. of NH_2Ph in such mixtures are calc. Extrapolation gives 2×10^{-10} as the val. for pure aq. solution (cf. A., 1930, 122). H. J. T. E.

Electrolytes in mixed solvents. V. Free energy of lithium chloride in water–alcohol mixtures and the salting-out of alcohol. J. A. V. BUTLER and D. W. THOMSON (Proc. Roy. Soc., 1933, **A, 141**, 86—94).—Earlier measurements of the partial v.p. of solutions of LiCl in H_2O–EtOH mixtures (A., 1931, 680) have been extended to solutions containing 2—4 mol.-% EtOH and in each case 0·5, 1·0, and 4·0*M*-LiCl. In a discussion of the thermodynamics of salting out it is shown that extent of the salting out is properly measured, not by the change of the activity of the non-electrolyte, but by the difference between the observed and normal effects. The free energies of transfer of LiCl from H_2O to EtOH solutions have been calc. from the partial pressures. L. L. B.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XVIII. Comparison of hydrolytic phenomena and aggregation processes in aqueous solutions of beryllium, magnesium, and aluminium salts. W. HEUKESHOVEN and A. WINKEL (Z. anorg. Chem., 1933, **213**, 1—11; cf. this vol., 580).—Diffusion coeffs. of $Be^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ were measured between p_H 0 and 5·8—6·6. The val. for $Mg^{\cdot\cdot}$ is const.; for $Be^{\cdot\cdot}$ it diminishes between p_H 2 and 6 from 0·45 to 0·35 and for $Al^{\cdot\cdot\cdot}$ the decrease is even greater. This is due to hydrolysis, aggregates of lower mobility being formed. The conductometric titration of $Be(ClO_4)_2+HClO_4$ with 2*N*-NaOH is described. H. J. E.

Amphoteric behaviour of metal hydroxides. R. SCHOLDER (Angew. Chem., 1933, **46**, 509—512).—A lecture. E. S. H.

Displacement of equilibrium by variation of mass. R. ÉTIENNE (Compt. rend., 1933, **197**, 149—151; cf. this vol., 783).—A graphical method of arriving at the result previously demonstrated. C. A. S.

Chemical law of mass action for concentrated non-ideal solutions. F. SAUERWALD (Naturwiss., 1933, **21**, 547).—The validity of the law of mass action in certain conc. non-ideal solutions may be due to special relations between the activity and the concn. A. J. M.

Thermodynamics of very dilute gases and solutions. W. NERNST (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1933, Reprint, 4 pp.).—Attention is directed to the difference between the formula $A=RT\log v/v_0$ in its application to a gas and the formula $EF=RT\log c/c_0$ as applied to a concn. cell. The mechanical work A cannot be actually realised when the gaseous system is very dil., although this is readily accomplished in the case of the electrical work EF even in the case of extremely dil. solutions. A. J. M.

Activity coefficients of the nitrobenzoic acids [at 50°]. P. H. SYKES and P. W. ROBERTSON (J. Amer. Chem. Soc., 1933, **55**, 2621—2625).—The activity coeffs. have been computed from the solubilities of the nitrobenzoic acids in *iso*amyl alcohol, xylene, H_2O, 1—5*N* aq. NaCl and $MgSO_4$, and from distribution ratios. *o*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ is much more highly polar than the other isomerides and has a very high activity coeff. in xylene. J. G. A. G.

Changes of chemical potential of concentrated solutions of certain salts. R. E. GIBSON and L. H. ADAMS (J. Amer. Chem. Soc., 1933, **55**, 2679—2695).—The relative lowering of the v.p. of conc. aq. solutions of LiCl, NH_4NO_3, KCNS, and Na_2SO_4 has been determined in the range 20—27·5° by a modified static method. The data are reproduced by empirical equations by means of which differences in the chemical potential of either component may be calc. J. G. A. G.

Thermodynamic ionisation constants of carbonic acid [at 25°]. D. A. MACINNES and D.

BELCHER (J. Amer. Chem. Soc., 1933, **55**, 2630—2646).—From the e.m.f. of the cell Ag,AgCl|$XHCO_3(m)+XCl(m)+CO_2$ (dissolved, 1 atm.)|glass|AcO′ buffer+KCl|AgCl,Ag, where X=Na or K, it is shown that the fugacity of 0·54—99·6 mol.-% of CO_2 in N_2 mixtures at 1 atm. total pressure is proportional to the mol. fraction, and the first ionisation const. of H_2CO_3 is computed to be $4{\cdot}54\times10^{-7}$, which, although it is much > previously accepted vals. (A., 1916, ii, 512), is in close accord with a redetermination by a conductivity method. From the e.m.f. of the cell Ag,AgCl|0·0011—0·04*M*-K_2CO_3+0·0025—0·047*M*-$KHCO_3$+0·0025—0·04*M*-KCl|H_2, the second ionisation const. of H_2CO_3 is computed to be $5{\cdot}61\times10^{-11}$, which is consistent with existing vals. J. G. A. G.

Application of Nernst's approximate formula to cases of complex heterogeneous equilibrium in organic chemistry. Z. E. ZINKOV (Anilinokras. Prom., 1933, **3**, 144—153).—A thermodynamic consideration of the system NaOPh–CO_2 leads to the conclusion that Davies' " ester salts I and II " (A., 1928, 1329) are respectively $PhNaCO_3$ and Na salicylate, which in Davies' experiments were in false equilibrium with the other phases of the system. Nernst's approx. formula is applicable to the above case of heterogeneous equilibrium. R. T.

Ionic activity at extremely high concentrations. F. TODT (Z. Elektrochem., 1933, **39**, 521—526).—The $H^{\cdot}$ activity in H_2SO_4 up to 37·4*N* has been measured with a H electrode. p_H vals. of 11·86 were observed. Similarly high vals. were obtained for conc. HNO_3 by the inversion of sucrose. H. J. E.

Thermodynamic treatment of stationary systems. B. BRUŽS (Z. Elektrochem., 1933, **39**, 642—645).—Theoretical. H. J. E.

Individual thermodynamic behaviour of tetra-alkylammonium halides in very dilute solution. J. LANGE (Z. Elektrochem., 1933, **39**, 545—549; cf. A., 1930, 1251).—The osmotic coeff. for NMe_4Cl, NPr_4Cl, NMe_4I, and NPr_4I, calc. from f.-p. measurements at concn. 0·1—0·001*M*, are compared with vals. calc. from electrostatic theory. For the chlorides changes in the hydration outweigh changes in the size of the cation. For the iodides partial association of the ions must be assumed. The conductivity data at 0° are discussed in relation to the Debye–Huckel–Onsager theory and the cryoscopic measurements. H. J. E.

Thermodynamic studies of mercurous bromide. F. ISHIKAWA and Y. UEDA (Sci. Rep. Tohoku, 1933, **22**, 249—262).—The e.m.f. at 25° of reversible cells containing HgBr lead to: standard free energy of formation −21,350 g.-cal., heat of formation −24,470 g.-cal., entropy change −10·5 g.-cal. per 1°, and entropy of the salt 27·2 g.-cal. per 1°. A. R. P.

Thermodynamic studies of cadmium bromide. F. ISHIKAWA and Y. UEDA (Sci. Rep. Tohoku, 1933, **22**, 262—287).—The % of $CdBr_2$ in a saturated solution at 20—35° is $52{\cdot}88+0{\cdot}653(t-25°)+0{\cdot}00243(t-25°)^2$. Below 36° $CdBr_2,4H_2O$ is the stable solid phase and above 36° $CdBr_2$; there are no intermediate hydrates. The heat of dissolution of $CdBr_2,4H_2O$ is −7340 g.-cal., the heat of formation of $CdBr_2$ from α-Cd 74·471 kg.-cal., and the entropy of $CdBr_2$ 36·8 g.-cal. per 1°. A. R. P.

Heats of combustion of carbon monoxide in oxygen and of nitrous oxide in carbon monoxide at constant pressure. J. H. AWBERY and E. GRIFFITHS (Proc. Roy. Soc., 1933, **A**, **141**, 1—16).—The heats of combustion of N_2O and of O_2 in CO, determined by a continuous-flame method involving combustion at const. pressure, are found to be 364,340 and 282,730 international joules per mol., respectively. The reaction was brought about by continuously burning one of the reacting gases in an excess of the other, using an adiabatic calorimeter to measure the heat evolved. From these two vals. the calc. heat of formation of N_2O at 20°/1 atm. is $19{\cdot}5_0$ kg.-cal.[15] L. L. B.

Bomb calorimeter determination of the heats of formation of nitrous oxide and carbon dioxide. R. W. FENNING and F. T. COLTON (Proc. Roy. Soc., 1933, **A**, **141**, 17—28).—From measurements of the heats of reaction of O_2 and N_2O in CO and H_2, the heats of formation of N_2O and CO_2 at a const. pressure of 1 atm. and at 20° were found to be $-19{\cdot}74\pm0{\cdot}07$ kg.-cal.[15], and $67{\cdot}65_5\pm0{\cdot}03_5$ kg.-cal.[15], respectively. L. L. B.

Perchlorates. II. Heats of dissociation and hydration. C. SMEETS (Natuurwetensch. Tijds., 1933, **15**, 105—124).—Data are given for the alkali and alkaline-earth perchlorates. For each group the heats of hydration diminish with increase of the at. vol. of the cation, and, correspondingly, the hydrated perchlorates of metals having very small at. vol. (Fe, Mn, Co, etc.) decompose at temp. < those at which they lose H_2O of crystallisation. H. F. G.

Heat of reaction of $2Fe(ClO_4)_3+2Hg=2Fe(ClO_4)_2+Hg_2(ClO_4)_2$ from equilibrium data. V. B. FLEHARTY (J. Amer. Chem. Soc., 1933, **55**, 2646—2649; cf. A., 1931, 802).—The effect of varying the concn. of $HClO_4$ and salts on the reaction $2Fe^{\cdot\cdot\cdot}+2Hg=2Fe^{\cdot\cdot}+Hg_2^{\cdot\cdot}$ has been determined at 35°. The true equilibrium const. is 0·0539, and the heat of reaction 20,000 g.-cal. J. G. A. G.

Thermal data on organic compounds. XI. Heat capacities, entropies, and free energies of ten compounds containing oxygen and nitrogen. G. S. PARKS, H. M. HUFFMAN, and M. BARMORE (J. Amer. Chem. Soc., 1933, **55**, 2733—2740).—From sp. heat determinations between 91° and 300° abs., the following entropies per mol., S_{298}, have been computed: $CO(NH_2)_2$ 25·2, glycine 26·1, EtOAc 62·0, *n*-amyl alcohol 60·9, *tert.*-amyl alcohol (I) 54·8, Pr^s_2O 70·4, PhOH 34·1, NH_2Ph 45·8, BzOH 40·8, and sucrose 86·1 g.-cal. per 1°. (I) has a transition point at 146·0° abs. Latent heats of fusion have been determined, and mol.-free energies have been calc. The val. of the latter for $CO(NH_2)_2$ agrees with the val. derived from independent equilibrium data, thus affording further evidence of the validity of the third law of thermodynamics. J. G. A. G.

Dissociation pressure of calcium carbonate. I. Differential thermocouple method. M. MATSUI, K. BITO, S. MURAYAMA, and M. KADONO. **II.**

Differential manometer method. M. MATSUI, K. BITO, and M. KADONO (J. Soc. Chem. Ind. Japan, 1933, **36**, 155—157B, 157—158B).—I. Results are given by $\log p = -37{,}251/4{\cdot}576T + 9{\cdot}9333$.

II. Observations are given by $\log p = -37{,}502/4{\cdot}576T + 10{\cdot}0092$. H. F. G.

Thermal dissociation of calcium carbonate in a carbon dioxide atmosphere. III. Primary and secondary dissociation points. IV. Thermal change of precipitated calcium carbonate. K. BITO and M. MATSUI (J. Soc. Chem. Ind. Japan, 1933, **36**, 152—153B, 154—155B). III. Heating and cooling curves for Iceland spar are recorded.

IV. Corresponding curves for pptd. $CaCO_3$ are given. H. F. G.

Composition and dissociation of thallium peroxide. M. CENTNERSZWER and T. TRĘBACZKIEWICZ (Z. physikal. Chem., 1933, **165**, 367—371).—Tl peroxide, formed at a Pt anode on electrolysis of Tl_2SO_4 solution, has the empirical formula TlO_2, the mol. formula probably being Tl_2O_4. In O_2 (1 atm.) it loses O_2 reversibly above 573°, forming Tl_2O_3. The dissociation pressure, p, between 350° and 573° can be represented by $\log p = -27055/(4{\cdot}571T) + 1{\cdot}751 \log T + 0{\cdot}0052T/4{\cdot}571 + 2{\cdot}8$. The heat of dissociation is 27,055 g.-cal. per mol. of O_2 lost. R. C.

System $BiCl_3$–$ZnCl_2$. E. JÄNECKE (Z. anorg. Chem., 1933, **213**, 149—154).—A simple eutectic is shown at 215°. Reported abnormalities (Herrmann, A., 1911, ii, 801) are due to BiOCl, formed by H_2O or by exposure to atm. O_2 at 300°. H. J. E.

Affinity of metals for sulphur. IV. Dissociation of zinc and manganese sulphides. E. V. BRITZKE, A. F. KAPUSTINSKI, and B. K. VESSELOVSKI. **V. General conclusions.** E. V. BRITZKE and A. F. KAPUSTINSKI (Z. anorg. Chem., 1933, **213**, 65—70, 71—76).—IV. From static measurements of the equilibrium between ZnS or MnS and gaseous HCl between 300° and 1100°, the dissociation pressures of ZnS and MnS and the affinity of Zn and Mn for S were calc. The heat of formation of MnS=44,600 g.-cal.

V. Dissociation pressures and heats of dissociation of metal sulphides and the order of affinity of metals for S are summarised. The more dissociated a metal sulphide is in solution, the less is its thermal dissociation. H. J. E.

M.-p. diagram of the system phenol–benzoic acid. N. F. MOERMAN (Rec. trav. chim., 1933, **52**, 601—606).—The system exhibits a eutectic at 31·5°. Liquid PhOH and BzOH have no measurable heat of mixing; their dipole moments are probably approx. equal. E. S. H.

Binary systems. III. Systems with ethane as volatile component. F. E. C. SCHEFFER and J. SMITTENBERG (Rec. trav. chim., 1933, **52**, 607—614; cf. A., 1932, 1204).—Data for *as*-*o*-xylidine, *p*-toluidine, *o*- and *m*-$C_6H_4Cl{\cdot}NO_2$, *o*-nitrophenol, and *p*-$C_6H_4Cl{\cdot}NH_2$ afford no evidence of compound formation. E. S. H.

Thermal analysis of certain organic compounds. F. ADAMANIS (Rocz. Chem., 1933, **13**, 351—359).—The fusion diagrams for 19 binary systems, comprising all possible combinations of quinine, carbamide (I), phenacetin (II), antipyrine, ethylurethane, menthol, and salol, have been determined. Compound formation is in no case indicated. The systems (I)–salol, –menthol, or –quinine yield two immiscible liquid phases, whilst the system (I)–(II) exhibits immiscibility between 3·7 and 65·8 mol.-% of (II). R. T.

System bismuth–tellurium–sulphur. Oruetite. J. GARRIDO (Anal. Fís. Quím., 1933, **31**, 99—102).—Although the analysis of oruetite conforms closely to the formula Bi_3TeS_4, *X*-ray analysis shows the mineral to consist of a eutectic mixture of various compounds interspersed with Bi. H. F. G.

Equilibria in the system $Ba(NO_3)_2$–HNO_3–H_2O at 18°. R. FRICKE and F. BRUMMER (Z. anorg. Chem., 1933, **213**, 319—320).—The solubility of $Ba(NO_3)_2$ in H_2O at 18° decreases almost hyperbolically with addition of HNO_3 from 0·6 g.-equiv. per 1000 g. of solution to 0·0256 g.-equiv. with 3·4372 g.-equiv. of HNO_3. A. R. P.

Thermodynamical study of systems of the type $PbCl_2$–RCl–H_2O at 25°. II. A. J. ALLMAND and L. J. BURRAGE (Trans. Faraday Soc., 1933, **29**, 679—689; cf. A., 1927, 1030).—Electrometric measurements have been made on the system $PbCl_2$–KCl–H_2O, and the activities of the three components evaluated. J. S. A.

Ternary system $K_4Fe(CN)_6$–K_2SO_4–H_2O. E. BOVALINI and E. FABRIS (Gazzetta, 1933, **63**, 338—344).—The equilibrium relations at 0°, 30°, 40°, 65°, 74°, 85°, and 90° have been examined. O. J. W.

Heterogeneous equilibrium of system CdI_2–KI–H_2O. H. HERING (Compt. rend., 1933, **197**, 243—245; cf. A., 1932, 574).—CdI_2 crystallises with $4H_2O$ at −2·9°; CdI_2,KI,H_2O exists up to 100°; CdI_2,2KI crystallises with 1 or $2H_2O$ above or below −15·3°, and above 76° with $0{\cdot}5H_2O$. $2CdI_2$,3KI,$4H_2O$ is formed between 10·3° and −27·6° from solutions containing 0·511—0·536KI per mol. of CdI_2. C. A. S.

System zinc oxalate, potassium oxalate, water. I. At 25°. V. METLER and W. C. VOSBURGH (J. Amer. Chem. Soc., 1933, **55**, 2625—2629).—The solubilities in aq. $K_2C_2O_4$ have been determined of ZnC_2O_4 and the complex *salt* $K_2Zn(C_2O_4)_2,7H_2O$ (I) which coexists with the more conc. solutions. (I) is metastable above 34°. J. G. A. G.

Preparation of ammonium phosphates. II. L. E. BERLIN and B. M. MANTZEV (J. Appl. Chem. Russ., 1933, **6**, 385—389).—The 25° isotherm for the system H_2O–NH_3–P_2O_5–SO_3 has been determined. R. T.

Reciprocal salt pair $CoSO_4 + K_2Cl_2 \rightleftharpoons CoCl_2 + K_2SO_4$. D. LANGAUER (Z. anorg. Chem., 1933, **213**, 180—182).—Equilibrium data for 25° are recorded. H. J. E.

Lowering of eutectic point of system H_2O–KNO_3–NH_4Cl. H. MULLER (Compt. rend., 1933, **197**, 241—243; cf. this vol., 566).—The mol. lowering for the eutectic (H_2O 100, KNO_3 11·9, NH_4Cl 25·1; −18·09°) is 13·1°. C. A. S.

Equilibria of the quaternary system Na_2SO_4–$(NH_4)_2SO_4$–NH_3–H_2O. A. P. Belopolski and N. P. Alexandrov (J. Appl. Chem. Russ., 1933, **6**, 390—415).—The solid phases at 0° and 15° are mirabilite (I), Na_2SO_4 (II), $Na_2SO_4,(NH_4)_2SO_4,4H_2O$ (III), and $(NH_4)_2SO_4$ (IV). (III) is unstable in solutions containing $>65{\cdot}25$ g. of NH_3 per 100 g. H_2O at 0°; the necessary NH_3 concn. rises with temp. A process is described for the prep. of almost pure (IV) from the mother-liquor (V) remaining after crystallisation of Na_2CO_3, prepared from (I) by the Solvay process. Most of (II) in (V) is removed by freezing at −10°, and (IV) is fractionally salted out by addition of NH_3. R. T.

Influence of small amounts of dissolved silicates on the conductance of conductivity water and very dilute solutions of electrolytes. T. I. Taylor (J. Physical Chem., 1933, **37**, 765—777).—The effect of the addition of small amounts of Na silicate on the conductance of conductivity H_2O collected and stored in vessels of pyrex or soft glass has been determined. If the H_2O contains CO_2 there is an initial decrease of conductance due to its reaction with the silicate. On storage CO_2 disappears at a rate depending on the nature and pre-treatment of the storage vessel, owing to reaction with silicates dissolved from it. Very dil. solutions of HCl, NaOH, and KCl have been similarly examined. The "solvent" correction to be applied in conductivity measurements is discussed. F. L. U.

Equivalent conductance of aqueous barium hydroxide solutions [at 28°]. H. G. Leopold and J. M. Luck (J. Amer. Chem. Soc., 1933, **55**, 2655—2656).—The data refer to 0·016—0·21*M*-$Ba(OH)_2$. J. G. A. G.

Conductivity of alkylammonium picrates in aqueous solution at 0°, 25°, and 90°. III. Hydrolysis of the salts examined. P. Ekwall (Z. physikal. Chem., 1933, **165**, 331—337).—From data for the degree of hydrolysis mobility data (this vol., 467) are revised, without, however, altering the conclusions as to the validity of Stokes' law originally reached. R. C.

Electrical conductivity of solutions of uni-univalent salts in ethyl alcohol. M. Barak and (Sir) H. Hartley (Z. physikal. Chem., 1933, **165**, 272—293).—The conductivities of alkali and NEt_4 salts, NaOEt, and $NaEtCO_3$ have been measured at 25° at concns. of 0·0001—0·0013*N*. For all these $\Lambda_c=\Lambda_0-xc^{\frac{1}{2}}$, where c is the concn., but for most x deviates considerably from the Debye–Huckel–Onsager val. The relation of the deviation to the ionic size as deduced from mobility data agrees with the theoretical connexion between the latter and the formation of ion pairs making no contribution to the conductivity. The mobilities of univalent ions in EtOH show that except for some Li salts all uni-univalent salts are somewhat associated even in dil. solution. In a group of analogous alkali salts the degree of association increases with the at. no. of the metal. The mobilities of the alkali ions increase from $Li^{\cdot}$ to $Cs^{\cdot}$, and their effective sizes are greater in EtOH than in H_2O. The effect of the addition of small amounts of H_2O on the conductivity of the EtOH solutions has been examined. R. C.

Anomalous electrolytes. II. Electrical conductivity of solutions of iodine and iodine compounds in ketones. E. J. Birr (Z. physikal. Chem., 1933, **165**, 311—322; cf. this vol., 354).—The nature of these solutions has been investigated by measurements of their conductivity and its change on keeping. I dissolved in $COPh_2$ is simply dissociated into $I^{\cdot}$ and I', whilst in *cyclo*hexanone solution a solvate is formed, which ionises largely. In $COMe_2$, COMeEt, and COPhMe solution the I adds itself to the enol form of the solvent, and the resulting iodohydrin, a pseudo-electrolyte, is more slowly transformed into a non-electrolyte, so that ultimately the conductivity falls to zero. ICN in COMeEt behaves similarly, but ICl_3 follows a more complicated scheme of reaction. R. C.

Conductivity and state of electrolytes dissolved in metal alkyls. F. Hein and H. Pauling (Z. physikal. Chem., 1933, **165**, 338—366, and Z. Elektrochem., 1933, **39**, 537—538).—The mol. conductivity, μ, of solutions of tetra-alkylammonium halides in $ZnEt_2$, $CdEt_2$, and $AlEt_3$ has been determined. The μ–concn. curve for tetra*iso*amylammonium iodide (I) in $ZnEt_2$ solution exhibits a max. This, however, disappears if μ is corr. for viscosity by multiplication with η_v/η_∞, and the curve can then be represented by $\mu_{corr.}v^n=$const., where v is the dilution and n a const. For a given cation μ increases with the at. wt. of the anion, and for a given anion with the mol. wt. of the cation. Owing to solvation the solutions exhibit high osmotic effects, *e.g.*, in $ZnEt_2$ (I) has the association factor 2. Solvent and dissociating powers decrease in the order $ZnMe_2$, $ZnEt_2$, $CdEt_2$, $AlEt_3$, $HgEt_2$, primarily because the solvating power decreases in the same order. The metal alkyls are to be regarded as insulators comparable with C_6H_6 and $CHCl_3$, although the osmotic effects of insulators are very small. In $ZnEt_2$ or $CHCl_3$ solution C_5H_5NEtI is gradually partly converted into an isomeride. The *compound* $2NEt_4I,ZnEt_2$ has been isolated. R. C.

Electrolytic solutions. V. Conductance of amido-salts in liquid ammonia. C. A. Kraus and W. W. Hawes (J. Amer. Chem. Soc., 1933, **55**, 2776—2785).—From conductivity measurements in liquid NH_3 at −33°, the limiting conductance and dissociation consts., K, of NHNaPh, $NNaPh_2$, $NH_2Na{\cdot}BPh_3$, $NKPh_2$, and $NH_2K{\cdot}BPh_3$ have been calc Vals. of K increase with increasing size of the negative ions, but bear no relation to their electron affinity. The results are consistent with the theory which attributes the process of ion association to Coulomb forces (this vol., 464). J. G. A. G.

Anhydrous hydrazine as an ionising medium for electrolytes and non-electrolytes. I. Behaviour of typical electrolytes and half electrolytes. P. Walden and H. Hilgert (Z. physikal. Chem., 1933, **165**, 241—271).—Conductivities of solutions of org. and inorg. salts and org. acids at dilutions up to 2500—5000 litres have been measured at 0° and 25 For all the solutes $\lambda_\infty=\lambda_c+a\sqrt{c}$ at dilutions $(272/\varepsilon)^3$, ε being the dielectric const. of N_2H_4. The vals. of $Kn_1n_2/\varepsilon\eta$, where n_1 and n_2 are the

valencies of the ions and η is the viscosity of N_2H_4, usually agree with the observed vals. of α (A., 1924, ii, 387), whilst some of the Debye–Hückel vals. are too small. N_2H_4 is a highly ionising medium, differences in strength between dissolved electrolytes being obscured. Already at a dilution of 375 litres all the solutes have the same degree of ionisation (0·935). The val. of is about the same for all the salts, but far exceeds the val. for other non-aq. media. Solutions of N_2H_4 salts have no detectable Grotthus conductivity. Mono-, di-, and tri-alkylammonium chlorides are solvolysed. The principle of independent migration of the ions is valid. In solvents of the N_2H_4 type the val. of $\varepsilon v^{\frac{1}{2}}$, where v is the dilution corresponding with a given degree of ionisation, is at high dilutions the same for all binary salts and is independent of the solvent. Many solutions of salts in differentiating solvents deviate widely from this relation. R. C.

Transport of matter and the passage of current in liquid alloys. K. Schwarz (Z. Elektrochem., 1933, **39**, 550—554; cf. A., 1931, 1236).—The transport nos. of Na and K in their amalgams at 26° agree with the vals. calc. from the diffusion potentials. In such liquids the metal is practically completely dissociated into electrons and metal ions of the lowest valency stage. In the electrolysis of binary liquid alloys the ion with the greater charge density moves to the cathode. H. J. E.

Electrical conductivity of solutions of electrolytes in strong fields and at high frequencies. P. Debye (Z. Elektrochem., 1933, **39**, 478—482).—A survey of recent developments. H. J. E.

Molecular conductivity of the hydrogen halide acids and nitric acid at high concentrations. E. Wilke (Z. Elektrochem., 1933, **39**, 526).—Between 0·1 and 10*N* the mol. conductivity of the four acids at the same concn. is equal. The conductivity is proportional to concn.$^{1/3}$ H. J. E.

Peculiarities in the conductivity relations of non-aqueous solutions. H. Ulich (Z. Elektrochem., 1933, **39**, 483—489).—Electrolytes are divided into (i) those in which the ions are already formed (*e.g.*, NaCl), and (ii) those in which the ions are formed in a reaction (*e.g.*, $NH_3+HX=NH_4^++X^-$; $HCl+Y=Cl^-+HY^+$). (ii) is subdivided into cases where transfer of a proton occurs, those in which an electron transition takes place, and those in which a halogen ion is transferred. This classification is illustrated for various electrolytes and solvents. H. J. E.

Conductivity in solvents of very low dielectric constant. R. M. Fuoss (Z. Elektrochem., 1933, **39**, 513—516; cf. this vol., 464).—The conductivity curves for tetra*iso*amylammonium nitrate in mixtures of dioxan (dielectric const. 2·2) and H_2O (78) show min. vals. at concns. which fall as the dielectric const. of the medium decreases. The increased tendency to form pairs and groups of ions due to the lower dielectric const. is discussed. H. J. E.

Electrical conductivity of some fused salt mixtures. E. Ryschkewitsch (Z. Elektrochem., 1933, **39**, 531—537).—The sp. conductivity of NaCl, KCl, Na_2CO_3, LiCl, LiF, NaCN, $CaCl_2$, and of NaCl–KCl, NaCl–$CaCl_2$, NaCl–KCl–$CaCl_2$, NaCl–KF, and NaCl–Na_2CO_3 mixtures has been measured between approx. 600° and 1000°. H. J. E.

Electrical conductivity of capillary and colloidal systems. J. J. Bikerman (Z. Elektrochem., 1933, **39**, 526—531).—Theoretical. The Debye theory is applied to colloidal particles, for which interionic forces are much stronger than in true solutions, and in which the colloid ion has a correspondingly lower mobility. H. J. E.

Electrostatic theory of the dependence of ionic mobility and dielectric constant on the frequency in mixed solutions of strong electrolytes. H. Falkenhagen and W. Fischer (Z. Elektrochem., 1933, **39**, 517—520; cf. this vol., 8).—Theoretical. Expressions are derived for the conductivity and change of dielectric const. for mixed electrolytes in a high-frequency field. These are applied to Spaght's experiments on aq. KCl+aq. $Ca_2Fe(CN)_6$ (A., 1932, 998). H. J. E.

Demonstration of the high-frequency effect in electrolytes. P. Debye and H. Sack (Z. Elektrochem., 1933, **39**, 512—513).—The conductivity cell is made to serve as a thermometer bulb (50 c.c.), by an attached capillary. Differences in conductivity using high frequency are demonstrated by a change in the rate of heating of the electrolyte as shown by the liquid rise in the capillary. H. J. E.

Electrostatic theory of dependence of ionic mobility on frequency and dielectric constants in mixed solutions of strong electrolytes. II. Generalisation of the Bennewitz–Wagner–Kuhler calculation for the non-stationary state. H. Falkenhagen and W. Fischer (Physikal. Z., 1933, 34, 593—602).—Theoretical. The general solution of the problem of dispersion of conductivity and dielectric consts. of mixed electrolytes is developed, and an explanation of Spaght's dispersion curve given. A. J. M.

Time factor in the conductivity and dielectric capacity of electrolytes in solvents of various viscosities. O. Dobenecker (Ann. Physik, 1933, [v], **17**, 699—715).—The time factor has been examined for wave-lengths of 13·5, 9·0, and 4·5 m. in solvents of high viscosity. The viscosity of the solvent was varied by adding sucrose. Sucrose solution shows a large anomalous dipole absorption, and a small dielectric dispersion for short waves, and the magnitudes of both these effects were determined by comparison with a $COMe_2$–H_2O mixture of the same dielectric const. and conductivity. The time factor was determined for NaCl, K_2SO_4, $MgSO_4$, and $Ba_3[Fe(CN)_6]_2$ in sucrose solutions of various concns., and for $K_4Fe(CN)_6$ in 67% sucrose solution. In accordance with theory, the time factor in the case of conductivity increases with the valency and with the frequency, but the effect is > that indicated by theory. The time factor in the case of dielectric capacity is < the theoretical. A. J. M.

Thermo-electric force and Ludwig–Soret effect in solid salts and mixed crystals, and their relation to electrolytic conductivity. H. Reinhold (Z. Elektrochem., 1933, **39**, 555—561; cf. this vol.,

677).—Theoretical. Systems of the type CuBr–AgBr and Ag_2S–Cu_2S are discussed. H. J. E.

Thermodynamic consideration of the system perfect electrode–dilute solution. K. Guminski (Rocz. Chem., 1933, **13**, 301—305).—Theoretical. R. T.

Potential difference between copper and its amalgam and the reproducibility of the copper electrode. M. Oku (Sci. Rep. Tohoku, 1933, **22**, 288—300).—A standard Cu electrode can be prepared by electrolysis of aq. $CuSO_4$ acidified with H_2SO_4 using a Pt anode and a high c.d. The c.m.f. of the cell Cu|aq. $CuSO_4$|Cu(Hg) is 0·00512 at 25° and dE/dT=0·0000737 volt per 1° between 0° and 35°. The standard free energy of formation of Cu amalgam is −236 g.-cal. and the heat of formation −1250 g.-cal. A. R. P.

Electrophoretic null point for mercury in aqueous solutions. S. R. Craxford (Phil. Mag., 1933, [vii], **16**, 268—274). The potential of the electrophoretic null point for a Hg drop in a series of solutions has been found to be identical, within experimental error, with the electrolytic null point given by the potential of the electrocapillary max., even when the salt from the solution is strongly adsorbed at the surface of the Hg drop. J. W. S.

Effect of sugars on the p_H of sodium molybdate solutions. P. Thomas and (Mlle.) C. Kalman (Compt. rend., 1933, **197**, 330—331).—Addition of mannose, fructose, xylose, or galactose increases the acidity or alkalinity of solutions of Na tungstate or molybdate (I), according to whether the solution is initially acid or alkaline. With (I) the effect of the sugars decreases in the order given and the point of inflexion is at p_H 5·7 in all cases. R. S. C.

Hydrolysis and the oxidation–reduction potential of the system $Fe^{\cdot\cdot\cdot}$–$Fe^{\cdot\cdot}$. P. A. Kriukov and G. P. Avsejevitsch (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 135—150).—Glass electrode data for the system are recorded. A. M.

Oxidation–reduction potentials of chlororaphin. B. Elema (Rec. trav. chim., 1933, **52**, 569—583).—Oxidation–reduction potentials of phenazine-1-carboxylamide (the oxidation product of chlororaphin; cf. A., 1932, 1043) have shown that in the acid region the reversible reaction occurs in two steps. The results cannot be explained by the formation of a meriquinone, as only one electron is involved in each step; a semiquinone, identical with chlororaphin, is probably formed. The two steps are definite at $p_H < 1$, but in less acid solutions they overlap. At $p_H > 4$ no semiquinone can be detected, and the usual one-step oxidation involving two electrons occurs. E. S. H.

Electrochemistry of photosensitive electrodes with copper salts. R. Audubert (J. Chim. phys., 1933, **30**, 389—395).—Cu coated with CuO, Cu_2O, CuI, CuBr, CuCl, or collodion containing an org. dye forms a photosensitive electrode, an illuminated electrode acting in general as anode to an unilluminated one. In contact with $Cu^{\cdot\cdot}$ ions, the latter behaves as a simple Cu electrode. The potential is identical in vac. or in presence of N_2 or H_2, but varies with $[O_2]$, the equilibria $2Cu^{\cdot} \rightleftharpoons Cu^{\cdot\cdot} + Cu$ and $4Cu^{\cdot} + O_2 + 2H_2O \rightleftharpoons 4Cu^{\cdot\cdot} + 4OH'$ being maintained at the electrode. D. R. D.

Boundary conditions for the wave equation. W. H. McCrea and R. A. Newing (Proc. Roy. Soc., 1933, **A**, **141**, 216—217).—Mathematical. L. L. B.

Homogeneous reaction between hydrogen and fluorine. H. Eyring and L. S. Kassel (J. Amer. Chem. Soc., 1933, **55**, 2796—2797).—There is no appreciable homogeneous reaction between H_2 and F_2 at room temp., but explosions are caused by introduction of extraneous matter. Thermal reaction by way of chains may be expected to begin at 150—250°. J. G. A. G.

Explosions of mixtures of hydrogen and air: specific heats of steam at high temperatures. G. B. Maxwell and R. V. Wheeler (J.C.S., 1933, 882—885).—From time–pressure curves of mixtures of H_2 and air fired centrally in a sphere 19·7 cm. diam., vals. of the sp. heat of steam have been calc. which are > those usually accepted. F. L. U.

Upper pressure limit in the chain reaction between hydrogen and oxygen. G. H. Grant and C. N. Hinshelwood (Proc. Roy. Soc., 1933, **A**, **141**, 29—40).—The influence of surface, diameter of vessel, H_2–O_2 ratio, inert gases, and temp. on the upper pressure limit of the low-pressure explosion of H_2 and O_2 has been investigated. The variation of the explosion pressure with H_2–O_2 ratio and with the pressure of the inert gas present can be quantitatively explained on the hypothesis that at the upper limit a branching chain process is balanced by gas phase deactivation in ternary collisions. The theory also explains the very different influences of temp. on the upper and lower limits. L. L. B.

Explosions of methane and air: propagation through a restricted tube. H. Robinson and R. V. Wheeler (J.C.S., 1933, 758—760).—No discontinuity in the combustion within the restricted zone, and no sudden increment in speed of the flame, such as occurs when a detonation wave is initiated, could be detected during the explosion of a mixture containing 10% CH_4 in an open-ended tube 32·3 m. long and 30·5 cm. in diam., provided with eleven rings reducing the diam. to 10·2 cm. (cf. B., 1926, 970). F. L. U.

Influence of temperature on limits of inflammation of combustible vapours. M. Briand, P. Dumanois, and P. Laffitte (Compt. rend., 1933, **197**, 322—323).—Temp.–concn. curves for the inflammation of mixtures of air and pure C_6H_6, PhMe, and *cyclo*-hexane and -hexene for temp. 100—300° in a wide pyrex vessel have been determined. They are straight lines slowly falling and rising from the temp. axis, respectively, save as regards the max. concn. of PhMe, which after rising falls slightly, indicating slow preliminary combustion. These results agree with those of White, but not with Berl and Fischer's, due probably to the doubtful purity of their materials and use of too narrow a tube (cf. A., 1925, ii, 553, 413). C. A. S.

Combustion of light hydrocarbons at constant volume. I—III. M. AKITA (J. Soc. Chem. Ind. Japan, 1933, **36**, 436—440B).—I. When a mixture of a *n*-paraffin or a *n*-primary alcohol and air or O_2 is heated in a SiO_2 vessel a no. of sudden pressure rises occurs and oxidation is complete at 570—580° (hydrocarbons) or 530—570° (alcohols). The no. of sudden rises is equal to the no. of C atoms in the mol., the temp. at each rise is equal to that of the next following rise for the next higher homologue, and the temp. (except the first) are the same for the alcohols and the hydrocarbons. The following reaction mechanism is suggested: $C_nH_{2n+2}+O\longrightarrow C_nH_{n+1}\cdot OH\longrightarrow CH_2O$; $CH_2O+O\longrightarrow CO(\text{or } CO_2)+H_2O$.

II. The heats of reaction at the three stages are +33·8, −11·9, and +21·9 g.-cal., respectively, independent of the val. of *n*. As *n* increases the flame propagation velocity (I) increases and the combustion velocity (II) diminishes. The initial reaction temp. is the same as the spontaneous ignition temp.

III. Knocking of hydrocarbons diminishes with increasing energy requirement for initiating combustion, with diminishing (I), with increasing (II), and (within a homologous series) with rising reaction temp. Anti-knock agents raise the reaction temp. When the energy required to initiate combustion is low sufficient is supplied by the engine compression and knocking occurs. A. G.

Explosion of carbon disulphide–nitric oxide mixtures. II. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1933, **52**, 549—566; cf. this vol., 355).—The degree of association of CS_2 at room temp. and 5—20 mm. is about 3%. The products of reaction differ according to the ratio CS_2 : NO; with increasing amount of NO the amount of S produced decreases. The variation of light energy with composition of the mixture, and the yield for the optimal mixture have been determined. The duration of the flash is shortest when CS_2 : NO = 1 : 3 or 1 : 4, and increases with increasing pressure or vol. For practical purposes (*e.g.*, photography) the duration of the flash may be taken as 0·02 sec.; the light intensity rises relatively slowly at first, then rapidly, to a max., after which it falls rapidly at first and then slowly. E. S. H.

Explosive properties of propylene dichloride–air mixtures. G. W. JONES, W. E. MILLER, and H. SEAMAN (Ind. Eng. Chem., 1933, **25**, 771—773).—The limits of inflammability of $CHMeCl\cdot CH_2Cl$ (I) in dry air at normal pressures and temp. up to 100° are from 3·4 to 14·5 vol.-%. The max. pressure developed in the apparatus used was 67 lb. per sq. in. above atm.; this was given by mixtures containing 5·02% of (I), *i.e.*, slightly > the amount (4·95%) necessary to consume all the O_2 present. (I)–air mixtures developed a max. pressure slightly > that for CH_4 (II)–air mixtures and considerably < that for $COMe_2$ (III), manufactured gas (IV), and HCO_2Me (V). The ignition temp. of (I) were < those for (II), approx.= those for (III) and (IV), and > those for (V). C. E. M.

Thermal decomposition of acetaldehyde and the existence of different activated states. C. J. M. FLETCHER and C. N. HINSHELWOOD (Proc. Roy. Soc., 1933, **A**, **141**, 41—55).—The rate of decomp. of MeCHO has been measured over a range of initial pressures 0·2—1100 mm. Abrupt changes of slope are shown by the curve connecting reciprocal of time of half decomp. with initial pressure. These results are explained on the assumption that the reaction, even when wholly homogeneous, is kinetically composite, and can be interpreted by the theory that the MeCHO mol. can be activated in a limited no. of ways, and that the different activated states are associated with different transformation probabilities. There are thus several virtually independent quasi-unimol. decomps. for the same chemical reaction. L. L. B.

Thermal decomposition of ethyl azide: homogeneous unimolecular reaction. J. A. LEERMAKERS (J. Amer. Chem. Soc., 1933, **55**, 2719—2729).—The thermal decomp. of 0·08—19·5 cm. of EtN_3 at 199—240° affords N_2, C_2H_4, HN_3, $CHMe{:}NH$, C_4H_{10}, and a solid. The reaction is of first order at high pressure, $k_\infty=2\times10^{14}e^{-39,740/RT}$, but k decreases when the pressure is depressed below 2 cm. For the theoretical expressions relating k and pressure to be consistent with the data, a mol. diam. of $6\cdot2\times10^{-8}$ cm. and fourteen classical oscillators are required. k is slightly and consistently diminished by increasing the surface : vol. ratio of the reaction vessel. J. G. A. G.

Effect of solvent on the reaction between iodine and hydrogen sulphide. M. R. A. RAO and B. S. RAO (J.C.S., 1933, 836—839).—I and H_2S do not interact in dry CCl_4 solution, but addition of C_5H_5N causes rapid and complete reaction. The reaction is slow and incomplete when small quantities of H_2O or EtOH are present in the solvent. In dry Et_2O the reaction is slow but nearly complete. The progress of the reaction in a given solvent depends on removal of the HI formed; *e.g.*, with C_5H_5N in CCl_4 it is pptd. F. L. U.

Spontaneous change in aqueous solutions of stannic chloride. J. GUERON (Compt. rend., 1933, **197**, 247—249).—The % of Sn not flocculated in aq. solutions containing 2—40 g. of $SnCl_4,5H_2O$ per litre at 20° when plotted against time give similar curves, showing first a period of induction decreasing with decreasing concn. and shorter when tested by ultrafiltration than by centrifuging, followed by a period of flocculation in which most of the Sn is removed by either method, and lastly a period in which the Sn in solution tends to a limit of about 1%. The p_H is always the same as that of the clear liquid, and remains const. as soon as the solution has become opalescent. Only $2\pm0\cdot5$% of the Cl is carried down with the ppt. when formed spontaneously, and this is wholly removed on agitation and centrifuging (cf. J.C.S., 1922, **121**, 441; A., 1929, 29; 1932, 692). C. A. S.

Velocity of bromination of ethyl acetoacetate. I. The water reaction. K. J. PEDERSEN (J. Physical Chem., 1933, **37**, 751—764).—The velocity has been measured at 18° when the ester is dissolved in H_2O, and in aq. solutions of HCl, NaCl, KCl, and KBr. It is independent of [Br] and is not catalysed by $H^\cdot$. The measurements indicate the occurrence of

the consecutive reactions (1) $\cdot CO\cdot CH_2\cdot \longrightarrow \cdot C(OH){:}CH\cdot$, (2) $\cdot C(OH){:}CH\cdot + Br_2 \longrightarrow \cdot CO\cdot CHBr\cdot + H^{\cdot} + Br'$, (3) $\cdot CO\cdot CHBr\cdot \longrightarrow \cdot C(OH){:}CBr\cdot$, (4) $\cdot C(OH){:}CBr\cdot + Br_2 \longrightarrow \cdot CO\cdot CBr_2\cdot + H^{\cdot} + Br'$. The observed velocity is determined by (1) and (3). F. L. U.

Increase in reaction velocity of tertiary acids by the presence of a carbonyl group in the γ-position. H. APPEL (Z. physiol. Chem., 1933, **218**, 202—208).—According to the accepted constitution of cholesterol the CO_2H group has a similar position in the acids $C_{24}H_{40}O_3$ (I) and $C_{23}H_{38}O_3$ (II) (A., 1923, i, 1204). The great difference in the saponification velocity of the respective esters is due to the position of the :CO group relative to the CO_2H, since on reduction of the :CO to :CH_2 the esters show a similar saponification velocity, both behaving as esters of *tert.* acids. Evidently the reaction velocity of a *tert.* CO_2H is considerably increased by the presence of :CO in the -position. This is further exemplified in the behaviour of camphononic acid (III) and its reduction product. (II) gave the *acid* $C_{23}H_{40}O_2$, m.p. 134—135° [*Me* ester (IV), an oil; *semicarbazone* of (IV), m.p. 182·5°], by Clemmensen reduction. (III) [*semicarbazone* (V), m.p. 225°] formed the *Me* ester, m.p. 29·5—30° (*semicarbazone*, m.p. 220—221°), with CH_2N_2. By Wolff–Kishner reduction at 180°, (V) afforded *camphonanic acid*, m.p. 190—191°, $[\alpha]_D^{15}$ + 17·1° in C_6H_6 (*Me* ester, m.p. —6°). J. H. B.

Mechanism of oxidation processes. XXXIV. Anaerobic fermentation of citric acid by yeast. H. WIELAND and R. SONDERHOFF. **XXXV. Aerobic dehydrogenation of alcohol by yeast.** H. WIELAND and F. WILLE.—See this vol., 865.

Heterogeneous reactions of the type $A_{solid} + B_{gaseous} \rightleftharpoons C_{solid}$. I. Inconstancy of equilibrium pressure, "apparent equilibria," and their interpretation. II. Kinetics of formation and decomposition of carbonates. J. ZAWADZKI and S. BRETSZNAJDER (Z. physikal. Chem., 1933, **B**, 22, 60—78, 79—96; cf. this vol., 474).—I. In such reactions as $CaCO_3 \rightleftharpoons CaO + CO_2$ there may be considerable delay in the establishment of the equilibrium pressure, p. Thus if CaO is subjected to a CO_2 pressure much $> p$ and the temp. varied the apparent equilibrium pressures are all too high, whilst if $CaCO_3$ is rapidly decomposed by vac. treatment the pressure–temp. curves are initially too low. Under some conditions the pressure–temp. curves ultimately become normal, but sometimes they fail to do this. A possible partial explanation of these phenomena is that when reaction is rapid a large no. of nuclei of resultant are formed which are so small as to have abnormal dissociation pressures. To arrive at a complete explanation it seems necessary to suppose that the chemosorption of CO_2 prior to the appearance of a second solid phase is not confined to a surface layer, but that between surface compounds in Langmuir's sense and systems of two solid phases there may exist stable intermediate systems with a decomp. tension depending on the composition, particle size, and no. and kind of the active centres.

II. Measurements of the effect of pressure, composition, structure, previous history of the system, and temp. on the rates of the reactions $CaCO_3 \rightleftharpoons CaO + CO_2$ and $CdCO_3 \rightleftharpoons CdO + CO_2$ have given results agreeing with the above theory. R. C.

Autoxidation. VIII. Decomposition of dithionic acid. P. GOLDFINGER and H. D. GRAF VON SCHWEINITZ (Z. physikal. Chem., 1933, **B**, 22, 117—133; cf. this vol., 25).—In acid solution at 85° the rate of decomp. is proportional to [H·] and $[S_2O_6'']$. From the experimental data the heat of activation, Q, is calc. to be 29·8 kg.-cal. for a frequency exponent of 14·2, whilst assuming 10 degrees of freedom to be involved in the decomp. of $H_2S_2O_6$ by H_2O in acid solution the val. of 32·6 kg.-cal. results. In alkaline solution at 120—180° there is decomp. into SO_3'' and SO_4'' at a rate which is proportional to $[S_2O_6'']$ and [OH'], unless either of these $> 0{\cdot}32N$, when the velocity coeff. increases with the concn. For this reaction the val. of Q is 25 kg.-cal. In neutral solution decomp. into SO_3'' and SO_4'' occurs at a rate independent of [H·] and [OH']. The addition of SO_3'', SO_4'', CrO_4'', and BrO_3' does not influence the rate of decomp. in acid, alkaline, or neutral solutions. It is considered that the process the velocity of which is measured is $S_2O_6'' + H_2O = SO_3'' + SO_4'' + 2H^{\cdot}$, not $H_2S_2O_6 = 2HSO_3$. The absorption of heat in the latter reaction is at least 37 kg.-cal., which also represents a lower limit for the firmness with which the S atoms in $H_2S_2O_6$ are linked. R. C.

Influence of magnetic field on corrosion of iron in solutions of salts of noble metals. H. FORESTIER and (MLLE.) M. HAURY (Compt. rend., 1933, **197**, 54—56; cf. A., 1930, 1002).—The ratio of the amounts of Fe dissolved in presence of a magnetic field to that dissolved in its absence increases with increasing field strength at a decreasing rate tending to a limit, the order of the effect being $HgCl_2 > AuCl_3 > AgF$. When these ratios are plotted against concn. of the other metal there is, except with AgF, first an increase, then a decrease tending to a limit increasing in the order AgF, $AuCl_3$, $HgCl_2$, $CuCl_2$, $CuBr_2$. The effect is attributed to increase in solution pressure of Fe by magnetisation. C. A. S.

Influence of fluid velocity on heterogeneous reactions. I. General theory. S. UCHIDA (J. Soc. Chem. Ind. Japan, 1933, **36**, 416—420B).—Heterogeneous reactions are dynamically similar to heat transfer processes, the temp. difference, thermal conductivity, and coeff. of heat transfer being replaced by the concn. difference, diffusion const., and reaction const., respectively. A. G.

Kinetics and heat of adsorption of oxygen on platinum. E. B. MAXTED and N. J. HASSID (Trans. Faraday Soc., 1933, **29**, 698—702).—The heat of adsorption of O_2 on Pt-black is const. up to the stage where adsorption becomes relatively slow. At advanced stages, the rate of adsorption accords with the expression: adsorbed concn. $= kt^n$, but in the initial stages, the rate is markedly dependent on the pressure. J. S. A.

Catalysis of the hydrogen–sulphur reaction by minute traces of oxygen. E. E. AYNSLEY, T. G. PEARSON, and P. L. ROBINSON (Nature, 1933, **132**, 101).—The curvature found by Norrish and Rideal (J.C.S., 1923, **123**, 696) in the $(\log d[H_2S]/dt)/(1/T)$

curve is due to traces of O_2 in the H_2–N_2 mixtures. As these traces are more and more completely removed by successive treatments of the H_2–N_2 mixture with alkaline pyrogallol or with $CrCl_2$ + Zn the rate of H_2S formation approaches that obtained with pure H_2. L. S. T.

Acceleration and retardation by various elements of the oxidation of materials by sulphuric acid. J. RANEDO (Anal. Fís. Quím., 1933, **31**, 195—200).—The influence of compounds of 36 elements on the rate of oxidation of org. matter by hot conc. H_2SO_4, as used in the Kjeldahl method, has been determined. Pt, Pd, Se, Mo, and Hg reduce the time required for complete oxidation from 4·5 hr. to < 1 hr., the three first-named being the most active; B, Al, La, Th, Pb, and Ta increase the time to 8—12 hr. The retarding agents are practically inoperative in presence of, *e.g.*, Pt. When Pt alone is used, the rate of oxidation falls considerably as the quantity of Pt present is reduced, whereas the rate in presence of Se falls but slowly as the Se concn. is reduced. H. F. G.

Inhibitors in reduction of vat dyes. E. BAUR (Z. physikal. Chem., 1933, **B**, **22**, 231—239).—The reduction of methylene-blue and phenosafranine with H_2 and the oxidation of the leuco-compounds with O_2 are retarded by various org. and inorg. substances capable of forming reduction–oxidation systems. The retardation varies with the concn. of inhibitor according to the formula previously published (A., 1931, 1250, 1378). R. C.

Relation of hydrogen to nickel with special reference to the catalytic power of the latter. H. N. HUNTZICKER and L. KAHLENBERG (Trans. Electrochem. Soc., 1933, **63**, 335—353).—Ni, free from S, was electrodeposited from $Ni(OAc)_2$ solution. After rubbing with sand, specimens were immersed in aq. solutions of various salts of Cu, Hg, and Ag. No displacement of these metals could be detected, but deposits of Cu_2Cl_2 and Hg_2Cl_2 were obtained from $CuCl_2$ and $HgCl_2$ solutions. From such experiments and from measurements of single potentials of Ni, Cu, Co, Ag, and Au in solutions of salts of Cu, Ag, and Ni, it is concluded that Ni is normally in a passive state which is not dependent on a surface effect. Immediately after cathodic treatment in H_3PO_4 solution Ni readily displaces Cu and Ag from their salt solutions, reduces $KMnO_4$, $FeCl_3$, KNO_3, etc., and, if the treatment has been sufficiently intensive or prolonged, will displace Co, Fe, and even Ni itself from their salt solutions. Raising the temp. of treatment above 35° gives a less active product. Ni charged with H exhibits no change in cryst. form according to the *X*-ray method. The H_2 liberated from Ni cathodes is markedly active even after it has completely left the metal surface; it will reduce S, P, As, Sb, and N_2. H. J. T. E.

Reaction mechanism. V. Active centres of typical hydrogenation catalyst. O. SCHMIDT (Z. physikal. Chem., 1933, **165**, 133—146; cf. A., 1932, 716).—For the hydrogenation of doubly linked C atoms the catalyst must have a porous fine-structure. Reaction probably takes place, not at active centres on the surface of the crystals, as Taylor supposes, but within the crystals in the cracks or pores visualised by Smekal; *i.e.*, it is not the adsorbed but the absorbed gases which react. The rate of hydrogenation is therefore to a large extent dependent on the closeness of the spacing of the catalyst mols. The active form of H which occurs within elements of the Fe and Pt group consists of positive ions, which could not exist on the surface of the crystals. For these catalysts the activation of the H and the hydrogenation is a reaction in solid solution. The mechanism of such hydrogenations as the above is not, however, necessarily identical with that of other catalysed reductions, such as the reduction of $PhNO_2$ with H_2. R. C.

Catalytic activity and potential of the catalyst. A. R. MIRÓ and N. G. MORALES (Anal. Fís. Quim., 1933, **31**, 103—114).—The activity of Pt in catalysing the decomp. of H_2O_2 solutions (0·4—0·5*N*) buffered with phosphate is a max. at p_H 12—13. The diminution of activity which is observed on repeated use of the catalyst is accompanied by an increase of the abs. potential of the Pt. A similar increase occurs in presence of a poison of the catalyst, whilst a reduction occurs during regeneration. When the catalyst is in contact for a prolonged period with strongly alkaline (4*N*-NaOH) solutions, gradual reduction of activity accompanied by slight change of potential is observed. The homogeneous unimol. velocity coeff. of the decomp. of H_2O_2 in $NaHCO_3$ solution passes through a min. at p_H 9·2 and a pronounced max. at p_H 9·7; in solutions buffered with phosphate there is a max. only, at p_H 12—13. H. F. G.

Catalytic activity of chromites for the oxidation of carbon monoxide. E. C. LORY (J. Physical Chem., 1933, **37**, 685—692).—The catalytic activity of Cu, Co, Ni, Fe^{II}, and Mn^{II} chromites in the oxidation of CO has been determined. The first three when heated undergo surface oxidation to chromate, and the last is reduced by CO at the temp. at which the substances are catalytically active. The catalytic action is explained on this basis. F. L. U.

Surface electrons in adsorption and catalysis. H. P. CADY and W. E. WHITE (J. Physical Chem., 1933, **37**, 823—824).—Currents up to 50 milliamp. at 50,000 cycles impressed on a Ni strip used to promote the reaction of H_2 and O_2 did not cause increased catalytic activity, such as would be expected on the theory developed by Nyrop (A., 1931, 1375; 1932, 553). F. L. U.

Influence of the shape and size of the pieces of contact substance on catalytic processes. I. E. ADADUROV and D. V. GERNET (J. Appl. Chem. Russ., 1933, **6**, 450—469).—A study of the process of oxidation of SO_2 to SO_3, using a Sn–Ba–V catalyst (I), indicates that % conversion depends not only on the free surface of the individual pieces of (I), but also on the mode of packing of these pieces, and on the resistance offered by them to flow of gas; for these reasons, hemispherical pieces, the sp. surface of which is much < that of rectangular prisms, give somewhat greater % conversion. For each size and shape of pieces of (I) there exist an optimum velocity of flow of gas, [SO_2], and duration of contact. R. T.

Catalysts for ammonia synthesis. D. A. Epstein and J. S. Upolovnikov.—See B., 1933, 668.

Influence of various factors on the synthesis of ammonia. C. Toniolo and G. Giammarco.—See B., 1933, 668.

Thermal reaction between acetaldehyde vapour and oxygen. R. N. Pease (J. Amer. Chem. Soc., 1933, **55**, 2753—2761; cf. A., 1932, 1210).—AcO_2H is the preponderant product of the interaction of 103—482 mm. MeCHO and 104—479 mm. O_2 at 90—150°, except when the reaction vessel is coated with KCl. The reaction is catalysed by broken glass packing and by coating the reaction vessel surface with KCl. H_2O, N_2, H_2, and C_2H_6 have no effect, but EtOH is an inhibitor. The reaction is autocatalytic, and the initial rate is proportional to the square of the MeCHO concn., but is independent of O_2 concn. The oxidation probably proceeds by way of reaction chains starting on the walls and terminating in the gas phase. J. G. A. G.

Reaction mechanism. VI. What elements catalyse hydrogenation ? O. Schmidt (Z. physikal. Chem., 1933, **165**, 209—227; cf. this vol., 912).—An extended account of work already noted (this vol., 680). With catalysts of the first class the activation of the H occurs on the surface with the aid of electrons and intermediate formation of H′, $H_2 + 2\ominus \quad 2Na^{\cdot} = 2NaH$, followed by decomp. of NaH giving H′ and H; the H then reacts with the C_2H_4. With catalysts of the second class activation occurs through the ionisation of the H_2 dissolved in the metal, giving $H_2^{\cdot}$, followed by $H_2^{\cdot} = H^{\cdot} + H$, and the $H^{\cdot}$ reacts with negatively-charged C_2H_4. R. C.

Reduction of sodium sulphate to sulphide. P. Budnikov (Compt. rend., 1933, **197**, 60—63).—When Na_2SO_4 is heated in a SiO_2 flask with sugar C reaction begins at 800°, with pine C at 750°, Acheson graphite at 880°, and lampblack at 750—800°, and proceeds rapidly, being autocatalysed by Na_2S, which lowers the m.p. of Na_2SO_4. With $3Na_2SO_4 : 1C$ the reduction at 850° is complete in 2—3 min., yield 95%; at 1000° in 40 sec., yield 88·6%. It is hence suggested that Na_2S be prepared by injecting powdered Na_2SO_4 into burners for powdered coal. Raising the temp. or prolonging the reaction reduces the yield, probably due to $2Na_2S \longrightarrow Na_2S_2 + 2Na$, and $Na_2SO_4 + Na_2S_2 \longrightarrow 4Na + 2SO_2 + S$ (cf. A., 1913, ii, 405). CO at 850° reduces Na_2SO_4, and at a lower temp. with a catalyst, *e.g.*, C or Ni, but the yield is >42—45% (cf. B., 1928, 111). H_2 in 45 min. at 800° gave 44% Na_2S, at 900° 68%, at 1000° 60%, and at 1100° 52%; or in presence of Ni 82, 83, 47, and ?, respectively. C. A. S.

Low-pressure hydrogen–oxygen reaction on platinum. E. O. Wiig (J. Amer. Chem. Soc., 1933, **55**, 2673—2679).—Contrary to Tanner and Taylor (A., 1931, 692) H_2 and O_2 at pressures $< 0{\cdot}1$ mm. react in the ratio 2 : 1 by vol. on a Pt catalyst when every possibility of change in composition of the gaseous mixture due to differential diffusion is eliminated. J. G. A. G.

[Interaction of] platinum oxide and carbon monoxide. P. V. McKinney and E. F. Morfit (J. Amer. Chem. Soc., 1933, **55**, 3050).—Unlike PdO (cf. this vol., 134), PtO is reduced by CO at temp. as low as 0°. The reaction is autocatalytic and has an induction period which is eliminated by the presence of freshly reduced Pt. J. G. A. G.

Electrolytic oxidisability of carbon monoxide. V. Sihvonen and P. Veijola (Suomen Kem., 1933, **B**, **6**, 63—64).—Experiments on the production of CO_2 and CO during electrolysis of aq. H_2SO_4 or NaOH with a graphite anode are described. The depolarising action of CO at a Pt or graphite anode is very slight. F. L. U.

Electrolysis of copper salts of organic acids. G. Kravtzoff (Compt. rend., 1933, **197**, 137—140).—The Cu deposited on electrolysis of solutions of the Cu salts of HCO_2H (I), AcOH (II), $EtCO_2H$ (III), chloro- (IV) and trichloro-acetic acid (V), and $PhSO_3H$ (VI), of concns. 3·65—41·5 g. Cu per litre with c.d. 0·2—0·8 amp. per sq. dm., give brittle deposits of colour varying from normal to bluish-black (II) and green (V). With (III), (IV), and (V) striæ along the lines of force are formed. The ratio of wt. of deposit on the electrode to that of deposit in a coulometer in series is almost always > 1 (1·47—0·96); it diminishes with increased c.d., acidity, dilution, or agitation. *X*-Ray examination of the deposit indicates presence of Cu_2O (cf. A., 1878, 706; 1907, ii, 548). C. A. S.

Electrolytic oxidation. III. Formation of dithionate by electrolytic oxidation of potassium sulphite. S. Glasstone and A. Hickling (J.C.S., 1933, 829—836; cf. this vol., 34).—The amount of S_2O_6'' formed by oxidation of K_2SO_3 at a Pt anode is nearly independent of temp., current strength, and $[SO_3'']$, if the electrode has previously been anodically polarised. If it has not been so treated the yield of S_2O_6'' is less, and still less if it has been polarised cathodically. The yield is a max. at p_H 8. Addition of catalysts for the decomp. of H_2O_2 decreases the yield. Efficiency of anode materials decreases in the order Ni>Pt,Au>platinised Pt>C. The oxidation is not due to a purely electrical process involving discharge of SO_3'', but is effected by H_2O_2. F. L. U.

Use of bimetallic anodes in the electrolytic synthesis of alloys. C. Béchard.—See B., 1933, 673.

Linear velocity of crystallisation of the cathode deposit in the electrolysis of certain lead salts. A. Glazunov and E. Bartunek (Chem. Listy, 1933, **27**, 172—175).—The linear velocity of crystallisation of Pb at the cathode in the electrolysis of aq. $PbCl_2$ or $Pb(OAc)_2$ is a function of their concn., and of the c.d. R. T.

Stick antimony electrode. [I.] Theory. [II.] Theoretical limitations. L. R. Parks and H. C. Beard (J. Physical Chem., 1933, **37**, 821—822, 822—823; cf. A., 1932, 470).—I. The Sb electrode is of the metal–metal oxide type, in which the oxide is in the form of an adsorbed film and the solution is not saturated with it. The electrode reaction is considered to take place at the interface metal–metal oxide.

II. As a means of determining [H·] the Sb electrode is theoretically correct only in the p_H range 1·60—7·87. F. L. U.

Prevention of injurious effect of antimony in electrodeposition of zinc and copper. N. KAMEYAMA and H. IIDA.—See B., 1933, 631.

Electrodeposition of metals and alloys from formamide solutions. R. D. BLUE and F. C. MATHERS (Trans. Electrochem. Soc., 1933, **63**, 327—334).—The physical character of Cu, Zn, Bi, Ni, Fe, and Cr electrodeposited from solutions of their anhyd. chlorides in $HCO{\cdot}NH_2$ was improved by the presence of HCl, but deposits of Sn, Pb, and Cd were unaffected. No deposits of Al or Mg were obtained, but Fe–Al alloys containing up to 17% Al were deposited from a solution of $FeCl_3$ and $AlCl_3$. Alloys of Al with Zn and Mn were obtained, but the Al content was very low. Good deposits of Zn and Ni were obtained from solutions of their thiocyanates in $HCO{\cdot}NH_2$, and a fair deposit of Cd from $Cd(CNS)_2$ solution. H. J. T. E.

Electrochemical reduction at the cathode, and its prevention in the electrolysis of barium chloride without a diaphragm. I. S. KATZEN (J. Chem. Ind. Russ., 1933, No. 4, 34—41).—In the electrolytic prep. of $Ba(ClO_3)_2$ (I) from $BaCl_2$, part of the (I) formed is reduced at the cathode by H. The addition of $K_2Cr_2O_7$ or of $MgCl_2$, $CaCl_2$, or $SrCl_2$ to the electrolyte and the use of a Cr-plated Fe cathode have very little or no influence on the yield per unit of current used (22—54% of theoretical after 4 hr.), whilst, using graphite electrodes, with 1% of $CaCl_2$ in the electrolyte, 84% yields are obtained. The addition of 0·3% of gum arabic to the electrolyte almost completely inhibits reduction (90% yields, in presence of $CaCl_2$), but leads to the production of large quantities of Cl_2 at the anode. Cathodic reduction is the greater the lower is the temp.; at 70° it is reduced to 3%. 80% yields of (I) are obtained even after 63 hr. under the following optimum conditions: 1% of $CaCl_2$ in the electrolyte, c.d.—anode 0·05 and cathode 0·5 amp. per sq. cm., temp. 50°, using graphite electrodes. R. T.

Influence of iron salts on the electrolytic reduction of benzophenone. S. SWANN, jun. (Trans. Electrochem. Soc., 1933, **63**, 227—228).—Fe salts inhibit the reduction of $COPh_2$ to $[CPh(OH){\cdot}]_2$ in aq. $EtOH–H_2SO_4$ when Al cathodes are used. H. J. T. E.

Formation of organic nitro-compounds by electrolytic action. D. F. CALHANE and C. C. WILSON (Trans. Electrochem. Soc., 1933, **63**, 117—127).—In a diaphragm cell with Al cathode and duriron anodes, the anode compartment being furnished with a stirrer and cooling coil, $C_{10}H_8$ suspended in aq. HNO_3 (d 1·25—1·29) is anodically nitrated at temp. $< 45°$ using 20 amp. per sq. dm. The HNO_3 concn. in the anode compartment rises, but remains much $<$ that needed for chemical nitration. The action of the current in promoting nitration is attributed to the formation of a film of much more conc. HNO_3 on the anode surface. H. J. T. E.

Primary process in the oxidation of tartrates in alkaline solution at a high anode potential. V. SIHVONEN (Suomen Kem., 1933, **B**, 6, 64—65).—By causing the electrolyte (alkaline Na tartrate solution) to stream past a Au anode, glyoxylic acid may be obtained with a max. current yield of 45%. If the anode liquid is not rapidly removed the glyoxylic acid is further oxidised to HCO_2H, $H_2C_2O_4$, and CO_2. F. L. U.

Influence of active nitrogen on oxidation. M. PRETTRE (Compt. rend., 1933, **197**, 328—330).—A mixture of 40% CO + 12% O_2 + 48% N_2, if the N_2 is activated by passage across a condensed spark and cooled, inflames at 620—655°, 560°, 520°, and 450° if the intervals between the N_2 leaving the spark and becoming mixed with the CO and O_2 are respectively 0·5, 0·2, 0·15, and 0·08 sec. If the active N is luminescent it inflames a mixture of CO and O_2 at room temp. (cf. A., 1927, 1156; this vol., 231). C. A. S.

Formation of ozone in the alternating-current corona discharge with tubes coated with paraffin, stearic acid, and platinum. H. G. THODE and A. C. GRUBB (Trans. Electrochem. Soc., 1933, **63**, 297—314).—The dependence of yield of O_3 on velocity of O_2 through an a.c. corona discharge tube has been investigated at various power inputs. The yield increases when the surface of the glass discharge tube has become sputtered with Pt, whereas coating the tube with paraffin decreases the yield, and coating with stearic acid causes further decrease. The corresponding thermal equilibrium temp., the electron efficiency, and the no. of mols. of O_3 formed per max. no. of ion pairs are calc. The nature of the wall effect is discussed in relation to theories of O_3 formation. H. J. T. E.

Behaviour of argon and krypton with fluorine in electrical discharges. O. RUFF and W. MENZEL (Z. anorg. Chem., 1933, **213**, 206—207; cf. this vol., 578).—No diminution in pressure or compound formation was observed. In presence of O_2, O_2F_2 was isolated. H. J. E.

Behaviour of argon and krypton with fluorine in electrical discharges. A. VON ANTROPOFF (Z. anorg. Chem., 1933, **213**, 208; cf. preceding abstract).—The author used different conditions (condensed discharge and circulating gas) in attempts to prepare rare gas halides. H. J. E.

Deposition of sputtered films. R. W. DITCHBURN (Proc. Roy. Soc., 1933, **A**, **141**, 169—188).—The deposition of sputtered Cd on glass and metal surfaces placed near the cathode has been investigated. There is no indication of a crit. density phenomenon similar to that found for the condensation of vapour. The rate of deposition for insulated surfaces is only slightly influenced by temp. changes from 30° to −150°, but it is affected by the conditions of the discharge and the potential of the target, being faster for surfaces collecting slow positive ions, slower for those collecting fast positive ions, and almost negligible for surfaces collecting electrons. In the last case the rate can be hastened by cooling. The sputtered metal giving these effects is uncharged. Experiments on the thickness and structure of the deposits are described, and a theory is suggested according to which the deposition is assisted by a surface cleaning effect of positive ions. L. L. B.

Photochemical union of chlorine and hydrogen in presence of oxygen, and relative rates of formation of water and hydrogen chloride in illuminated mixtures of the three gases rich in oxygen. D. L. CHAPMAN and J. S. WATKINS (J.C.S., 1933, 743—745; cf. *ibid.*, 1923, **123**, 3062).—When the proportion of Cl_2 is small, illumination of such mixtures may cause a greater no. of H_2O than of HCl mols. to be formed. The theoretical bearing of this result is considered. F. L. U.

Photographic sensitivity of silver sulphide. K. HICKMAN and W. WEYERTS (Nature, 1933, **132**, 134—135).—Colloidal Ag_2S suspended in solutions of $NaAgS_2O_3+Na_2SO_3$ is darkened by light and deposits Ag. The darkening occurs best in solutions of Ag_2SO_3 in excess of alkali sulphite and in $AgNO_2$ in alkali nitrite. The sulphide is slightly sensitive in double Ag tartrates, formates, and NH_3–Ag complexes. The darkening is due to the deposition of Ag on or near the sulphide surface. The reaction appears to concern adsorbed ions and the speed is approx. proportional to [Ag']. The limiting factor is apparently the exclusion of light from the active surface by the reduced Ag. Spectral sensitivity extends from the violet into the infra-red. The reaction is practically independent of p_H between 11 and 5, is depressed by gelatin, and shows a negative temp. coeff. with NO_2' and a positive coeff. with SO_3''. With photographic materials it affords a kind of image building or optical intensification. L. S. T.

Topography of the latent *X*-ray image. LUPPO-CRAMER and H. STEPS (Z. wiss. Phot., 1933, **32**, 113—128).—Ripening (*i.e.*, production of sensitive nuclei), without increase of grain size, increases the sensitivity of pure AgBr emulsions to *X*-rays. Treatment with CrO_3 or desensitising dyes reduces the sensitivity to some extent (much < the desensitisation to ordinary light). CrO_3, and also AcOH with developing agents, strongly attack a latent *X*-ray image. Pure AgBr emulsion is more sensitive than emulsion containing AgI, but the former is always larger-grained. From these results it is concluded that the primary Ag (" ripening " nuclei) is sensitive to *X*-ray action, and that the latent *X*-ray image cannot lie very deep in the grain of AgBr. J. L.

Schwarzschild effect with colloid-free silver bromide. A. J. RABINOVITSCH and C. S. BAGDASSARJAN (Z. wiss. Phot., 1933, **32**, 110—112).—Reciprocity failure is found to occur with varying exposure of pure AgBr (activated with dil. NaOH) to light, the results being measured by determining the amount of Ag pptd. J. L.

Influence of hydrogen-ion concentration on the light-sensitivity of colloid-free silver bromide. A. J. RABINOVITSCH and C. S. BAGDASSARJAN (Z. wiss. Phot., 1933, **32**, 97—109).—The sensitivity of AgBr suspensions increases with increased particle size (which reaches a max. on keeping). Using buffer solutions, the sensitivity increases rapidly with alkalinity above p_H 7·5. The adsorption of OH' also increases markedly at this point. Presence of a large excess of Br' greatly reduces the effects. The OH' also strongly sensitises AgBr to red light. J. L.

Photo-activity in anodic polarisation at peroxide-forming metals. V. SIHVONEN and A. JUSSILA (Suomen Kem., 1933, **B**, 6, 65—66).—When Pb or Ag in *N*-H_2SO_4 and *N*-NaOH, respectively, are anodically polarised in the dark, illumination causes the anode potential to decrease. If the potential is maintained const., the increase of current caused by illumination $\propto$ the light intensity. The metals are photosensitive only over a limited range of c.d. Pb responds to light extending to the orange, Ag to the red. Cu, Fe, Ni, Pt, and graphite do not show the effect, which is probably related to decomp. of metal peroxide. F. L. U.

Chemical reactions induced by light. V. L. VECCHIOTTI and C. PICCININI (Gazzetta, 1933, **63**, 319—322; cf. this vol., 602).—The action of sunlight for several months on a mixture of $PhNO_2$ and *m*-$C_6H_4Me{\cdot}NH_2$ gave orange *2'-hydroxy-3-methylazobenzene*, m.p. 105°. O. J. W.

Formation of sugars in mixtures of tartaric acid and aldehydes in tropical sunlight. V. GORE (J. Physical Chem., 1933, **37**, 745—749).—Sugar formation has been detected (by Benedict's solution) in mixtures of aq. tartaric acid with EtOH, BuOH, $C_5H_{11}{\cdot}OH$, CH_2O, and MeCHO, exposed to tropical sunlight. None was found in similarly treated solutions of tartaric acid or CH_2O separately. F. L. U.

Photovoltaic effects in Grignard solutions. III. R. T. DUFFORD (J. Physical Chem., 1933, **37**, 709—721; cf. A., 1931, 802).—Further experiments are described. The photovoltaic effect can be affected by, but is not caused by, surface films on the electrode. The response to *X*-rays is large compared with that to visible light. The origin of the effect is discussed. F. L. U.

Colloid substrate in photosynthesis. M. COPISAROW (Nature, 1933, **132**, 67). L. S. T.

Action of electrons on nitrogen iodide and other explosives. J. J. TRILLAT and H. MURAOUR (Bull. Soc. chim., 1933, [iv], **53**, 443—445).—NI_3, picric acid, Pb picrate, trinitrotoluene, glyceryl nitrate, and nitrated cotton do not explode when bombarded by electrons in a Coolidge–Lenard tube. E. S. H.

Effect of electronic bombardment on lead azide and silver acetylide. Thermal decomposition of explosives. H. MURAOUR (Chim. et Ind., 1933, **30**, 39—40T).—On bombardment with electrons both explosives blacken, the metals being liberated. No explosion was observed with $Pb(N_3)_2$, whilst of three experiments with Ag_2C_2 only one resulted in explosion and that after 3 min. The slow decomp. is analogous to that on heating the compounds. It is concluded that the decomp. of a single mol. is insufficient to initiate decomp. of the whole mass, but that the development of a combustion or detonation wave is dependent on the simultaneous decomp. of a large no. of mols. in the same region. J. W. S.

Chemical action of audible sound. E. W. FLOSDORF and L. A. CHAMBERS (J. Amer. Chem. Soc., 1933, **55**, 3051—3052).—Sound of high energy density and of frequency between 1000 and 15,000 causes coagulation of albumins, hydrolysis of carbo-

hydrates and esters, and pptn. of the hydroxides of Cu, Mn, Al, Ni, and Cr from their chlorides. In the presence of O_2, halides afford free halogen and H_2S gives S. Au is pptd. from $AuCl_3$. The reactions may be due to a conversion of sound into heat. J. G. A. G.

Action of quartz and alkali silicates on alkali carbonates. C. KROGER and E. FINGAS (Z. anorg. Chem., 1933, **213**, 12—57).—The dissociation pressures of $LiCO_3$ between 750° and 1100° were measured. Equilibria in the systems Li_2O–SiO_2–CO_2, K_2O–SiO_2–CO_2, and Na_2O–SiO_2–CO_2 were studied between approx. 400° and 1100° by measurement of the equilibrium CO_2 pressure. The conditions of formation of the following silicates were determined: Li_2SiO_3, Li_4SiO_4, Li_6SiO_5 (or Li_8SiO_6), K_2SiO_3, K_2SiO_5, K_4SiO_4, Na_2SiO_3, $Na_2Si_2O_5$, $Na_2Si_3O_7$, Na_4SiO_4. The heats of formation of these silicates were calc. from the temp. dependence of the equilibrium CO_2 pressures. H. J. E.

Dissolution of salt in metal. T. PECZALSKI (Compt. rend., 1933, **197**, 227—229).—When a Cu rod was heated for 8 hr. at 700° in $CaCl_2$ the salt became red and the rod lost 3% of its wt. If the rod is wrapped around with steel wire the salt is blackened by dissolved Fe and the wire covered with Cu; the Cu rod is strongly cemented and its $d^{19°}$ reduced from 8·90 to 8·484. KCl, KF, and $BaCl_2$ behave similarly. When a current of 3 amp. per sq. cm. is passed between two such Cu rods in $CaCl_2$ at 700° for 1 hr., the cathode was much, the anode little, cemented. The positive ions of the salt thus enter the metal; a Debye–Scherrer photograph shows the effect. C. A. S.

Oxidation of colloidally-dissolved substances. II. S. VOSNESSENSKY and V. SKVORZOV (Kolloid-Z., 1933, **64**, 205—209; cf. A., 1932, 1002).—The amount of 0·04*N*-HCl reacting with colloidal Ag at 20° is equiv. to the [Ag^+] of the intermicellar liquid, but at 100°, using 1*N*-HCl, it is equiv. to the amount of Ag^+ in the micelles. The metallic Ag of the colloidal particle does not in any circumstances react. $FeCl_3$, however, converts colloidal Ag into AgCl. $KMnO_4$ oxidises colloidal Ag to Ag_2O_2. E. S. H.

Higher valency states of silver. M. S. EBERT, E. L. RODOWSKAS, and J. C. W. FRAZER (J. Amer. Chem. Soc., 1933, **55**, 3056—3057).—By interaction of Ag and F_2 at 300°, an unstable black material which is a powerful oxidising agent and contains > 75% of AgF_2 has been prepared. Other properties are described. J. G. A. G.

Hydrates of magnesium perchlorate. E. MOLES and C. ROQUERO (Anal. Fis. Quím., 1933, **31**, 175—184).—The *d* of $Mg(ClO_4)_2$ and of the tri- and hexa-hydrates are 2·208 (lit. 2·600), 2·06, and 1·906, respectively. It is probable, from spatial considerations, that the so-called trihydrate is not a true compound but consists of mixed crystals. The dihydrate is probably a hydroxonium derivative, in which the mol. vol. of the H_2O is 10, whilst in the hexahydrate the mol. vol. of each of the four additional H_2O mols. is 13. H. F. G.

Calcium silicates. I. Synthesis. S. KONDO and T. YAMAUCHI (J. Soc. Chem. Ind. Japan, 1933, **36**, 167B).—The reactions between 3 : 1, 2 : 1, 3 : 2, and 1 : 1 mixtures of $CaCO_3$ and SiO_2 when heated at temp. between 600° and 1800° have been studied. Four very pure Ca silicates have been prepared. H. F. G.

Hydrothermal synthesis of calcium silicates under pressure. III. S. NAGAI (J. Soc. Chem. Ind. Japan, 1933, **36**, 403—407B).—When CaO and SiO_2 in the proportions 1 : 1—5 : 1 are heated in an autoclave with H_2O most of the SiO_2 and a part of the CaO and H_2O combine. The compounds are considered to be $CaO,SiO_2,0{\cdot}25H_2O$, $3CaO,2SiO_2,8H_2O$, $3CaO,2SiO_2,H_2O$, and $2CaO,SiO_2,H_2O$ or mixtures of these. A. G.

Synthesis of calcium silicates. VI. S. NAGAI and K. MURAKAMI (J. Soc. Chem. Ind. Japan, 1933, **36**, 326—330B).—Thermal synthesis of Ca silicates from a mixture of $CaCO_3$ and SiO_2 showed that the reaction is almost completed in 3 hr. at 1450°. $3CaO,SiO_2$ can be produced easily at this temp., one heating giving 99·65% purity. When further heated at 1150° $3CaO,SiO_2$, but not $2CaO,SiO_2$, showed slight decomp., which was accelerated by the presence of CaO, CaF_2, and $CaSO_4$. The dissociation was unaffected by $Ca_3(PO_4)_2$, MgO, or $2CaO,SiO_2$. C. A. K.

Calcium sulphate hemihydrate and its products of dehydration. P. GAUBERT (Compt. rend., 1933, **197**, 72—75).—Crystals of $2CaSO_4,H_2O$ obtained by evaporation of a boiling solution of $CaSO_4$ in HNO_3 are rhombohedral, not rhombic (cf. A., 1916, ii, 450), *d* 2·735, n_ω 1·558, n_ϵ 1·586. When heated in air the crystals are dehydrated at 130° forming van 't Hoff's γ-anhydrite, *d* 2·61, n_ω 1·505, n_ϵ 1·548. At 170° this passes into the β-form, which appears to be rhombic, and seems to be Lacroix's "probably triclinic form," *d* 2·85, n_β 1·595, n_α 1·562. When heated in vaseline $2CaSO_4,H_2O$ loses no H_2O below 170°, and if rapidly heated passes directly into β-anhydrite. The β-form at 650° is transformed into the α-form (cf. A., 1932, 482). C. A. S.

Properties of tricalcium silicate from basic open-hearth steel slags. O. ANDERSEN and H. C. LEE (J. Washington Acad. Sci., 1933, **23**, 338—351).—Crystals of $3CaO,SiO_2$ isolated from the non-magnetic fraction of basic slags by treatment with a mixture of CH_2I_2 and CCl_4 (*d* 3·24), on which they floated, contained SiO_2 22·77, TiO_2 0·18, P_2O_5 1·72, Al_2O_3 0·20, Fe_2O_3 0·76, FeO 2·01, MnO 1·20, MgO 1·29, and CaO 68·65%. About 12% of the 14% of impurities present was in solid solution. The crystals are trigonal with rhombohedral development, *c*/*a* 1·773, d_4^{20} 3·224, n_D 1·724, and birefringence (ω—ϵ) = 0·005. At 1400° the substance is decomposed into β-$2CaO,SiO_2$ and free CaO. A. R. P.

Calcium carbide and calcium cyanamide. J. GELHAAR.—See B., 1933, 668.

Calcium arsenate. G. FESTER and F. BERTUZZI (Angew. Chem., 1933, **46**, 477—478).—A suspension of As_2O_3 in H_2O is treated with bleaching powder (containing 7·1% active Cl) with const. stirring at 25—30°. $Ca_3(AsO_4)_2$ is pptd. and is rapidly removed, as it reacts further to form $CaCl_2$. E. S. H.

Hydrated calcium aluminates. A. TRAVERS and P. LEDUC (Compt. rend., 1933, **197**, 252—253).—The transformation of hexagonal into cubic Ca aluminate (cf. this vol., 794) is the more rapid the higher is the p_H, *e.g.*, with $p_H > 12$ in 30 min. at 40—45°, or 24 hr. at room temp., although sometimes it occurs more slowly, or there may be false equilibria. The transformation is reversible (cf. A., 1930, 162, 436, 1262). C. A. S.

Oxidation of zinc dimethyl. H. W. THOMPSON and N. S. KELLAND (J.C.S., 1933, 746—756).—The velocity of oxidation of $ZnMe_2$ vapour by O_2 at low pressures and room temp. is very high but measurable. The product is ZnMe·OMe. At higher pressures the reaction is explosive, the principal products being CO, CH_4, and H_2. Both reactions are preceded by an induction period. The mechanism is discussed. F. L. U.

Oxidation of zinc diethyl. H. W. THOMPSON and N. S. KELLAND (J.C.S., 1933, 756—757; cf. preceding abstract).—The vapour is oxidised by O_2 with measurable rapidity at 50°, giving rise to a peroxide $ZnEt_2O_2$, which does not decompose explosively. F. L. U.

Mechanism of precipitation processes. XIII. Processes in which $HgCl_2$ participates. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1933, **213**, 155—160; cf. this vol. 564).—The HgS pptd. from excess of aq. $HgCl_2$ by aq. Na_2S contains the *compound* $2HgS,HgCl_2$, which increases in amount on keeping. Formation of this compound is hindered by HCl or NaCl. Aq. $HgCl_2$ and aq. NaOH form the compound $4HgO,HgCl_2$ similarly. HgO and $HgCl_2$ react more readily than do HgS and $HgCl_2$. This is due to the greater solubility of HgO. Undissociated mols. of $HgCl_2$ take part in these reactions. H. J. E.

Action of phosphorus trichloride on boron tribromide. E. WIBERG and K. SCHUSTER (Z. anorg. Chem., 1933, **213**, 94—96).—With excess of either PCl_3 or BBr_3 only the solid white *compound* BBr_3,PCl_3 (m.p. 42°) is formed. It is decomposed by H_2O (cf. Tarible, A., 1901, ii, 153). H. J. E.

Dimethylamino-substituted boron trichlorides. E. WIBERG and K. SCHUSTER (Z. anorg. Chem., 1933, **213**, 77—88; cf. A., 1912, i, 171).—The *compounds* BCl_2NMe_2, $BCl(NMe_2)_2$ and $B(NMe_2)_3$ were isolated from the reaction products of BCl_3 with various proportions of $NHMe_2$. They are colourless liquids with f.p. —46°, —54°, and —40° and b.p. 111·9°, 146·1°, and 147·5°, respectively. The v.p. were measured. They react with H_2O forming H_3BO_3, HCl, and $NHMe_2$. With HCl they form the solid *compounds* $BCl_2·NMe_2,HCl$, $BCl(NMe_2,HCl)_2$, and $B(NMe_2)_3,5HCl$, respectively. H. J. E.

Different chemical compounds of the formula BCl_2,NMe_2. E. WIBERG and K. SCHUSTER (Z. anorg. Chem., 1933, **213**, 89—93; cf. preceding abstract).—Liquid $BCl_2·NMe_2$ deposits on keeping or warming white monoclinic crystals of the same composition (*a* 6·47, *b* 6·63, *c* 6·47 Å.; 2 mols. in unit cell). The crystals are unattacked by H_2O or gaseous HCl. The mol. wt. in C_6H_6 show a double mol. The mol. of the liquid is single in C_6H_6. The constitution of the solid is discussed. H. J. E.

Action of boric acid on alkaline-earth chlorides and nitrates. PENG CHUNG-MING (Compt. rend., 1933, **197**, 153—155).—By heating in steam at 150—300° mixtures of H_3BO_3 and MCl_2 or $M(NO_3)_2$ (M=Ca, Sr or Ba) in ratios 1 : 10 to 6 : 1, HCl is rapidly, H_3BO_3 slowly evolved. In all cases $MO,4B_2O_3$ is formed (cf. A., 1927, 325), but (especially for M=Ca) is gradually destroyed on continued heating. Formation of $3CaO,B_2O_3,CaCl_2$ was not confirmed (cf. A., 1884, 1261). C. A. S.

Amorphous aluminium carbide. L. WOHLER and K. HOFER (Z. anorg. Chem., 1933, **213**, 249—254).—Electric furnace preps. of Al_4C_3 consist of a mixture of yellow crystals (I) and a chrome-yellow amorphous powder (II), of the same composition. (I) remains undecomposed when heated at 1000°, whereas (II) decomposes slowly into Al and C at >700°. (II) reacts readily with conc. HCl, (I) only slowly, and with H_2O at 50° (II) evolves twice the vol. of CH_4 evolved by (I) in the same time. The difference in behaviour is ascribed to the larger surface of (II). A. R. P.

New phosphors from the hydrated sulphates of aluminium and other metals with organic luminous substances. M. TRAVNIČEK (Ann. Physik, 1933, [v], **17**, 654—678).—A new class of phosphors can be prepared from $Al_2(SO_4)_3,18H_2O$ and similar sulphates with org. mols. like fluorescein and uranin. For the successful prep. of phosphors the org. mol. must be molecularly dispersed in the ground material. A certain amount of H_2O in the mol. of the ground material is necessary. The effect of concn. of fluorescein and temp. on the phosphorescence of the $Al_2(SO_4)_3,18H_2O$–fluorescein phosphors was investigated. In these phosphors the Al can be replaced by Be, Zr, or Th, whilst the SO_4 may be replaced by SeO_4. A. J. M.

Chemistry of indium. A. W. DOWNES and L. KAHLENBERG (Trans. Electrochem. Soc., 1933, **63**, 163—166).—Determinations of replacing power and electrode potential indicate that In is slightly less noble than Sn. The electrode potential is scarcely affected by gases. Passage of H_2 over molten In gives a brown coating of *hydride* which decomposes at 330°. H. J. T. E.

Indium sulphate. R. P. SEWARD (J. Amer. Chem. Soc., 1933, **55**, 2740—2744).—At room temp. in presence of excess of H_2SO_4, $In_2(SO_4)_3,H_2SO_4,7H_2O$ crystallises, but in the absence of excess of acid $In_2(SO_4)_3,9H_2O$ crystallises, whilst EtOH ppts. $In_2O(SO_4)_2,6H_2O$. $In_2(SO_4)_3,6H_2O$ and $In_2(SO_4)_3,3H_2O$ exist. The decomp. pressure of anhyd. $In_2(SO_4)_3$ is 1 atm. at 810°. The salt is hydrolysed in aq. solution. J. G. A. G.

Stability of methane, ethane, and carbon monoxide at low temperature. F. E. C. SCHEFFER (Bull. Soc. chim. Belg., 1933, **42**, 251—268).—A lecture on the reactions (*a*) $x\text{Ni}+CH_4 \rightleftharpoons \text{Ni}_x\text{C}+2H_2$, (*b*) $x\text{Ni}+2CO=\text{Ni}_x\text{C}+CO_2+49{\cdot}5$ kg.-cal., (*c*) $x\text{Ni}+2C_2H_6=\text{Ni}_x\text{C}+3CH_4$. Ni_xC is an exothermal com-

pound, stable below 420°, but decomposing at 420° according to $Ni_xC=xNi+C-7{\cdot}4$ kg.-cal. E. S. H.

Influence of combined oxygen on determination of vapour isothermals on porous solids. II. L. J. BURRAGE (J. Physical Chem., 1933, **37**, 735—744; cf. this vol., 563).—CCl_4 vapour used to flush out adsorbed H_2O from SiO_2 gel reacts with the former at 100° to give $COCl_2$ and HCl. Part of the structural H_2O is also removed, thereby diminishing the capacity of the gel. C_6H_6 is less effective than CCl_4 for removing H_2O, but at 100° it produces a definite cleansing effect, resulting in increased capacity. At 230°, however, the gel structure is affected and the capacity diminished. Further experiments with C as adsorbent have shown that rapid equilibrium and a stepped isothermal can be obtained by flushing at 110° as well as at 800°. It is considered that in all previous work isothermals on C relate to surfaces poisoned by CO_2. F. L. U.

Zirconium sulphides. PICON (Compt. rend., 1933, **196**, 2003—2006).—By the action of H_2S on ZrO_2 at 1100—1700° three sulphides, ZrS_2, Zr_2S_3, and Zr_3S_5, $d^{\prime\prime}$ 3·87, 4·10, and 4·62, respectively, have been obtained. In H_2 (in a graphite boat) S is lost and a carbide (5% C) is formed; in N_2 at 2000° a nitride (volatile) and carbide are formed. C. A. S.

Properties of zirconium sulphides. PICON (Compt. rend., 1933, **197**, 151—153; cf. preceding abstract).—The sulphides are referred to in the order ZrS_2, Zr_3S_5, Zr_2S_3. Dry Cl_2 reacts at 250°, 235°, 250°; HCl at 165°, 210°, 280°; O_2 forms SO_2, basic sulphate, and oxide from 180°, 225°, 350°; SO_2 oxidises from 140°, 170°, 175°; Br reacts at room temp., more rapidly if moist; S with H_2 at 1000° converts all into ZrS_2; H_2O at 200° slowly forms sulphate and oxide; aq. HCl acts slowly on ZrS_2 and Zr_3S_5, not on Zr_2S_3; 10% aq. H_2SO_4 attacks all slowly; NH_3 at 1000° forms a nitride to the extent of 25%; aq. NH_3 attacks only ZrS_2; conc. HNO_3 attacks all violently, dil. does not attack ZrS_2; CO_2 at 500° gives CO, S, and ZrO_2; Mg (in H_2) removes S at 1000°; aq. NaOH attacks ZrS_2 rapidly, Zr_3S_5 slowly, Zr_2S_3 not at all; no compound is formed with PtS or Sb_2S_3 (in H_2) at 1000°; H_2O_2 attacks all with decreasing rapidity; aq. $KMnO_4$ attacks all slowly; aq. $K_3Fe(CN)_6$ more slowly. C. A. S.

Stannous oxide. M. STRAUMANIS and C. STRENK (Z. anorg. Chem., 1933, **213**, 301—309).—Pure SnO is obtained as a bluish-black cryst. powder by dehydration of $Sn(OH)_2$ at 50° in the presence of small quantities of NaOH, Na_2CO_3, or HCl; it has a tetragonal structure, a 5·364±0·003, c 4·833±0·003 Å., c/a 0·901; $d_{calc.}$ 6·393. With larger amounts of acid or alkali grey to brown hydrated oxides of indefinite composition are formed. On heating a thick paste of hydroxide with a few crystals of $SnCl_2$ at 100° a yellowish-red hydroxide $2SnO,H_2O$ is formed; the air-dried hydroxide (white) has the composition $3SnO,2H_2O$. A. R. P.

Intensive drying. II. Reaction between ammonia and phosphorus pentoxide. E. MOLES and J. SANCHO (Anal. Fís. Quím., 1933, **31**, 172—174).—Pure and intensively dried NH_3 (gas) reacts instantaneously when brought into contact with sublimed P_2O_5; the product is vitreous on the surface and apparently unchanged in the interior. The ratio $NH_3:P_2O_5$ varies between 0·58 and 1·40 according to the conditions of the experiment. H. F. G.

Preparation of phosphorus oxychloride. N. A. ELMANOVITSCH and L. C. MAJOFIS (J. Chem. Ind. Russ., 1933, No. 4, 59—62).—90% yields of $POCl_3$ are obtained by passing Cl_2 through a solution of 1 mol. of P_2O_5 in 3 mols. of PCl_3, with the addition of 0·5 vol. of $POCl_3$; the process is complete in 6·5 hr. at 80°. R. T.

Phosphates. I. Ammonium magnesium phosphate and related compounds. II. Orthophosphates of the type $M_3(PO_4)_2,xH_2O$. III. Complex orthophosphates of sodium and a bivalent metal, and some orthophosphate solid solutions. H. BASSETT and W. L. BEDWELL (J.C.S., 1933, 854—871, 871—876, 877—882).—I. Salts of the type $NH_4M^{II}PO_4,6H_2O$ show strong incandescence on ignition, in contrast to the corresponding monohydrates, in which it is very faint. When M=Co or Ni the hexahydrates have colours characteristic of the cation, the monohydrates mixed colours indicating that part of the bivalent metal is anionic. The salts are true NH_4 compounds and not ammines, since NH_3 cannot be replaced by C_5H_5N. The hexahydrates are considered to be unimol., and the monohydrates quadrimol. On ignition they yield $M_2P_2O_7$ and $(M_2P_2O_7)_2$, respectively, of which the first is unstable, its heat of transformation into the second causing the observed incandescence. All the compounds $KMPO_4$ and most of the type $MHPO_4,xH_2O$ are probably quadrimol. The following *salts* are described: $KNiPO_4,6H_2O$; $KMPO_4,H_2O$ (M=Mg, Mn, Co, Ni, Cu, Cd); $CoHPO_4,2H_2O$; NH_4CoPO_4; $CuHPO_4,H_2O$.

II. Normal orthophosphates of Mg, Co, Ni, and Zn have been prepared and studied. Those of Cu, Mn, and Cd could not be obtained. The *compounds* $Cu_4P_2O_9,1{\cdot}2H_2O$ and $Cu_4P_2O_9,1{\cdot}6H_2O$ are described. The normal salts become incandescent on ignition, the heat evolved during the change being nearly the same as for the pyrophosphate of the same metal. The hydrates have usually 4 or 8 H_2O. Pink $Co_3(PO_4)_2,8H_2O$ has a blue (probably non-ionic) isomeride.

III. Na_2HPO_4, when used to ppt. salts of bivalent metals, may give normal phosphates as described in Part II, or compounds or solid solutions containing Na. The following *salts* are described: $Na_3MgH(PO_4)_2$; solid solutions $xNaMPO_4,yNa_2HPO_4$ (M=Mn, Cu, Cd), and $2CdHPO_4,Cd_3(PO_4)_2,12H_2O+2K_2HPO_4,Cd_3(PO_4)_2,4H_2O$. Structural formulæ are developed for all the compounds described. F. L. U.

Decomposition of arsenites by heat. R. RAT (Compt. rend., 1933, **197**, 59—60).—Na, K, and Ba di-, meta-, pyro-, and ortho-arsenites were heated rapidly to 730°. The diarsenites were undecomposed after several hr. at that temp. With the others conversion into arsenate and As is more rapid as the base is stronger and in greater proportion relatively to As_2O_3, and proceeds until an approx. fixed proportion of As_2O_3 has been so converted,

12·9—14·4% for meta-, 72—74% for pyro-, and 100% for ortho-arsenites. The temp. at which conversion begins is the lower the greater is the proportion of base, and its strength (cf. A., 1932, 810). C. A. S.

Formulæ of antimonic acid and the antimonates. L. PAULING (J. Amer. Chem. Soc., 1933, 55, 3052).—Concerning priority (cf. this vol., 664). J. G. A. G.

Amorphous sulphur. O. VON DEINES (Z. anorg. Chem., 1933, **213**, 183—188).—The soft amorphous S obtained by acidifying aq. $Na_2S_2O_3$, aq. thionates, or aq. Na polysulphide, or from aq. SO_2 and aq. H_2S always contains S-rich H_2S_x, and may be made to yield H_2S. The only amorphous form of S is the solid, insol. in CS_2. H. J. E.

Sulphur sesquioxide. L. WOHLER and O. WEGWITZ (Z. anorg. Chem., 1933, **213**, 129—148; cf. A., 1925, ii, 890).—The chemical identity of S_2O_3 has been confirmed. The thermal decomp. of S_2O_3 at 40—80° yields $S+SO_3$ (20%), and $SO+SO_2$ (80%). The SO is not isolated. It decomposes into S and SO_2. No $EtNaSO_2$ or Na_2SO_2 was detected in the reaction of S_2O_3 with NaOEt. The products were S, Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, $Na_2S_3O_6$, and EtSH (or MeSH when NaOMe was used). The occurrence of these products is correlated with the mechanism of decomp. of S_2O_3. The formula is $\overset{S}{O}\!>\!S\!<\!\overset{O}{O}$. H. J. E.

" Blue acid " of the lead chamber process. II. W. MANCHOT (Z. anorg. Chem., 1933, **213**, 255—256; cf. this vol., 240).—A reply to Berl (this vol., 580). The formation of " blue acid " decreases with decreasing $OH{\cdot}SO_2{\cdot}NO_2$ content of the H_2SO_4; it can be obtained with oleum and $OH{\cdot}SO_2{\cdot}NO_2$ instead of $NaNO_2$. A. R. P.

Action of thiosulphate on dilute acid solutions. F. PRAKKE and E. STIASNY (Rec. trav. chim., 1933, **52**, 615—639).—The main reactions are (*a*) $H^{\cdot}+S_2O_3''\rightleftharpoons HSO_3'+S$, and (*b*) $6H^{\cdot}+5S_2O_3''\rightleftharpoons 2S_5O_6''+3H_2O$. The influence of each of the products is examined from the viewpoint of the law of mass action. Reaction (*b*) is very slow; no S_3O_6'' appears to be formed. At p_H 0—0·3 (*a*) occurs to the extent of 92·5%, whilst at $p_H>3$ (*b*) proceeds to the extent of 92%. The p_H at which $Na_2S_2O_3$ begins to react with acids depends on the concns. of the reagents. At room temp. only traces of H_2S are formed. H_2S is not a primary product and its formation is explained on the assumption of two tautomeric forms of $Na_2S_2O_3$. E. S. H.

Action of thiosulphate on dilute chrome alum solutions. E. STIASNY and F. PRAKKE (Rec. trav. chim., 1933, **52**, 640—656).—In addition to the reaction products obtained from $Na_2S_2O_3$ and acids (cf. preceding abstract), a sulphito-sulphato-Cr complex is produced to an extent which varies with the proportions in which the reagents are mixed. Determinations have been made of SO_4'' bound with (*a*) the Cr complex, (*b*) $Cr^{\cdot\cdot\cdot}$, (*c*) $Na^{\cdot}$, SO_3'' bound with Cr complex or $Cr^{\cdot\cdot\cdot}$, S_2O_3'' bound with Cr complex or $Cr^{\cdot\cdot\cdot}$, polythionates, $Cr^{\cdot\cdot\cdot}$, $Ba^{\cdot}$, and pptd. S. E. S. H.

Preparation of heavy metal polythionates. O. VON DEINES and E. CHRISTOPH (Z. anorg. Chem., 1933, **213**, 209—239).—Heavy metal polythionates can be prepared by double decomp. of the K polythionate with the tartrate, fluosilicate, or, best, perchlorate of the heavy metal. Conc. ice-cold solutions must be used and the filtrate from the insol. K salt must be evaporated rapidly in vac., since the heavy metal polythionates soon decompose in presence of H_2O. The following have been prepared: *pentathionates*, $Cu(xH_2O)$, $Co(6H_2O)$, $Ni(7H_2O)$, $Mn(7H_2O)$, $Zn(6H_2O)$, $ZnH_2(S_5O_6)_2,xH_2O$; *tetrathionates*, $Cu(xH_2O)$, Cu en, $Ni(7H_2O)$, Co, Zn, $ZnH_2(S_4O_6)_2$, $Mn(5H_2O)$, $Bi_2O(S_4O_6)_2$; *trithionates*, Cu en, $(BiO)_2S_3O_6$. Cu, Ni, Co, and Zn trithionates are unstable, decomposing immediately into thiosulphates and sulphates; pure $Cu_2S_2O_3$, NiS_2O_3, CoS_2O_3, and ZnS_2O_3 have been prepared. A. R. P.

Co-ordination compounds of chromic chloride. D. R. CHESTERMAN (J.C.S., 1933, 796—798).—The *compounds* $[CrCl_2,4MeOH]Cl$, $[CrCl_3,3Pr^{\alpha}OH]$, and $[CrCl_3,3Pr^{\beta}OH]$ have been prepared. The last two, with the known $[CrCl_3,3EtOH]$, are differentiated from the first and the hexahydrate in that increasing size of the co-ordinating mol. causes fewer mols. to be co-ordinated. In the prep. of the compounds from metallic Cr chromous products were first formed, but not isolated. Compounds (not purified) were also formed with COMe$_2$ and BuOH. F. L. U.

Decomposition of permanganic acid in the presence of certain acids. J. CHLOUPEK (Chem. Listy, 1933, **27**, 217—222, 270—275).—$KMnO_4$ decomposes in the presence of H_2SO_4, AcOH, and H_3PO_4, but not H_3AsO_4, to yield MnO_2 and O_2; the velocity of decomp. increases with concn. of acid. At equiv. concns., the activity of acids increases in the order $H_3PO_4<AcOH<H_2SO_4$. The degree of oxidation of Mn in strongly acid solutions can be determined by potentiometric titration with $Fe^{\cdot\cdot}$ salts. R. T.

Topochemical transformations. VI. Reactions of crystalline ferric sulphate. I. H. W. KOHLSCHUTTER [with L. SPRENGER and H. SIECKE] (Z. anorg. Chem., 1933, **213**, 189—205; cf. A., 1932, 822).—Cryst. $Fe_2(SO_4)_3$ reacts with aq. NaOH, forming pseudomorphic Fe_2O_3,xH_2O (I). Better results are obtained with aq. NH_3. Reaction occurs very near the crystal surface. The dehydration and hydration of (I) resembles that of zeolites, although the substance is not cryst. H. J. E.

Ferrous ferrites. II. Constitution and ferromagnetism of the ferrous ferrites, and the autoxidation of ferrous hydroxide. A. KRAUSE and J. TULECKI (Z. anorg. Chem., 1933, **213**, 292—300).—For the prep. of Fe^{II} ferrite from γ-FeO_2H an excess of $Fe(OH)_2$ is required, since part of the latter is oxidised with the simultaneous formation of H_2O_2. The constitutional formula of the ferrite is similar to that of spinel, but not all the cation positions are occupied. The ferromagnetism of the compound is explained by the presence of $\cdot Fe:(O_2):Fe\cdot$ groups. The ferrites produced from α-FeO_2H are formed by the substitution of FeO for the co-ordinately combined H_2O. Fe_2O_3 prepared by gentle ignition of γ-FeO_2H

or by strong ignition of α-Fe_2O_3 adsorbs up to 0·5 mol. FeO per mol. of Fe_2O_3. $BaSO_4$ accelerates oxidation of $Fe(OH)_2$ in air probably owing to the formation of a Ba salt of ferrisulphuric acid. A. R. P.

Composition of Prussian blue and Turnbull's blue. Influence of adsorption on the composition. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1933, **213**, 240—248).—The compositions of the reaction products of $FeCl_3$ and $K_4Fe(CN)_6$ and of $FeSO_4$ and $K_3Fe(CN)_6$ tend to approach $Fe_2(CN)_5$ on ageing owing to oxidation and reduction reactions between the anion and cation. When an excess of the cyanide is used in the pptn. the " sol. Prussian (or Turnbull's) blue " obtained is a colloid containing adsorbed $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$; adsorption is more marked in the first case. A. R. P.

Contamination of nickel crystals grown in a molybdenum resistance furnace. A. Dingwall, J. Zacharias, and S. L. Siegel (Trans. Electrochem. Soc., 1933, **63**, 395—400).—Specially pure Ni after melting in an alundum crucible in a Mo resistance furnace was found to contain 0·1% Mo homogeneously distributed throughout it. Such contamination was avoided by use of a modified furnace in which the crucible was surrounded with a gas-tight porcelain tube, but some contamination with Si resulted. H. J. T. E.

Compounds of tartaric acid and nickel. J. P. Mathieu (Compt. rend., 1933, **197**, 56—59).—Absorption and rotation determinations of solutions containing Na_2 tartrate and $NiSO_4$ in varying proportions indicate formation of $NiC_4H_4O_6$. On addition of NaOH there are indications of formation of a complex nickelotartrate in which Ni : Na=1. The solutions exhibit mutarotation and gradually acquire colloidal properties and are then separable by ultra-filtration into a dextrorotatory filtrate and lævorotatory suspension (cf. A., 1900, i, 587). C. A. S.

Affinity. LIX. Ruthenium sulphides. R. Juza and W. Meyer (Z. anorg. Chem., 1933, **213**, 273—282).—Tensimetric measurements and *X*-ray examination show that RuS_2 is the only stable Ru sulphide; certainly no lower sulphide exists and no pure higher sulphide can be obtained by dehydration of pptd. sulphides. The heat of formation of RuS_2 at 1170° is 77 kg.-cal. per g.-mol. A. R. P.

New methods in analytical chemistry. G. G. Longinescu (Bul. Chim. Soc. Romane, 1933, **34**, 81—96).—An account of the author's researches in analytical chemistry during the past 12 years. A. R. P.

Chemical analysis of things as they are. G. E. F. Lundell (Ind. Eng. Chem. [Anal.], 1933, **5**, 221—225).—A criticism of present-day analytical procedure. E. S. H.

Comparative chemistry. I. General introduction. II. Classifications. I. N. Longinescu (Bul. Chim. Soc. Romane, 1933, **34**, 97—100, 100—104). A. R. P.

Quantitative analysis by spectroscopic methods. O. S. Duffendack, R. A. Wolfe, and R. W. Smith (Ind. Eng. Chem. [Anal.], 1933, **5**, 226—229).—Modifications of technique are described. Each plate is calibrated by putting upon it an intensity pattern, and a means of standardising the arc source used in analysing alloys has been devised. Results for Ba–Ni alloys show that the accuracy is approx. equal to that attained by chemical means. E. S. H.

Technique of spectrographic analysis. O. Feussner (Arch. Eisenhüttenw., 1932—1933, **6**, 551—556).—The conditions necessary for obtaining reproducible spectrographs are discussed and modern electrical apparatus for producing standardised spark discharges and optical apparatus for measuring the intensity of the lines are described. A. R. P.

Sedimentation analysis. R. Loebe and R. Köhler (Mitt. Lab. preuss. geol. Landesanst., 1932, No. 17, 13 pp.; Chem. Zentr., 1933, i, 838).—Sedimentation analysis with Köhn's pipette apparatus gives trustworthy vals. for the determination of fine fractions (< 50 μ). Coarser fractions require elutriation. $Na_2C_2O_4$ in general produces a higher degree of dispersion. L. S. T.

Recommended specifications for analytical reagent chemicals. Benzoic, boric, formic, sulphanilic, and sulphurous acids, aniline, hydrogen peroxide, mercuric bromide, potassium biphthalate, potassium oxalate, sodium sulphite anhydrous. W. D. Collins and collaborators (Ind. Eng. Chem. [Anal.], 1933, **5**, 289—292).—Requirements and tests are specified. Corrections are made to published specifications for H_3PO_4, $(NH_4)_2SO_4$, $CaCl_2,2H_2O$, and $NaBiO_3$. E. S. H.

Sources of error in the use in water analysis of Fairchild's method for determination of fluoride in phosphate rock. M. D. Foster (Ind. Eng. Chem. [Anal.], 1933, **5**, 238).—The method (A., 1930, 725) is accurate only to 0·2—0·4 mg. F. E. S. H.

Determination of hypochlorite. F. K. Revva and V. V. Illarionov (J. Appl. Chem. Russ., 1933, **6**, 568—570).—Equally accurate results are obtained by titrating excess of H_3AsO_3 not oxidised by HOCl with I, $KMnO_4$, or $HBrO_3$. R. T.

Determination of traces of bromine in presence of great excess of chlorine. F. Hahn (Compt. rend., 1933, **197**, 245—247).—To about 1 c.c. of the solution to be examined a drop of 0·0005*M*-Na fluoresceinate is added with 3 drops of aq. NaOAc of p_H 5·5—5·6 and a drop of 0·1*M*-$C_6H_4Me{\cdot}SO_2{\cdot}NClNa$ as oxidiser; after 1—2 min. further reaction is stopped by addition of a drop of aq. $Na_2S_2O_3$; the amount of Br is then determined colorimetrically. The method is suitable for determining blood-Br. C. A. S.

Bromo-acidimetric processes. V. L. Rosenthaler (Pharm. Acta Helv., 1932, **7**, 223—226; Chem. Zentr., 1932, ii, 3925).—The following reactions can be utilised : $HCO_2Na + Br_2 = HBr + NaBr + CO_2$, $H_2C_2O_4 + Br_2 = 2HBr + 2CO_2$, $K_2S_2O_5 + 2Br_2 + 3H_2O = 2KHSO_4 + 4HBr$, $NaNO_2 + Br_2 + H_2O = NaNO_3 + 2HBr$. L. S. T.

Potentiometric silver–halogen titration with indifferent electrodes. W. Böttger and B. M. Schall (Z. physikal. Chem., 1933, **165**, 398—410).—

An attempt to find why such indifferent materials as Pt, Au, Hg, and C may serve as indicator electrodes in the above titration has yielded inconclusive results. A possible explanation is the formation of a film of Ag on the indifferent electrode. R. C.

Determination of iodates in presence of hypochlorites, bromates, and chlorates. F. K. Revva and V. V. Illarionov (Z. anal. Chem., 1933, **93**, 344—345).—Two rapid and exact methods depend on the reduction of the salts with $Na_2S_2O_3$ or $Na_2S_2O_4$ in acid solution, and determination of I in the resulting iodide. F. L. U.

Colorimetric determination of fluoride in water using ferric chloride. M. D. Foster (Ind. Eng. Chem. [Anal.], 1933, **5**, 234—236).—The intensity of the coloration produced by a given amount of $FeCl_3$ in presence of NH_4CNS, the $FeCl_3$ being in excess, decreases in proportion to the amount of F′ present. Special precautions are necessary if SO_4'' and Cl′ are present. The F′ contents of several natural waters have been determined. E. S. H.

Determination of fluorides in Illinois waters. C. S. Boruff and G. B. Abbott (Ind. Eng. Chem. [Anal.], 1933, **5**, 236—238).—H_2O containing small amounts of F′ can be conc. without loss of F if made alkaline to phenolphthalein. F is distilled as H_2SiF_6, and the distillate is titrated with 0·01*N*-$Th(NO_3)_4$, using a mixture of $Zr(NO_3)_4$ and alizarin-red in aq. EtOH as indicator. The accuracy is about ± 0·1 p.p.m. Results for H_2O from different districts do not show the presence of F′ to be characteristic of any one stratum. E. S. H.

Colorimetric determination of nitrites in water. R. Uzel.—See B., 1933, 654.

Determination of ammonia by steam distillation in a vacuum. D. Bach (Bull. Sci. pharmacol., 1932, **39**, 607—615; Chem. Zentr., 1933, i, 820).—A method for the determination of NH_3, especially in biological liquids, is described. L. S. T.

Differentiation of the three stages of dissociation of phosphoric acid. J. V. Dubsky and A. Langer (Z. anal. Chem., 1933, **93**, 272—273).—The colour reactions of 13 indicators with 0·1*N*-aq. Na_3PO_4, Na_2HPO_4, and NaH_2PO_4 are recorded. H. J. E.

Rapid iodometric determination of phosphites and hypophosphites isolated or mixed. D. Raquet and P. Pinte (J. Pharm. Chim., 1933, [viii], **18**, 5—10).—Phosphites (I) are oxidised by I to phosphate in alkaline solution, whilst hypophosphites (II) are oxidised in acid solution. For determination of (I), 0·1*N*-I and $Na_2B_4O_7$ are added and after 15 min. the solution is acidified with AcOH and the excess of I is titrated with $Na_2S_2O_3$. (II) is determined by the addition of 0·1*N*-I and HCl, heating at 70—80° for 15 min., and cooling. $Na_2B_4O_7$ is added and after 15 min. the mixture is acidified with AcOH and the excess of I titrated with $Na_2S_2O_3$. When both (I) and (II) are present the first process determines (I), whilst the second determines both (I) and (II). W. O. K.

Rapid determination of arsenates. M. Fitz-Gibbon (Analyst, 1933, **58**, 469—470).—The use of large amounts of acid and KI, the possibility of back reaction, and the lengthy time required to ensure reduction in Williamson's method are avoided by reduction at the b.p. in the presence of H_2SO_4, 0·1*N*-I, and 0·2 g. of 100-mesh amorphous P, any I formed from the HI being automatically reduced by the P. When colourless (I-free), the solution is filtered, almost neutralised with NaOH, and titrated with 0·1*N*-I in presence of excess of $NaHCO_3$. J. G.

Distinction between ter- and quinque-valent arsenic by the formation of iodoantipyrine antimonate. P. Duquenois (Compt. rend., 1933, **197**, 339—341).—Antipyrine and KI in HCl with Sb''' and Sb''''' compounds give golden-yellow and brick-red ppts., respectively. In the latter case Sb''''' liberates I from KI, thus forming iodoantipyrine which gives the insol. antimonate (called "antipyrine iodoantimonate"). R. S. C.

Determination of ozone. III. Influence of the alkalinity on the iodometric method. R. Ruyssen (Natuurwetensch. Tijds., 1933, **15**, 125—130).—Concordant results (deviation ⩾ 0·5%) are obtained with pure KI solution, *N*-KI in 0·1*N*-NaOH, and *N*-KI buffered (with phosphate or borate) to p_H 7—9. In presence of air or N oxides, however, the use of the unbuffered solutions leads to errors of several %. H. F. G.

Approximate determination of sulphate in drinking water. L. W. Winkler.—See B., 1933, 654.

Quantitative precipitations in highly concentrated solutions. IV. V. Njegovan and V. Marjanovic (Z. anal. Chem., 1933, **93**, 353—358; cf. A., 1928, 497).—Further details regarding the pptn. of $BaSO_4$ are given. F. L. U.

Nephelometric determination of sulphurous acid and its salts. Bycichin and Laska (Chem. Listy, 1933, **27**, 269—270).—The SO_3'' content of solutions can be determined by oxidation by means of H_2O_2 to SO_4'', which is determined nephelometrically. R. T.

Volumetric determination of hydrogen peroxide and Caro's acid in the presence of perdisulphuric acid. A. J. Berry (Analyst, 1933, **58**, 464—467).—H_2O_2 is determined by direct titration with $Ce(SO_4)_3$ at 0°, no indicator being necessary. The Caro's acid (I) is then reduced at room temp. by a measured excess of $(VO)_2(SO_4)_3$ which is then titrated with $KMnO_4$ without an indicator, whilst $H_2S_2O_8$ is obtained by repeating this reaction at the b.p.; alternatively (and more conveniently) (I) and $H_2S_2O_8$ are determined together at this stage by the usual $FeSO_4$ and $KMnO_4$ method. J. G.

Simplification of the Treadwell and Mayr method [for the determination of thiocyanate]. Bromometric determination of bismuth. R. Montequi and J. G. Carreró (Anal. Fís. Quím., 1933, **31**, 242—254).—The CNS′ solution (⩾ 75 mg. KCNS) is treated with 0·5 g. of KBr and 15 c.c. of conc. HCl; 0·1*N*-$KBrO_3$ is added until the colour of Br persists, starch and KI are added, and the solution is titrated with 0·1*N*-$Na_2S_2O_3$. In the determination of Bi (⩾25 mg.), the solution, which should be free

from halogen and 0·5—1*N* with respect to free acid, is treated with a freshly prepared solution of $K_3Cr(CNS)_6$; pptn. is facilitated by adding a trace of the solid reagent. PhMe (5—10 drops) is added, and the ppt. is removed, washed, and treated with about 5—10 c.c. of a solution containing 150 g. Na K tartrate, 108 g. NaOH, and 100 g. KBr per litre. The clear solution is heated until its colour changes to green, when it is cooled and treated with 150 c.c. of conc. HCl and sufficient 0·1*N*-$KBrO_3$ to yield an excess of Br, which is titrated with 0·1*N*-$Na_2S_2O_3$ after addition of KI and starch. The method requires only 10—15 min. H. F. G.

Detection of traces of carbon monoxide in air. H. R. Ambler and T. C. Sutton.—See B., 1933, 653.

Acidimetric method for the determination of the alkali metals. V. M. Gortikov (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 211—223).—A modification of Wohlk's method (A., 1929, 163) is proposed. A. M.

Volumetric cobaltinitrite method for [determining] potassium. I. N. Antipov-Karataiev and A. M. Miasnikova (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 69—80).—The technique of Druschel's method (A., 1908, ii, 66, 735) as applied to aq. and acid extracts from soils is described. The accuracy is given as ±3%. A. M.

Colorimetric picrate method for [determining] potassium. I. N. Antipov-Karataiev and A. M. Miasnikova (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 81—88).—The picrate method suggested by Caley (A., 1931, 452) was tested under varying conditions. Pptn. can be carried out at 12—15°; stirring for 10—15 min. after addition of reagent gives larger crystals which are best filtered through a plug of glass wool in an ordinary funnel. $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, P, and Si do not interefere, but if Na is > twice K the results are poor. A. M.

Potentiometric determination of potassium. B. P. Nikolski and I. N. Lavrov (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 45—55).—K is pptd. as $K_2CaFe(CN)_6$ and the excess $Ca_2Fe(CN)_6$ is titrated potentiometrically with standard $ZnSO_4$ solution. The solubility of the ppt. is reduced by the addition of EtOH–$CaCl_2$. With a K content between 40 and 130 mg. the error is ⩾ 0·5 mg. $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, SO_4'', CO_3'', and SiO_3''' do not interfere. Details of the prep. of $Ca_2Fe(CN)_6$, the method of titration, and calculation of results are given. A. M.

Determination of potassium and sodium as sulphates. H. Remy and R. Siegmund (Z. anal. Chem., 1933, **93**, 321—331).—To expel H_2O completely K_2SO_4 must be heated at 400° and Na_2SO_4 at 900°. K_2SO_4 begins to volatilise appreciably above 800°. Loss by decrepitation, with K_2SO_4, can be avoided by introducing some H_2SO_4 before heating. The last traces of SO_3 are removed by heating at 400—800° after addition of $(NH_4)_2CO_3$. F. L. U.

Application of mercurimetry in the determination of silver. J. V. Dubsky and J. Trtilek (Z. anal. Chem., 1933, **93**, 345—348; cf. this vol., 364).—The Ag solution is treated with excess of 0·1*N*-KCl and the excess is titrated with 0·1*N*-$Hg(NO_3)_2$, using diphenylcarbazide or diphenylcarbazone as indicator. F. L. U.

Adsorption indicator system silver iodide–starch; modification of the Haen–Low method for the determination of copper. F. Sierra (Anal. Fís. Quím., 1933, **31**, 26—33).—The indicator is prepared by adding 5 c.c. of starch paste and 5 drops of 0·1*N*-$AgNO_3$ to 20—30 c.c. of 0·2*N*-KI. It is added to 20—25 c.c. of $Na_2S_2O_3$ solution which has been standardised against $Cu(NO_3)_2$ solution, and the solution under examination is added from a burette until the ppt. becomes blue. The [Cu] should be 0·14—3 g. per litre, and the solution should not contain SO_4''. H. F. G.

Determination of Ca and Mg in presence of NH_4Cl and NaCl. E. N. Nabilkova (Trans. Dokuchaiev Soil Inst., 1933, **8**, No. 8, 43—51).—Ca and Mg may be determined in NH_4Cl and NaCl soil extracts without removal of these salts. A. M.

Effect of the presence of perchloric acid in the proximate analysis of limestone. F. H Fish and F. M. Taylor (J. Chem. Educ., 1933, **10**, 246—247).—The use of $HClO_4$ for dehydrating SiO_2,xH_2O involves one evaporation and no baking. $HClO_4$ in the solution does not affect later determinations. Ch. Abs.

General method of quantitative microchemical analysis. I. Determination of calcium. L. T. Fairhall and R. G. Howard (J. Roy. Microscop. Soc., 1933, [iii], **53**, 129—138).—CaC_2O_4 is pptd. under regulated conditions by the neutralisation of an acid solution by NH_3 evolved from boiling $(NH_4)_2CO_3$ solution. The ppt. is centrifuged into a calibrated capillary with sides ground plane and parallel, and the length occupied is measured with an eyepiece micrometer. 10^{-5} g. may be determined within 5%. J. S. A.

Determination of beryllium. L. Fresenius and M. Frommes (Z. anal. Chem., 1933, **93**, 275—279, 285—307; cf. B., 1932, 429).—A crit. review of the literature. A ppt. of $Be(OH)_2$ may be ignited before it is washed free from NH_4Cl. No loss due to volatilisation of $BeCl_2$ occurs. $BeCl_2$ on ignition is transformed quantitatively into BeO. H. J. E.

Determination of metals by means of 8-hydroxyquinoline. I. Effect of p_H on the precipitation of Mg, Zn, Co, Ni, Cu, and Mo from acetate solutions. H. R. Fleck and A. M. Ward (Analyst, 1933, **58**, 388—395).—Complete pptn. of Mg with 8-hydroxyquinoline, under specified conditions, takes place in the p_H range 9·44—12·66, of Zn, 4·58—13·4, of Co, 4·33—14·5, of Ni, 4·33—14·58, of Cu, 5·33—14·55, of Mo, 3·60—7·33. Of the possible separations, those of Mo from Co, of Ni from Mg, of Mo from Zn, and of Mg from Zn have been successfully carried out. E. C. S.

Microchemical determination of magnesium as magnesium calcium hexamethylenetetramine ferrocyanide. L. Debucquet and L. Velluz (Compt. rend., 1933, **196**, 2006—2007).—To determine approx. 0·1 mg. of Mg the solution is evaporated to dryness and 2·5 c.c. of 2·5% $K_2CaFe(CN)_6,C_6H_{12}N_4,6H_2O$ (cf. A., 1930, 752) in 10% aq. $C_6H_{12}N_4$ are added. On keeping

for 1 hr. the Mg is entirely converted into insol. $3CaMgFe(CN)_6,4C_6H_{12}N_4,40H_2O$, which after washing with 20% $C_6H_{12}N_4$ and $COMe_2$ and drying is dissolved in H_2O and determined colorimetrically as $Fe_4[Fe(CN)_6]_3$. C. A. S.

Volumetric determination of lead by the nickel dioxide–arsenite process. R. Lang and J. Zweřina (Z. anal. Chem., 1933, **93**, 248—260; cf. A., 1927, 126).—To 50 c.c. of the neutral aq. Pb solution (up to 0·45 g. Pb) 20—25 c.c. of 2·5*N*-NaOH, 20 c.c. of aq. $Ni(NO_3)_2$ (135 g. per litre), 2 g. of $K_2S_2O_8$, and 60—80 c.c. of 1 : 1 HNO_3 are added. A ppt. of PbO_2 forms. Excess of 0·1*N*-Na_3AsO_3, 10 c.c. of 1 : 1 HCl, and 1 drop of 0·005*M*-KIO_3 are added, and the excess Na_3AsO_3 is determined with 0·1*N*-$KMnO_4$. The potentiometric titration of Pb is described. PbO_2 is first pptd., and converts $Mn^{\cdot\cdot}$ into $Mn^{\cdot\cdot\cdot}$, which is titrated with Na_3AsO_3. Errors up to 1% are due to incomplete pptn. of PbO_2. The method is inapplicable in presence of Co, Bi, Sb, Sn, halides, and phosphates. The determination of Pb and Mn together is described. Sn and Sb may be removed from Pb–Sn–Sb alloys by dissolving in H_2SO_4 and heating with HCl and KBr. H. J. E.

Microchemical determination of heavy metals with dithizone (diphenylthiocarbazone). I. Lead. II. Copper. H. Fischer and G. Leopoldi (Wiss. Veroff. Siemens-Konz., 1933, **12**, No. 1, 44—52, 52—60).—I. The Pb solution is made just ammoniacal (litmus), treated with an excess of KCN, and shaken with a green CCl_4 solution of dithizone (6 mg. per 100 c.c.) until the CCl_4 ceases to turn red. After removal of the aq. layer the red CCl_4 is shaken with very dil. aq. NH_3 to remove excess of dithizone and treated with dil. H_2SO_4 until the colour changes to green, and this colour is compared with that produced by a standard Pb solution treated similarly using a wedge colorimeter. The method can be used for the determination of Pb >0·0005% in Zn, Cd, Cu, Hg, Ag, As, Sb, Al, and Be.

II. Prolonged shaking of a dil. acid (H_2SO_4 or HNO_3) solution containing Cu with the CCl_4 dithizone solution results in all the Cu passing into the CCl_4 layer. Excess of reagent is removed and the analysis finished as above. In acid solution large amounts of Pb, Zn, Cd, Ni, Co, Al, As, Sb, and $Sn^{\cdot\cdot\cdot\cdot}$ do not interfere. A. R. P.

Dithizone reactions. H. Fischer (Angew. Chem., 1933, **46**, 517).—A criticism of procedure (cf. this vol., 798). E. S. H.

Separation and determination of traces of lead in the presence of small amounts of bismuth. J. H. Hamence (Analyst, 1933, **58**, 461—464).—Addition of $FeCl_3$ to the sample followed by aq. NH_3 removes Bi and Pb by adsorption (cf. A., 1932, 1223), the ppt. being then dissolved in 25 c.c. of H_2O and 0·5 c.c. of HNO_3, and 2 c.c. of saturated NH_4CNS and 1 c.c. of C_5H_5N are added. The Bi and Fe are then removed by extraction twice in a mixture of Et_2O and $C_5H_{11}\cdot OH$ (1 : 1), and the Pb is determined colorimetrically as PbS in the filtered residual liquid. J. G.

Analytical scheme for the toxicological investigation of metals, including thallium, uranium, and vanadium. L. S. Guisande (Arch. Med. leg., 1930, **3**, 205—218).—Org. matter is destroyed by repeated heating with HNO_3, and with mixed HNO_3 and H_2SO_4; on dilution Pb, Ba, Sr, Ca are pptd. as MSO_4. After filtration (I) Pb is separated with $[CH(OH)\cdot CO_2NH_4]_2$ and aq. NH_3, the residue fused with Na_2CO_3, Ba separated as $BaCrO_4$, Sr as $SrSO_4$, Ca as $Ca_2Fe(CN)_6$. From (I) Hg, Ag, Bi, Cu, Cd, As, Sb, Sn are pptd. with H_2S (II), and As, Sb, Sn, dissolved out with hot KOH (III). Hg is separated with HNO_3, Ag with HCl, Cu with $K_4Fe(CN)_6$, Bi with aq. NH_3, Cd with KCN and H_2S. As is separated from (III) with HCl, Sb with Pt and Zn, Sn with Fe and $HgCl_2$. From (II) Tl is pptd. with KI, and the other metals with Na_2S. The ppt. is dissolved in 2*N*-HCl (IV); Ni and Co are insol. and are identified with $[CMe{:}N\cdot OH]_2$ and nitroso-β-naphthol, respectively. (IV) is oxidised with HNO_3 and with H_2O_2 in alkaline solution; Fe, Mn, and U are pptd. (V) Zn, Al, Cr, V remain in solution (VI). From (V), U is separated with $NaHCO_3$, Fe identified with $K_4Fe(CN)_6$ or KCNS, Mn with PbO_2 and HNO_3, Zn (if present) with Na_2S; in (VI) Cr is detected with H_2O_2 and Et_2O and separated with $BaCl_2$, V with cupferron, Al with aq. NH_3, Zn with Na_2S. Confirmatory tests are given for all metals. R. N. C.

Separation and determination of copper and nickel by salicylaldoxime. H. L. Riley (J.C.S., 1933, 895; cf. this vol., 478).—Details of procedure are given. The method for Ni compares favourably with that using dimethylglyoxime, the reagent giving slight turbidity in a neutral solution containing 1 part Ni in 10,000,000. Co must be absent. F. L. U.

Analysis of pure synthetic ultramarine. K. Leschewski (Z. anal. Chem., 1933, **93**, 273—274).—1 g. of the sample is treated with Br and HNO_3; SiO_2 is determined, and the filtrate diluted to 1000 c.c. In this solution the total S is determined as $BaSO_4$, Al as Al_2O_3, and alkali as sulphate (after removing Al). H_2S liberated by dil. H_2SO_4 is determined iodometrically. H. J. E.

Analysis of aluminium acetate solution. C. Rohmann.—See B., 1933, 668.

Determination of small amounts of manganese in salt solutions. N. A. Clark (Ind. Eng. Chem. [Anal.], 1933, **5**, 241—243).—The colorimetric method involving oxidation of $Mn^{\cdot\cdot}$ with KIO_4 in H_3PO_4 can detect a difference of 0·001 mg. Mn in 50 c.c. The blue coloration formed by benzidine can be stabilised by addition of small quantities of KNO_3, NH_4Cl, NH_4NO_3, or $MgCl_2$ and is suitable for determining about 0·005 mg. of Mn, but at higher dilutions the colour fades. E. S. H.

Colorimetric determination of manganese by means of persulphate. F. Alten and H. Weiland (Z. Pflanz. Düng., 1933, **30**, A, 193—198).—The use of H_3PO_4 instead of H_2SO_4 in this method permits the oxidation of larger amounts of $Mn^{\cdot\cdot}$ and prevents pptn. of MnO_2. Accuracy is not affected

by the presence of AgCl. The method is applicable to the examination of soil extracts and plant ash. A. G. P.

Colorimetric determination of iron by the thiocyanate procedure. L. DE BROUCKERE and A. E. GILLET (Bull. Soc. chim. Belg., 1933, **42**, 281—293).—The colour produced varies with the prep. and age of the solutions used. A considerable excess of KCNS is advisable. Results are accurate to about 1% when the solution is *N* with respect to NH_4Cl, KCl, KNO_3, $MgCl_2$, $Ca(NO_3)_2$, $BaCl_2$, or $AlCl_3$. Large quantities of Mn produce a positive error. In presence of SO_4'' or PO_4''' the concn. of acid in the solutions used should be about *N*. E. S. H.

Iodometric determination of Fe" in the presence of organic matter. N. F. SOLOVEVA (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 21—28).—Fe" is oxidised with I solution, and Fe''' is removed from solution by $NH_4F+K_2C_2O_4$ (5 : 1), 6 g. of the mixture being used for each determination. Methylene-blue is used as indicator. The presence of humus, as in acid extracts, does not affect the determination appreciably. Potentiometric methods may be used. Mohr's iodometric method for the determination of Fe''' is untrustworthy in the presence of org. matter. A. M.

Phenanthrolene-ferrous ion: a reversible oxidation-reduction indicator of high potential and its use in oxidimetric titrations. G. H. WALDEN, jun., L. P. HAMMETT, and R. P. CHAPMAN (J. Amer. Chem. Soc., 1933, **55**, 2649—2654; cf. A., 1931, 1385).—The *o*-phenanthrolene-ferrous ion is a completely reversible indicator for the titration of $FeSO_4$ in 0·3—5*M*-H_2SO_4 with $K_2Cr_2O_7$, $Ce(SO_4)_2$, and 0·01*N*-$KMnO_4$. In general, the mean error is $<\pm 0{\cdot}7$ part per 1000. The prep. of the indicator is described. J. G. A. G.

Simultaneous potentiometric determination of ferricyanide and chromate in alkaline solution by means of vanadous sulphate. C. DEL FRESNO and E. MAIRLOT (Anal. Fís. Quím., 1933, **31**, 122—128).—Two well-defined breaks in the potential curve are observed, corresponding with reduction to $Fe(CN)_6''''$ and Cr''', respectively. The solution should contain 13—18% of free NaOH, the temp. should be 50—70°, and air must be excluded. H. F. G.

Volumetric determination of cobalt by means of ferrous sulphate and potassium dichromate. L. A. SARVER (Ind. Eng. Chem. [Anal.], 1933, **5**, 275—276).—Dil. H_2SO_4 and $NaBO_3$ are added to the Co" solution, and $Co(OH)_3$ is pptd. by excess NaOH. Excess of $FeSO_4$ solution is introduced with exclusion of air; the ppt. is dissolved by adding H_2SO_4 and then H_3PO_4. Excess of Fe is titrated with $K_2Cr_2O_7$, using Ba diphenylamincsulphonate as indicator. Nitrates and other oxidising substances must be absent. Ni does not interfere. E. S. H.

Determination of metals with anthranilic acid. II. Cobalt, nickel, and copper. H. FUNK and M. DITT (Z. anal. Chem., 1933, **93**, 241—247; cf. this vol., 244).—Neutral aq. solutions of Co, Ni, or Cu salts are pptd. at the b.p. with 3% aq. Na anthranilate. The ppts. of metal salts are cryst., readily filtered, and coloured rose-yellow, bluish-green, and green, respectively. The ppt. is washed with EtOH, dried at 105—110°, and weighed. The sensitivities of the reactions are 1 in 8×10^5, 1 in $4{\cdot}45\times10^5$, and 1 in 10^6, respectively. A volumetric method depends on the dissolving of the ppt. of Co, Ni, or Cu anthranilate in acid and determining the org. acid with bromide–bromate solution. H. J. E.

Potentiometric determinations on nickel and cobalt ferrocyanides. I. A. ATANASIU and A. I. VELCULESCU (Bul. Chim. Soc. Romane, 1933, **34**, 71—75).—Potentiometric titrations of $CoSO_4$ and $NiSO_4$ (I) with $K_4Fe(CN)_6$ (II) give curves which show inflexions at a mol. ratio (I) : (II) of 5 : 4, indicating that the ppts. are probably mixtures of $3K_2MFe(CN)_6$ with $1M_2Fe(CN)_6$, where M=Ni or Co. In the presence of NH_4 or alkali salts, mixed ferrocyanides of high absorptive powers are formed; in mixed Ni and Co solutions the two metals behave as one. A. R. P.

Increased sensitivity of a microchemical reaction for chromium. I. M. KORENMAN (Z. anal. Chem., 1933, **93**, 268—271).—The sensitivity of the reaction for the detection of Cr by oxidation and pptn. as Ag_2CrO_4 is increased from 1 in 80,000 to 1 in 571,000 by co-pptn. with Ag_2SO_4. The ratio Cr : SO_4 should be between 1 : 50 and 1 : 200. H. J. E.

Rapid macro- and micro-determination of bismuth. G. SPACU and P. SPACU (Z. anal. Chem., 1933, **93**, 260—265).—The Bi solution is made slightly acid with HNO_3, excess of KI is added, and Bi is pptd. at the b.p. with hot conc. aq. $[Co\,en_2(SCN)_2](SCN)(\frac{1}{6})$ (cf. Werner, A., 1900, i, 86). The orange-yellow cryst. ppt. of $[BiI_4][Co\,en_2(SCN)_2](\frac{1}{6})$ (20·65% Bi) is washed with EtOH and Et_2O, dried in a vac. desiccator, and weighed. The method is applicable for micro-determinations. H. J. E.

Determination of bismuth in copper. ANON.—See B., 1933, 631.

Inhibiting action of certain ions on the fluorescence of the uranyl ion and its applications to inorganic chemical analysis. VOLMAR and MATHIS (Bull. Soc. chim., 1933, [iv], **53**, 385—392).—The fluorescence of UO_2'' is destroyed by Cl', Br', I', SCN', $Fe(CN)_6''''$, $Fe(CN)_6'''$, NO_2', S', S_2O_3'', CrO_4'', Cr_2O_7'', MnO_4', AsO_3''', and salicylate. The limiting quantity of each ion required has been determined. The concn., temp., and p_H of the UO_2'' solution have practically no influence. Iodides at a concn. of *N*/3000 destroy the fluorescence. The phenomenon may be adapted for methods of analysis. E. S. H.

Application of the micropolychromar to micro-determination of m.p. K. RICHTER and H. DAMM (Naturwiss., 1933, **21**, 517—518).—The micropolychromar can be applied to the micro-determination of m.p. of cryst. substances and particularly of fats. A. J. M.

Radiation thermopiles for use at liquid air temperatures. C. H. CARTWRIGHT (Rev. Sci. Instr., 1933, [ii], **4**, 382—384).—Bi+11% Sb is the best combination. C. W. G.

Refrigeration with ammonium thiocyanate. H. SEEKAMP and W. PFAHLER.—See B., 1933, 607.

Ice calorimeter to measure very small thermal effects. W. SWIENTOSLAWSKI, A. ZMACZYNSKI, I. ZLOTOWSKI, J. USAKIEWICZ, and J. SALCOWICZ (Compt. rend., 1933, **196**, 1970—1973).—The apparatus has a useful space of 500 c.c., and is accurate to $\pm 0{\cdot}03$ g.-cal. per hr., and in the case described was able to detect a heat evolution of $1—3\times10^{-5}$ g.-cal. per g. per hr. C. A. S.

Apparatus for producing a controlled temperature programme. W. B. WARREN (Ind. Eng. Chem. [Anal.], 1933, **5**, 285—286).—The apparatus enables the rate of rise of temp. of an electric furnace to be controlled at will, with complete reproducibility. E. S. H.

Air thermostat for solubility determinations. H. G. BEIER and H. BRINTZINGER (Kolloid-Z., 1933, **64**, 173—175).—The electrically-controlled apparatus is const. to 0·1° over the range 20—80° and can be used below room temp. E. S. H.

Thermo-electric temperature scale of Pt|Pt–Rh thermocouple. K. BITŌ and M. MATSUI (J. Soc. Chem. Ind. Japan, 1933, **36**, 421—424B).—Temp. scales based on the two sets of fixed points Sb, Ag, Au (I) and Zn, Sb, Ag (II) and on the two equations $E=a+bt+ct_2$ (III) and $t=a+bE+cE^2$ were compared, using five Pt|Pt–Rh couples. Using equation (III) and fixed points (I) and (II) the deviations at the m.p. of Zn and Au, respectively, were $>0{\cdot}5°$, but the differences between the two equations were greater. A. G.

Pt|Pt–Rh thermocouple. K. BITŌ and M. MATSUI (J. Soc. Chem. Ind. Japan, 1933, **36**, 424—426B).—Under-cooling of Ag used for calibrating thermocouples is avoided if the rate of cooling is small. Zn can be used as a secondary fixed point. A. G.

Microphotometer for registering the blackening of a photographic plate. W. SCHÜTZ (Physikal. Z., 1933, **34**, 566—569).—The apparatus is described. A. J. M.

Air chamber for studying photosynthesis under natural conditions. A. J. HEINICKE (Science, 1933, **77**, 516—517). L. S. T.

Calcium target for *X*-rays. H. KERSTEN and J. MAAS (Rev. Sci. Instr., 1933, [ii], **4**, 381).—The target is made by melting and grinding 5 g. of SiO_2, 5 g. of CaO, and 0·3 g. of clay. C. W. G.

Demountable metal *X*-ray tube. E. P. MILLER (Rev. Sci. Instr., 1933, [ii], **4**, 379—380).—The cathode assembly is made completely of Cr-plated brass. Vac.-tightness is obtained by means of rubber gaskets. C. W. G.

Spectroscopic examination of thin metallic films. A. HARVEY and E. S. DREBLOW (J. Sci. Instr., 1933, **10**, 224—225).—A spark between a Cu electrode and the thin film on glass is examined. C. W. G.

Method of taking *X*-ray photographs of crystalline powders at the temperature of liquid air. J. A. SANTOS and J. WEST (J. Sci. Instr., 1933, **10**, 219—221).—A small fountain of liquid air is caused to play over the specimen. C. W. G.

Photo-electric spectrophotometer. A. G. WINN (Trans. Faraday Soc., 1933, **29**, 689—697).—Two photo-electric cells are used, an electrometer triode being employed as null-reading, amplifying voltmeter. Calibration against a rotating variable sector is obviated, and the range of the instrument thereby extended. J. S. A.

Photo-electric comparator for precise and rapid measurement of reflexion and transmission. C. H. SHARP and H. J. ECKWEILER (J. Opt. Soc. Amer., 1933, **23**, 246—250). N. M. B.

Constant deviation *X*-ray vacuum monochromator. G. I. HARPER (Proc. Camb. Phil. Soc., 1933, **29**, 408—416).—An instrument which provides an accurately monochromatised beam by reflexion at a crystal, and permits the wave-length to be changed without moving either the *X*-ray tube or the measuring apparatus, is described. N. M. B.

Measurement of light absorption. Accuracies of several spectrophotometric methods. R. FONTEYNE (Natuurwetensch. Tijds., 1933, **15**, 131—137).—A theoretical discussion is given of the relative degrees of accuracy obtainable by the spectrophotometric, photographic, and photo-electric methods. H. F. G.

Determination of conductivity and dielectric constants of electrolytes for wave-lengths of 1 m. P. WENK (Ann. Physik, 1933, [v], **17**, 679—698).—An accurate barretter method for carrying out the above determinations simultaneously is described. The results are compared with those derived from the Debye–Falkenhagen dispersion theory. There is good qual. agreement, but deviations increasing with concn., valency, and frequency are found. A. J. M.

Electron-tube potentiometer for the determination of reduction–oxidation potentials. C. H. WERKMAN, C. A. JOHNSON, and H. D. COILE (Iowa State Coll. J. Sci., 1933, **7**, 163—175).—Simple apparatus is employed. CH. ABS.

Use of micro-coulometers in the determination of transport numbers by the moving boundary method. W. O. REEVELY and A. R. GORDON (Trans. Electrochem. Soc., 1933, **63**, 261—265).—For the measurement of small quantities of electricity, a Ag coulometer consisting of a Pt crucible containing about 3 c.c. of 10% aq. $AgNO_3$, with a fine linen bag or glass tray to catch anode slimes, gives accurate and reproducible results by using a micro-balance for the weighings. Determinations of the transport no. of $K^{\cdot}$ in 0·1*N*-KCl by the moving boundary method, using this type of coulometer, give $0{\cdot}4899\pm0{\cdot}0003$ at 25°. H. J. T. E.

Apparatus for measuring hydrogen-ion concentration. G. DEMORTIER (Bull. Inst. agron. Gembloux, 1932, **1**, 65—73).—Details of new types of compact standard cell, HgCl electrode, and H_2 electrode are given. NUTR. ABS. (*b*)

Use of the vacuum-tube electrometer with extremely high input resistance. R. E. BURROUGHS and J. E. FERGUSON (Rev. Sci. Instr., 1933,

[ii], 4, 406).—The method is suitable for use with cells of very high internal resistance. C. W. G.

Portable double Geiger counter. R. D. Bennett, J. C. Stearns, and W. P. Overbeck (Rev. Sci. Instr., 1933, [ii], 4, 387—390).—A thermionic valve method is described. C. W. G.

Amplified ballistic method for measurement of glass electrode electromotive force. A. Hemingway and E. L. Arnow (Ind. Eng. Chem. [Anal.], 1933, 5, 278).—A new circuit is described. The bulb of the electrode is filled with HCl–KCl buffer saturated with quinol and contact is made by a bare Pt wire. E. S. H.

Application of compensated valve-voltmeter to measurements of glass electrode potentials. A. S. McFarlane (J. Sci. Instr., 1933, 10, 208—212).—An instrument having a grid-input impedance of 5000 megohms is described. Glass electrode potentials can be measured to 0·05 mv. C. W. G.

Apparatus glass. I, II. F. H. Zschacke (Chem.-Ztg., 1933, 57, 521—523, 542—544).—A review of recent improvements in glass and its application in chemical industry. Compositions of modern glasses are given and their properties (chemical resistance, expansion coeff., softening temp., hardness, and homogeneity) are discussed. E. S. H.

Apparatus for the separation and measurement of steam distillates. W. H. Simmons and C. A. Hills (Analyst, 1933, 58, 396). E. C. S.

[Laboratory] fractional distillation. R. McIntyre (Chem. and Ind., 1933, 578—579).—In the American "single condenser" system of distillation the vapour from the still head is completely condensed and divided, part being run back down the column. This is applied to laboratory fractionation by the use of a vertical Liebig condenser fitted above the column having an expansion at its lower end and a side tube with tap. The latter allows the proportion of distillate removed to be controlled. C. I.

Fractional distillation. R. G. W. Eadie (Chem. and Ind., 1933, 618).—Modifications of McIntyre's apparatus (preceding abstract) are suggested. E. S. H.

Arsenic distillation apparatus without ground-glass connexions. B. S. Evans (Analyst, 1933, 58, 470—471).—A modified Wurtz flask, in which a T-piece is inserted in the neck and the side tube is bent vertically and attached to a Liebig condenser by corks in both cases, is described. During distillation a slow stream of air passed in through one arm of the T-piece prevents the acid from attacking the cork. J. G.

Fractional distillation at reduced pressure. A. G. Banús (Anal. Fís. Quím., 1933, 31, 311—313).—Brühl's apparatus has been modified to render it suitable for use with substances of high m.p. A Hg-in-glass manometer for use in reduced pressure distillation is described. H. F. G.

Glass packing for laboratory fractionating columns. C. D. Wilson, G. T. Parker, and K. C. Laughlin (J. Amer. Chem. Soc., 1933, 55, 2795—2796).—The coils are made by winding softened glass on a metal rod. Single and double turns from such coils afford highly efficient packing for fractionating columns. J. G. A. G.

Efficiency of the standard and some new types of reflux condenser. F. Mach and R. Herrmann (Chem. Fabr., 1933, 6, 199—201, 211—213).—The results of comparative tests on the efficiency of nineteen types of reflux condensers are tabulated and discussed. The standardised German type is among the most efficient; more complicated forms are therefore unnecessary. A. R. P.

Handling of distilled water in aluminium. H. V. Churchill (Ind. Eng. Chem. [Anal.], 1933, 5, 264—266).—A review, favouring the use of Al. E. S. H.

Large-capacity extractor. N. L. Drake and J. R. Spies (Ind. Eng. Chem. [Anal.], 1933, 5, 284).—The apparatus, having a capacity of 12 litres, is designed for use with MeOH, but can be used with few changes for any solvent having b.p. $< 100°$. E. S. H.

Micro-extractor. L. Titus and V. W. Meloche (Ind. Eng. Chem. [Anal.], 1933, 5, 286—288).—The apparatus may be used with 5 c.c. of Et_2O. E. S. H.

Divided titration pipette-stirring rod. R. Richardson (J. Amer. Chem. Soc., 1933, 55, 2794—2795).—Part of the liquid to be titrated is sucked through the narrow jet into the hollow barrel of the pipette-stirring rod, which has a tap at the upper end. When a slight excess of reagent has been added rapidly from the burette, the liquid in the pipette is added by opening the tap and the titration completed dropwise. Rapid titrations in a fixed time can be effected in this way. J. G. A. G.

Measurement of the permeability of porous media for homogeneous fluids. R. D. Wyckoff, H. G. Botset, M. Muskat, and D. W. Reed (Rev. Sci. Instr., 1933, [ii], 4, 394—405).—Detailed descriptions of technique, using both gases and liquids, are given for substances such as rocks. C. W. G.

Gas bubbler for very small pressure drops. C. C. Furnas (Ind. Eng. Chem. [Anal.], 1933, 5, 250).—The apparatus is satisfactory for absorbing CO_2 from gases containing 1—90% at velocities up to 50 c.c. per min. E. S. H.

Measurement of viscosities of liquids saturated with gases at high pressures. B. H. Sage (Ind. Eng. Chem. [Anal.], 1933, 5, 261—263).—A viscosimeter suitable for studying the effect of dissolved gas on the viscosity of crude oils is described. The time required for a sphere to roll or slide down an inclined tube filled with the liquid is determined. A wide range of viscosity can be covered by using spheres of different sizes. E. S. H.

Water-motor stirrer. R. E. Dunbar (Ind. Eng. Chem. [Anal.], 1933, 5, 266). E. S. H.

Chain arrangement for rubber stoppers. R. A. Osborn and A. G. Sterling (Ind. Eng. Chem. [Anal.], 1933, 5, 274).—A device for attaching the stopper to the neck of the container. E. S. H.

Simple laboratory tachometer. W. A. SPERRY (Ind. Eng. Chem. [Anal.], 1933, 5, 288).—An automobile speedometer may be converted suitably. E. S. H.

Simple hygrometer. K. MELLANBY (Nature, 1933, 132, 68).—A simple method for measuring humidity in small or inaccessible places is described. Humidity at a leaf surface or among vegetation can thus be determined. L. S. T.

Telephonic drop counter. C. F. GRAHAM (Science, 1933, 77, 542—543). L. S. T.

Stop-cock clamp. A. F. ROE (Science, 1933, 77, 566).—A spring clamp suitable for manometers, vac.-pump distributors, etc. is described. L. S. T.

Laboratory measurement of gas currents. C. PADOVANI and G. MONTI (Giorn. Chim. Ind. Appl., 1933, 15, 331—334).—The principles and apparatus involved in measuring gas flow are discussed. Contrary to makers' guarantees, capillary fluxometers of the Riesenfeld type obey the Poiseuille linear law within only very narrow load limits. Experiments on the flow of gas through such porous diaphragms as filter-paper, porous glass, graphite, and refractories show that many of these substances behave absolutely as capillary systems and that the gas flow through them obeys Poiseuille's law over very wide ranges of load. Porous diaphragm fluxometers are thus distinctly advantageous, and may, moreover, be used to measure the flow of gas under high pressure. T. H. P.

Rotatable wooden burette holder as titration stand. H. HARDTL (Z. anal. Chem., 1933, 93, 332—335). F. L. U.

Phosphoric anhydride as drying agent. W. A. BONE (Chem. and Ind., 1933, 246—247).—The necessity of purifying P_2O_5 before using it as a drying agent in studying gas reactions is emphasised. A. R. P.

Terpenes, sesquiterpenes, and related compounds. II. Micro-method for mol. wt. determination using camphene as a cryoscopic solvent. S. UCHIDA and K. SHIMOYAMA (J. Soc. Chem. Ind. Japan, 1933, 36, 388—392B).—Camphene has the advantage of a lower m.p., but has a low solvent power for polar compounds, especially acids. The use of a more accurate method of calculation than van 't Hoff's equation is discussed. A. A. L.

Precision weights. J. J. MANLEY (Phil. Mag., 1933, [vii], 16, 489—504).—Experiments on the corrosion of wts. by fumes from glue are described. Other sources of error in wts. are discussed. H. J. E.

Mass spectrometer with directional and velocity focussing. H. BONDY and K. POPPER (Ann. Physik, 1933, [v], 17, 425—444).—The spectrometer has been constructed according to the theory of Bartky and Dempster. By combining a radial electric field with a homogeneous transverse magnetic field the directional and velocity focussing can be obtained in one and the same position. W. R. A.

Production of highly concentrated emanation preparations. O. WERNER (Z. physikal. Chem., 1933, 165, 391—397).—A simple apparatus for the purification and concn. of Ra emanation, starting from highly emanating dry preps., and an electric oven suitable for the production of glass capillaries with a wall thickness of 10 μ or less, which can be filled with emanation and are permeable to α-particles, are described. R. C.

Nomograph for rapid calculation of sulphate : carbonate ratios. R. T. SHEEN (Ind. Eng. Chem. [Anal.], 1933, 5, 276—277). E. S. H.

Geochemistry.

Determination of atmospheric ozone by visual photometry. J. GAUZIT (Compt. rend., 1933, 197, 178—180; cf. this vol., 45).—A modification of the method is described. The mean equiv. thicknesses of the O_3 layer at Montpellier during the months Feb. to June 1933 have been 0·29, 0·33, 0·38, 0·37, and 0·32 cm., respectively, or substantially > the corresponding vals. for 1931 (cf. A., 1927, 1164). C. A. S.

Chloride and sulphate in rain-water. W. D. COLLINS and K. T. WILLIAMS (Ind. Eng. Chem., 1933, 25, 944—945).—Data are reviewed. The average contents of Cl and SO_4 in rain-H_2O on reaching the earth in the U.S.A. are approx. 0·3 and 2 p.p.m., respectively. H. J. E.

Characteristics of the newly discovered lakes to the north of the Volga delta : Deschscheschak, Bekesch-Sor, etc. V. I. NIKOLAEV and B. I. STEPANOV (J. Appl. Chem. Russ., 1933, 6, 436—449).—Analytical data are given for a no. of salt lakes, possessing an unusually high NaCl content, and depositing on evaporation $NaCl,MgSO_4,4$, 5, 6, and $7H_2O$, $KCl,MgCl_2,6H_2O$, $MgCl_2,6H_2O$, and $MgSO_4,Na_2SO_4,4H_2O$. R. T.

Batalpaschinsk (N. Caucasus) salt lake. P. N. LASCHTSCHENKO and A. I. MOROZOVA (J. Appl. Chem. Russ., 1933, 6, 416—435).—The composition of the saline varies considerably with the season, and from year to year. During the winter months mirabilite is pptd. and is redissolved during the summer months; the ratios $[Na^{\cdot}]/[Mg^{\cdot\cdot}]$ and $[Cl']/[SO_4'']$ remain fairly const. The lake is fed by ground-H_2O, the composition of which becomes more nearly that of the lake the closer it is to the latter. Na_2SO_4 originates from interchange of Na and Ca between soil colloids or mud from the lake-bottom and dissolved $CaSO_4$. R. T.

Lithium in sea-water. B. D. THOMAS and T. G. THOMPSON (Science, 1933, 77, 547—548).—A method for the spectrographic determination of Li is described. Sea-H_2O contains 0·1 mg. Li per litre. L. S. T.

Boron content of sea-water. E. G. MOBERG and M. W. HARDING (Science, 1933, **77**, 510; cf. this vol., 802).—Sea-H_2O from N. California and Tortugas, Florida, contains 4·30—4·80 mg. per kg. The variation corresponds with the variation in salinity, the average ratio of B to halides being 0·000239. L. S. T.

Lepidolite system. A. N. WINCHELL (Amer. Min., 1932, **17**, 551—553).—Structural relations are discussed; a diagram shows the variations of optical properties with composition. CH. ABS.

Serendibite from Warren County, N.Y., and its paragenesis. E. S. LARSEN and W. T. SCHALLER (Amer. Min., 1932, **17**, 457—465).—Serendibite, $3Al_2O_3,4MgO,2CaO,B_2O_3,4SiO_2$, of hydrothermal-contact-metamorphic origin, is triclinic, n_α 1·701, n_β 1·703, n_γ 1·706. Polysynthetic twinning is prominent. CH. ABS.

Magnesiosussexite. J. W. GRUNER (Amer. Min., 1932, **17**, 509—513).—Magnesiosussexite, $2(Mg,Mn)O,B_2O_3,H_2O$, found as a veinlet in hæmatite, had hardness 3, d 2·83 approx., n_α 1·595, n_γ 1·660, and contained MgO 29·32, MnO 23·48, R_2O_3 0·34, B_2O_3 36·18, H_2O+ 10·18, H_2O- 0·22, SiO_2 0·43, CaO 0·05, total 100·20%. The mineral is isomorphous with sussexite and camsellite. CH. ABS.

Refractive indices of bloedite. W. T. SCHALLER (Amer. Min., 1932, **17**, 530—533).—Bloedite has n_α 1·4826, n_β 1·4855, n_γ 1·4868. CH. ABS.

Castanite from Chuquicamata, Chile. M. C. BANDY (Amer. Min., 1932, **17**, 534—537).—Castanite, $Fe_2O_3,2SO_3,8H_2O$, associated with amarantite and other Fe sulphates, has hardness 2·5, n_α 1·550, n_β 1·645, n_γ 1·660. CH. ABS.

Mellite. T. F. W. BARTH and C. J. KSANDA (Amer. Min., 1933, **18**, 8—13).—Mellite, $Al_2C_{12}O_{12},18H_2O$, a mellitate, has a 22·0, c 23·3 Å., $d_{calc.}$ 1·65; the unit cell, a tetragonal prism, contains 16 mols. CH. ABS.

Balkashite. G. L. STADNIKOV (Brennstoff-Chem., 1933, **14**, 227—229; cf. B., 1931, 4).—A no. of different varieties of balkashite (I), distinguished as ordinary, young, old, and weathered (I), respectively, have been examined. The variation in composition, particularly in O content, is discussed. It is assumed that oxidation proceeded most vigorously during the formation (by polymerisation etc. of the fatty acids) of the (I), the O content, therefore, as well as other characteristics, being determined more by the conditions prevailing during formation than by those to which (I) has subsequently been exposed. Ordinary (I) on carbonisation in the Al assay apparatus yielded: tar 69·4% (d 0·844; bases 0·42%; carboxylic acids 1·86%; phenols and asphaltenes nil); semi-coke 5·5%; gas 16·3%; H_2O of decomp. 8·8%. A. B. M.

Thorianite from Easton, Pa. R. C. WELLS, J. G. FAIRCHILD, and C. S. ROSS (Amer. J. Sci., 1933, [v], **26**, 45—54).—Analyses are given and the age is calc. to be pre-Cambrian. C. W. G.

Insolation hypothesis of rock weathering. E. BLACKWELDER (Amer. J. Sci., 1933, [v], **26**, 97—113).—A discussion adversely criticising the theory for lack of supporting evidence. C. W. G.

Magnetic properties of certain igneous rocks. A. F. HALLIMOND [in part with E. F. HERROUN] (Proc. Roy. Soc., 1933, **A**, **141**, 302—314).

Thermal expansion of plagioclase. S. KOZU and J. UEDA (Proc. Imp. Acad. Tokyo, 1933, **9**, 262—264).—Vals. for plagioclase from five different sources are given. C. W. G.

Triangular biotitic phlogophite in basalt from Mutsure-jima and its chemical composition. S. KÔZU and S. TSURUMI (Proc. Imp. Acad. Tokyo, 1933, **9**, 269—272).—Analyses are given. There are 4 mols. to the unit cell, which has a_0 5·29, b_0 9·27, $d_{(001)}$ 20·05 Å. C. W. G.

Mica basalt from Mutsure-jima. S. KOZU and B. YOSHIKI (Proc. Imp. Acad. Tokyo, 1933, **9**, 265—268).—Analyses are given. C. W. G.

Geochemistry of boron. V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Gottingen, 1932, 402—407; Chem. Zentr., 1932, ii, 3857).—With a Cu arc 0·0005% B_2O_3 can be detected and the method is quant. Volcanic and sedimentary rocks, meteorites, coal and wood ashes have been examined. A German granite and gabbro contained 0·001% B_2O_3, whilst meteorites showed a somewhat lower B content than volcanic rocks. Argillaceous sedimentary rocks contain larger quantities of B_2O_3 (approx. 0·1%). This high B content must come from the hydrosphere, especially sea-H_2O, and it appears that in phyllite and micaceous schists, the regional metamorphic descendants of such sediments, considerable amounts of freshly-formed tourmaline are widespread. A marked concn. of B occurs in coal ash. L. S. T.

Emery [rocks] of Greece and bauxites. J. DE LAPPARENT (Compt. rend., 1933, **197**, 75—77).—The emery rock from Samos, which resembles that from Naxos, was probably originally a metamorphic bauxite. It is pisolitic, and consists essentially of diaspore with particles of anatase and rutile, and some hæmatite, united by a siliceous cement; corundum occurs occasionally in fair-sized crystals with inclusions of anatase and rutile. C. A. S.

Chemical and mineralogical changes in a miocene marl at contact with a granite laccolite. L. GLANGEAUD and BOUTIRON (Compt. rend., 1933, **197**, 164—166).—In Jebel Al-rujaud, 15 km. W. of Cherchel (Algeria), a laccolite has been intruded into marl, which has been metamorphosed below it. The first change of the marl is into a felspathic and pyroxenic hornfels; nearer the laccolite appears spherulitic prehnite, which is gradually on still nearer approach replaced by diopside, evidently the result of fumarole action. Analyses are given of the marl, hornfels, and the prehnite- and diopside-containing rocks. C. A. S.

Physical properties of colloidal clay. II. C. LA ROTONDA (Z. Pflanz. Düng., 1933, **30**, **A**, 269—284; cf. A., 1932, 806).—Experimental data confirmatory of earlier work are recorded. Addition of electrolytes in artificial fertilisers to acid soils

improves their physical condition by transformation of colloids from sol into gel forms. A. G. P.

X-Ray examination of ceramic raw materials. II. T. NAKAI and Y. FUKAMI (J. Soc. Chem. Ind. Japan, 1933, **36**, 434—435B).—Kaolin begins to lose its cryst. structure at 350—400° and is completely amorphous at 780°. The amorphous Al_2O_3 begins to crystallise at 900—1000°. Quartz is unaffected by temp. up to 1000°. A. G.

Chemical composition of mechanical fractions of podsols and bog soils. A. A. RODE (Trans. Dokuchaiev Soil Inst., 1933, **8**, No. 3, 1—56).—The chemical composition of the fractions (1—0·0025 mm., 0·0025—0·00025 mm., and $<$ 0·00025 mm.) is used to show the successive stages of podsolisation and gley formation. A. M.

Icelandic soil types. F. WEISS (Kong. Vet.-Landb. København, Aarsskr., 1933, 1—18).—These soils are derived from materials of glacial or volcanic origin. Although they contain no free CaO they have a p_H varying from 6 to 7. The fraction sol. in $(NH_4)_2C_2O_4$ is high, as is the total N. The C : N ratio varies from 10 to 18. The ratio hygroscopic H_2O : total absorption complex is fairly const. A. M.

How can the " descriptive " soil map be used in soil valuation. A. TILL (Z. Pflanz. Düng., 1933, **30, A**, 319—323).—Extension of the uses of the author's method of charting soils (this vol., 369) is described. A. G. P.

Characteristics of the organic matter of soils of the U.S.S.R. I. N : C ratio of the organic matter. N. P. REMEZOV. **II. Approximate qualitative composition of the organic matter.** N. P. REMEZOV and (MME.) M. M. VLASOVA (Z. Pflanz. Düng., 1933, **30, A**, 285—299, 299—311).—I. The significance of the C : N ratio of soil org. matter is discussed and data for numerous soils of various types are recorded.

II. The methods of Waksman (B., 1930, 633) are applied to the examination of Russian soils. In the grey-soil area, the org. matter contains little cellulose or hemicellulose, and the proportion of " protein " substance exceeds that of the lignin–humus (I) complexes. In chestnut-coloured soils hemicellulose is present and the (I) fraction occurs in greater proportion than " protein " matter. In chernozems the total org. matter content is high, and the (I) fraction averages 2·5—3 times the " protein " fraction. The podsolisation process is associated with a decrease in the (I) fraction. A. G. P.

Soil classification based on the composition of the colloidal clay fraction. III. Terra rossa formation in comparison with limestone weathering under varied climatic conditions. IV. Comparison between the weathering of limestone and basic eruptive rocks in the Mediterranean area. A. REIFENBERG and S. ADLER (Z. Pflanz. Düng., 1933, **30, A**, 345—356, 356—358; cf. B., 1933, 559).—III. Soils derived from limestone may be classified according to the SiO_2 : sesquioxide ratio of their colloid fractions. The importance of the $SiO_2 : Fe_2O_3$ ratio as well as the $SiO_2 : Al_2O_3$ ratio is emphasised. Whilst desert and steppe soils have a particularly wide $SiO_2 : Fe_2O_3$ ratio, the terra rossa have a wide $SiO_2 : Al_2O_3$ and relatively narrow $SiO_2 : Fe_2O_3$ ratios. This results in the accumulation of both SiO_2 and sesquioxide, and with it is associated the protective action of SiO_2 against pptn. of sesquioxides by $Ca^{\cdot\cdot}$ during dry periods. In neighbouring brown-earth soils the apparent enrichment in Fe_2O_3 and Al_2O_3 is due to the removal of SiO_2. In tropical areas this removal of SiO_2 is intensified and the apparent enrichment in Fe_2O_3 and Al_2O_3 still greater. Such soils are, however, sharply differentiated from terra rossa in both origin and properties. Max. apparent accumulation of sesquioxides occurs in tropical laterites, in which sesquioxide sols are flocculated during dry periods and the SiO_2, more stable in low concns. of electrolytes, is leached away. Complete latérisation may not occur over limestone rock owing to partial pptn. of SiO_2 by $Ca^{\cdot\cdot}$.

IV. Soils derived from eruptive rocks (basalt etc.) have a smaller SiO_2 : sesquioxide ratio than those from limestone. Both Fe_2O_3 and Al_2O_3 are equally concerned in this difference. The presence of $Ca^{\cdot\cdot}$ tends to restrict the leaching of SiO_2. A. G. P.

Iodine content of soil in Kentucky. J. S. MCHARGUE and D. W. YOUNG (Soil Sci., 1933, **35**, 425—434).—In the area examined I was highest in soils derived from limestone strata and lowest in those from sandstone. The I content of phosphatic and non-phosphatic profiles varied considerably at different depths, but no correlation between I and PO_4''' contents was apparent. Soils from limestone rock contained much more I than the unaltered rock. A. G. P.

Formation of muscovite in soils, and refinements in specific gravity separations. N. J. VOLK (Amer. J. Sci., 1933, [v], **26**, 114—129).—Detailed descriptions of the use of s-$C_2H_2Br_4$ and $PhNO_2$ for the mechanical separation of minerals are given. C. W. G.

Occurrence of sphaerosiderite in a sub-bituminous coal from Hsian coal mine, Liaoning Province. C. Y. HSIEH (Contrib. Sin Yuan Fuel Lab., China Geol. Survey, 1932, No. 7).—Small oolites in Chinese Cretaceous coal contained FeO 51·62, CO_2 30·95, org. matter 2·62, insol. 1·06%. CH. ABS.

Organic Chemistry.

Origin of petroleum. I. E. BERL and H. BIEBESHEIMER. **II.** E. BERL and W. DIENST (Annalen, 1933, **504**, 38—61, 62—71).—I. The possibility is investigated that vegetable material is the precursor of petroleum and that the transformation of the material is conditioned by the chemical and physical action of inorg. deposits commonly associated with petroleum. Treatment of cotton wool with

N-NaOH at 310—330°/180—200 atm. ($CaCO_3$ or dolomite behave similarly) gives gases, mainly CO_2 and H_2, and a "protoproduct" (I) which gradually passes into a black, asphalt-like mass when exposed to air. (I) is strongly unsaturated, and contains small amounts of acidic material and naphthenes; alcoholic OH is present. Hydrogenation of (I) (Fe reductum and I) at 420—460° gives a liquid resembling petroleum physically and containing aliphatic, olefinic, naphthenic, and aromatic hydrocarbons the distribution of which in the various fractions is similar to that in natural petroleum. The isolation of a hydrocarbon, $C_{24}H_{50}$, m.p. 50·5°, is described. The possibility of the production of H_2 by the following reactions is considered: (1) $Fe(OH)_2+H_2O=Fe(OH)_3+H$; (2) $FeCO_3+H_2O=CO_2+Fe(OH)_2$, and thence as in (1); (3) $FeS+H_2O=FeO+H_2S$ and $FeO+2H_2O=Fe(OH)_3+H$; (4) $H_2S=H_2+S$. Considerable amounts of H_2 are evolved from FeS and H_2O at 420—430°/133 atm.

II. Cracking of (I) at 400°/110 atm. yields liquid hydrocarbons containing traces of oxygenated material. They comprise paraffins, olefines, and aromatics closely resembling those of natural petroleum. In the more volatile fractions paraffins predominate (C : H~2), whereas the less volatile portions consist mainly of aromatics and olefines. Formation of liquid hydrocarbons rich in H_2 during cracking is accompanied by the production of a coke-like residue poor in H or, under milder conditions, probably of an asphalt-like residue. The ratio C : H in (I), cracked product, residue, and natural asphalt is 1 : 1·09, 1 : 2·1—1·08, 1 : 0·7—0·6, and 1 : 0·7—0·8, respectively. H. W.

Thermal decomposition of organic compounds from the viewpoint of free radicals. III. Calculation of the products formed from paraffin hydrocarbons. F. O. Rice (J. Amer. Chem. Soc., 1933, 55, 3035—3040; cf. A., 1932, 1108).—The decomp. products of paraffin hydrocarbons can be calc. by assuming that they decompose by a chain mechanism, that Me and Et are the only stable radicals, and that the relative chances of reaction of primary, *sec.*, and *tert.* H atoms are 1 : 2 : 10, respectively. Results are in accord with experiments. R. S. C.

Two reactions of gaseous methyl and ethyl. J. H. Simons and M. F. Dull (J. Amer. Chem. Soc., 1933, 55, 2696—2701).—Me from $PbMe_4$ forms NaMe with Na and MeI with CI_4. Et from $PbEt_4$ reacts analogously. J. G. A. G.

M.p. of naturally occurring *n*-nonacosane. A correction. K. S. Markley and C. E. Sands (J. Biol. Chem., 1933, 101, 431).—The val. 63·5—63·7° is substituted for 64·7—65·1° previously given (this vol., 104; cf. A., 1923, i, 990; 1932, 203). F. O. H.

Microanalysis of gases. II. Carbon monoxide, ethylene, and acetylene. F. E. Blacet, G. D. MacDonald, and P. A. Leighton (Ind. Eng. Chem. [Anal.], 1933, 5, 272—274).—The apparatus (A., 1931, 1027) has been improved. CO is determined by Ag_2O, C_2H_4 by $H_2S_2O_7$, and C_2H_2 by a mixture of CuCl and KOH. E. S. H.

Synthesis of acetylene by pyrolysis of methane. H. H. Storch and P. L. Golden (Ind. Eng. Chem., 1933, 25, 768—771).—Pyrolysis of CH_4, and CH_4 diluted with H_2O or CO_2, using a rapid cooling device, yields a product containing approx. 10% of unsaturated compounds (I), chiefly C_2H_2, with mixtures containing 75—90% of CO_2, in contact with a surface at 1500° for 0·03—0·04 sec. With longer contact the % of H_2 and CO increases, (I) remaining const. There is little C deposition. The use of steam as a diluent causes polymerisation and C formation. A. A. L.

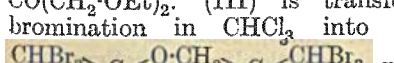
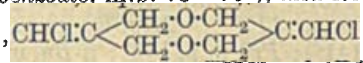
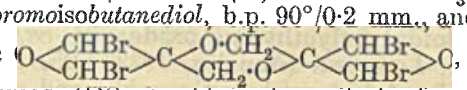
α-Iodo-Δ$^{\alpha}$-butinene. T. H. Vaughn and J. A. Nieuwland (J.C.S., 1933, 741—743).—Δ$^{\alpha}$-Butinene in NH_3 at −34° with I gives α-iodo-Δ$^{\alpha}$-butinene, b.p. 71·5—71·6°/102 mm. (yield 96%; cf. this vol., 694), which undergoes polymerisation and oxidation (retarded by lower temp. and by antioxidants) at room temp. to an inflammable resin sensitive to shock. The change under various conditions is followed by means of the refractive index. Separation of the polymerides from the partly changed products with solvents is described. These polymerides are very sensitive to O_2, to heat, and to shock (less inflammable in the earlier stages of polymerisation). Similar products obtained from material stabilised with antioxidants are difficultly inflammable, and insensitive to shock. A. A. L.

Acetylene polymerides. XV. δ-Halogeno-Δ$^{\alpha\beta}$-butadienes. Mechanism of 1 : 4-addition and of αγ-rearrangement. XVI. Preparation of orthoprenes by the action of Grignard reagents on δ-chloro-Δ$^{\alpha\beta}$-butadienes. W. H. Carothers and G. J. Berchet (J. Amer. Chem. Soc., 1933, 55, 2807—2813, 2813—2817; cf. this vol., 694).—XV. Vinylacetylene, when passed into liquid HBr, gives *δ-bromo-Δ$^{\alpha\beta}$-butadiene* (I) (53·5%), b.p. 64—66°/181 mm., 109—111°/760 mm., and βδ-dibromo-Δ$^{\beta}$-butene (II) (36%). δ-Chloro-Δ$^{\alpha\beta}$-butadiene (III) with NaBr in $COMe_2$–H_2O gives (I) (25% yield) and with NaI in 80% EtOH or $COMe_2$ *δ-iodo-Δ$^{\alpha\beta}$-butadiene*, b.p. 43—45°/38 mm., which reacts instantly with aq. $AgNO_3$ and is very rapidly polymerised as a result of previous isomerisation to the very unstable β-*iodo-Δ$^{\alpha\gamma}$-butadiene* (*iodoprene*), b.p. 111—113°, rapidly formed therefrom with much tar at 125—130°. (III) or (I) and aq. Na_2CO_3 at 60—90° give *δ-hydroxy-Δ$^{\alpha\beta}$-butadiene* (IV) (50% yield), b.p. 68—70°/53 mm., 126—128°/760 mm. (IV) is hydrogenated to Bu$^{\alpha}$OH, is unaffected by NaOEt, 25% H_2SO_4, or 2% HCl, but gives with boiling 18% HCl a 9%, or with PCl_3 and a little C_5H_5N a 62%, yield of (III), and with Ac_2O and a drop of H_2SO_4 (75% yield) or NaOAc in AcOH (59% yield) affords *δ-acetoxy-Δ$^{\alpha\beta}$-butadiene*, b.p. 85—86°/125 mm., 140—140·5°/780 mm. [also obtained from (I) in 73% yield], hydrogenated to Bu$^{\alpha}$OAc and hydrolysed to (IV). No rearrangement occurred during the above reactions. (III) with 18% HCl at 70—80° gives a little chloroprene, obtained in 70% yield if CuCl, is added and to a considerable extent by dry $FeCl_3$. These and the results reported below show that αγ-rearrangements are not a preliminary to 1 : 4-addition and cannot proceed by any mechanism involving free ions. The αγ-change is

considered to be brought about by co-ordination of the atom or group attached to the α-C atom with the γ-C atom. If this atom or group is small, co-ordination and consequently the αγ-change is assisted by a salt which can form a co-ordination complex. An explanation of the "abnormal" nature of the Grignard reaction is offered.

XVI. β-Substituted $\Delta^{\alpha\gamma}$-butadienes are termed "orthoprenes." δ-Chloro-$\Delta^{\alpha\beta}$-butadiene and MgMeI or MgMeCl in Bu^{a}_2O give isoprene. MgBuBr gives β-*butyl*-$\Delta^{\alpha\gamma}$-*butadiene* (not isolated pure), giving with naphthaquinone 2-n-*butyl*-1 : 4 : 4a : 9a-*tetrahydroanthraquinone*, m.p. 63—64°. *n*-C_7H_{15}·MgBr gives tetradecane and β-n-*heptyl*-$\Delta^{\alpha\gamma}$-*butadiene* (*heptoprene*), b.p. 52—54°/5 mm., affording 2-n-*heptyl*-1 : 4 : 4a : 9a-*tetrahydroanthraquinone*, m.p. 81°, and thence β-n-*heptylanthraquinone*, m.p. 87°. MgPhBr gives (*a*) β-*phenyl*-$\Delta^{\alpha\gamma}$-*butadiene* (*phenoprene*), b.p. 60—61°/17 mm., affording 2-*phenyl*-1 : 4 : 4a : 9a-*tetrahydroanthraquinone*, m.p. 146—147°, and thence 2-phenylanthraquinone, double m.p. 145° (decomp.) and 161—165°, but only 163—164° if previously dried in vac. at 125°, (*b*) δ-*phenyl*-$\Delta^{\alpha\beta}$-*butadiene*, b.p. 72—73°/17 mm., which does not react with naphthaquinone and is hydrogenated to $PhBu^{a}$, (*c*) a *dimeride*, m.p. 62°, b.p. 220—225°/10 mm., of phenoprene, and (*d*) some Ph_2. CH_2Ph·MgCl affords $(\cdot CH_2Ph)_2$ and δ-*benzyl*-$\Delta^{\alpha\beta}$-*butadiene*, b.p. 76—77°/7 mm., oxidised by $KMnO_4$ to BzOH and by O_3 in $CHCl_3$ to γ-*phenylpropaldehyde*, an oil (*oxime*, m.p. 95—97°). M.p. were taken on a Cu block.

R. S. C.

Elimination of the nitro-group from tertiary nitro-compounds. III. H. Kleinfeller and H. Stahmer (Ber., 1933, **66**, [*B*], 1127—1137).—Trichloronitro*iso*butane (I) is converted by KOH in EtOH–H_2O or by NaOEt into α-*chloro*-γ-*ethoxy*-β-*ethoxymethyl*-Δ^{α}-*propene* (II), b.p. 81°/11 mm., oxidised by $KMnO_4$ to Cl_2 and AcOH and by H_2O_2 or HNO_3 to $H_2C_2O_4$; ozonisation does not yield $CO(CH_2\cdot OEt)_2$. Treatment of (II) with 3 : 5-dinitrobenzoyl chloride and $ZnCl_2$ at 120° yields 3 : 5-$(NO_2)_2C_6H_3\cdot CO_2Et$, m.p. 89°. Catalytic hydrogenation (PtO_2 in EtOH) follows a complex course, C_2H_6 and $CHMe_3$ being evolved. α-*Bromo*-γ-*ethoxy*-β-*ethoxymethyl*-Δ^{α}-*propene*, b.p. 90—91°/11 mm., is similarly obtained from tribromonitro*iso*butane. Hydrogenation of (II) in presence of KOH–EtOH (Pd–$CaCO_3$) leads to γ-*ethoxy*-β-*ethoxymethyl*-Δ^{α}-*propene* (III), b.p. 160°, also obtained by dehydration with $KHSO_4$ of αγ-*diethoxy*-β-*methylpropan*-β-*ol*, b.p. 71—74°/14 mm., prepared from MgMeI and $CO(CH_2\cdot OEt)_2$. (III) is transferred by energetic bromination in $CHCl_3$ into the *bromide* (IV)  , m.p. 101° Treatment of (I) with boiling 11% KOH affords α-*chloro*-γ-*hydroxy*-β-*hydroxymethyl*-Δ^{α}-*propene* (V), b.p. 102—105°/0·2 mm. (*di*-3 : 5-*dinitrobenzoate*, m.p. 73—76°), and its *dimeric anhydride* (VI),  m.p. 47—48°, which is stable to HCl and Br, but oxidised by HNO_3 to mesoxalic acid. (VI) absorbs almost 6 H_2 in EtOH in presence of PtO_2. (V) is converted by H_2SO_4 into the *trimeric anhydrides*, $OH\cdot CH_2\cdot[C(:CHCl)\cdot CH_2\cdot O\cdot CH_2]_2\cdot C(:CHCl)\cdot CH_2\cdot OH$, incipient decomp. 75—80°, $CH_2\cdot[C(:CHCl)\cdot CH_2\cdot O\cdot CH_2]_2C(:CHCl)\cdot CH_2$, m.p. 125—130° (decomp.), and a *substance* $C_3H_4O_2$, m.p. 160—165° (decomp.). Treatment of (II) with PCl_5 at 100° in absence of solvent leads to *tetrachloroisobutanediol Et*$_2$ *ether*, b.p. 84—87°/11 mm. (II) and Br in $CHCl_3$ yield *chlorotribromoisobutanediol*, b.p. 90°/0·2 mm., and the *substance*  , m.p. 97°, whereas (IV) is obtained similarly from the corresponding Br-ether. H. W.

Amyl alcohol. I. M. Korenman (Pharm. Zentr., 1933, **74**, 453—454).—The colour reactions of Ekkert (A., 1928, 733) are extended. J. L. D.

Configurative relationship of *iso*propylcarbinols. P. A. Levene and R. E. Marker (J. Biol. Chem., 1933, **101**, 413—418).—Et *l*-α-hydroxybutyrate with EtI and dry Ag_2O yields *Et* l-α-*ethoxybutyrate*, b.p. 67°/12 mm., $[\alpha]_D^{25}$ −36·45°, converted by MgMeI into l-γ-*ethoxy*-δ-*methylpentan*-δ-*ol*, b.p. 162—163°/760 mm., $[\alpha]^{25}$ −8·3°, which affords l-γ-*ethoxy*-δ-*methyl*-Δ^{δ}-*pentene*, b.p. 120—130°, $[\alpha]_D^{25}$ −17·8°, reduced to l-γ-*ethoxy*-β-*methylpentane*, b.p. 126°, $[\alpha]_D^{25}$ −2·78°. *d*-β-Methylpentan-γ-ol, +9·8°, is similarly converted into d-γ-*ethoxy*-β-*methylpentane*, b.p. 124—126°/760 mm., $[\alpha]^{25}$ +5·00°. The above syntheses permit correlation of CHEtPr·OH and $CHEtPr^{\beta}\cdot OH$, the results being compared with those of Stevens (A., 1932, 1109). The trustworthiness of the indirect method (A., 1932, 1027) is confirmed.

F. O. H.

Partly acylated sugar alcohols. III. Products of the toluenesulphonation of mannitol αζ-dibenzoate. A. Müller and L. von Vargha (Ber., 1933, **66**, [*B*], 1165—1168).—The material described previously as *d*-mannitol αζ-dibenzoate tri-*p*-toluenesulphonate is a mixture of d-*mannitol* αζ-*dibenzoate* βγδε-*tetra*-p-*toluenesulphonate* (I), m.p. 159°, $[\alpha]_i^{s}$ +42·02°, in $CHCl_3$, and *anhydro*-d-*mannitol di*-p-*toluenesulphonate* (II), m.p. 142°, $[\alpha]_D^{s}$ +56·1° in $CHCl_3$. (II) is converted by NaOH–EtOH into *dianhydro*-d-*mannitol* p-*toluenesulphonate*, m.p. 98—99°, $[\alpha]_D^{20}$ −57·17° in $CHCl_3$, under conditions which do not affect (I). Treatment of (I) with boiling Ac_2O and NaOAc affords d-*mannitol diacetate* αζ-*dibenzoate di*-p-*toluenesulphonate*, m.p. 108—109°, $[\alpha]^{20}$ +74·3° in $CHCl_3$. H. W.

Favourable influence of lead on hydrogenation by sodium amalgam. G. Bertrand and (Mme.) S. Delauney-Auvrey (Compt. rend., 1933, **197**, 6—9).—Amalgams were prepared containing 2·5% Na and up to 0·5% Pb from vac.-distilled Hg and pure Na and Pb; with > 0·2% Pb the amalgams acted slowly. In the reduction of galactose in presence of H_2SO_4, addition of 0·1 and 0·2% Pb gave increased yields, *e.g.*, 75·8 and 90·9% of possible dulcitol as against 62·1—64·2% without Pb. C. A. S.

Quantitative isolation of ether from dilute solutions. A. A. Benedetti-Pichler and F. Schneider (Ind. Eng. Chem. [Anal.], 1933, **5**, 255—257).—Et_2O is separated from dil. aq. solutions by

distilling from a specially-constructed flask and collecting the distillate in a receiver cooled with $COMe_2$ and solid CO_2, which freezes out the H_2O vapour. The contents of the receiver are then centrifuged. The procedure gives a const. error of −9 mg. with solutions containing 10—300 mg. Et_2O in 60 c.c. H_2O. E. S. H.

Highly polymerised compounds. LXXXI. Eucolloidal polyethylene oxide. H. Staudinger and H. Lohmann (Annalen, 1933, **505**, 41—51).—Sluggish catalysts such as the oxides and carbonates of Ca, Sr, or Zn cause the conversion of $(CH_2)_2O$ into polymerides of very high mol. wt. Since these products are formed at room temp. or at 100°, the type of change depends on the catalyst. Oxides of Fe, Mg, Pb, SiO_2 gel, and C are without action. Al_2O_3 slowly yields hemicolloids. The best results are obtained with ZnO, nearly all of which can be subsequently removed without accompanying depolymerisation; the small residue is regarded as an impurity. Solutions of eucolloidal polyethylene oxides do not follow the Hagen–Poiseuille law; the deviations are slight in dil. solution, but increase with increasing chain-length of the polymerides. In the polymeric-homologous series of polyethylene oxides (n = 2—2700), elasticity and hardness are functions of n. Very hard, tenacious products occur only when n is very great, and the power of forming hard, tenacious films is confined to such materials. All polyethylene oxides are cryst., and differences are not observable between the higher and lower polymerides. A "meander" form of the mol. is postulated which explains the free solubility and low m.p. in contrast with the paraffins and polyoxymethylenes. H. W.

Organic reactions with boron fluoride. IV. Ether cleavage in the presence of organic acids. G. F. Hennion, H. D. Hinton, and J. A. Nieuwland (J. Amer. Chem. Soc., 1933, **55**, 2857—2860; cf. A., 1932, 1125).—Et_2O, Bu^{α}_2O, or di*iso*amyl ether with various acids or PhOH and BF_3 ($< 0{\cdot}3$ mol.; modified prep.) at 200° give up to 55% yields of the esters, possibly by preliminary cleavage of the ether to the alcohol. R. S. C.

Synthesis of dimethyl ether of *n*-pentitol. Lespieau and Wiemann (Compt. rend., 1933, **197**, 69—70).—Hydrogenation of δ-hydroxy-αε-dimethoxy-Δ^{β}-pentinene (cf. A., 1928, 989) (Pd–H_2) gives *cis*-*δ-hydroxy-αε-dimethoxy-*Δ^{β}*-pentene*, b.p. 107°/14 mm., oxidised by $AgClO_3$ in presence of OsO_4 to *βγδ-trihydroxy-αε-dimethoxy*-n-*pentane*, b.p. 129—131°/0·34 mm. H. A. P.

Monoalkyl carbonates. V. Mono-*n*-propyl carbonate. C. Faurholt and I. C. Jespersen (Z. physikal. Chem., 1933, **165**, 79—88; cf. A., 1927, 515).—If CO_2 is passed into aq. PrOH and NaOH there occur simultaneously the reactions $CO_2 + PrO' = PrCO_3'$, $CO_2 + OH' = HCO_3'$, and $PrO' + H_2O = PrOH - OH'$. Combining the first and last gives $CO_2 + PrOH + OH' \longrightarrow PrCO_3' + H_2O$, the rate of which has been measured at 0°. $PrHCO_3$ decomposes rapidly in acid solution, $PrHCO_3 = CO_2 + PrOH$; in an acetate buffer the rate is proportional to the $H^{\cdot}$ activity. In slightly alkaline solution in presence of an appropriate amount of PrOH there is established the equilibrium $NaPrCO_3 + H_2O \rightleftharpoons PrOH + NaHCO_3$, the equilibrium const. of which has been measured at 0°. The rate of reaction in strongly alkaline solution has also been determined. R. C.

Ribosephosphoric acid from yeast adenylic acid. P. A. Levene and S. A. Harris (J. Biol. Chem., 1933, **101**, 419—429).—Hydrolysis of yeast adenylic acid (I) (A., 1925, i, 487) yields methylribosidephosphoric acid, converted by exhaustive methylation into tetramethylphosphomethylriboside, $[\alpha]_D^{25}$ −26·4° in abs. EtOH, also produced by similar treatment of NH_4 guanylate or xanthylic acid. Dephosphorylation by $Ba(OMe)_2$ of the riboside from guanylic acid yields dimethylmethylriboside (II), b.p. 90—93°/< 1 mm., $[\alpha]_D^{22}$ −48·7° in MeOH, −47·4° in H_2O (that from adenylic acid has $[\alpha]_D^{21}$ −55·8° in H_2O), hydrolysed by 6% aq. HCl to dimethylribose, b.p. 132—136°/< 1 mm., $[\alpha]_D^{1}$ −16·7° in dil. aq. NH_3, which is reduced by Adams' catalyst to dimethylribitol. The product was not optically inactive [due to presence of γ-glucoside in (II)], and hence the structure of (I) cannot be rigidly concluded. Deamination of (I), however, yields inosine-3-phosphoric acid, $[\alpha]_D^{22}$ −41·0° in H_2O, which, in aq. solution at its own p_H, is readily hydrolysed to a ribosephosphoric acid identical with the corresponding acid from xanthylic acid. Thus (I) is l-adenine-*d*-ribofuranoside-3-phosphoric acid. F. O. H.

Thermal behaviour of sulphur compounds in hydrocarbon solvents. II. *n*-Butyl sulphide in benzene. W. M. Malisoff and E. M. Marks (Ind. Eng. Chem., 1933, **25**, 780—783; cf. A., 1931, 1393).—The thermal stability of n-butyl sulphide (I) in C_6H_6 solution is studied at various temp., concns., and times of exposure. For exposures up to 50 sec. in 0·05 mol. solution (I) is thermally stable at 400°, slightly decomposed at 450°, whilst a 30-sec. exposure at 515° yields only a 20% conversion into H_2S. On exposure up to 55 sec. at ≯ 515° the products are only H_2S and mercaptan unless a large amount of H_2S is present, in which case S and thiophens are also formed. The rates of decomp. are decidedly < those for aliphatic mercaptans under similar conditions. The reactions are partly heterogeneous, being promoted by surface and length of exposure. The inequality of rates of decomp. in C_6H_6 and in n-C_7H_{16} (II) suggests that C_6H_6 may affect the velocity of the reaction or (II) may be an inhibitor. C. E. M.

Sulphoxides and other derivatives of tetrathiolmethylmethane. H. J. Backer and N. D. Dijkstra (Rec. trav. chim., 1933, **52**, 701—708; cf. this vol., 48).—Tetrathiolmethylmethanes (I) (1 mol.) with H_2O_2 (4 mols.) in AcOH at room temp. afford the following tetrasulphoxides, which yield cryst. mercurichlorides: *Me*, m.p. 205° (+2$HgCl_2$, m.p. 143°); *Et*, m.p. 137° (+2$HgCl_2$, m.p. 157·5°); *Pr*$^{\alpha}$, m.p. 117° (+2$HgCl_2$, m.p. 88°; +4$HgCl_2$, m.p. 141°); *Pr*$^{\beta}$, m.p. 165°; n-*Bu*, m.p. 123° (+$HgCl_2$, m.p. 51°; +2$HgCl_2$, m.p. 97°; +4$HgCl_2$, m.p. 149°); tert.-*Bu*, m.p. 212° (+2$HgCl_2$, decomp. > 300°); n-*amyl*, m.p. 143° (+2$HgCl_2$, m.p. 84°; +4$HgCl_2$, m.p. 128°); n-*hexyl*, m.p. 159·5°. (I)

with Br (4 mols.) in C_6H_6 or PhMe afford the following octabromides, decomposed by cold H_2O: *Me*, m.p. 107° (decomp.); *Et*, m.p. 93° (decomp.); *Pr*$^{\alpha}$, m.p. 80° (decomp.); *Pr*$^{\beta}$, m.p. 80° (decomp.); tert.-*Bu*, m.p. 130° (decomp.). $C(CH_2{\cdot}SPh)_4$ (1 mol.) in CCl_4 with Br (4 mols.) affords *tetra*-p-*bromophenylthiolmethylmethane*, m.p. 110° [also formed by interaction (II) of *p*-$C_6H_4Br{\cdot}SNa$ and $C(CH_2Br)_4$ at 150° during 8 hr.] [*sulphone*, m.p. 328°, which is not obtained from $C(CH_2{\cdot}SO_2Ph)_4$ and Br in CCl_4]. By a method similar to (II), the *tetra*-p-*chlorophenyl*, m.p. 96° (*sulphone*, m.p. 276°), and the *tetra*-p-*tolyl* compounds, m.p. 103° (*sulphone*, m.p. 249°), are prepared. J. L. D.

Mercaptides of selenium and tellurium. T. Bersin and W. Logemann (Annalen, 1933, **505**, 1—16).—Absorption of O_2 by Na α-thiolpropionate (I) is not accelerated by $CH_2I{\cdot}CO_2Na$ (II). Repetition of the observations with thiolacetanilide (III) shows this substance to behave similarly when sufficiently purified; the previously observed activity is due to traces of Se present in the NH_4CNS used in the prep. Addition of Na_2SeO_3 (IV) increases the rate of oxidation of (III). If the amount of (IV) is reduced so that only a slight acceleration is observable, addition of (II) causes absorption at a marked rate. (I) behaves similarly. Se and Te likewise accelerate, surpassing Cu and As. (IV) and (I) under N_2 or O_2 give a ppt. of red Se after a transient yellow colour. If the amount of (IV) is diminished and shaking is continued in O_2, the ppt. re-dissolves and the solution contains only (IV) and disulphide. If the concn. of (I) is sufficiently diminished, Se is not pptd., but sufficient O_2 is invariably absorbed for the oxidation of Se to SeO_2 and 2RSH to R_2S_2. Protracted action carries the oxidation beyond the S_2 stage. H_2TeO_3 behaves similarly, but the intermediate compound is more stable. Also, in the presence of an equiv. amount of Na_2TeO_3, the rate of absorption of O_2 exhibits a sharp decline corresponding with the point of complete dissolution of the pptd. Te. The intermediate compound of (IV) and (I) or (II) is too unstable for isolation. Na_2TeO_3 and (I) yield *Te di-α-carboxyethyl disulphide*, $Te(S{\cdot}CHMe{\cdot}CO_2H)_2$, m.p. 114°, which gives the *product* $Te(S{\cdot}CHMe{\cdot}CO_2H)_2,SH{\cdot}CHMe{\cdot}CO_2H$, decomp. 84°, readily hydrolysed by H_2O. SeO_2 and 3-bromo-2-hydroxy-5-methylthiophenol in Et_2O yield *Se di-3-bromo-2-hydroxy-5-methylphenyl disulphide*, m.p. 98°. H. W.

Hexadecanesulphonic acid. R. C. Murray (J.C.S., 1933, 739—740).—An improved prep. is described for hexadecyl mercaptan, m.p. 47—48° (*Pb mercaptide*), containing approx. 25% disulphide, and oxidised (98% yield) to the sulphonic acid, which may be determined as the Ba salt. A. A. L.

Determination of formic, acetic, and propionic acids in a mixture. O. L. Osborn, H. G. Wood, and C. H. Werkman (Ind. Eng. Chem. [Anal.], 1933, **5**, 247—250).—HCO_2H is determined by oxidising with HgO and absorbing the CO_2 in aq. KOH. AcOH and $EtCO_2H$ are determined by the partition method, using Et_2O and titrating with 0·05*N*-NaOH and phenolphthalein. E. S. H.

Identification of hexoic [acids]. M. Hommelen (Bull. Soc. chim. Belg., 1933, **42**, 243—250).—The prep. of the following acids is described: *γ-methylvaleric* (I) (b.p. 199·1°/752 mm., m.p. −33°), β-*methylvaleric* (II) (b.p. 197·8°, m.p. −41·6°), ββ-*dimethylbutyric* (III) (b.p. 183·1—183·8°/741 mm., m.p. +5·6°), α-*ethylbutyric* (IV) (b.p. 192·6—193·0°/754 mm., m.p. −31·8°), αβ-*dimethylbutyric* (V) (b.p. 191·4—191·9°/760 mm., m.p. −1·5°), α-*methylvaleric* (VI) (b.p. 192·0—193·6°/748 mm.), αα-*dimethylbutyric* (VII) (b.p. 186·8—187·2°/750 mm., m.p. −15·0°). Data are given for derivatives as follows: (*a*) b.p. of *chlorides*, (I) 143·8—144·6°/745 mm., (II) 142·5—143·0°/749 mm., (III) 129·5—130·3°/746 mm., (IV) 138·0—138·8°/750 mm., (V) 140—140·8°/745 mm., (VI) 135·9—136·6°/751 mm., (VII) 131·8—132·4°/748 mm.; (*b*) m.p. of *amides*, (I) 118·8°, (II) 124·9°, (III) 132·0°, (IV) 111·8°, (V) 79·6°, (VI) 130·9°, (VII) 99·8°; (*c*) m.p. of *anilides*, (I) 112·0°, (II) 95·2°, (III) 87·0°, (IV) 126·8°, (V) 91·4°, (VI) 131·6°, (VII) 78·4°; (*d*) m.p. of p-*toluidides*, (I) 63·0, (II) 80·5°, (III) 74·8°, (IV) 116·2°, (V) 83·3°, (VI) 134·4°, (VII) 112·6°. E. S. H.

Ester-interchange. IV. Ester-interchange between two fats, and between ethylene glycol and a mixture of two fats. V. Ether-interchange. R. Oda (J. Soc. Chem. Ind. Japan, 1933, **36**, 331—334B, 334B; cf. B., 1933, 197, 476).—IV. Olive oil (I) or linseed oil (II) at 200° in presence of H_2 and a little K_2CO_3 undergoes ester-interchange (III) with coconut oil (IV), but not with hardened oil. From experiments with mixtures of two fats with glycol it is concluded that the acids of (IV) undergo (III) with glycol more easily than those of (I) or (II).

V. An extension of the double linking rule (this vol., 256) indicates that certain ethers should undergo (I) in a similar manner to esters. EtOBz and PrOBz with EtOH at 200° give a little Et_2O and EtOPr, respectively. A. A. L.

Ester-interchange. VI. Ester-interchange between fatty oils, fatty acids, and ethylene glycol. R. Oda (J. Soc. Chem. Ind. Japan, 1933, **36**, 376—377B; cf. preceding abstract).—Interchange of free and combined fatty acid radicals occurs on autoclaving coconut oil (I) with oleic acid (II) at 200°, and to a smaller extent between linseed oil and stearic acid. With castor oil and (II), ester-interchange accompanies ester formation at the OH group: similarly, both reactions take place when a mixture of (I), (II), and $C_6H_4(OH)_2$ is heated at 200° for 2 hr. E. L.

Olefinic compounds. II. Orienting influence of the carboxyl group. G. F. Bloomfield, E. H. Farmer, and C. G. B. Hose (J.C.S., 1933, 800—806; cf. A., 1932, 930).—α-Methylacrylic acid, from α-bromo*iso*butyric acid by an improved process, with HOCl gives α-chloro-β- and β-chloro-α-hydroxy-*iso*butyric acid (90%), m.p. 110°, the latter being also obtained by hydrolysis of chloroacetone cyanohydrin. Et α-methylacrylate similarly gives (?) Et αβ-dichloro-, β-chloro-α-hydroxy-, and α-chloro-β-hydroxy-*iso*butyrate (70% of the chlorohydrins), separated as the corresponding acids. Tiglic acid gives α-*chloro*-β- (I), m.p. 113° (38%), and β-*chloro*-

α-*hydroxy*-α-*methylbutyric acid* (II), m.p. 89°. The proportion of isomerides is found by determination of the Cl content after reduction with Na–Hg in presence of CO_2, only the α-Cl-acids being attacked. Et tiglate gives a (?) dichloride and equal quantities of the Et esters of (I) and (II), isolated as the acids, one of which is a *stereoisomeride* of (II), m.p. 114°. The proportions were found by the above reduction method, and by actual separation. Na tiglate gives (I) and (II) (80%), determined by the reduction method. Crotonic acid gives β-chloro-α- and α-chloro-β-hydroxybutyric acid (26% by the reduction method); this mixture when oxidised with $K_2Cr_2O_7$ or HNO_3 gave AcOH and $CHMeCl{\cdot}CO_2H$, isolated as $CHMe(CO_2H)_2$. ββ-Dimethylacrylic acid gives α-chloro*iso*butylene and other neutral compounds, impure β-*chloro*-α-, and α-*chloro*-β-*hydroxy*-β-*methylbutyric acid* (80%), m.p. 69°, converted by conc. H_2SO_4 into α-chloro-ββ-dimethylacrylic acid. In determining the isomerides the neutral compounds are considered to arise from the latter acid. It is suggested that the O of the CO group has no attraction for the components of HOCl, so that the proportion of isomerides is a measure of the orienting influence of the CO_2H group. This influence is greatly affected by the state of ionisation of the CO_2H group, and appears to be small with the CO_2Et group. Δ^{α}-Acids, and especially their esters, add more slowly than the Δ^{β}- and Δ^{γ}-compounds. A. A. L.

Olefinic acids. VII. Preparation of Δ^{β}-acids. R. P. Linstead, E. G. Noble, and (in part) E. J. Boorman. **IX. Addition of hydrogen bromide to unsaturated acids.** E. J. Boorman, R. P. Linstead, and H. N. Rydon. **X. Formation of lactones from Δ^{α}- and Δ^{β}-*n*-butenoic and -pentenoic acids.** E. J. Boorman and R. P. Linstead. **XI. Formation of lactones from Δ^{γ}-unsaturated acids, and an example of ring–chain (lacto–enoic) tautomerism.** R. P. Linstead and H. N. Rydon (J.C.S., 1933, 557—561, 568—576, 577—580, 580—586; cf. A., 1932, 251).—VII. EtCHO and malonic acid in presence of $N(C_2H_4{\cdot}OH)_3$ (cf. A., 1931, 935) give β-ethylglutaric acid and Δ^{β}-*n*-pentenoic acid, m.p. 1°, b.p. 90°/10 mm. (32—36% yield). Δ^{β}-*n*-Hexenoic acid, m.p. 12°, b.p. 110°/15 mm. (40—52% yield), and β-*n*-propylglutaric acid (and its anhydride) are similarly obtained, whilst vinylacetic acid is obtained only in small yield by this process, being best prepared by an improvement in Bruylants' method (A., 1924, i, 1053). Other methods for Δ^{β}-olefinic acids are less good.

IX. With the exception of Δ^{α}-acids, addition of HBr is independent of the position of the double linking with respect to CO_2H. In hydrocarbon solvents the acids behave as H esters, so that Br goes entirely to the C atom of the double linking more distant from CO_2H. Addition is considered to be controlled by the polar effect of CO_2H acting either through the C chain, or as a direct field effect if > one CH_2 intervenes. In other solvents (H_2O, AcOH, Et_2O), or with the free acid, addition proceeds according to the Markovnikov rule, being controlled by the no. of the alkyl substituents at the double linking. Application of these rules provides convenient preps. for acids with Br distant from CO_2H. A method for the analysis of mixtures of β- and γ-Br-acids depends on the formation of OH-acid by the former, and lactone by the latter, when the Ba salts are boiled with H_2O. The hydrobromides obtained in the following reactions are individuals except where stated. Crotonic acid at 80° with HBr gives β-bromobutyric acid (I) (Et ester, b.p. 81°/17·5 mm.). Similarly, vinylacetic acid (II) alone, with 0·5% H_2O, in Et_2O, or in AcOH gives (I), whilst in petrol or PhMe it gives γ-bromobutyric acid (III), converted by boiling with $Ba(OH)_2$ into the γ-lactone, m.p. —48°. The Et ester of (II) gives the Et ester of (III), b.p. 94°/18 mm., converted by suitable treatment with Et sodiomalonate into adipic acid, a method also applied to the synthesis of glutaric and β-methylglutaric acids. Δ^{α}-*n*-Pentenoic acid, m.p. 9·5°, b.p. 106°/20 mm., alone gives β-bromovaleric acid (IV). Δ^{β}-*n*-Pentenoic acid alone or with 0·5% H_2O gives 8% of (IV) and 92% γ-bromovaleric acid (V), the Et ester of which by the above treatment gives β-methyladipic acid. (V) is converted as for (III) into γ-valerolactone, m.p. —35·5°, b.p. 92—93°/18 mm. Δ^{γ}-*n*-Pentenoic acid [Et ester (VI), b.p. 144—144·5°], alone, with 0·5% H_2O, or in Et_2O gives (V), whilst in PhMe it gives δ-bromovaleric acid (VII), m.p. 40°, also obtained from δ-valerolactone with HBr. (VI) alone gives the Et ester of (VII), converted as above into pimelic acid. Δ^{α}-*iso*-Hexenoic acid alone gives β-bromo*iso*hexoic acid, converted (also as Na salt) by boiling H_2O into the β-hydroxy-acid and a little (?) β-lactone. Δ^{β}-*iso*-Hexenoic acid (pyroterebic acid), m.p. —2°, b.p. 84°/4 mm., alone or with 0·5% H_2O gives γ-bromo*iso*-hexoic acid, also obtained from, and converted into, the γ-lactone, m.p. 8·4°, b.p. 94°/20 mm. Δ^{γ}-*iso*-Heptenoic acid (see below) alone or with 0·5% H_2O gives δ-*bromo*-δ-*methylhexoic acid*, m.p. 45°, also obtained from the δ-lactone. γ-*Bromo*-δ-*methylhexoic acid*, m.p. 41°, is obtained from the γ-lactone.

X (cf. A., 1932, 251). Vinylacetic acid when boiled alone, with 50% H_2SO_4, or in decahydronaphthalene yields crotonic acid without appreciable lactone formation, whilst in cold 60% H_2SO_4 tautomeric change is slow, and unaccompanied by lactonisation. Crotonic acid and γ-butyrolactone, m.p. —48°, b.p. 83·5°/12 mm., are stable under similar conditions. The latter is obtained by the action of KCN on trimethylene chlorohydrin, followed by hydrolysis and distillation of the acid. Δ^{α}-*n*-Pentenoic acid is stable to cold 60% H_2SO_4, but with boiling 50% H_2SO_4 gives γ-valerolactone (I), m.p. —36°, b.p. 102—103°/28 mm. (hydroxyamide, m.p. 51·5—52°), also obtained by the reduction of lævulic acid (improved prep.). Δ^{β}-*n*-Pentenoic acid is stable when boiled alone, gives (I) slowly with cold 60% H_2SO_4, and rapidly with hot 50% H_2SO_4. The results are correlated with theory previously discussed. The rates of formation of lactone from γ-hydroxy-butyric and -valeric acids are recorded, and the amounts of hydrolysis of the above lactones by H_2O at 100° are determined by a method of direct titration with $Ba(OH)_2$.

XI. An extension of previous theory indicates that if R=R′=H in the acid $CRR'{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$

it should give a γ-lactone, whereas if R and R′ are alkyl groups a δ-lactone should be formed. Δ^{γ}-*n*-Pentenoic acid, m.p. −22·5°, b.p. 90°/16 mm. (from Et allylmalonate), gives γ-valerolactone slowly when boiled alone in the absence of air, or rapidly with H_2SO_4. Dimethylmalonic acid, obtained by an improved method from the ester (A., 1922, i, 978; also obtained from dimethyltrimethylene dibromide), gives δ-*iso*heptolactone (I), m.p. 28°, b.p. 94°/6 mm. (? second form, m.p. 8°), and Δ^{γ}-*iso*heptoic acid (II), m.p. −33°, b.p. 105°/5 mm., separated by acidifying the $NaHCO_3$ extract in presence of a solvent, and converted into (I) with H_2SO_4. (I) is also obtained from *iso*amylmalonic acid, m.p. 94°, which is converted into *iso*heptoic acid. Oxidation of the K salt of this with $KMnO_4$ gives (I). The "lacto–enoic" tautomerism (I) ⇌ (II) takes place at the b.p., and was studied quantitatively. A method for the analysis of mixtures of (I) and (II) is described. Trimethylene chlorohydrin with $CHNa(CO_2Et)_2$ gives a *substance*, $C_{11}H_{16}O_2$, m.p. 148°. An improved prep. is described for δ-*n*-valerolactone, m.p. −12·5°, b.p. 88°/4 mm. (A., 1928, 737), from Et γ-phenoxypropylmalonate (acid, m.p. 65—66°; cf. A., 1928, 990). β-Carbethoxypropionyl chloride with $CHMe_2$·ZnI gives γ-keto*iso*heptoic acid, which, after reduction with Na–Hg, gives the γ-lactone, b.p. 98°/15 mm. The hydrolysis of the above lactones and the lactonisation of the corresponding OH-acids were followed quantitatively. A. A. L.

Catalytic hydrogenation of unsaturated compounds. I. Additive mode in relation to selectivity of attack and catalyst activity. E. H. Farmer and R. A. E. Galley (J.C.S., 1933, 687—696; cf. A., 1932, 365).—In mixtures of Δ^{γ}-pentenoic acid or allyl alcohol with a hexenoic acid (I) the former is reduced first, whilst the components of mixtures of (I) are hydrogenated side by side. This is in agreement with the principle that monosubstituted olefines are selectively reduced before disubstituted etc. (cf. A., 1925, i, 350). In the reduction of sorbic acid (II), hexoic acid (III) and (I) are produced side by side. Since the amount of II required to effect complete disappearance of the (II) is unchanged by previous addition of (I), all the (III) is formed by αβγδ addition to (II) so long as some is present, and not by reduction of the (I). With an "aged" catalyst (from PtO_2,H_2O) αβγδ addition is decreased, whilst αβ, αδ, and γδ additions are increased, the last to the greatest extent. Hence the state of the catalyst may affect the additive mode with a polyolefine. The bearing of this on the assessment of constitutive influences is discussed. The rate of reduction of (I) increases with increasing remoteness of the double linking from the acid group. The rate of hydrogenation is independent of the concn. of the olefine within wide limits, but the sudden increase in rate just before saturation with certain substances is confirmed (*loc. cit.*). A. A. L.

So-called polyundecenoic acids. A. Barbot (Compt. rend., 1933, 197, 65—67).—The spongy residue left on distillation of castor oil on alcoholysis (EtOH) gives 8 wt.-% of glycerol, Et heptoate (0·4%), *n*-nonoate (0·5%), undecenoate (I) (11·1%), palmitate (2·4%), ricinoleate (II) (2·4%), oleate (III) (6·5%), stearate (0·8%), the Et ester of an unidentified acid, m.p. 85—86° (0·4%), and an undistillable residue (IV) (75%), mol. wt. approx. 700°, apparently the ester of a dibasic acid. Interruption of the distillation at an early stage gives the same products in very different proportions, (I), (II), (III), and Et linoleate comprising the bulk of the product. Abundant evolution of H_2O occurs during the distillation, and it is concluded that (IV) is formed by condensation of linoleic acid with itself or with other unsaturated acids produced by decomp. of ricinoleic acid. H. A. P.

Calorimetric researches. XX. Alternation phenomena. VI. Alternations in the properties of *n*-monoalkylmalonic acids. P. E. Verkade and J. Coops, jun. (Rec. trav. chim., 1933, 52, 747—767).—The *n*-monoalkylmalonic acids fall into two groups, that with term no. (cf. A., 1930, 848) 2—5, and that from 6 onwards. The heats of combustion are determined (cf. A., 1925, ii, 490); those from the "lower" group exhibit definite, although weak, odd alternation, whereas those of the "higher" group are const. These results strongly contrast with those of Coster and van der Ziel (A., 1932, 682) and previous work on the alternation of other physical properties. The significance of the results is discussed and Malkin's views (A., 1932, 326) are criticised. J. L. D.

Modes of addition to conjugated unsaturated systems. V. Hydrogenation of ethyl muconate and of sorbic and β-vinylacrylic acids in presence of platinum. C. K. Ingold and L. D. Shah (J.C.S., 1933, 885—890).—Treatment of Et muconate, sorbic (I) or β-vinylacrylic acid with 1 mol. of H_2 in presence of Pt gives equal proportions of tetrahydro-derivative and unchanged material, the amount of dihydro-compounds being < a few % (cf. A., 1932, 365; this vol., 935). Analyses by ozonisation, followed by treatment with H_2O_2, and with $KMnO_4$ in the case of (I) (*loc. cit.*) are described. The mixtures of unchanged and hydrogenated substances could not be completely separated by distillation. $CH_2(CO_2H)_2$ may be titrated with Br in $CHCl_3$ in the presence of HCl. Similar results are obtained with (I) and an "aged" catalyst. Reduction of dihydro-derivatives is slower than the complete reduction of butadiene derivatives. *Et* Δ^{α}-*dihydromuconate* (from the chloride) has b.p. 125—126°/14 mm. The results are in agreement with theory previously discussed. A. A. L.

Emetics derived from mandelic and malic acids. Volmar and Betz.—See this vol., 948.

Synthesis of substances analogous to bile acid degradation products. II. Synthesis of some straight-chain polycarboxylic esters. J. W. Baker. **III. Attempted use of diallyl as an agent to introduce the requisite side-chain in the synthesis of the acid $C_{13}H_{20}O_6$.** J. W. Baker and H. Burton (J.C.S., 1933, 811—815, 815—818).—II. $CH_2(CO_2Me)_2$ and Me γ-bromovalerate condense to *Me* β-*methyl*-n-*butane*-αα*δ*-*tricarboxylate*, b.p. 145°/3 mm. $CH_2(CO_2Me)_2$ and $CHMeBr{\cdot}CO_2Me$ form *Me* n-*propane*-αα*β*-*tricarboxylate*, m.p. 48—49° [*triamide*,

m.p. 249° (decomp.); *amide-imide*, m.p. 162°], brominated to the α-*Br*-ester, b.p. 150°/7 mm., which with C_5H_5N gives *Me* Δ$^{\alpha}$-*propene-ααβ-tricarboxylate* (I), b.p. 178°/53 mm. [*amide*, m.p. 198° (decomp.)]. (I) condenses with $CH_2Ac{\cdot}CO_2Me$ to Me paraorsellinate and with HBr gives *Me* β-*bromo*-n-*propane-ααβ-tricarboxylate* (II), b.p. 158—165°/5 mm., m.p. 68° (*l*-ester, b.p. 165—175°/10 mm., m.p. 72°). (II) condenses with $CH_2(CO_2Me)_2$ to *Me* β-*methyl*-n-*propane-ααβγγ-pentacarboxylate*, m.p. 58°, and with Me β-methyl-*n*-butane-ααδ-tricarboxylate to *Me* βγ-*dimethyl*-n-*butane-ααβγδδ-hexacarboxylate*, m.p. 179°. $CH_2Ac{\cdot}CO_2Me$ and $CHMeBr{\cdot}CO_2Me$ give *Me* β-*keto*-n-*pentane-γδ-dicarboxylate*, b.p. 146°/30 mm. (*semicarbazone*, m.p. 159°). Et ethane-ααβ-tricarboxylate with Et bromosuccinate yields *Et* n-*butane-αβγγδ-pentacarboxylate*, b.p. 210°/5 mm., but with Et β-bromo-*n*-propane-αβ-dicarboxylate the required product is not obtained. Bromination of Et β-methyl-*n*-propane-αγγ-tricarboxylate affords the *γ-Br*-ester, b.p. 184°/9 mm., which does not give the required condensation product with Et αβ-dicyano-β-methylglutarate (III). Hydrolysis of (III) gives a *substance*, m.p. 109—110°, and subsequently an *acid*, $C_7H_9O_4N$, m.p. 133°.

III. Diallyl and HBr give the *mono-* (I), b.p. 41—43°/13 mm., and the *di-hydrobromide*, b.p. 82—84°/5 mm. Ozonolysis of diallyl yields some MeCHO, showing the presence of a small amount of isomerides. Decomp. of the ozonide of (I) affords some MeCHO and a Br-aldehyde. The *trimeride* of β-bromo-*n*-butaldehyde, m.p. 98°, prepared from crotonaldehyde and HBr, is not found in the ozonolysis product, indicating that the amount of $CHMeBr{\cdot}CH_2{\cdot}CH{:}CHMe$ is small. *Me* cyclo*pentanone*-2 : 3-*dicarboxylate*, b.p. 162°/15 mm. (*semicarbazone*, m.p. 188—189°), prepared from *Me* n-*butanetricarboxylate*, b.p. 168°/16 mm., by the Dieckmann reaction, is methylated to the 2-*Me* derivative (II), b.p. 146°/4 mm. [*semicarbazone*, m.p. 234° (decomp.)]. Condensation of (II) and (I) and subsequent ozonolysis and oxidation does not give the required OH-acid ester or the unsaturated derivative, but *n*-pentane-αγδ-tricarboxylic acid or unchanged ester. F. R. S.

Influence of solvents and other factors on the rotation of optically active compounds. XXXI. Rotation dispersion of the nitrobenzyl tartrates. T. S. Patterson and D. McCreath (J.C.S., 1933, 760—768).—*m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ and *d*-tartaric acid at 140° for 15 hr. in a current of dry air give m-*nitrobenzyl* d-*tartrate*, m.p. 119° (Ac_2 derivative, m.p. 107°; Bz_2 derivative, m.p. 109°). *o*-Nitrobenzyl *d*-tartrate (Ac derivative, m.p. 118—120°; Ac_2 derivative, m.p. 75°) is similarly prepared. Rotation–temp. curves for the *m*- and *p*-NO_2-esters and their derivatives in C_5H_5N, quinoline, and $MeNO_2$ lie in a comparatively restricted part of the general curve for tartrates already described, whilst the *o*-NO_2-esters lie in widely separated regions. The curves for *o*-nitrobenzyl dibenzoyl-*d*-tartrate in quinoline suggest that the general curves should be extended to include a second point of visible anomalous dispersion, and possibly should rise to another max. with fall of temp. A. A. L.

Primary process in the oxidation of tartrates in alkaline solution at a high anode potential. V. Sihvonen.—See this vol., 914.

Derivatives of hydroxymethoxysuccinic and methoxymalonic acids. J. Pryde and R. T. Williams (J.C.S., 1933, 642—644).—The [α] of derivatives of α-hydroxy-β-methoxysuccinic acid (*Me* ester, b.p. 119—122°/1·6 mm.; *diamide*, m.p. 190—191°; *methylamide*, m.p. 129°) are approx. the means of the pairs of corresponding derivatives of tartaric and dimethoxysuccinic acids (cf. J.C.S., 1915, **109**, 5). Tartronic acid (improved prep.) with Ag_2O and MeI gives *Me* αβ-*dimethoxyethane-ααββ-tetracarboxylate*, m.p. 76°. A. A. L.

Constitution of vitamin-*C*. V. F. Micheel and K. Kraft (Z. physiol. Chem., 1933, **218**, 280—282; cf. this vol., 698).—Catalytic hydrogenation of ascorbic acid yields *l*-idonic acid, whereas the authors' proposed constitution should give anhydrohexonic acid. Hydrogenation in AcOH gives a cryst. acetylhexonolactone, which from its stability contains a 1 : 4-ring. Oxidation with $Pb(OAc)_4$ of dimethylascorbic acid affords CH_2O. In the light of this evidence the constitution advanced by Hirst *et al.* (cf. this vol., 594) is accepted. J. H. B.

Synthesis of ascorbic acid. W. N. Haworth and E. L. Hirst (Chem. and Ind., 1933, 645—646).—*d*- and *l*-Xylosone, aq. KCN, and $CaCl_2$ give a reducing acid converted by 8% HCl at 50° into ascorbic acid, identical with the natural acid (cf. this vol., 698). The substance of Reichstein *et al.* (this vol., 594) is a derivative of *d*-ascorbic acid. F. R. S.

Preparation from glucose of an acid $C_6H_8O_6$ equal to ascorbic acid in reducing power. K. Maurer and B. Schiedt (Ber., 1933, **66**, [*B*], 1054—1057).—Me α-ketogluconate is converted by NaOMe in MeOH, C_5H_5N, or their mixtures into an *acid*, probably $\begin{matrix}OH{\cdot}C{=}{=}{=}C(CO_2H)\\ (OH{\cdot}CH{\cdot}CH(CH_2{\cdot}OH)\end{matrix}{>}O$), m.p. 168°, $[\alpha]_D$ −16·3° in H_2O (*K* salt, $[\alpha]_D$ +91·8° in H_2O), which gives all the reactions of vitamin-*C*. Treatment of the *Na* salt with H_2SO_4, $COMe_2$, and anhyd. $CuSO_4$ gives a strongly reducing *substance*, m.p. (indef.) 150—160°, $[\alpha]_D$ −16·8° in H_2O, which is not a mono*iso*propylidene compound; it appears to acquire 2 Me when treated with CH_2N_2. H. W.

Preparation of aldehydes and ketones by dehydrogenation of alcohols over copper–chromium oxide. H. Adkins, C. E. Kommes, E. F. Struss, and W. Dasler (J. Amer. Chem. Soc., 1933, **55**, 2992—2994).—Dehydrogenation of alcohols by $CuO{-}Cr_2O_3$ may lead to four products, *e.g.*, $Bu^{\alpha}OH \longrightarrow$ (*A*) $Pr^{\alpha}{\cdot}CHO+H_2$ or (*B*) $C_4H_8+H_2O$; $2Pr^{\alpha}{\cdot}CHO \longrightarrow$ (*C*) $CHPr^{\alpha}{:}CEt{\cdot}CHO+H_2O$ or (*D*) $Pr^{\alpha}{\cdot}CO_2Bu$. With primary alcohols at 300° reaction (*B*) occurs only slightly. At 300—400°/100—300 atm. reactions (*C*) and (*D*) mainly occur, and even at 1 atm. reaction (*D*) may take place to 20%, although it rarely exceeds 10%. Reaction (*C*) does not usually occur greatly at 1 atm. with primary alcohols, but *cyclo*hexanol at 360° gives 2-*cyclo*hexylidene*cyclo*hexan-1-one, b.p. 274—276° (20%), *cyclo*hexanone (I) (56%), and *cyclo*hexene (II), b.p. 81—83° (6%); at 360° and (?) 300 atm. it gives

26% of (I) and 51% of (II). The activity of the catalyst can be revived by heating in H_2O at 250° for 1 hr. R. S. C.

Anhydrous formaldehyde. F. WALKER (J. Amer. Chem. Soc., 1933, **55**, 2821—2826).—The preps. of liquid CH_2O (I) and its anhyd. polymeride are modified. The solubility of (I) in H_2O, MeOH, $Pr^{\alpha}OH$, and $Bu^{\alpha}OH$ is recorded, the heat of dissolution for these solvents being 14·2—15·0 kg.-cal. (I) does not react with ice and is fairly stable when pure. Primary aliphatic amines cause very rapid, *tert.* less rapid, polymerisation. The polymerides can be differentiated by the rate of their reaction with H_2O. R. S. C.

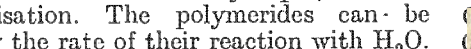
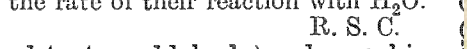
Reductone (enol-tartronaldehyde) and ascorbic acid. H. VON EULER and C. MARTIUS (Annalen, 1933, **505**, 73—87; cf. this vol., 699).—Equally conc. solutions of fructose, glucose, mannose, and maltose when heated with the same amount of alkali under similar conditions consume equal amounts of 2 : 6-dichlorophenol-indophenol (I), galactose somewhat less, and hexose phosphate only so much as corresponds with the amount of ester hydrolysed. Glyceraldehyde, AcCHO, and, particularly, dihydroxyacetone require about twice as much (I). Pentoses behave similarly to hexoses. The resulting reductone (II) differs quantitatively from ascorbic acid in behaviour towards I and (I). Sudden polymerisation occurs when conc. acid solutions of (II) are heated to rather above 100°; the viscous, amorphous products are devoid of reducing power, which they regain when treated with alkali. The high m.p. is explained by polymerisation during heating. (II) does not show antiscorbutic action. H. W.

Determination of acetone [in the presence of acetaldehyde]; catalysts in the synthesis of acetone from acetaldehyde. S. YAMADA (J. Soc. Chem. Ind. Japan, 1933, **36**, 193—195B).—MeCHO is determined in presence of $COMe_2$ by oxidation with Ag_2O. The total aldehyde and ketone is then determined with $NaHSO_3$ and I, and the $COMe_2$ by difference. A mixture of ZnO and CaO is more effective than either alone as a catalyst in the conversion of MeCHO into $COMe_2$ with steam. A. A. L.

Preparation of mesityl oxide by Bodroux and Taboury's method. R. JACQUEMAIN (Compt. rend., 1933, **196**, 1622—1624).—Fractionation of the product gives 18% of mesityl oxide (I), 40% of $COMe_2$, and 14% of a forerun containing $COMe_2$ (59·1%), H_2O (2·7%), and (I) (29·5%). The last fraction, b.p. > 132°, contains β-hydroxy-δ-keto-β-methylpentane and *ketones*, $C_9H_{18}O$ and $C_{12}H_{18}O$, b.p. 80°/6 mm. and 104—106°/6 mm. (*semicarbazones*, m.p. 206° and 150°, respectively) (cf. A., 1909, i, 699). R. S. C.

Formation of sugar from formaldehyde in presence of alcohols. G. GORR and J. WAGNER (Biochem. Z., 1933, **262**, 351—354).—Details of the rapid polymerisation of CH_2O into sugar by heating with various alcohols and CaO are given. Using 30% CH_2O and MeOH the yield of sugar calc. as glucose was 82—93% of the aldehyde. P. W. C.

Reducing sugars. III. L. MARCHLEWSKI and W. URBAŃCZYK (Biochem. Z., 1933, **262**, 248—259; cf. this vol., 810).—Addition of 0·5*N*-NaOH to *l*-arabinose (I) solutions leads to the appearance in the originally continuous spectrum of two bands, max. at 2690 and 3095 Å., and on keeping for 2 hr. with NaOH rhamnose solutions show a band at 2675 Å. With (I) immediate neutralisation restores the continuous spectrum. P. W. C.

Transformation of glucals into γ-keto-acids. M. BERGMANN and H. MACHEMER (Ber., 1933, **66**, [*B*], 1063—1065).—Glucal triacetate is converted by boiling 0·5% HCl–MeOH into a *substance*, possibly  or  , b.p. 53°/1·5 mm., and *Me δ-methoxymethyl-lævulate* (I), b.p. 90°/3 mm. [*phenylhydrazone*, m.p. 74°; *semicarbazone*, m.p. 117° (corr.)]. (I) is obtained in similar yield from ψ-glucal triacetate, in poorer yield from glucodeose or galactal triacetate. Xylal diacetate similarly affords Me lævulate, b.p. 85°/14 mm. [phenylhydrazone, m.p. 105°; semicarbazone, m.p. 151° (corr.)], also obtained from arabinal diacetate. H. W.

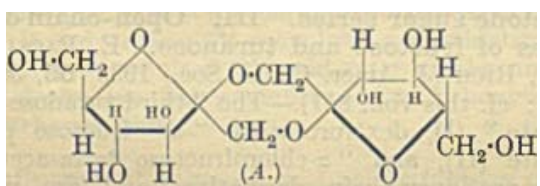
Simultaneous preparation of 2 : 3 : 4- and 2 : 3 : 6-trimethylglucose. G. J. ROBERTSON (J.C.S., 1933, 737—739).—2 : 3-Dimethyl-α-methylglucoside in C_5H_5N with CPh_3Cl gives 6-*triphenylmethyl*-2 : 3-*dimethyl*-α-*methylglucoside*, m.p. 169—170°, $[\alpha]_D$ +66·4° in $CHCl_3$ [4-*Bz* derivative, m.p. 60°; 4-*Ac* derivative (I), m.p. 153—154°]. 4-*Acetyl*-2 : 3-*dimethyl*-α-*methylglucoside* [from (I)] on repeated methylation with MeI and Ag_2O yields a Me_3 derivative, from which 2 : 3 : 6- (separated by conversion into the methylglucoside) and 2 : 3 : 4-trimethylglucose (1 : 6-dinitrate, m.p. 84° and 86°) are obtained in approx. equal amounts. The wandering of Ac groups during treatment with MeI and Ag_2O is discussed. A. A. L.

Ketone sugar series. III. Open-chain derivatives of fructose and turanose. E. PACSU and F. V. RICH (J. Amer. Chem. Soc., 1933, **55**, 3018—3024; cf. this vol., 811).—The "third turanose octa-acetate" (I), dextrorotatory "α" fructose penta-acetate (II), and "α-chlorofructose tetra-acetate" (III) are open-chain derivatives and are named *keto*turanose octa-acetate, *keto*fructose penta-acetate, and 6-chloro*keto*fructose tetra-acetate, respectively. (I) is hydrogenated (Pt) in EtOH to a mixture, yielding on acetylation 5-*glucosido-sorbitol nona-acetate* (IV), m.p. 116·5°, $[\alpha]_D^{20}$ +70·9° in $CHCl_3$, and -*mannitol nona-acetate*, m.p. 142°, $[\alpha]_D^{20}$ +89·3° in $CHCl_3$. (IV) when deacetylated by 5% H_2SO_4 and then with yeast gives *d*-sorbitol hexa-acetate. The prep. of fructose tetra-acetate, $[\alpha]_D^{20}$ −101·6° ⟶ −99·9° in C_5H_5N, −97·2° in C_6H_6, and −74·4° (stable) in H_2O, is modified. (II) by reduction and acetylation gives similarly sorbitol and mannitol hexa-acetates. β-Fructose penta-acetate is not reduced similarly. (III) with AgOAc and Ac_2O gives β-fructose penta-acetate and on reduction and acetylation a mixture of (probably) 6-chloro-sorbitol and -mannitol tetra-acetates. R. S. C.

Alcoholysis of sucrose. I. E. BERNER (Ber., 1933, **66**, [*B*], 1076—1080).—The action of MeOH on

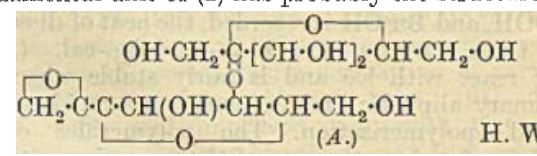
sucrose (I) at 150—155° during 8—10 hr. causes change of about half of (I) into glucose and γ-methylfructoside (II) $[\alpha]_D$ ≯ +54°. Prolongation of the reaction is accompanied by isomerisation of (II), which is partly prevented by the alkali of the glass. Since the determinations of reducing sugar and of aldose (Willstatter–Schudel) gives identical results, free fructose is not formed. (II) is identified by conversion into 1 : 3 : 4 : 6-tetramethyl-methylfructoside and -fructose. In accordance with Hudson's rule, (II) is regarded as α-methylfructofuranoside. Provided that a Walden inversion does not occur during alcoholysis, the configuration of (II) must be identical with that of the fructose residue in sucrose. H. W.

Natural polylævans. V. Carbohydrates of the Jerusalem artichoke. II. H. H. Schlubach and H. Knoop (Annalen, 1933, **504**, 19—30).—Repeated dissolution in MeOH of the dextrorotatory material (I) derived from the Jerusalem artichoke and subsequent pptn. with Et_2O permits the separation of mannitol without leading to a product of established homogeneity. Characterisation of fructose anhydrides is facilitated by hydrolysis with N-H_2SO_4 in 1% solution at 20° or 60°, respectively, the course of the change being followed by determination of reducing power (Bertrand) rather than of [α]. The fructose anhydrides are thereby differentiated into two distinct classes: irisin, sucrose, inulin, and the dilævan of artichoke are readily hydrolysed, whereas (I) and Jackson's difructose anhydride I and III are difficultly hydrolysed. A simple relationship does not exist between the rates of hydrolysis at the different temp. Treatment of (I) with Ag_2O and MeI yields mainly a *hexamethyldifructose anhydride*, b.p. 143°/0·18 mm., $[\alpha]^{20}$ +149·2° in $CHCl_3$, hydrolysed by N-H_2SO_4 at 95° chiefly to 3 : 4 : 6-trimethylfructose, b.p. 90°/0·1 mm., $[\alpha]_D^{20}$ +24·9° in $CHCl_3$ (phenylosazone, m.p. 77—79°). (I) has therefore



the constitution *A*. Jackson's compound III is probably identical with (I) and is an accompaniant of his inulin, whilst his substance I is regarded as a reversion product. H. W.

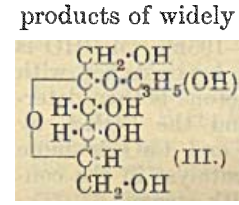
Fructose anhydrides. XII. Constitution of irisin. H. H. Schlubach, H. Knoop, and M. Y. Liu (Annalen, 1933, **504**, 30—37).—Extraction of the powdered rhizomes of *Iris pseudoacorus* mixed with $CaCO_3$ by EtOH and successive treatment of the extracts with $Pb(OAc)_2$, H_2S, and NH_3 leads to irisin (I), which, after repeated dissolution in H_2O and pptn. with EtOH, has m.p. 210° (decomp.) after softening at 160°, $[\alpha]^{20}$ −53·3° in H_2O, ash 0·08%. Under standard conditions it is more readily hydrolysed than any other fructose derivative; the discrepancy between the results obtained by using Bertrand's method and measuring $[\alpha]_D$ points to the production of intermediate compounds during hydrolysis. (I), Ac_2O, and C_5H_5N afford irisin acetate, m.p. 217°, $[\alpha]^{20}$ −23·1° in AcOH, which, with Me_2SO_4 and NaOH in $COMe_2$, gives *methylirisin* (II), m.p. 187—188·5°, $[\alpha]^{20}$ −63·2° in $CHCl_3$. (II) is hydrolysed by $H_2C_2O_4$ in boiling 70% EtOH to 1 : 3 : 4 : 6-tetramethyl- and an unidentified dimethyl-fructose. The fundamental unit of (I) has probably the structure *A*.



Optical superposition and the 4 : 6-benzylidenemethylglucosides. D. S. Mathers and G. J. Robertson (J.C.S., 1933, 696—698).—4 : 6-Benzylidene-α-methylglucoside 2 : 3-di-*p*-toluenesulphonate, m.p. 148—149°, has $[\alpha]_D$ +13° in $CHCl_3$ (cf. A., 1929, 50). A comparison of mol. rotations of 4 : 6-benzylidene-α- and -β-methylglucosides, and their Bz_2, Me_2, Ac_2, and di-*p*-toluenesulphonyl derivatives shows that the rule of optical superposition is not applicable, probably owing to the influence of :CHPh. A. A. L.

Properties of *d*-β-5-chloro-, -5-bromo-, and -5-iodo-salicylglucosides. P. Delauney (Compt. rend., 1933, **197**, 70—72; cf. A., 1927, 174; 1928, 201; 1930, 57).—Solubility in H_2O and EtOAc, m.p., $[\alpha]_D$, reducing power, and behaviour on hydrolysis with dil. H_2SO_4 and emulsin are given. All crystallise with $1H_2O$. *d*-β-5-Iodosalicylglucoside has m.p. 172° (block, anhyd.). H. A. P.

Alcoholytic degradation of inulin. E. Berner (Annalen, 1933, **505**, 58—72).—Treatment of inulin (I) with glycerol (II) in the proportion used by Vogel and Pictet occasions slight degradation, leading to products of widely differing mol. wt. Increase in the amount of (II) and prolongation of the time of reaction leads to *glycerylfructofuranoside* (III), which is treated with Ac_2O and C_5H_5N and then with Me_2SO_4 and NaOH in $COMe_2$, thereby giving *glyceryl-fructofuranoside Me_6 ether*, b.p. 126°/0·03 mm., $[\alpha]_D^{20}$ +19·4° in $CHCl_3$, hydrolysed by 1% HCl to 1 : 3 : 4 : 6-tetramethylfructofuranose, b.p. 99°/0·05 mm., $[\alpha]_D^{20}$ +27·1° in H_2O (final val.), further identified as 5-methoxymethylfurfuraldehydesemicarbazone, m.p. 165—166°. Depolymerisation of (I) is greatly accelerated by a little H_3PO_4 (*d* 1·75). Treatment of (I) with $[\cdot CH_2\cdot OH]_2$ is described. Anhyd. MeOH and (I) at 170—175° yield γ-methylfructoside, $[\alpha]_D^{20}$ +41·3° in H_2O, converted by Me_2SO_4 and 30% NaOH into tetramethylmethylfructofuranoside, b.p. 85°/0·04—0·05 mm., $[\alpha]_D^{20}$ +76·3° in H_2O, whence 1 : 3 : 4 : 6-tetramethylfructose, b.p. 95°/0·1 mm., $[\alpha]_D$ about +40° in H_2O. (I) is therefore a α-fructofuranose anhydride of high mol. wt. Trimethylinulin is more stable than (I), but is degraded by MeOH at 220—230° to a trimethylmethylfructoside, b.p. 100°/0·03 mm., $[\alpha]_D$ +44° in $CHCl_3$. H. W.



Factors influencing the conversion of cellulosic material into sugar. G. J. Ritter, R. L. Mit-

CHELL, and R. M. SEBORG (J. Amer. Chem. Soc., 1933, **55**, 2989—2991).—With the 2-hr. treatment of spruce cellulose with 72% H_2SO_4 the optimum temp. is 35°, with 6-hr. treatment 16° (99·7% conversion), conversion being partial below the optimum temp. and reduced by charring above it. R. S. C.

Complete nitration of cellulose. A. BOUCHONNET, M. TROMBE, and G. PETITPAS (Compt. rend., 1933, **197**, 63—65).—Nitration of cellulose (linters) with a mixture of 50 parts of 99·9% HNO_3, 25 of AcOH, and 25 of Ac_2O for 5 hr. at 15°, and stabilisation with EtOH gives a stable trinitrate with the calc. N content. Only slightly inferior results are obtained with ramie and α-cellulose. H. A. P.

Osmometric investigation of dilute solutions of polymeric carbohydrates. IV. Mol. wt. of crystalline cellulose acetate II. K. HESS and M. ULMANN (Annalen, 1933, **504**, 81—94).—The mol. wt. of cryst. cellulose acetate II (I) in glacial AcOH depends greatly on the concn. In solution more conc. than 0·25% at 20°, osmotic pressure is scarcely detectable, so that the colloidal state must be assumed. Between 0·25 and 0·19%, 0·16 and 0·08%, and 0·07 and 0·01% the apparent mol. wt. corresponds with $(C_6)_{16}$, $(C_6)_8$, and $(C_6)_2$, respectively. Since the region of concn. within which a colloidal solution passes into one with mols. $(C_6)_{16}$ is very narrow, a possible equilibrium between colloidal and cryst. phases must be assumed which is very readily displaced in either direction by slight changes of concn. An almost instantaneous change is indicated. The changes $(C_6)_{16} \longrightarrow (C_6)_8 \longrightarrow (C_6)_2$ are even more definitely marked, and in suitably conc. solution are functions of the time. Delay in the establishment of equilibrium is frequently observed. Thus, in 0·07% solution the $(C_6)_8$ stage may persist at 20°; if the solution is warmed for 1 hr. at 50° and then cooled to 20°, the $(C_6)_2$ stage is attained. Freezing and subsequent thawing of the solution leads to the $(C_6)_8$ condition, which gradually passes within a few hr. to $(C_6)_2$, and then remains const. Evaporation of a solution of $(C_6)_2$ leads to regeneration of (I), m.p. 280—286° (decomp.), $[\alpha]_D^{20}$ +23·0° in $CHCl_3$. In analogy with "hendecamethylcellotriose" the possible dispersal of (I) to the (C_6) stage is discussed. Since (I) has low viscosity and does not form films or swell, it appears that there is no relation between these properties and mol. size. H. W.

Primary, secondary, and tertiary cellulose acetates. I. SAKURADA and T. FURUKAWA (J. Soc. Chem. Ind. Japan, 1933, **36**, 400—403B).—Primary (I), *sec.* (II), and *tert.* (III) cellulose acetates were prepared by acetylation (60·5% AcOH), by partial hydrolysis (56·3%), and by subsequent re-acetylation (61·8%). (I) and (III) were similar in solubility and swelling in a no. of solvents and in their *X*-ray diagrams. (I) and (III) swell > (II) in non-polar liquids but less in polar liquids. The different solubilities of (I) and (II) are due to different mol. arrangements conditioned by the different Ac contents. A. G.

Identification of amines as 3 : 5-dinitrobenzoates. C. A. BUEHLER, E. J. CURRIER, and R. LAWRENCE (Ind. Eng. Chem. [Anal.], 1933, **5**, 277—278).—The m.p. of the amine salts of 3 : 5-dinitrobenzoic acid are recorded: NH_2Ph 134·7°, *o*- 134·9°, *m*- 139·0—144·0°, and *p*-$C_6H_4Me{\cdot}NH_2$ 145·0—147·4°, *m*-4-xylidine 169·6—170·4°, *o*- 152·7°, *m*- 121·8°, and *p*-$C_6H_4Cl{\cdot}NH_2$ 133·0°, *p*-$C_6H_4Br{\cdot}NH_2$ 126·9°, *m*- 112·0—114·4°, *p*-$C_6H_4(NH_2){\cdot}NO_2$ 128·6°, *p*-$NH_2{\cdot}C_6H_4{\cdot}OH$ 178·2—178·8°, *o*- 205·2—205·6°, *m*- 167·0—172·2°, *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ 196·7°, $NHMePh$ 121·8°, NMe_2Ph 114·8—115·6°, $NHPh{\cdot}CH_2Ph$ 133·0°, $NHPhAc$ 129·1—130·1°, *o*- 177·3°, *m*- 158·7°, *p*-$C_6H_4(NH_2)_2$ 177·3—178·0°, α- 200·5°, β-$C_{10}H_7{\cdot}NH_2$ 156·5—157·2°, benzidine 205·7°, C_5H_5N 171·3°, quinoline 151·4—152·2°, NH_3 246·7°, $CH_2Ph{\cdot}NH_2$ 210·0°, $NHEt_2$ 163·4°, NEt_3 138·0—150·0°, $CO(NH_2)_2$ 120·5°, NH_2Ac 93·9—103·0°, NH_2Bz 138·6—140·4°. E. S. H.

Acyl peroxides and secondary amines. S. GAMBARJAN and L. KAZARJAN (J. Gen. Chem. Russ., 1933, **3**, 222—228).—The reaction between Bz_2O_2 (I), Ac_2O_2 (II), and BzO_2Ac (III) and *sec.* amines yields acyldialkylhydroxylamines. (III) gives in every case the Ac, not the Bz, compound and BzOH, and under more drastic conditions the corresponding dialkylacetamide. $C_5H_{11}N$ was the most active amine examined; *tert.* amines also react. (I) and $NHEt_2$ in Et_2O gave *N*-*benzoyloxydiethylamine*, b.p. 92°/0·12 mm. (II) and $NHEt_2$ give without cooling NEt_2Ac, and with cooling *acetoxydiethylamine*, b.p. 32°/0·01 mm., also obtained from (III) and $NHEt_2$. (I) and $NHPr^{\alpha}_2$ give *N*-*benzoyloxydipropylamine*, b.p. 40—41°/0·01 mm., also obtained from (III) and $NHPr^{\alpha}_2$. (I) and $C_5H_{11}N$ give *N*-benzoyloxypiperidine (A., 1925, i, 1260). (II) and $C_5H_{11}N$ give without cooling *N*-acetylpiperidine, b.p. 44°/0·01 mm., and with cooling *N*-acetoxypiperidine, b.p. 50—51°/0·01 mm., also obtainable from (III) and $C_5H_{11}N$. (I) and NEt_3 give $NHEt_2$. G. A. R. K.

Reaction of alkylchloroamines with Grignard reagents. G. H. COLEMAN (J. Amer. Chem. Soc., 1933, **55**, 3001—3005).—The following % yields of (*a*) primary, (*b*) *sec.*, and (*c*) *tert.* amines were obtained. (*a*), (*b*), and (*c*): $NEtCl_2$ with $MgPr^{\alpha}Cl$ 52, 12, and 8, $MgBu^{\alpha}Cl$ 36, 11, and 9, *n*-$C_5H_{11}{\cdot}MgCl$ 34, 12, and 8, and $CH_2Ph{\cdot}MgCl$ 28, 19, and 6; $NMeCl_2$ with $MgBu^{\alpha}Cl$ 43, 22, and 5, and $CH_2Ph{\cdot}MgCl$ 43, 25, and 3. (*a*) and (*b*): $CH_2Ph{\cdot}MgCl$ with $NHMeCl$ 70 and 14, and $NHEtCl$ 75 and 12; $MgBu^{\alpha}Cl$ with $NHMeCl$ 72 and 14. (*b*) and (*c*): $CH_2Ph{\cdot}MgCl$ with NMe_2Cl 95 and 5, NEt_2Cl 76—90 and 5—7, and NPr^{α}_2Cl 78 and 5; $MgBu^{\alpha}Cl$ with NBu^{α}_2Cl 85 and 4, respectively. The following b.p. are recorded: *n*-ethylamylamine, 134—136°/745 mm., $NHMe{\cdot}CH_2Ph$ 77·5—78°/17 mm., $NMe_2{\cdot}CH_2Ph$, 98—99°/24 mm., $NHEt{\cdot}CH_2Ph$ 88·5—89°/18 mm., $NEt_2{\cdot}CH_2Ph$ 96—98°/17 mm., and $NPr^{\alpha}_2{\cdot}CH_2Ph$ 120—122°/17 mm. R. S. C.

Stereochemistry of organic compounds. III. Spatial configuration of aliphatic and alicyclic amino-acids. L. ORTHNER and R. HEIN (Biochem. Z., 1933, **262**, 461—479).—The acid and basic dissociation consts. of various aliphatic and alicyclic NH_2-acids are calc. from the hydrolysis const. of their hydrochlorides and Na salts, and it is shown

that the strength of the CO_2H group in these compounds is increased in comparison with that of the corresponding carboxylic acids, the extent of the increase decreasing as the NH_2 group passes from the α- to the δ-position. The basic nature of the NH_2 group is increased as the CO_2H group passes from the α- to the δ-position. In aq. solutions the C chains are so arranged that the NH_2 and CO_2H groups are as far removed from one another as is possible. P. W. C.

Hydrolysis of amino-acids by aqueous extracts of bone charcoal. E. Baur and K. Wunderly (Biochem. Z., 1933, **262**, 300—307).—Aq. extracts of bone black hydrolytically deaminate glycine, alanine, aspartic acid, leucine, and phenylalanine (I), the activity except in the case of (I) being < that of the charcoal itself. The salts contained in the extracts have relatively a feeble deaminating activity. P. W. C.

Amino-acids and related compounds. III. Electrolytic oxidation of arginine. IV. Electrolytic reactions of leucic acid. Y. Takayama (Bull. Chem. Soc. Japan, 1933, **8**, 169—173, 173—178; cf. this vol., 720).—III. Electrolysis of arginine sulphate in dil. H_2SO_4 using PbO_2–Pb electrodes at 2 amp. per sq. dm. and 25° gives NH_3, guanidine, and succinic acid. γ-Guanidinobutyric acid was not detected as an intermediate product.

IV. Electrolysis of leucic acid (I) as above but at 38·5° gives *iso*valeric acid, its *iso*amyl ester, *iso*amyl alcohol, *isovaleryl-leucic acid* (II), b.p. 165—175°/24 mm. (*Ag* salt), and gases. (II) was synthesised for comparison from (I) and *iso*valeryl chloride. H. A. P.

Synthesis of aspartic acid. M. S. Dunn and S. W. Fox (J. Biol. Chem., 1933, **101**, 493—497).—Aspartic acid (I) is readily prepared (59% yield) by heating for 24 hr. in sealed vessels at 100° NH_3 (4·8 mols.) and Et_2 fumarate (1·0 mol.) in abs. EtOH to yield crude diketopiperazinediacetamide, which is hydrolysed by 6*N*-NaOH and (I) separated by its Cu salt. F. O. H.

Hydroxyamino-acids. E. Abderhalden and F. Broich (Biochem. Z., 1933, **262**, 321—328).—The formation of Bz_2 derivatives of serine and *iso*serine on benzoylating in slightly alkaline solution is confirmed. *O*-Bz in these compounds is, however, immediately removed by stronger alkali. Serine is readily decomposed both by acids and alkalis, forming on heating with 25% H_2SO_4 lactic and pyruvic acids, CO_2, glycine, and NH_3. Serine ester on distillation at 2 mm. is considerably decomposed, and the amount of serine isolated from proteins containing it is only about ⅓ the actual content. P. W. C.

Sulphur–lead union. H. Bauer and K. Burschkies (Ber., 1933, **66**, [*B*], 1041—1046).—Cysteine (I) and $Pb(OAc)_2$ in H_2O yield the insol. *salt*, $Pb[\cdot S\cdot CH_2\cdot CH(NH_2)\cdot CO_2\cdot]_2$:Pb, decomp. 215—220°, converted by Na_2CO_3 into (I) and the *salt* $NH_2\cdot CH<\begin{matrix}CH_2\cdot S\\ CO-O\end{matrix}>Pb$, sol. without decomp. in Na_2CO_3, NaOAc, and NaCl, but from which all the Pb is pptd. by H_2S. α-Thiolpropionic acid similarly yields the compounds $Pb[\cdot S\cdot CHMe\cdot CO_2]_2$:Pb and $\begin{matrix}CO-O\\ CHMe\cdot S\end{matrix}>Pb$, whereas *o*-thiolbenzoic acid gives a *Pb* salt $C_7H_4O_2SPb$, decomp. 350°, completely decomposed by Na_2CO_3. *Pb* 3-*amino*-4-*thiolbenzenesulphonate* is partly stable to Na_2CO_3. The *Pb* salt of 2-*aminothiophenol*, m.p. 185—186° (decomp.), is decomposed by Ac_2O, and the NH_2 group cannot be substituted by $HCHO$–$NaHSO_3$, whereas *Pb* p-*aminophenyl sulphide*, m.p. 185° (decomp.), gives an Ac_2 derivative, decomp. 330—331°, and the *substance* $(SO_3Na\cdot CH_2\cdot NH\cdot C_6H_4\cdot S)_2Pb$. *Pb* m-*aminophenyl sulphide*, decomp. 174°, occupies an intermediate position. H. W.

Crystalline derivatives of dithiocyanostearic acid. I. Synthesis of thiocyanogen derivatives of benzoylmethyl and *p*-halogenobenzoylmethyl esters of oleic acid. W. Kimura (J. Soc. Chem. Ind. Japan, 1933, **36**, 234—236B).—Na oleate with ω-bromoacetophenone or its *p*-halogen derivatives, followed by treatment with $(CNS)_2$ (cf. B., 1930, 429), gives *benzoylmethyl*, m.p. 54°, and p-*iodo*-, m.p. 48°, p-*bromo*-, m.p. 43·5°, and p-*chloro*-*benzoylmethyl* η9-*dithiocyanostearate* (oily). A. A. L.

Salts of diguanide and of guanidine. C. Manuelli (Annali Chim. Appl., 1933, **23**, 235—244).—Priority is claimed for the industrial prep. of guanidine nitrate by heating a mixture of NH_4NO_3 and dicyanodiamide (I) and of the interpretation of the reaction through the intermediate formation of diguanide nitrate. The *mono*- and *di*-*nitrates* and the $(NO_2)_2$-derivative of diguanide (II), and some guanidine salts are described. The analytical reactions of guanidine, (II), and (I) have been studied. O. J. W.

Additive compounds of mercuric cyanide with hydriodides of organic bases. G. Ragni (Gazzetta, 1933, **63**, 303—304).—$Hg(CN)_2$ forms with guanidine and dicyanodiamide hydriodides the *complexes* $CH_6N_3I,Hg(CN)_2$, m.p. 210° (decomp.), and $C_2H_7ON_4I,Hg(CN)_2$, decomp. about 300°; the conductivity of the former shows that it is strongly dissociated in solution. E. W. W.

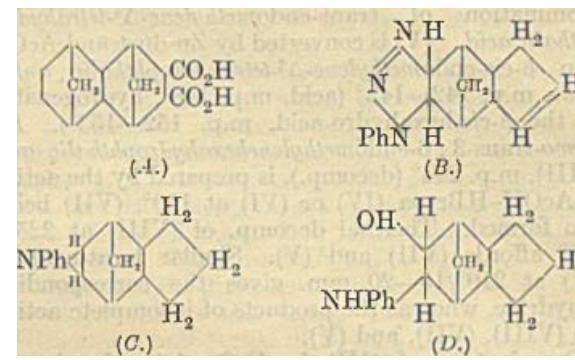
Nitriles of Δ^α- and Δ^β-olefinic acids. R. A. Letch and R. P. Linstead (J.C.S., 1933, 612—614; cf. A., 1932, 371).—A reply to Bruylants (A., 1932, 1119). The bromometric method for the determination of Δ^β-nitriles (A., 1931, 205) is applicable provided sufficient time is allowed for complete reaction. A. A. L.

Relative reactivity of various functional groups towards a Grignard reagent. C. E. Entemann, jun., and J. R. Johnson (J. Amer. Chem. Soc., 1933, **55**, 2900—2903).—When 1 mol. of MgMeBr in Et_2O reacts with 1 mol. each of two reactants, PhX, the proportions of the products formed indicate the following reactivities: X=CHO>COMe>NCO>COF>COPh>COCl, COBr>CO_2Et>CN. The order, COF>COCl, shows that Grignard reactions proceed by addition rather than by direct metathesis. R. S. C.

Reactions catalysed by aluminium chloride. VI. Isomerisation of *cyclo*hexane into methyl-*cyclo*pentane. C. D. NENITZESCU and I. P. CANTUNIARI. **VII. Hydrogenation phenomena in the customary Friedel–Crafts reaction.** C. D. NENITZESCU and D. A. ISACESCU (Ber., 1933, **66**, [*B*], 1097—1100, 1100—1103).—VI. *cyclo*Hexane (I) is scarcely affected by protracted ebullition with freshly-sublimed, anhyd. $AlCl_3$. With $AlCl_3$ containing H_2O, equilibrium is established when about 1/5 of (I) has been converted into methyl*cyclo*pentane (II) containing a little *n*-hexane. Under similar conditions (I) is formed from (II). The transformation of (I) into (II) is not due to the smaller strain of the *cyclo*pentane ring; the strain-free *cyclo*hexane ring appears more stable and less reactive.

VII. Treatment of C_6H_6 with allyl chloride (I) in presence of $ZnCl_2$ or preferably $FeCl_3$ leads to CHPhMe·CH_2Ph (II) and β-*chloropropylbenzene* (III), b.p. 79°/10 mm., characterised by transformation into propenylbenzene, b.p. 73°/20 mm., and thence into CHPhBr·CHMeBr, m.p. 66·5°. Anhyd. $AlCl_3$, C_6H_6, and (I) afford almost exclusively (II), the intermediate production of (III) being postulated. With moist $AlCl_3$ the production of (II) is accompanied by that of PhPr (IV) and 9 : 10-*diethylanthracene* (V), m.p. 146°. Formation of (IV) is intimately connected with that of (V). H. W.

Polymerisation of cyclic hydrocarbons. V. Degradation of polymeric *cyclo*pentadienes with selenious acid. K. ALDER and G. STEIN [with W. GRASSMANN]. **VI. Stereochemistry of *cyclo*pentadiene polymerisation.** K. ALDER and G. STEIN [with W. ECKARDT, R. VON BUDDENBROCK, and S. SCHNEIDER] (Annalen, 1933, **504**, 205—215, 216—257).—V. Dihydro-α-di*cyclo*pentadiene (I) is converted by H_2SeO_3 in boiling MeOH into *dihydro-α-dicyclopentadien-3-ol Me ether*, b.p. 106—109°/15 mm.; the *Et ether*, b.p. 106—109°/15 mm., and *amyl ether*, b.p. 122—138°/13 mm., are obtained similarly. Treatment of (I) with Ac_2O and H_2SeO_3 leads to *dihydro-α-dicyclopentadien-3-yl acetate*, b.p. 116—120°/12 mm., hydrolysed by KOH–MeOH to *dihydro-α-dicyclopentadien-3-ol*, b.p. 114°/12 mm., m.p. about 30°, which is oxidised by CrO_3 in AcOH to *dihydro-α-dicyclopentadien-3-one* (II), b.p. 110°/12 mm., m.p. about 40° (*semicarbazone*, m.p. 213—214°). (II) is hydrogenated to tetrahydro-α-di*cyclo*pentadien-3-one, m.p. 99°, and oxidised by $KMnO_4$ in $COMe_2$ to *α-cis*-3 : 6-*endo*methylenehexahydro-*o*-phthalic acid, m.p. 165° (anhydride, m.p. 170°). A mixture of (I) and dihydro-β-di*cyclo*pentadiene is similarly treated, and β-*cis-endo*methylenehexahydro-*o*-phthalic acid, m.p. 151° (anhydride, m.p. 80°), is isolated from the product of the oxidation of the ketone mixture. Dihydro-α-tri*cyclo*pentadiene is transformed successively into *dihydro-α-tricyclopentadien-3-yl acetate*, b.p. 180—185°/11 mm., *dihydro-α-tricyclopentadien-3-ol*, m.p. 135°, *dihydro-α-tricyclopentadien-3-one*, m.p. 162°, and the α_1-*cis*-dicarboxylic acid (cf. *A*), m.p. 174° (anhydride, m.p. 156°; Me_2 ester, m.p. 101°, transformed by NaOEt into the *trans*-acid, m.p. 248—249°). Similarly, dihydro-β-tri*cyclo*pentadiene yields successively *dihydro-β-tricyclopentadien-3-yl acetate*, b.p. 180—182°/11 mm., *dihydro-β-tricyclopentadien-3-ol*, m.p. 140°, *dihydro-β-tricyclopentadien-3-one*, and the 3-*cis*-*dicarboxylic acid* (cf. *A*), m.p. 184—185° (decomp.) [*anhydride*, m.p. 143—144°; Me_2 ester, m.p. 95—96°, converted by NaOEt in boiling EtOH into the *trans*-acid, m.p. 248—249° (see above)].

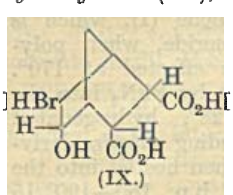


VI. The evidence obtained above gives proof of the existence of β-di*cyclo*pentadiene (I), which is isolated, mixed with the α-isomeride, when polymerisation of *cyclo*pentadiene is effected at 170°. (I) is characterised by conversion by PhN_3 into the *hydrotriazole* (*B*), m.p. 127—128°, hydrogenated (Pd in EtOH) to the corresponding *dihydro*-derivative, m.p. 142°, which passes when heated into the *phenylimine* base (*C*), m.p. 68°, b.p. 180—190°/15 mm., and when treated with dil. H_2SO_4 into the *OH*-base (*D*), m.p. 95°. Hydrogenation of the mixed di*cyclo*pentadienes and treatment of the product with Br does not lead to a homogeneous β-Br-derivative. The conversion of dihydro-β-di*cyclo*pentadiene into the β-acid (see above) is very circuitous. Reduction of 3 : 6-*endo*methylene-Δ^1-tetrahydrophthalic acid or its anhydride leads exclusively to the known *α-cis*-3 : 6-*endo*methylenehexahydrophthalic acid (anhydride, m.p. 167°). Condensation of *cyclo*pentadiene with Me_2 maleate affords Me_2 *α-cis*-3 : 6-*endo*methylene-Δ^4-tetrahydrophthalate, b.p. 145—147°/18 mm., reduced (Pd–H_2) to the H_6-ester, b.p. 142—143°/15 mm., which is isomerised and hydrolysed by NaOMe to the *trans*-acid (II). Distillation of (II) gives a mixture of anhydrides from which, by treatment with H_2O, β-cis-3 : 6-endo*methylenehexahydrophthalic acid* (II), m.p. 152—153° (decomp.) (*anhydride*, m.p. 78—79°; *Me H* ester, m.p. 96—97°), is obtained. Treatment of (II) with conc. HCl at 180—190° or, successively, with CH_2N_2 and NaOMe affords the *trans*-acid, m.p. 193—194°. The *α-cis*-acid at 215—220° passes exclusively into the *α-cis*-anhydride, m.p. 167°.

Distillation of *trans*-3 : 6-*endo*methylene-Δ^4-tetrahydrophthalic acid gives mainly *cyclo*pentadiene and fumaric acid with a small amount of *α-cis*-anhydride. On the assumption that the transition of CO_2H from the α- into the β-position is possible only when the Δ^4 double linking is saturated, *α-cis-endo*methylene-Δ^1-tetrahydrophthalic anhydride (III) is converted by Br in $CHCl_3$ (free from H_2O and EtOH) into *dibromo-α*-cis-endo*methylenehexa-*

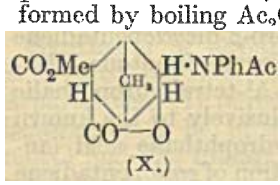
hydrophthalic anhydride, m.p. 206°, converted by Zn dust and AcOH into (III) [corresponding *acid* (IV), m.p. 188° (decomp.), transformed by AcCl into (III)]. (IV) passes at 210—220° into *dibromo*-β-cis-endo*methylenehexahydrophthalic anhydride* (V), m.p. 248—249° [corresponding *acid* (VI), m.p. 248° after loss of H_2O at 220°], and the *bromo*-trans-*lactonic acid*, $C_9H_9O_4Br$ (VII), m.p. 186°, also obtained by bromination of trans-endo*methylene*-Δ^4-*tetrahydrophthalic acid*. (V) is converted by Zn dust and AcOH into β-cis-endo*methylene*-Δ^4-*tetrahydrophthalic anhydride*, m.p. 142—143° (acid, m.p. 148°, hydrogenated to the β-*cis*-hexahydro-acid, m.p. 152—153°). *Dibromo*-trans-3 : 6-endo*methylenehexahydrophthalic acid* (VIII), m.p. 244° (decomp.), is prepared by the action of AcOH–HBr on (IV) or (VI) at 160°, (VII) being also formed. Thermal decomp. of (VIII) at 225—230° affords (VII) and (V). Similar treatment of (IV) at 210°/15—20 mm. gives the corresponding anhydride, whereas the products of incomplete action are (VIII), (VII), and (V).

Bromination of (III) in H_2O gives the *bromohydroxy-acid* (IX), m.p. 116° (decomp.), which passes readily into the *bromo*-cis-*lactonic acid*, $C_9H_9O_4Br$, m.p. 157° (*Me* ester, m.p. 77°). The *trans*-Δ^4-acid is similarly readily converted into the corresponding lactone.



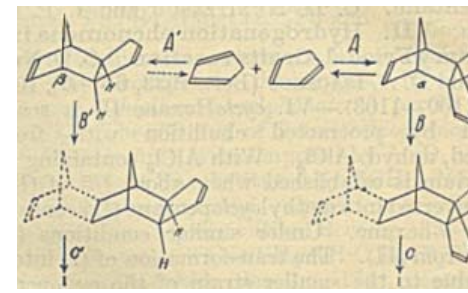
(IX.)

Addition of PhN_3 to Me_2 *trans*-3 : 6-*endo*methylenehexahydrophthalate occurs smoothly with production of the *hydrotriazole*, $C_{17}H_{19}O_4N_3$, m.p. 115°, which readily passes into the *base*, $C_{17}H_{19}O_4N$, m.p. 156°, transformed by boiling Ac_2O into the *compound* (X), m.p. 188—189°. Conditions are therefore similar to those of the *cis*-α-series. The β-*cis*-anhydride similarly yields a *hydrotriazole*, m.p. 220° (decomp.), readily passing into the *phenylimine* base, m.p. 189° (decomp.), transformed by CH_2N_2 into the corresponding *Me*$_2$ ester, m.p. 138°, which is stable to boiling Ac_2O.



(X.)

Treatment of Me_2 α-*cis*-3 : 6-*endo*methylene-Δ^4-tetrahydrophthalate with BzO_2H in $CHCl_3$ leads to the corresponding *oxide*, b.p. 162—169°/13 mm., converted by boiling Ac_2O into the *acetylated Me ester lactone*, m.p. 64—65°. Likewise the Me_2 *trans*-ester yields an *oxide*, b.p. 150—160°/15 mm., and the trans-*acetyl-lactone acid*, m.p. 152° (*Me* ester, m.p. 98°). *Me*$_2$ β-cis-3 : 6-endo*methylene*-Δ^4-*tetrahydrophthalate*, b.p. 136°/13 mm., m.p. 51—52° (from the anhydride and MeOH–H_2SO_4), affords an *oxide*, m.p. 86—87°, stable to boiling Ac_2O. Oxidation of *cis*-α-acid with $KMnO_4$ in alkaline solution and treatment of the product with AcCl gives the *diacetoxy*-α-cis-*anhydride*, m.p. 161—162° [corresponding *acid*, m.p. 197° (decomp.)]. Similar treatment of the *trans*-acid and β-*cis*-anhydride yields the *diacetoxy*-trans-*acid*, m.p. 205—206°, and the *diacetoxy*-β-cis-*anhydride*, m.p. 155—156°; lactone formation does not occur in any instance. Determination of the configuration of the acids establishes that of the *cyclo*pentadiene polymerides in the sense of the following scheme, in which the only doubtful positions are indicated by the dotted lines :



Formation of α-di*cyclo*pentadiene is reversible; at room temp. the equilibrium is almost completely in favour of the α-dimeride, and is noticeably displaced towards the monomeride only at 140—160°. In a closed vessel at 170° equilibrium is disturbed by the formation of the α-tri*cyclo*-compound, which is stable at this temp., but is capable of further addition of monomeride. The only complication arises from the ability of the monomeride to yield the β- as well as the α-dimeride at higher temp. H. W.

Slow oxidation of aromatic hydrocarbons at high pressures. D. M. Newitt and P. Szego (Chem. and Ind., 1933, 645).—Oxidation of PhMe by air at 210°/50 atm. gives chiefly $CH_2Ph{\cdot}OH$, with some PhCHO, BzOH, and 2 : 4-dihydroxytoluene, corresponding with 60% of PhMe burned. The mechanism is one of hydroxylation of side-chain and nucleus. F. R. S.

Bromination of bromobenzene in the gaseous phase at high temperatures. *m*-Directing influence of the bromine atom above 450°. J. P. Wibaut, L. M. F. van de Lande, and G. Wallagh (Rec. trav. chim., 1933, **52**, 794—807).—Freezing curves for *o*- and *m*-$C_6H_4Br_2$ are determined; the m.-p. curve shows that an additive *compound*, m.p. −15·9°, of 2 mols. *m*- and 1 mol. *o*- is formed. Employing the *p*–*o* curve of van der Linden (A., 1912, i, 20) as well, the % composition of a mixture of isomerides is determined to 2%. Interaction of Br (1 mol.) and PhBr (2 mols.) at 480° by a streaming technique (cf. A., 1932, 1260) affords a little 1 : 3 : 5-$C_6H_3Br_3$, but mainly $C_6H_4Br_2$. At 400°, *o*-*p*-substitution predominates, but > 450° the *m*-isomeride is the main product, the proportions of isomerides varying only slightly from 450° to 630°, so that Scheffer's suppositions (cf. A., 1926, 913) do not apply over a wide temp. range. J. L. D.

Decomposition of iodobenzene dichloride. VII. Action of solutions in various solvents on Zerevitinov's reagent. VIII. Analogy with the action of equimolecular solutions of chlorine, iodine, and iodine mono- and tri-chloride on the same reagent. E. V. Zappi and H. Degiorgi (Anal. Asoc. Quím. Argentina, 1933, **21**, 12—23).—When a solution of $PhICl_2$ in a polar solvent is treated with MgMeI, only one Cl reacts. In a non-polar solvent, only about 20% of the theoretical quantity of C_2H_6 is produced. The substance is therefore [PhICl]Cl. H. F. G.

Tervalent carbon. XII. Rate of dissociation and energy of activation of hexaphenylethane. K. ZIEGLER, P. ORTH, and K. WEBER. **XIII. Chain reactions during the autoxidation of radicals.** K. ZIEGLER and L. EWALD. **XIV. Rates of autoxidation and decomposition of dissociable ethanes.** K. ZIEGLER, L. EWALD, and A. SIEB. **XV. New tautomerism of dichromenylenes.** K. ZIEGLER and H. LÜTTRINGHAUS (Annalen, 1933, **504**, 131—161, 162—181, 182—189, 189—204; cf. A., 1930, 711, 762).—XII. The rate of absorption of NO by C_2Ph_6 in PhMe at 0° is not entirely controlled by the rate of union of CPh_3 with NO. In presence of NH_2Ph the change is strictly unimol. with NO at 1 atm. or more, but not at 0·2 atm. Similar observations are made in $CHCl_3$. Under 1 atm. the rate of the "removal" reaction exactly suffices to render NO a useful reagent. The vol. of NO absorbed exceeds 1 mol. (in presence of NH_2Ph exceeds 3 mols.), so that primary formation of CPh_3·NO is followed by one or two changes shown to be immeasurably rapid in comparison with that of radical formation. The half-period of the change in $CHCl_3$ at 0° is 3·30 min., whereas the I method indicates 2·75 min., attributed to errors in the latter process. Observations in CCl_4, $CHCl_3$, $C_2H_4Br_2$, NH_2Ph, EtOH, PhMe, $PhNO_2$, $NPhMe_2$, $CH_2Cl·CH_2·OH$, $CH_2(CO_2Et)_2$, $OH·CH_2·CH_2·OMe$, C_5H_5N, $NAcEt_2$, $CMe_2{:}CHAc$, *o*-$OH·C_6H_4·CO_2Me$, and $CN·CH_2·CO_2Et$ show the rate of decomp. of C_2Ph_6 to depend relatively very little on the solvent, and a relationship between dipole moment of the medium and rate of change is not apparent. Measurements of the rate of change between −20° and 10° in $CHCl_3$ and PhMe lead to the val. 19—20±1 kg.-cal. for the energy of activation at room temp. Since the heat of dissociation of C_2Ph_6 is 10—12 kg.-cal., the compound at the moment of dissociation contains more energy than is found later in 2 mols. of normal CPh_3 and the difference may be regarded as the equiv. of a certain stabilisation of the true radical mol. primarily produced by dissociation of the ethane.

XIII. In presence of pyrogallol, CPh_3 absorbs exactly 1 mol. of O_2; the normal peroxide is not produced and the formation of $CPh_3·O_2H$ is considered probable. A labile, primary peroxide is regarded as the carrier of chain reactions, and such a reaction is postulated for the absorption of O_2 by C_2Ph_6, which proceeds much more rapidly than accords with the dissociation of C_2Ph_6 into CPh_3. Mixtures of CPh_3 and oxidisable substances usually absorb more O_2 than both components under like conditions, as shown with NHPh·NHPh. The catalytic activity of CPh_3 is more pronounced in presence of aldehydes and unsaturated hydrocarbons, the following chain lengths varying with concn. of acceptor and radical being observed: crotonaldehyde (35), anisaldehyde (49—43), 1 : 4-dihydronaphthalene (7·5), styrene (20—16), indene (9, 51), diphenylfulvene (17, 25), dimethylfulvene (14, 35, 65). Dimethylbenzofulvene (I) is a particularly suitable acceptor without proper O_2 absorption. It appears that a "limiting chain length" exists dependent on the radical solution and hence on the concn. and also on the solvent, and therefore independent of the concn. Purification of (I) increases the chain length to 11,000 without difficulty, whilst substitution of hexahydrotoluene or CCl_4 for PhMe causes increases to 12,000—19,000 and 48,000—55,000, respectively.

XIV. The influence of pyrogallol on the absorption of O_2 in EtOBz, $CHCl_3$, and PhMe is examined in greater detail. In the case of tetraphenyldidiphenylylethane the absorption is strictly unimol. and the reaction coeff. is independent of the O_2 pressure over a certain range.

XV. The reaction between I and dichromenyls is not strictly of the first order, and the irregularities are particularly marked with di-2 : 4-diphenyl-3-benzyl-6-methylchromenyl. Since the compound absorbs O_2 abnormally in EtOBz containing pyrogallol, the irregularity is not due to an exceptional course of the changes, but is attributable to the dichromenyls. Mathematical examination of the I absorption graphs discloses the presence of a material (I) which behaves like C_2Ph_6, has a mean const. 0·0346, and a half-period of 20 min., and a substance (II) with dissociation const. 0·77 and a half-period of 0·9 min. The presence of 73% of (I) and 27% of (II) in the initial solution is calc., but the presence of a third form, not disclosed by the method of calculation, is postulated. It is not considered that chemical investigation will throw light on this type of tautomerism, but the utility of physical methods is indicated. $CH_2Ph·CH_2·COCl$, *p*-$C_6H_4Me·OMe$, and $AlCl_3$ in CS_2 yield β-*phenylpropionyl*-p-*cresol*, m.p. 62—63°, converted by Bz_2O and PbO at 180° into 3-*benzyl*-6-*methylflavone*, m.p. 118—119°, which yields 4-*phenyl*-3-*benzyl*-6-*methylflavylium perchlorate*, decomp. 227° after softening at 218°, when treated successively with MgPhBr and $HClO_4$ and Ac_2O. H. W.

Relative stability of penta-arylethanes. II. Reactions of penta-arylethanes. W. E. BACHMANN (J. Amer. Chem. Soc., 1933, **55**, 3005—3010: cf. this vol., 703).—Nine compounds, $CPh_2·CHArAr'$, dissociate when heated (usually at 85—105°) to CPh_3 and $(·CHArAr')_2$, are reduced by boiling HI–AcOH to $CHPh_3$ and CH_2ArAr', give the bromides with Br in $(CH_2Br)_2$ at 100°, are stable to 1% Na–Hg (differentiation from hexa-arylethanes), and are cleaved by Na–K. Some are stable to 40% Na–Hg. Since chemical cleavage is usually more rapid than dissociation, the effect of the five aryl groups is to weaken the C·C linking rather than break it. The order of effect is α-$C_{10}H_7$>*p*-C_6H_4Ph>anisyl>*p*-C_6H_4Me>Ph>$·C_6H_4·C_6H_4·$. R. S. C.

Oxidation of aromatic hydrocarbons. B. A. BUYLLA and J. M. PERTIERRA (Anal. Fís. Quím., 1933, **31**, 59—64).—A yield of about 40% of phthalic anhydride is obtained by passing $C_{10}H_8$ and air over V_2O_5 on porous pot at 400—450°. *o*-$C_6H_4Me_2$ appears to yield the same product. R. K. C.

Constitution of some acenaphthenesulphonic acids. M. T. BOGERT and R. B. CONKLIN (Coll. Czech. Chem. Comm., 1933, **5**, 187—203).—The orientations of 3-nitroacenaphthene and its -4-sulphonic acid (B.P. 274,902; B., 1928, 293) and of acenaphthene-3-sulphonic acid are confirmed as follows. 3-Aminoacenaphthene (I) (from the product of direct nitration; cf. A., 1922, i, 1142) is converted

by the diazo-reaction into *acenaphthene-3-sulphinic acid* (II), which is oxidised by alkaline $KMnO_4$ to the 3-sulphonic acid (III) [*Me*, m.p. 131—132°, and *Et*, m.p. 140—141° (lit. 137—139°), esters; chloride (IV), m.p. 110—111°]. (II) is more conveniently prepared by reduction of (IV) with aq. Na_2SO_3 and $NaHCO_3$. 4-Nitroacenaphthene-3-sulphonic acid (V), prepared by direct nitration of (III), is also obtained by nitration of (IV) in AcOH at 10°, reduction of the resulting *4-nitroacenaphthene-3-sulphonyl chloride*, decomp. 190·3—191·3° (very rapid heating) [accompanied by the (?)5-NO_2-compound, m.p. 167·5—168·5°], to the *-3-sulphinic acid*, and oxidation of this with neutral $KMnO_4$. Other methods of conversion of the chloride into (V) or its derivatives failed. The orientation of (V) is confirmed by reduction to the 4-NH_2-compound (*Na* salt) with Zn–Cu and HCl, which gives *acenaphthenesultone*, m.p. 173°, when diazotised and boiled, and (I) when reduced in aq. solution with Na–Hg. All m.p. are corr. H. A. P.

Ring closure and radical formation. V. 9 : 10 - Tetraphenyldihydrophenanthrene and 4 : 5-dimethoxy - 9 : 10 - tetraphenyldihydrophenanthrene. G. Wittig and H. Petri (Annalen, 1933, **505**, 17—41).—Me_2 diphenate is converted by LiPh in Et_2O into *oo'*-di(diphenylhydroxymethyl)diphenyl (I), m.p. 252—253°, transformed by K in boiling dioxan into the *K* compound, which with MeI affords the *Me_1 ether* (II), m.p. 209·5—211°. (II) and K phenyl-*iso*propyl give *oo'-di(diphenylmethoxymethyl)diphenyl* (III), m.p. 186—187·5°, converted by successive treatment with HCl in AcOH and NaOH into 9 : 9-diphenyl-5-diphenylhydroxymethylfluorene, m.p. 256°, whence 9 : 9-diphenyl-5-benzhydrylfluorene (IV), m.p. 219·5—221°. (I) is converted by HCl in hot C_6H_6 into the corresponding *anhydride*, m.p. 291—292°, also obtained from (III) and conc. H_2SO_4 and converted by K–Na in dioxan into *o-benzhydryl-o'-diphenylhydroxymethyldiphenyl*, m.p. 242—243°, whence (IV) by HCl in boihng AcOH. (III) is transformed by the successive action of K–Na and MeOH into *oo'*-dibenzhydryldiphenyl (V), m.p. 238—239·5°. Treatment of (III) with K–Na in dioxan followed by tetramethylethylene dibromide leads to 9 : 10-*tetraphenyldihydrophenanthrene* (VI), m.p. 339·5—341°, which resembles CPh_3 in its ready addition of K or Na [whence (V)], but is analogous to C_2Ph_4 in that it is indifferent to Br or O_2 and is converted by SO_2Cl_2 containing AcOH into *oo'-di(diphenylchloromethyl)diphenyl*, which passes into 9 : 9-*diphenyl-5-diphenylchloromethylfluorene*.

In the hope of forcing radical dissociation, compounds with substituents in the free *o*-positions of the Ph·Ph residue are investigated. *r-oo'*-Dimethoxydiphenic acid is converted into 2 : 2'-dimethoxy-6 : 6' - di(diphenylhydroxymethyl)diphenyl, which, with K in dioxan, gives the *K_1* compound, transformed by MeI into the *Me_1 ether* (VII), m.p. 256—257·5°. Successive action of K phenyl*iso*propyl in dioxan and MeI on (VII) yields the *Me_2 ether* (VIII), m.p. 206·5—208°, transformed by K–Na and MeOH into 2 : 2'-*dimethoxy*-6 : 6'-*dibenzhydryldiphenyl* (IX), m.p. 204·5—205·5° (*K* derivative). (VIII) treated successively with Na–K and $C_2Me_4Br_2$ gives 4 : 5-*dimethoxy*-9 : 10 - *tetraphenyldihydrophenanthrene* (X), m.p. 231·5—232°, transformed by Na–K and subsequent alcoholysis into (IX). Since (X) is stable to Br, is colourless, and shows no tendency to radical dissociation in solution, the introduction of OMe appears to cause no change in the union of the radical C atoms.

The possibility that (X) is a racemate is examined as follows. (—)-2 : 2'-Dimethoxydiphenic acid, m.p. 293·5—294·5°, $[\alpha]_D^{20}$ —116° in anhyd. $COMe_2$, is converted by CH_2N_2 into the *Me_2* ester (XI), m.p. 101—102°, $[\alpha]_D$ —160° in $COMe_2$, the racemisation consts. of which are determined in PhCl at 100° and 118·5°. (XI) is transformed into (—)-2 : 2'-*dimethoxy*-6 : 6'-*di(diphenylhydroxymethyl)diphenyl* (XII), m.p. 284°, $[\alpha]_D^{25}$ —220° in $CHCl_3$ [*anhydride* (XIII), m.p. 242·5—243°, $[\alpha]_D^{25}$ —393° in $CHCl_3$, completely racemised when heated at 315°]. (XII) is converted into its *Me_1 ether* (XIV), m.p. 238—239°, $[\alpha]_D^{25}$ —157° in $CHCl_3$, converted by HCl in C_6H_6 into (XIII), whilst the *Me_2 ether* (XV), m.p. 218—220°, $[\alpha]^{20}$ —150° in $CHCl_3$ [converted by conc. H_2SO_4 into (XIII)], is derived from (XII) or (XIV). (XV) with Na–K followed by MeOH gives (—)-2 : 2'-*dimethoxy*-6 : 6'-*dibenzhydryldiphenyl*, m.p. 170—170·5°, $[\alpha]_D$ —298° in $CHCl_3$, whereas the 4 : 5-dimethoxy-9 : 10-tetraphenyldihydrophenanthrene obtained from it is optically inactive. It cannot therefore be decided whether the dihydrophenanthrene derivative is plane or asymmetric in structure. H. W.

Polycyclic compounds. I. Synthesis of perylene and its mechanism. II. Four new methods of preparing perylene and their mechanisms. III. Constitution of α- and β-tetradecahydroperylenes formed by the hydrogenation of perylene under high pressure. S. Uchida and S. Takata (J. Soc. Chem. Ind. Japan, 1933, **36**, 222B, 223—224B, 224—226B).—I. A mechanism for the synthesis of perylene (I) from di-β-naphthol (II) is suggested.

II. (II) heated with H_3PO_3, H_3PO_4, $H_4P_2O_7$, or Japanese acid clay, or 2-$C_{10}H_7Cl$ (from β-$C_{10}H_7$·OH and PCl_5) heated with acid clay gives (I). Mechanisms are suggested.

III. Treatment of (I) with Pd and H_2 in decahydronaphthalene at 150° under pressure gives *α-tetradecahydroperylene*, m.p. 180—181·5° (and a little of a *substance*, m.p. 170—171·3°), a *β-isomeride*, m.p. 161—162°, being formed under similar conditions at 82°. Constitutions are suggested for these. A. A. L.

Diphenylguanidine. K. Shimada and T. Kimishima (J. Soc. Chem. Ind. Japan, 1933, **36**, 210—211B).—Thiocarbanilide with $PbSO_4$ in EtOH–NH_3 gives pure diphenylguanidine (yield 94%). PbO, $PbCO_3$, $Pb(OAc)_2$, $Pb(NO_3)_2$, ZnO, $ZnCl_2$, HgO, and $HgCl_2$ are less effective. A. A. L.

Synthetic menthol. II. Synthesis of 2-nitro-*p*-cymene, and properties of its derivatives. H. Inoue and H. Horiguchi (J. Soc. Chem. Ind. Japan, 1933, **36**, 189—190B).—Improved preps. are given for 2-nitro-, b.p. 129—132°/15 mm., 2-amino-, b.p. 116—119°/15 mm. (Bz derivative, m.p. 100°; Ac derivative, m.p. 71°; benzenesulphonamide, m.p. 151°), chloronitro-, b.p. 146—148°/15 mm., and chloroamino-*p*-cymene, b.p. 156—157°/15 mm. (Bz deriv-

ative, m.p. 134°; azo-β-naphthol derivative, m.p. 162°). The last is converted into α-chlorocymene. Physical consts. of the above compounds are recorded. A. A. L.

Four dinitrodimethyl-*p*-anisidines. H. H. Hodgson and J. H. Crook (J.C.S., 1933, 825—827).—Nitration of 3-nitrodimethyl-*p*-anisidine gives 2 : 3-, m.p. 130° [the corresponding $(NH_2)_2$-derivative condensing with benzil to *5-dimethylamino-8-methoxy-2 : 3-diphenylquinoxaline*, m.p. 233° (decomp.)], and 2 : 5-*dinitrodimethyl*-p-*anisidine*, m.p. 137°, also obtained by nitration of the 2-NO_2-compound. Dimethyl-*p*-anisidine is nitrated in H_2SO_4 and HNO_3 to the 2 : 6-$(NO_2)_2$-derivative, m.p. 151°, and in aq. H_2SO_4 and HNO_3 to a mixture of the 3 : 5-$(NO_2)_2$-derivative (I), m.p. 90°, and 3 : 5-*dinitro*-N-*nitrosomethyl*-p-*anisidine*, m.p. 113°, which with $CO(NH_2)_2$ and H_2SO_4 forms 3 : 5-*dinitromonomethyl*-p-*anisidine*, m.p. 130°. 3 : 5-Dinitro-*p*-toluenesulphonyl-*p*-anisidine after hydrolysis is converted (Sandmeyer) into 4-*chloro*-3 : 5-*dinitroanisole*, m.p. 123°, which gives (I) with $NHMe_2$. F. R. S.

Nitration of *o*- and *p*-aminodiphenyl derivatives. M. H. Werther (Rec. trav. chim., 1933, 52, 657—677).—Interaction of *p*-aminodiphenyl (I) and EtNCO in C_6H_6 affords N-4-*diphenylyl*-N′-*ethylcarbamide* (II), m.p. 208°, decomp. 290° into $(CO{\cdot}NHEt)_2$, and *s*-di-(4-diphenylyl)carbamide. (I) with $ClCO_2Me$ in boiling C_6H_6 containing Na_2CO_3 affords *Me diphenyl*-4-*carbamate* (III), m.p. 124°. (II) and abs. HNO_3 at 0° afford N-4-(3 : 5 : 4′-*trinitrodiphenylyl*)-N′N′-*ethylnitrocarbamide*, which is converted by boiling H_2O into 3 : 5 : 4′-*trinitro*-4-*aminodiphenyl* (IV), m.p. 280° (*Ac* derivative, m.p. 212°), whereas boiling MeOH or EtOH affords *Me* (V), m.p. 184°, and *Et* 3 : 5 : 4′-*trinitrodiphenyl*-4-*carbamate* (VI), m.p. 180°, respectively, both of which are converted by EtOH–NH_3 into (IV). (III) and its Et analogue with abs. HNO_3 at 0° afford *Me*, m.p. 189°, and *Et* 3 : 5 : 2′ : 4′-*tetranitrodiphenyl*-4-*carbamate* (VII), m.p. 149°, respectively [also formed from (V) and (VI) with abs. HNO_3 at 0°], hydrolysed by EtOH–NH_3 to 3 : 5 : 2′ : 4′-*tetranitro*-4-*aminodiphenyl* (VIII), m.p. 253°. 4-Bromo-3 : 2′ : 4′-trinitrodiphenyl when heated with NH_2Me in EtOH under pressure at 100° for 10 hr. affords 3 : 2′ : 4′-*trinitro*-4-*methylaminodiphenyl* (IX), m.p. 227° (*Ac* derivative, m.p. 197°) [whereas EtOH–NH_3 affords no 3 : 2′ : 4′-trinitro-4-aminodiphenyl (*Ac* derivative, m.p. 203°)], converted by abs. HNO_3 at 0° into 3 : 5 : 2′ : 4′-*tetranitro*-4-*methylnitroaminodiphenyl*, m.p. 172°, which with EtOH–NH_3 under pressure yields (VIII), also formed from (VII) and EtOH–NH_3. (IX) affords a 5-*Br*-derivative, m.p. 218°, whereas (IV) and (VIII) cannot be brominated similarly. The orientation of (VII) is thereby established. Reduction of 4 : 4′-dinitrodiphenyl (A., 1930, 762) affords a *by-product*, m.p. 235°, and 4-amino-4′-nitrodiphenyl, which reacts with EtNCO in C_6H_6 under pressure to give N-4-(4′-*nitrodiphenylyl*)-N′-*ethylcarbamide*, m.p. 248°, the NO_2-derivative of which is hydrolysed to (IV), thus establishing the orientation of (IV), (VII), and (VIII). 2-Aminodiphenyl with EtNCO in warm Et_2O during 0·5 hr. affords N-2-*diphenylyl*-N′-*ethylcarbamide* (X), m.p. 118°, and with $ClCO_2Me$ (or Et) in C_6H_6 containing Na_2CO_3 affords *Me* (XI), m.p. 50°, and Et diphenyl-2-carbamate (XII), b.p. 198—211° (cf. A., 1896, i, 483), respectively. (X) with excess abs. HNO_3 affords a NO_2-derivative, converted by boiling H_2O into 3 : 5 : 4′-*trinitro*-2-*aminodiphenyl* (XIII), m.p. 227°, and by boiling MeOH or EtOH into *Me*, m.p. 77°, and *Et* 3 : 5 : 4′-*trinitrodiphenyl*-2-*carbamate*, m.p. 65°, respectively. Both urethanes are formed by nitration of (XI) and (XII), respectively, and either with EtOH–NH_3 under pressure affords (XIII). Decomp. of the diazonium derivative of (XIII) affords 3 : 5 : 4′-*trinitrodiphenyl*, m.p. 170°, also obtained from the diazonium derivative of (IV). This orients the NO_2-groups in (XIII). Benzidine and EtNCO in boiling Et_2O during 6 hr. affords 4 : 4′-*diethylureidodiphenyl* (XIV), decomp. at 240°, decomposed by heat into $(CO{\cdot}NHEt)_2$ and carbonylobenzidine. Nitration of (XIV) affords only resinous products. J. L. D.

Mechanism of Hofmann, Curtius, and diazo-reactions. F. Bell (Chem. and Ind., 1933, 584).—An amine with the same direction of rotation is obtained from optically active 6-nitro-2-methyldiphenyl-2′-carboxylic acid by the Hofmann or Curtius reaction. The time of existence of the free radicals, therefore, is much < that of mutual rotation of the nuclei. H. A. P.

Proof of the unsymmetrical structure of the azoxy-group. T. T. Chu and C. S. Marvel (J. Amer. Chem. Soc., 1933, **55**, 2841—2850).—The compound described as 2 : 2′-azoxydiphenylethylmethane-4 : 4′-dicarboxylic acid (A., 1930, 774) is multimol. *dl*-α-Phenylbutyric acid (I) (modified prep. from the amide) gives the p-NO_2-*acid*, m.p. 118—120°, which affords a mixture of dl- (II) and meso- (III) -α-p-*azophenylbutyric acids*, $(N{\cdot}C_6H_4{\cdot}CHEt{\cdot}CO_2H)_2$, m.p. 197—199° (decomp.) and 211—212° (decomp.), respectively. (I) is resolved into the d- and l-*acids*, m.p. 120—122°, $[\alpha]^{25}$ ±17·7° in EtOAc (*quinine* salts, m.p. 183—185° and 180—182°, $[\alpha]_D^{25}$ −42·2° and $[\alpha]_D$ −53·8° in C_5H_5N, respectively). These acids afford dl-, d-, and l-α-p-*aminophenylbutyric acids* (IV), m.p. 142—143° and 138—140°, $[\alpha]_D^{25}$ ±12·3° in EtOH, respectively, dl-α-p-*hydroxylaminophenylbutyric acid* (V), double m.p. 112—113° (decomp.) and 166—168°, the corresponding d-*acid*, $[\alpha]^{25}$ +38° in EtOH, and dl-α-p-*nitrosophenylbutyric acid* (VI), m.p. 182—186° (decomp.) (crude d-*acid* has $[\alpha]^{25}$ +42·1° in EtOH), also obtained by oxidation of (V). (VI) and (IV) give (III), which is irresolvable (*strychnine* salt, m.p. 148—150°, $[\alpha]^{25}$ −83·5°), but is oxidised by H_2O_2 to dl-α-p-*azoxyphenylbutyric acid*, m.p. 199—201°, resolved by *d*-CHPhMe·NH_2 into the d-(*CHPhMe·NH*$_2$ salt, m.p. 192—196°, $[\alpha]_D^{25}$ +9·7° in MeOH) and l-*acids*, m.p. 206—208°, $[\alpha]_D^{25}$ +14·7° and −13·3° in MeOH. The fact that the *meso*-azo-compound gives a *dl*-azoxy-compound proves the asymmetric nature of the N_2O group. (II) is resolved by strychnine into d- and l-*azophenylbutyric acids*, m.p. 195—196° (decomp.), $[\alpha]_D^{25}$ +52·6° and −42·2° in EtOH, respectively (*strychnine* salts, m.p. 197—199° and 140—146° after softening at 130°, $[\alpha]_D^{25}$ −79·6° and −94·7° in C_5H_5N, respectively).

(II) with H_2O_2 gives a second dl-α-p-*azoxyphenylbutyric acid*, m.p. 178—180°, resolved into the d- and l-*acids*, m.p. 182—184°, $[\alpha]^{25}$ ±3·8° in MeOH (d-*CHPhMe·NH*$_2$ salts, m.p. 204—206° and 201—203°, $[\alpha]_D$ +7·8° and +5·5° in MeOH, respectively). R. S. C.

Colour and constitution from viewpoint of recent electronic theory. VI. H. H. Hodgson (J. Soc. Dyers and Col., 1933, **49**, 213—216; cf. A., 1931, 835).—Electronic explanations are offered of the substantivity (or otherwise) of benzidine derivatives, the possibility of successive coupling with the two diazonium groups in $(\cdot C_6H_4\cdot N_2X)_2$, etc., the coupling of diazonium salts with $NHPh_2$, but not with α-$C_{10}H_7\cdot NH_2$, in suspension in mineral acid, the replacement of Br by H in 4-bromo-3 : 5-dinitrobenzaldehyde, the ease of dinitration of the *p*-$C_6H_4Me\cdot SO_2\cdot$ derivatives of α-$C_{10}H_7\cdot NH_2$ and 3 : 5 : 4-$C_6H_2Me(NO_2)_2\cdot NH_2$, the separation of *m*- and *p*-xylidines by Limpach's method (cf. J.C.S., 1900, **77**, 65), and bromination of phenols in aq. as contrasted with inert solvents. It is suggested that benzidine dyes are substantive to cotton only when the two C_6 nuclei are co-planar. H. A. P.

Azo-chromophore. V. J. S. P. Blumberger (Chem. Weekblad, 1933, **30**, 538—547).—The powerful bathochromic effect of the co-ordinated *o*-hydroxy-azo-group is termed "chromophoric inversion." Usually a *p*-hydroxymonoazo-dye shows a bathochromic colour change with OH′, but with *o*-hydroxymonoazo-dyes the colour change may be absent or hypsochromic (fifty-four examples are quoted). Parallel effects are observed with aminomonoazo-dyes and H′ (forty examples quoted), the influence of various substituents being similar in the two cases. The colour changes are satisfactorily explained on the simple electronic views developed previously (cf. A., 1932, 1243; 1927, 142). The NHNa group is suggested as a new auxochrome. It is unnecessary to assume a quinonoid structure for either type of dye. The azo-chromophore is considered to be mainly responsible for absorption in the visible part of the spectrum, the ethylenic linking contributing very little to this effect. Eighty-one absorption curves for mono-azo-dyes are illustrated. S. C.

Constitution of acyl derivatives of *o*-hydroxy-azo-compounds. A. Burawoy and I. Markowitsch (Annalen, 1933, **504**, 71—80).—The azoid structure of the compound obtained by benzoylation of β-naphthaquinone-1-phenylhydrazone follows from the difference of its absorption spectrum from that of the quinonoid lactam of β-naphthaquinone-1-phenylhydrazone-8-carboxylic acid and its close similarity to that of 1-benzeneazo-β-naphthyl Me ether. Similarly, the absorption of the benzoate of β-naphthaquinone-2-phenylhydrazone (by benzoylation of the parent material or from β-naphthaquinone and $NH_2\cdot NPhBz$) resembles that of 2-benzeneazo-α-naphthyl Me ether and differs from that of the parent, so that the derivative is azoid. The benzoate of *o*-hydroxyazobenzene resembles *o*-ethoxyazobenzene and differs from the parent compound. Contrary to Tuck, the benzoate of benzeneazo-*p*-cresol is azoid, thus differing from the parent material. H. W.

Preparation of azo-dyes from brominated β-naphthol. V. Vesely and F. Šťursa (Chem. Listy, 1933, **27**, 126—128).—1 : 6-Dibromo-β-naphthol combines with diazotised *p*-$NO_2\cdot C_6H_4\cdot NH_2$ to yield 6-*bromo*-1-(4′-*nitrobenzeneazo*)-β-*naphthol*, m.p. 272°, identical with the product obtained from 6-bromo-β-naphthol. Similarly, both 1 : 4 : 6-tribromo- and 4 : 6-dibromo-β-naphthol yield 4 : 6-*dibromo*-1-(4′-*nitrobenzeneazo*)-β-*naphthol*, m.p. 221—222°. R. T.

Diethyl azobenzoate. G. Lock (J. pr. Chem., 1933, [ii], **138**, 51—54).—*o*-$C_6H_3Me\cdot NO_2$ and $SnCl_2$ give *o*-azoxytoluene, m.p. 59° (cf. A., 1911, i, 932), oxidised by $KMnO_4$ to *o*-azoxybenzoic acid (Et_2 ester, m.p. 77·5°), which is reduced by Zn dust and aq. NH_3 to the hydrazo-compound. This is oxidised by $AgNO_3$ to *o*-azobenzoic acid (Et_2 ester, m.p. 85°), also (better) obtained from *o*-$NO_2\cdot C_6H_4\cdot CHO$ or *o*-$NO_2\cdot C_6H_4\cdot CH_2\cdot OH$. *o*-Azotoluene is volatile in steam. R. S. C.

Mechanism of the oxidation of primary hydrazines. I. Reaction of primary aromatic hydrazines with salts of heavy metals. O. A. Seide, S. M. Scherlin, and G. J. Bras (J. pr. Chem., 1933, [ii], **138**, 55—68).—$NHPh\cdot NH_2$ (I) with $FeCl_3$ gives PhCl (62%), with $FeBr_3$ PhBr (50%), with $Fe(CNS)_3$ Ph_2S_2, and with $K_3Fe(CN)_6$ PhCN (10%) and Ph_2. These reactions are considered to proceed by way of the *syn*-diazonium salts. The oxidation of (I) by $Hg(OAc)_2$ to $HgPh_2$ is believed to take place by way of $NHPh\cdot NH\cdot Hg\cdot OAc$, which is oxidised to *syn*-benzenediazonium mercuriacetate; this decomposes in absence of Cu into C_6H_6, N_2, and $OH\cdot Hg\cdot OAc$, but in presence of Cu into phenylmercuriacetate (II). In conformity with this view, $Hg(OAc)_2$, $Cu(OAc)_2$, and dil. AcOH and the appropriate hydrazine give (II), m.p. 146—147°, p-*nitro*-, m.p. 202—203·5°, and p-*bromo-phenylmercuriacetate*, m.p. 194—195°, in 70, 42, and 87% yield, respectively. However, α-quinolylhydrazine (III) gives carbostyril (IV) by this reaction. (II) in hot dil. AcOH gives N_2, Hg, and $HgPh_2$, but the yield is increased by the presence of Cu, which proves the existence of an equilibrium $2HgPh\cdot OAc \rightleftharpoons HgPh_2 + Hg(OAc)_2$. (I), aq. $Cu(OAc)_2$, and (III) give (IV) and $HgPh_2$. R. S. C.

Constitution of tribromophenol bromide and analogous compounds. J. Ssuknewitsch and S. Budnitzki (J. pr. Chem., 1933, [ii], **138**, 18—22).—4-Chloro-1 : 6-dibromophenol (I) and Br-H_2O give 4-*chloro*-2 : 6-*dibromophenyl hypobromite* (II), $C_6H_2ClBr_2\cdot OBr$, m.p. 94° (decomp.), which (*a*) with NH_2Ph in $CHCl_3$ gives (I) and 2 : 4 : 6-tribromoaniline, and (*b*) with hot EtOH affords (I), HBr, and paracetaldehyde. 2 : 4 : 6-Tribromophenol (III) and aq. Cl_2 give 2 : 4 : 6-*tribromophenyl hypochlorite* (IV), $C_6H_2Br_3\cdot OCl$, m.p. 115—116°, which affords similarly (*a*) (III) and 2 : 4 : 6-trichloroaniline, and (*b*) (III), Cl_2, and only traces of Br. The given structures of (II) and (IV) are proved by these differences, which refute the usually accepted (quinonoid) formula common to both substances. R. S. C.

Decomposition of iodophenols. G. H. Woollett, F. W. Vaughan, M. L. Burks, and C. O. Hinton (J. Amer. Chem. Soc., 1933, **55**, 2909—2911).—Guaiacol, I–aq. KI, and aq. NH_3 give *di-iodo-*

guaiacol, m.p. 92·4°, and resorcinol Me ether gives the I_3-compound, m.p. 123°. The Na salts of these substances and of di-iodo-*o*- and -*m*-cresol with aq. NaOH or Na_2CO_3 give red, amorphous, multimol. *compounds*, corresponding in composition to loss of 1 mol. of NaI per mol. The Na salt of di-iodo-*p*-cresol loses only a part of its NaI. Quinol Me ether is only partly iodinated under similar conditions. R. S. C.

Halogen derivatives of dehydro-β-naphthol 1-disulphide. J. A. C. McClelland and S. Smiles (J.C.S., 1933, 786—788).—Bromination of β-naphthol 1-disulphide gives 6 : 6′-*dibromo*-β-*naphthol* 1-*disulphide*, m.p. 174°, oxidised by Br and AcOH to the corresponding *dehydro*-derivative, m.p. 190°. 6-*Bromo*-2-*naphthylene* 1-*thiolcarbonate*, m.p. 167°, 3 : 3′-*dibromo*-, m.p. 176°, and its *dehydro*-derivative, m.p. 184—185°, and 3 : 3′ : 6 : 6′-*tetrabromo*-β-*naphthol* 1-*disulphide*, m.p. 221°, and its *dehydro*-derivative, m.p. 189°, are similarly obtained. F. R. S.

Laccol. G. Bertrand and G. Brooks (Bull. Soc. chim., 1933, [iv], **53**, 432—443; cf. A., 1932, 943).—Laccol, b.p. about 220°/low vac. (decomp. at b.p., 280—290°/10—15 mm.) (Ac_2 derivative, b.p. 240—250°/0·5 mm.), gives tetrahydrolaccol, b.p. 265—275°/8—10 mm., m.p. 62·6° (*Pb* salt), best purified by the Ac_2, m.p. 58·7°, or dipropionyl derivative, m.p. 34·8°. R. S. C.

Action of nitrous acid on pyrocatechol-4-sulphonic acid. J. Frejka and J. Zika (Coll. Czech. Chem. Comm., 1933, 5, 253—262).—The action of excess of HNO_2 on pyrocatechol-4-sulphonic acid (*Ba*, *Na*, and *K* salts) gives 3 : 5-*dinitroso*- [Na_2 *H* ($+1·5H_2O$), K_2 *H*, *Ba H* ($+1·5H_2O$), *Sr H* ($+1·5H_2O$), *Ca H* ($+3H_2O$), and Ag_2 *H* salts], reduced by Fe and HCl to 3 : 5-*diamino*-*pyrocatechol*-4-*sulphonic acid* [*dihydrochloride* ; *dipicrate* ($+5H_2O$), decomp. 148—150° ; Ac_4 derivative]. This cannot be isolated in a pure state, since it is readily oxidised by air or by $FeCl_3$ in aq. solution to 3 : 5-*diamino*-*o*-*benzoquinone*-4-*sulphonic acid*. H. A. P.

Separation of two desmotropic forms of some polyhydric phenols derived from naphthalene. A. Madinaveitia and E. Olay (Anal. Fís. Quím., 1933, **31**, 134—138).—Using Meyer's method of fusion and extraction of the cooled, pasty melt with $CHCl_3$, the following ketonic (β-)forms have been separated and the phenylsemicarbazones prepared (m.p. in parentheses) : β-*dihydro*-2-*methyljuglone* (β-*dihydroplumbagin*), m.p. 86° (232°) ; β-1 : 4-*dihydroxy*-2-*methylnaphthalene*, m.p. 60° (260°) (diphenylsemicarbazide yields a *product*, m.p. 260°) ; β-1 : 4-*dihydroxynaphthalene*, m.p. 99° (250°) (*oxime*, m.p. 220°, darkens at 190°). Reversion to the α-form results on dissolution in NaOH containing stannite and repptn. by HCl. R. K. C.

Direct halogenation of arylaliphatic alcohols. (Mlle.) D. Sontag (Compt. rend., 1933, **197**, 159—161 ; cf. this vol., 501).—γ-Phenylpropyl alcohol (*benzoate*, b.p. 207°/20 mm.) is brominated (in Ph group) to the *Br*-compound, b.p. 157—158°/14 mm. (*acetate*, b.p. 168—170°/17 mm. ; *bromide*, b.p. 161—163°/17 mm.), and is chlorinated to a mixture of alcohols, difficult to separate [γ-*chlorophenylpropyl alcohol*, b.p. 149—150°/18 mm. (*benzoate*, b.p. 163—165°/2 mm.)]. F. R. S.

Cholesterol. XVI. I. Montignie (Bull. Soc. chim., 1933, [iv], **53**, 370—372 ; cf. A., 1932, 381).—Cholesterol gives a *gynocardate*, m.p. 110—112° (Br_4-derivative, m.p. 77—78°), and *bromoacetate*, m.p. 117—118°. R. S. C.

Synthesis in sterol and sexual hormone series. W. Schlenk, O. Bergmann, and E. Bergmann (J.S.C.I., 1933, **52**, 209—210T).—An attempt to prepare the hydrocarbon $C_{17}H_{14}$ (? or $C_{18}H_{16}$), previously obtained by dehydrogenation of cholesteryl chloride or cholic acid, by dehydrogenation with Se of 1-*allyl*-3 : 4-*dihydrophenanthrene* (I), m.p. 129—130·5°, gave 1 : 2-*cyclo*pentenophenanthrene (?) (cf. this vol., 710), m.p. 118—120·5° (picrate, m.p. 134—136°). α-$C_{10}H_7$·MgBr and CH_2Cl·CH_2·OH in presence of MgEtBr give β-1-*naphthylethyl alcohol*, m.p. 61°, b.p. 174—176°/14 mm., converted by $SOCl_2$ into its *chloride*, b.p. 165—166°/16 mm., which with $CHNa(CO_2Et)_2$ gives *Et* γ-1-*naphthylpropane*-αα-*dicarboxylate*, b.p. 234—236°/15 mm. ; the corresponding free *acid*, m.p. 150—150·5°, is readily decarboxylated by heat to γ-1-naphthylbutyric acid. Interaction of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene with Mg allyl bromide gives 1-*hydroxy*-1-*allyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 102—104°, dehydrated by 85% H_2SO_4 at 100° to (I). The crude dehydration product with Se at 300—340° gives a further *hydrocarbon*, $C_{17}H_{14}$, m.p. 164—168° (clear and mobile at 205—207°), b.p. 178—183°/0·1—0·3 mm. H. A. P.

β-Ergostenol. II. F. W. Heyl, M. C. Hart, and H. Emerson (J. Amer. Chem. Soc., 1933, **55**, 2870—2871 ; cf. A., 1932, 511).—β-Ergostenol gives a *propionate*, m.p. 110°, *phthalate*, m.p. 152—154°, *benzoate*, m.p. 158°, (22·5°), p- and m-*nitro*- and 3 : 5-*dinitro*-*benzoate*, m.p. 180°, 148°, and 164° (25·0°, 21·5°, and 15·0°), respectively, and a *phenylurethane*, m.p. 146—147° (16·1°), the figures in parentheses being $[\alpha]_{5461}$. α-*Ergostenol* 3 : 5-*dinitrobenzoate* and *phthalate* have m.p. 197° (—2·8°) and 185° (1·45°), respectively. R. S. C.

Increase in reaction velocity of tertiary acids by the presence of a carbonyl group in the γ-position. H. Appel.—See this vol., 911.

Racemisation of chaulmoogric and hydnocarpic acids. W. S. Hinegardner (J. Amer. Chem. Soc., 1933, **55**, 2831—2834).—*d*-Chaulmoogramide (I), $[\alpha]_D$ +57·1°, when distilled with P_2O_5 at 3—4 mm., gives dl-*chaulmoogronitrile*, b.p. 155—158°/2·5 mm., hydrolysed to dl-*chaulmoogric acid*, m.p. 68·5° (dl-*amide*, m.p. 105—106°). The *dl*-amide and -acid do not depress the m.p. of the *d*-compounds. (I) and $SOCl_2$ in C_6H_6 give d-*chaulmoogronitrile*, $[\alpha]_D^{25}$ +55·2° in $CHCl_3$, hydrolysed to the *d*-acid (II), $[\alpha]_D^{25}$ +61·4° in $CHCl_3$, and racemised by distillation with P_2O_5. (II) is not racemised by PCl_3 or $POCl_3$ at 100° or PCl_5 at 150°, and is decomposed by distillation with P_2O_5 in vac. *d*-Hydrocarpamide, $[\alpha]_D^{25}$ +69·4°, gives similarly the dl-*nitrile*, b.p. 155—156°/2—3 mm., hydrolysed to the dl-*acid*, m.p. 58·5—59°, alone or mixed with the *d*-acid. R. S. C.

Alkyl and alkylamine esters of *p*-aminothiobenzoic acid and related compounds. H. L. HANSEN and L. S. FOSDICK (J. Amer. Chem. Soc., 1933, **55**, 2872—2874).—*p*-Nitrothiobenzoic acid (modified prep.) affords the *Me*, m.p. 96—97°, *Et*, m.p. 67—68°, *Pr*, m.p. 30—31°, *Bu*, m.p. 13—15°, and β-*chloroethyl*, m.p. 91—92°, esters, whence were obtained *Me*, m.p. 113—114°, *Et*, m.p. 79—79·5°, *Pr*, m.p. 60—61°, *Bu*, m.p. 37—38°, β-*chloroethyl*, m.p. 99—101°, and p-β-*diethylaminoethyl*, m.p. 52—52·5° (*hydrochloride*, m.p. 177·6—178°) p-*aminothiobenzoate*. These compounds have strong anæsthetic properties, the last-named (thiocaine) being very rapid in action and having a low toxicity. R. S. C.

Preparation of some alkyl-substituted phenylacetonitriles in liquid ammonia. L. H. BALDINGER and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1933, **55**, 2851—2853).—Na and $CH_2Ph{\cdot}CN$ in liquid NH_3 give the Na derivative, which with alkyl halides (best, chlorides) give 35—50% yields of α-*phenyl*-n-*propio*-, b.p. 118—120°/19 mm., -n-*butyro*-, b.p. 126—129°/19 mm., -n-*valero*-, b.p. 120—123°/7 mm., -n-*hexo*-, b.p. 152—155°/20 mm., and -n-*heptonitrile*, b.p. 165—168°/22·5 mm. Some PhMe is also formed. R. S. C.

Stereoisomeric phenylmethylethyl and phenylmethylpropyl betaines. (MME.) GUAISNET-PILAUD (Compt. rend., 1933, **197**, 156—157).—The betaine monohydrate from Et phenylmethylethyliodoaminoacetate (cf. this vol., 387) when heated gives *Et phenylmethylaminoacetate*, b.p. 137—138°/14 mm. (with NH_3, *phenylmethylaminoacetamide*, m.p. 162°, formed), and the dihydrate yields *Me phenylethylaminoacetate*, b.p. 147—148°/15 mm. (*phenylethylaminoacetamide*, m.p. 108°). Ag_2O and methylpropylaniline iodoacetate afford a *monohydrate*, m.p. 172°, and a *dihydrate*, m.p. 81·5°, with elimination of I, which give similar results when heated. F. R. S.

Synthesis of α-naphthylacetic acid. DEW. T. KEACH (J. Amer. Chem. Soc., 1933, **55**, 2974—2975).—1-Allylnaphthalene and $KMnO_4$ in EtOH–H_2O give a 43% yield of α-naphthylacetic acid, m.p. 106° (lit. 131°), and a little αβ-*dihydroxy*-γ-1-*naphthylpropane*, m.p. 110°. R. S. C.

Synthesis of some alkylphenanthrenes and alkylphenanthrene-10-carboxylic acids by the Pschorr reaction. M. G. BOGERT and G. S. STAMATOFF (Rec. trav. chim., 1933, **52**, 584—592).—Interaction of *p*-ethyl-, 2 : 4-dimethyl-, and 2-methyl-5-*iso*propyl-benzyl chloride (A., 1923, i, 549) with KCN in boiling EtOH–H_2O affords p-*ethyl*- (I), b.p. 123·5—125·5°/12 mm. (hydrolysed to the *acid*, m.p. 88·5—89·5°), 2 : 4-*dimethyl*- (II), b.p. 140°/11 mm., and 2-*methyl*-5-*isopropyl*-*phenylacetonitrile* (III), b.p. 144°/14 mm., respectively. The *K* salts of the acids from (I), (II), and (III) with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ and Ac_2O during many hr. at 100° afford α-(p-*ethylphenyl*)-, m.p. 172·8—173·2°, α-(2 : 4-*dimethylphenyl*)-, m.p. 187—188°, and α-(2-*methyl*-5-*isopropylphenyl*)-o-*nitrocinnamic acid*, m.p. 183—184°, respectively, reduced by boiling aq. $FeSO_4$–NH_3 to NH_2-compounds, m.p. 200—201° (IV) (*Ac* derivative, m.p. 256—257°), 217·5—218° (V) (*hydrochloride*), and a tar (VI) which cannot be purified, respectively. (IV), (V), and (VI) in HCl at 0° with amyl nitrite, followed by Cu powder, afford 3-*ethyl*-, m.p. 195—196° (*picrate*, m.p. 166—167°), 1 : 3-*dimethyl*-, m.p. 188—189°, and 1-*methyl*-4-*isopropyl*-*phenanthrene*-10-*carboxylic acid*, m.p. 201—202°, respectively, which are decarboxylated to 3-*ethyl*-, an oil (*picrate*, m.p. 119·5—120·5°; *quinone*, m.p. 168·2—169°), 1 : 3-*dimethyl*-, m.p. 76—77° (*picrate*, m.p. 153—155°; *quinone*, m.p. 218—219°), and 1-*methyl*-4-*isopropyl*-*phenanthrene*, m.p. 68—68·5° (*picrate*, m.p. 113·6—114·1°), which is different from retene. J. L. D.

Phenolic acids. III. Esters of aspirin. P. P. T. SAH, T. S. MA, and H. H. LEI (Sci. Rep. Nat. Tsing Hua Univ., 1933, **2**, 13—17).—*Ac* derivatives of the following salicylates are described: Me, m.p. 48—49°, Et, b.p. 155—158°/15 mm., 281—283°/760 mm., Pr^{α}, b.p. 162—164°/10 mm., 291—293°/760 mm., Bu^{β}, b.p. 165—168°/10 mm., 293—295°/760 mm., Bu^{α}, b.p. 175—178°/10 mm., 303—305°/760 mm., and *iso*amyl, b.p. 175—178°/10 mm., 301—303°/760 mm. Pr^{β} salicylate did not acetylate, and acetylsalicyl chloride with $Pr^{\beta}OH$ gives $Pr^{\beta}OAc$ and Pr^{β} salicylate. Nitration of the above esters gives 3 : 5-$(NO_2)_2$-derivatives of the deacetylated esters (A., 1932, 1246). A. A. L.

Amino-acids and related compounds. V. Electrolytic oxidation of tyrosine and phenylalanine. Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, **8**, 178—188; cf this vol., 940).—More energy is absorbed in the electrolytic oxidation of phenylalanine than of tyrosine. In both cases NH_3 is produced rather less rapidly than is accounted for by the disappearance of N as NH_2, due it is suggested to the formation of melanine. The same products are obtained in both cases, viz., CO_2, NH_3, AcOH, succinic acid, p-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, quinol, benzoquinone, and melanine. H. A. P.

Emetics derived from mandelic and malic acids. VOLMAR and BETZ (Compt. rend., 1933, **197**, 414—416).—A mixture of equiv. concns. of mandelic acid and Na mandelate fixes the max. amount of Sb_2O_3. *Na antimonyl mandelate* is isolated cryst. having the composition $Sb(OH)(\cdot O{\cdot}CHPh{\cdot}CO_2H)(\cdot O{\cdot}CHPh{\cdot}CO_2Na)$. Max. fixation by *l*-malic acid occurs with a mixture of 2 mols. of acid and 1 mol. of neutral Na salt, yielding *Na antimonyl* l-*malate*, $Sb(OH)[\cdot O{\cdot}CH(CH_2{\cdot}CO_2Na)(CO_2H)]_2$+ $Sb(OH)[\cdot O{\cdot}CH(CH_2{\cdot}CO_2H)(CO_2H)]_2$?, $[\alpha]_D$ +83·4°. These compounds are more stable to H_2O than the corresponding lactic acid derivative (this vol., 376). A. C.

Synthesis of phenolic long-chain fatty acids. J. B. NIEDERL and C. LIOTTA (J. Amer. Chem. Soc., 1933, **55**, 3025—3026).—Oleic acid (I), *m*-cresol, and H_2SO_4–AcOH give ι-m-*tolyloxystearic acid*, b.p. 280°/23—24 mm., rearranged to ι-3-*hydroxy*-p-*tolylstearic acid*, m.p. 37° (II). (I) and HBr give ι-bromostearic acid, the structure of which is proved by its reaction with m-$C_6H_4Me{\cdot}OK$ and subsequent rearrangement to (II). R. S. C.

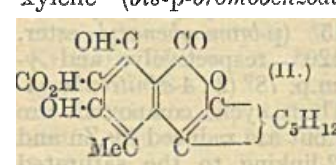
β-Anthronyl-β-phenylpropionic acid and its derivatives. Synthesis of 3-(9-anthronyl)hydrindone. P. E. GAGNON and L. GRAVEL (Canad. J. Res., 1933, 8, 600—615).—*Et*$_2$ *benzylidene-*, b.p. 176—177°/5 mm., and *o-chlorobenzylidene-malonate*, b.p. 182—183°/5 mm., m.p. about 30°, and *Me*$_2$ *o-chlorobenzylidenemalonate*, b.p. 175°/3 mm., m.p. 58—59°, with anthrone and piperidine in MeOH give *Et*$_2$ β-9-*anthronyl-β-phenyl-*, m.p. 104—105°, and -β-*o-chlorophenyl-ethane-αα-dicarboxylate*, m.p. 119—120° (corresponding *Me*$_2$ ester, m.p. 148—149°), $C_{10}H_9O{\cdot}CHAr{\cdot}CH(CO_2Et)_2$, which afford β-*anthronyl-β-phenyl-* (I), m.p. 196—197° (*Ag* salt), and -β-*o-chlorophenyl-propionic acid*, m.p. 159—161°. (I) and PCl_5 give the *chloride* (II), m.p. 115—116°, whence were obtained the *Me*, m.p. 111—112°, and *Et* ester, m.p. 88—89°, *amide*, m.p. 181—182°, and *anilide*, m.p. 168—169°, and β-9-anthronyl-β-phenylpropiophenone, m.p. 115—116°. (I) and H_2SO_4, or (II) and $AlCl_3$, best in CS_2, give 3-(9-*anthronyl*)*hydrindone*, enolic *form*, m.p. 188°, and ketonic *form*, $CO<^{C_6H_4}_{CH}>CH{\cdot}C_{14}H_9O$, m.p. 162° (*hydrazone*, m.p. 176°; *phenylhydrazone*, m.p. 224—225°; *semicarbazone*, m.p. 243°; *oxime*, m.p. 181—184°), both giving the same 2-*Br*-derivative, m.p. 169—171° (by Br–Et_2O), and oxidised by HNO_3 (*d* 1·2) quantitatively to phthalic acid and anthraquinone, whereby the alternative constitution, 13-hydroxy-11-phenylbenzanthrone, is excluded.

R. S. C.

Biochemistry of micro-organisms. XXIX. 2 : 5-Dihydroxybenzoic acid (gentisic acid), a new product of the metabolism of glucose by *Penicillium griseo-fulvum*, Dierckx. H. RAISTRICK and P. SIMONART. **XXX, XXXI. Molecular constitution of the metabolic products of *Penicillium brevi-compactum*, Dierckx, and related species. (I) Acids $C_{10}H_{10}O_5$, $C_{10}H_{10}O_6$, and $C_{10}H_{10}O_7$.** A. E. OXFORD and H. RAISTRICK. **(II) Mycophenolic acid.** P. W. CLUTTERBUCK and H. RAISTRICK (Biochem. J., 1933, **27**, 628—633, 634—653, 654—667).—XXIX. The metabolic products from the growth of *P. griseo-fulvum*, on Czapek–Dox medium containing 8% glucose and 0·25% $NaNO_3$, at 30° gives 2-hydroxy-6-methylbenzoic acid (cf. A., 1931, 524), mannitol, fumaric and gentisic acids (2 : 5-dihydroxybenzoic acid).

XXX. The three acid metabolic products (cf. A., 1932, 1289), $C_{10}H_{10}O_5$ (I), $C_{10}H_{10}O_6$ (II), and $C_{10}H_{10}O_7$ (III), are 3 : 5-dihydroxy-2-carboxylbenzyl Me ketone, -2-carboxyphenylacetylcarbinol (or a mixture of its tautomerides), and a hydrated form of -2-carboxybenzoyl Me ketone, respectively. A *substance*, $C_{11}H_{10}O_5$, m.p. 173—175°, has also been isolated. (I) is converted into $C_{10}H_8O_4$ (IV) by dehydrating agents. (I) forms a *mono-2 : 4-dinitrophenylhydrazone*, m.p. 224—226° (decomp.), (II) gives the *mono-2 : 4-dinitrophenylhydrazone* of $C_{10}H_8O_5$, m.p. 232° (decomp.), and (III) the *mono-2 : 4-dinitrophenylhydrazone* of $C_{10}H_8O_6$, m.p. 216° (decomp.); (II) and (III) form the same *monophenylhydrazone*, m.p. 214° (decomp.). (III) yields a supposed *quinoxaline* (+H_2O), m.p. 210° (decomp.), which is abnormal. (I) affords the *Ac*$_2$ derivative of (IV), m.p. 123—124°; (II) forms (?) *Ac*$_3$ derivative of $C_{10}H_8O_5$, m.p. 172—174°. Methylation of (I) by CH_2N_2 gives the *Me ether* of the *Me* ester, m.p. 88—91°, which is converted by MeI–K_2CO_3 into the *Me*$_2$ *ether* of (IV), m.p. 149—151°, hydrolysed to the *Me*$_2$ *ether* of (I), m.p. 139—141°. Methylation of (IV) by CH_2N_2 yields the *Me ether* of $C_{11}H_{10}O_4$, m.p. 124—125°, whilst (II) similarly gives the *Me ether* of the *Me* ester, m.p. 82°. (III) is reduced (Pd–H_2) to (II), and the Na salt of (II) is oxidised by $CuSO_4$ to (III), whilst both (II) and (III) are reduced (Zn–H_2SO_4) to (I), and (III) and (I) reduced (Zn–Hg) to (IV). Oxidation of (III) by H_2O_2 affords 3 : 5-dihydroxyphthalic acid, and of the Me_2 ether of (IV) by $KMnO_4$ gives 3 : 5-dimethoxyphthalic acid. The Me_2 ether of (I) when heated gives a ketone, oxidised ($KMnO_4$) to 3 : 5-dimethoxybenzoic acid and when treated with I–NaOH yields CHI_3 (side-chain must be $CH_2{\cdot}COMe$). The Me_2 ether of (IV) and EtOH–NH_3 form 6 : 8-dimethoxy-3-methyl*iso*carbostyril.

XXXI. Mycophenolic acid (I), $C_{17}H_{20}O_6$, m.p. 141° (*Ac* derivative, m.p. 158—160°), contains one OMe and is demethylated to *normycophenolic acid* (II), m.p. 184°. By titration, (I) is shown to contain one CO_2H and a lactonic ring, the OH of which is not phenolic. (I) and give the *Me* ester of the *Me ether*, m.p. 58°, hydrolysed to the *Me ether* of the acid, m.p. 112°, which is oxidised ($KMnO_4$) to a dilactonic acid, $C_{16}H_{14}O_6(OMe)_2$, m.p. 153°, and subsequently to the anhydride of 1 : 5-dimethoxybenzene-2 : 3 : 4 : 6-tetracarboxylic acid, m.p. 220°. Reduction (Pd–H_2) of (I) gives *dihydromycophenolic acid*, m.p. 139°. Fusion of (I) with KOH affords 3 : 5-dihydroxy-*o*-xylene (*bis*-p-*bromobenzoate*, m.p. 144—145°) and oxidation with HNO_3 gives a lactonic *acid*, $C_7H_{10}O_4$ (*Me* ester, b.p. 100°/0·1 mm.), isomerised by NaOH to a dibasic acid, m.p. 163°, and resistant to oxidation by $KMnO_4$. The annexed formula is suggested for (II), the position of the Me group in (I) being unknown.



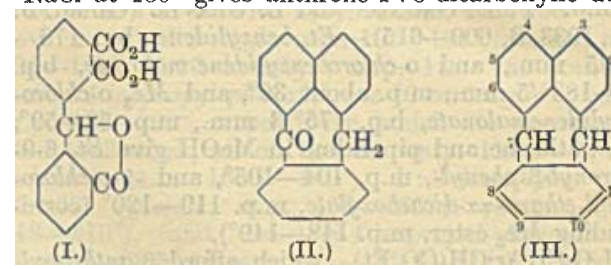
F. R. S.

γ-Iodopropyl chloride as a synthetic reagent. Synthesis of α-phenyl-dibasic acids. F. H. CASE (J. Amer. Chem. Soc., 1933, **55**, 2927—2932).—$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, red P, and I give γ-iodopropyl chloride (I), b.p. 169—173° (58·3% yield), which with KCN gives *γ-iodobutyronitrile* (II), b.p. 113—116°/7 mm. Hydrogenation (PtO_2) of β-chloropropiophenone in AcOH gives *γ-chloro-α-phenylpropyl alcohol*, b.p. 130—132°/8 mm. (p-*nitrobenzoate*, m.p. 62—63°). $CNaPh(CO_2Et)_2$ (III) and (II) in PhMe give an ester, hydrolysed to *α-phenyladipic acid*, m.p. 132—133°. $CHNa(CO_2Et)_2$, NaI, and (I) in EtOH give *Et*$_2$ *γ-iodopropylmalonate*, b.p. 164—168°/8 mm., which with (III) affords esters, hydrolysed to $CH_2Ph{\cdot}CO_2H$ and *cyclo*butane-1 : 1-dicarboxylic acid, and with $CHNaPh{\cdot}CN$ (IV) gives esters, hydrolysed to yield a little *α-phenylpimelic acid*, m.p. 92—93°. (IV) and (I) in Et_2O give a nitrile, hydrolysed to an *acid*, $C_{11}H_{12}O_2$, m.p. 106—107°, probably 1-*phenylcyclobutane-1-carboxylic acid* (since it resists hydrogenation), also obtained from (III) and (I) in EtOH, and from $CNa_2Ph{\cdot}CN$ and $CH_2(CH_2I)_2$ in Et_2O. $CNaEt(CO_2Et)_2$ and (I) in EtOH give impure *Et*$_2$

γ-iodopropylethylmalonate, b.p. 162—167°/9 mm., which with (III) in PhMe affords *α-phenyl-α'-ethylpimelic acid*, α-, m.p. 138—139°, and β-, m.p. 149—150°, forms. *Et κ-bromoundecoate*, b.p. 175—179°/6 mm., and (III) in PhMe afford an ester, hydrolysed to *α-phenylundecane-αα'-dicarboxylic acid*, m.p. 87—88°. (III) and $(CH_2I)_2$ in EtOH give esters, yielding $CH_2Ph{\cdot}CO_2H$ and αβ- (α- or β-form) -diphenylsuccinic acid; $(CH_2Br)_2$ gives similarly only $CH_2Ph{\cdot}CO_2H$; $CH_2(CH_2I)_2$ gives $CH_2Ph{\cdot}CO_2H$ and an oily acid. R. S. C.

Additive reactions of phenyl vinyl ketone. III. Methyl malonate. C. F. H. Allen and H. W. J. Cressman (J. Amer. Chem. Soc., 1933, **55**, 2953—2960; cf. A., 1932, 385).—β-Chloropropiophenone, NaOAc, and an excess of pure $CH_2(CO_2Me)_2$ in MeOH give *Me*$_2$ *β-benzoylethylmalonate* (I), m.p. 42°, b.p. 165—176°/5—6 mm. (decomp.) (*Et*, ester, an oil; 2 : 4-*dinitrophenylhydrazone*, m.p. 139°), hydrolysed by 10% aq. KOH to the corresponding *acid*, m.p. 168—170°, which at 175—180° gives CO_2 and γ-benzoylbutyric acid. Under other conditions the condensation affords *Me*$_2$ *di-(β-benzoylethyl)malonate*, m.p. 132°. (I) and Br give mixtures, whence by KOAc–MeOAc *Me*$_2$ 2-*benzoylcyclopropane*-1 : 1-*dicarboxylate* (II), m.p. 74°, b.p. 185—190°/4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 169°), was obtained. This is stable to dry NaOMe–MeOH or $Mg(OMe)_2$, but with NaOMe and a trace of H_2O gives an oil, whence aq. KOH forms 2-*benzoylcyclopropane*-1 : 1-*dicarboxylic acid* (III), m.p. 170—172°, which loses CO_2 to give cis- and trans-2-*benzoylcyclopropane*-1-*carboxylic acid*, m.p. 145° (p-*bromophenacyl* ester, m.p. 122°), and 118—120°, respectively, and *γ-benzoylbutyrolactone* (IV), m.p. 78° (2 : 4-*dinitrophenylhydrazone*, m.p. 174°). These cyclic compounds are all stable to conc. H_2SO_4, but are reduced by Zn and 80% AcOH at the 1 : 2-linking to the saturated aliphatic compounds. (III) and HBr–AcOH at 100° gives an oil, containing Br, which slowly passes into *α-carboxy-γ-benzoylbutyrolactone*, m.p. 122° (decomp. 125—130°); this at 150—155° or in hot KOAc–MeOH gives (IV). (II) gives similarly a halogenated oil, whence (II) is regenerated by KOAc–MeOAc. *Me γ-benzoylbutyrate*, m.p. —2°, b.p. 147—148°/8 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 149°), with Br in CCl_4 gives an oil, which with KOAc–MeOAc forms *Me γ-benzoyl-γ-acetoxybutyrate* (V), m.p. 60° (2 : 4-*dinitrophenylhydrazone*, m.p. 158°), and with NaOMe gives (IV), also obtained from (V) by alkaline or, better, acid hydrolysis, and by bromination of γ-benzoylbutyric acid followed by treatment with cold, aq. Na_2CO_3. In all these reactions fission occurred at the 1 : 2-linking. R. S. C.

Synthesis of phthaloylnaphthol. L. F. Fieser and (Mrs.) M. Fieser (J. Amer. Chem. Soc., 1933, **55**, 3010—3018).—The oxidation product of phthaloyl-β-naphthol, benzhydrol-2 : 3 : 2'-tricarboxylic acid lactone (A., 1931, 1292) (I) (modified prep.) (*imide*, m.p. 303—304°) titrates as a lactonic dicarboxylic acid, and with KOH at 180° (with or without HCO_2K) is reduced to *diphenylmethane*-2 : 3 : 2'-*tricarboxylic acid*, +1·5H_2O, m.p. about 145° (decomp.) and 200° (anhydride) (*Me*$_3$ ester, m.p. 79°; *anhydride*, m.p. 202°), which with conc. H_2SO_4 at 150° or $AlCl_3$–NaCl at 150° gives anthrone-1 : 5-dicarboxylic acid,



oxidised to anthraquinone-1 : 5-dicarboxylic acid. 2-(2'-Methoxy-1'-naphthoyl)benzoic acid, m.p. 196° (modified prep.), with Zn dust and aq. NaOH gives the *lactone*, m.p. 139°, of *phenyl-2'-methoxy-1'-naphthylcarbinol-2-carboxylic acid*, further reduced by the same reagents to the methanecarboxylic acid. Similarly were prepared: phenyl-2' : 3'-, m.p. 254°, 2' : 6'-, m.p. 218°, and -2' : 7'-*dimethyl*-1'-*naphthylmethane*-2-*carboxylic acid*, m.p. 211°. The acid chlorides, prepared from these and similar acids (finely divided) by $SOCl_2$, give with $AlCl_3$ in $PhNO_2$ (less well with conc. H_2SO_4) the following derivatives of 7-*pleiadone* (II) (derived from the hypothetical *pleiadene* (III): 1-*MeO*- (IV), m.p. 160°; 1-*Me*- (V), m.p. 128°; 1 : 2-, m.p. 195°, 1 : 5-, m.p. 159°, and 1 : 6-*Me*$_2$-, m.p. 172°. (IV) with $AlCl_3$ in hot C_6H_6 gives 1-*hydroxy*-7-*pleiadone*, m.p. 232° (*Ac* derivative, m.p. 195°), and with MgPhBr gives (probably) 7-*hydroxy*-1-*methoxy*-7-*phenyl*-7 : 12-*dihydropleiadene*, m.p. 186°. (V), however, gives a *hydrocarbon*, m.p. 237°. The pleiadones with CrO_3 in hot AcOH give 1-*methyl*-, m.p. 183°, 1 : 2-, m.p. 175°, 1 : 5-, m.p. 179°, and 1 : 6-*dimethyl*-, m.p. 241°, and 1-methoxy- (VI) -7 : 12-*pleiadenedione*. (VI) is identical with phthaloyl-β-naphthol Me ether; with MgPhBr it gives a *compound*, $C_{31}H_{22}O_2$, m.p. 183—184° (*acetate*, m.p. 212°). Reiche's formula for phthaloyl-β-naphthol (A., 1931, 1060) and Fieser's for (I) (*loc. cit.*) are thus confirmed, but the mechanism of the oxidation of the former to the latter remains obscure. R. S. C.

Colour and chemical constitution. Effect of auxochromic groups on phthalophenone (lactone of triphenylcarbinol-o-carboxylic acid). N. Ghatak (Bull. Acad. Sci. U.P., Allahabad, 1933, **2**, 253—258).—Condensation with H_2SO_4 of *p*-hydroxybenzoylbenzoic acid with the appropriate phenol has given the following: 4 : 4'-*di*-, m.p. 252°, 4 : 4' : 5'-*tri*-, m.p. 148—149°, 4 : 4' : 6'-*tri*-, m.p. 164°, 4 : 3' : 6'-*tri*-, m.p. 153—155°, 4 : 3' : 4' : 5'-*tetra*- m.p. 147—148°, and 4 : 2' : 4' : 6'-*tetra-hydroxy*-, m.p. 256°; 4 : 4'-*dihydroxy*-5'-*methyl*-, m.p. 117°, -6'-*methyl*-, m.p. 131°, -6'-*methyl*-3'-iso*propyl*-, m.p. 231—232°, and -3'-*methyl*-6'-iso*propyl*-, m.p. 178—179°, 4 : 6'-*dihydroxy* -*methyl*-, m.p. 135°, -4'-*dimethylamino*-, m.p. 142°, and -*diethylamino-phthalophenone*, m.p. 93; also 4-*hydroxydiphenyl*-4'-*hydroxy*-α-*naphthyl*-, m.p. 171°, -2'-*hydroxy*-α-*naphthyl*-, m.p. 153°, and -2' : 7'-dihydroxy-α-naphthyl-, m.p. 261°, -*carbinol*-2''-*carboxylic lactone*. The substances afford reddish-violet solutions in aq. NaOH, blue in the case of the α-naphthol derivative. Absorption max. are given. F. R. S.

Aminoguanidine derivatives. (Miss) V. A. Conard and R. L. Shriner (J. Amer. Chem. Soc., 1933, **55**, 2867—2870).—Aminoguanidine (modified prep.) and *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ give *ωω-di(guanidinamino)dimethyl-p-toluidine*, *p*-$NMe_2{\cdot}C_6H_4{\cdot}CH[NH{\cdot}NH{\cdot}C(:NH){\cdot}NH_2]_2$, $+H_2O$, m.p. 178—179° (*hydrochloride*), and p-*dimethylaminobenzylideneaminoguanidine*, $+2H_2O$ (lost at 105°), m.p. 149° [*hydrochloride*, $+2H_2O$, m.p. 210° (decomp.); *dihydrochloride*, m.p. 221—227° (decomp.)]. The salts have no hypoglycæmic action. R. S. C.

Phenanthrene series. III. Hydroxy-aldehydes and -ketones. E. Mosettig and A. Burger. **IV. Phenanthrene-2-, -3-, and -9-aldehydes.** E. Mosettig and J. van de Kamp (J. Amer. Chem. Soc., 1933, **55**, 2981—2989, 2995—2999; cf. A., 1932, 1029).—III. The structures of 2-hydroxyphenanthrene-1-aldehyde, m.p. 172—173° (*Schiff's base*, m.p. 160—161°), and 9-hydroxyphenanthrene-10-aldehyde, m.p. 133—134° (*Schiff's base*, m.p. 160—161°), are confirmed by oxidation (Dakin–Barger and H_2O_2–O_2, respectively) to 1 : 2-dihydroxyphenanthrene and phenanthraquinone, respectively. 3-Acetoxyphenanthrene is decomposed by $AlCl_3$ or $AlBr_3$, but with $AlCl_3$ and AcCl (1 mol.) in $PhNO_2$ gives a 30% yield of 3-*acetoxy-*(? 6- or 7-)*acetylphenanthrene*, m.p. 155° (*semicarbazone*, m.p. 218°; -9 : 10-*quinone*, m.p. 206—208°), also obtained from 3-hydroxyphenanthrene, AcCl (2 mols.), and $AlCl_3$, leading to a 3-*hydroxyacetylphenanthrene*, m.p. 180—181° [*Me ether*, m.p. 106—107° (*semicarbazone*, m.p. 203—205°)], and a 3-*methoxyphenanthrenecarboxylic acid* (this and all the acids prepared from ketones are obtained by NaOCl), m.p. 238—239° (*Me* ester, m.p. 125—126°). Arguments are presented confirming the structure assigned to 3-hydroxyphenanthrene-2-carboxylic acid. 3-Methoxyphenanthrene gives (Friedel–Crafts) a 3-*methoxyacetylphenanthrene*, m.p. 98—99° (*semicarbazone*, m.p. 217—219°), affording a 3-*methoxyphenanthrenecarboxylic acid*, m.p. 200° (*Me* ester, m.p. 81·5—82·5°). Fries rearrangement of 2-acetoxyphenanthrene (I) and the Friedel–Crafts reaction with 2-hydroxy- or 2-methoxy-phenanthrene (*A*) give 2-*methoxy*-1-*acetylphenanthrene*, m.p. 175—176°, oxidised to 2-*methoxyphenanthrene*-1-*carboxylic acid*, m.p. 244—246° (decomp.) [*Me* ester, m.p. 145—146°, also obtained from 2-*methoxyphenanthrene*-1-*aldehyde*, m.p. 160° (*semicarbazone*, m.p. 300—315°)], identical with Werner's "2-hydroxyphenanthrene-3-carboxylic acid" (A., 1903, i, 173). However, the Friedel–Crafts reaction with 2-acetoxyphenanthrene gives a 2-*acetoxyacetylphenanthrene*, m.p. 120—122·5° [-9 : 10-*quinone*, m.p. 238—240° (decomp.)], leading to a 2-*hydroxyacetylphenanthrene*, m.p. 186° [*Me ether*, m.p. 117° (*semicarbazone*, m.p. 241—242°)], and a 2-*methoxyphenanthrenecarboxylic acid*, m.p. 251—252° (*Me* ester, m.p. 79—80°). Reaction *A* leads also to a little 2-*methoxyacetylphenanthrene*, m.p. 132—133° (*semicarbazone*, m.p. 223°). The Fries rearrangement of 9-acetoxyphenanthrene (II) and the Friedel–Crafts reaction with 9-hydroxyphenanthrene (III), m.p. 155°, give 9-*hydroxy*-10-*acetylphenanthrene*, m.p. 96° [rearranges to a second *form*, m.p. 101·5—102°, when melted; *Me ether*, an oil (*picrate*)], oxidised by CrO_3 to 9 : 10-phenanthraquinone. (II) and (III) with 1 and 2 mols., respectively, of AcCl give, however, 9-*hydroxy*-10 : 3-(or : 6-)-*diacetylphenanthrene*, m.p. 175·5—176·5° (*Me ether*, m.p. 111·5—112·5°), oxidised to 3-acetyl-9 : 10-phenanthraquinone. The following are also described: 3-*methoxy-*, m.p. 80° [*semicarbazone*, m.p. 237—239° (decomp.)], and 3-*acetoxy-phenanthrene*-4-*aldehyde*, m.p. 98—99°; 9-*methoxyphenanthrene*-10-*aldehyde*, m.p. 79—81° (*semicarbazone*, m.p. 211°); 3-*methoxyphenanthrene*-4-*carboxylic acid*, m.p. 153—154° (decomp.) (*Me* ester, m.p. 122°), prepared from the aldehyde; 3-*hydroxyphenanthrene*-4-*carboxylic acid*, m.p. 125° (decomp.) (loses CO_2 quantitatively at 130° [*Ac* derivative, $+H_2O$ (lost at 95° in vac.), m.p. 105—115°, anhyd., m.p. 162—163° (decomp.); *Me ether* of *Me* ester, m.p. 133—133·5°]; and 9-*methoxyphenanthrene*-10-*carboxylic acid*, m.p. 113°, prepared from the aldehyde.

IV. Hydrogenation (Pd–$BaSO_4$ in decahydronaphthalene) of *phenanthroyl*-2-, m.p. 101—101·5°, -3-, and -4-*chlorides* gives *phenanthrene*-2-, m.p. 59—59·5°, -3-, m.p. 79·5—80°, and -4-*aldehyde*, m.p. 100·5—101° (*oximes*, m.p. 194—195°, 145—145·5°, and 157—157·5°; *semicarbazones*, m.p. 281—282°, 274—275°, and 221—222°, respectively), reduced (PtO_2 in EtOH) to 2-, m.p. 125—125·5°, 3-, m.p. 103—103·5° (*benzoate*, m.p. 84·5—85°), and 4-*phenanthrylmethyl alcohol*, m.p. 149—149·5°, whence the corresponding *bromides*, m.p. 111—111·5°, 114·5—115°, and 103—103·5°, and *cyanides*, m.p. 106—106·5°, 84·5—85°, and 96·5—97°, respectively, were obtained. Hydrolysis of the cyanides by 25% KOH–EtOH gives 2-, m.p. 183·5—184·5° (*Me* ester, m.p. 78—78·5°), 3-, m.p. 177—177·5° [*Me* ester, an oil (*picrate*, m.p. 103·5—104°)], and 4-*phenanthrylacetic acid*, m.p. 220—221° (*Me* ester, m.p. 75—75·5°). R. S. C.

Poly-membered ring systems. I. Synthesis of polymethylene ketones with more than six-membered rings. K. Ziegler, H. Eberle, and H. Ohlinger (Annalen, 1933, **504**, 94—130).—Successive addition of $NHEt_2$ and MeCN to 1·06*N*-LiPh in Et_2O at −10° and decomp. of the product with H_2O affords $CH_2Ac{\cdot}CN$ in 86% yield. Similarly $Pr^{\alpha}CN$ and $LiNEt_2$ afford *α-butyrylbutyronitrile* (I), b.p. 96°/11 mm., in 71·5% yield, hydrolysed by 70% H_2SO_4 to $COPr^{\alpha}_2$ (semicarbazone, m.p. 133°). (I) is obtained in 90% yield from $Pr^{\alpha}CN$ and LiNPhEt (from LiBu and NHPhEt) in Et_2O. Sebaconitrile (II) and $LiNEt_2$ in conc. solution give a 13% yield of *cyanocycloheptanone* (III), b.p. 140—141°/12 mm. (*semicarbazone*, m.p. 162°), hydrolysed by conc. H_2SO_4 or 48% HBr to suberone in poor yield. In more dil. solution and with apparatus to ensure the invariable ratio 1 : 1 of reactants, the yield rises to 71%. (III) is unusually readily hydrolysed by NaOH to the *Na* salt of sebacoheminitrile. A 90% yield of (III) is obtained from (II) and LiNPhEt. In special apparatus, azelaodinitrile is transformed into *cyanocyclooctanone*, b.p. 158—160°/13 mm., m.p. 55—56° (*semicarbazone*, m.p. 161°), readily hydrolysed by 48% HBr to *cyclo*octanone (semicarbazone, m.p. 167—168°) and 2 : 9-*dicyano*-1 : 8-*diketocyclohexadec-*

ane, m.p. 171°, hydrolysed to 1 : 8-diketo*cyclo*hexadecane, m.p. 83—84° (dioxime, m.p. 185—186°). Treatment of αζ-dicyanotetradecane with $LiNEt_2$ and subsequently with H_2O and 20% H_3PO_4 leads to *dicyanodi-iminocyclotriacontane* (hydrolysed to *cyclo*triacontanedione) and *cyanocyclopentadecanoneimine*, m.p. 142° (yield 30—40%), hydrolysed by boiling dil. H_2SO_4 to *cyclo*pentadecanone, b.p. 120°/0·1 mm. In like manner are prepared *cyanocyclo-heptadecanoneimine*, m.p. 108—109° [hydrolysed by 70% H_2SO_4 to *cyclo*heptadecanone (dihydrocivetone)], and *tetratriacontane-αζ-dione*, m.p. 84°. H. W.

Beckmann change. I. Spontaneous rearrangement of oxime picryl ethers. A. W. Chapman and C. C. Howis (J.C.S., 1933, 806—811).—*Benzophenoneoxime benzoate*, m.p. 99°, gives on heating dibenzanilide; *benzophenoneoxime* o-*nitrobenzoate*, m.p. 185—188°, chars. *Benzophenoneoxime picryl ether*, m.p. 103—105°, rearranges to benz-*N*-picrylanilide on heating alone or in a solvent. *Acetophenoneoxime picryl ether*, m.p. 112°, rearranges to *acet*-N-*picrylanilide*, m.p. 198°; p-*chlorobenzophenone-α-oxime picryl ether*, m.p. 117°, forms p-*chlorobenz*-N-*picrylanilide*, m.p. 223—224°, whilst the -β-*oxime*, m.p. 109—110°, yields *benz*-N-*picryl*-p-*chloroanilide*, m.p. 208—210°. Similar rearrangements have been obtained: *benzophenoneoxime* 2 : 4 : 6-*trinitro*-m-*tolyl ether*, m.p. 127° [*benz*-2 : 4 : 6-*trinitro*-m-*tolylanilide*, m.p. 255° (decomp.)]; *di*-p-*tolylketoxime picryl ether*, m.p. 106—107° (p-*toluo*-N-*picryl*-p-*toluidide*, m.p. 166—169°), and 2 : 4 : 6-*trinitro*-m-*tolyl ether*, m.p. 114° (p-*toluo*-2 : 4 : 6-*trinitro*-m-*tolyl*-p-*toluidide*, m.p. 144° and 168—170°); *di*-p-*chlorophenylketoxime picryl ether*, m.p. 129° (p-*chlorobenz*-N-*picryl*-p-*chloroanilide*, m.p. 194—195°), and 2 : 4 : 6-*trinitro*-m-*tolyl ether*, m.p. 129° (p-*chlorobenz*-2 : 4 : 6-*trinitro*-m-*tolyl*-p-*chloroanilide*, m.p. 166—168°); and p-*chloroacetophenoneoxime picryl ether*, m.p. 133° (p-*chloro*-N-*picrylacetanilide*, m.p. 191°). The velocity of the rearrangements changes with the solvent, indicating that the rearrangements are probably intramol. F. R. S.

Reaction of aromatic ketones with sodium. II. Reactions of sodium pinacolates. W. E. Bachmann (J. Amer. Chem. Soc., 1933, **55**, 2827—2830; cf. this vol., 505).—Na_2 pinacolates (prepared from Na and $COPh_2$, *p*-$C_6H_4Ph{\cdot}COPh$, or fluorenone) in Et_2O–C_6H_6 with MgX_2 or MgRX (X=halogen) give red solutions of the MgX-derivatives of the pinacols, which with H_2O afford 80—90% yields of pinacols. $(\cdot CHPh_2{\cdot}ONa)_2$ does not react with NaPh. The preps. of $HgPh_2$ and NaPh are modified. R. S. C.

Grignard reaction in the synthesis of ketones. III. Preparation and characterisation of a series of mono- and di-chlorodeoxybenzoins. S. S. Jenkins (J. Amer. Chem. Soc., 1933, **55**, 2896—2899; cf. this vol., 610).—The benzyl Grignard reagents (3 mols.) and appropriate amides afford *Ph* m-*chlorobenzyl ketone*, m.p. 43° (101—102°), m-*chlorophenyl benzyl*, m.p. 62° (120°), m-, o-, and p-*chlorobenzyl*, m.p. 65°, 71°, and 74·5° (103—104°, 130·5—131·5°, and 100°), respectively, *ketones*, o-*chlorophenyl* m-*chlorobenzyl ketone*, b.p. 185—190°/6 mm. (86—87°), and p-*chlorophenyl* m-*chlorobenzyl ketone*, m.p. 75·5° (127—128°), the m.p. in parentheses being those of the anti-(benzyl)-*oximes*, which rearrange to the following anilides, also prepared from the appropriate acid and basic components: m-*chlorophenylacetanilide*, m.p. 130°, *phenylaceto*-m-*chloroanilide*, m.p. 95°, m-*chlorophenylaceto*-m-, -o-, and -p-*chloroanilide*, m.p. 120°, 120°, and 150·5°, respectively, and o- and p-*chlorophenylaceto*-m-*chloroanilide*, m.p. 154° and 137·5°, respectively. *m*-$C_6H_4Cl{\cdot}CH_2Br$, b.p. 103—105°/8 mm., m.p. 15—15·5°, is prepared from *m*-C_6H_4ClMe and Br in CCl_4 at 60—80° in light, and m-*chlorophenylacetic acid*, m.p. 77·5—78·5°, from *m*-$C_6H_4Cl{\cdot}CH_2{\cdot}MgBr$. All m.p. are corr. R. S. C.

True nature of a so-called dihydropyrocatechol. G. Dupont and E. Urion (Compt. rend., 1933, **197**, 158—159).—The "dihydropyrocatechol," obtained from the sol. tar of pine (B., 1931, 467), has been identified as 3-methyl*cyclo*pentane-1 : 2-dione in its enolic form. F. R. S.

Strainless monocyclic rings. M. Qudrat-i-Khuda (Nature, 1933, **132**, 210).—Direct reduction (Clemmensen) of dimethyldihydroresorcinol gives a second isomeric ketone (semicarbazone, m.p. 162°), supporting the view of a strain-free configuration of the substituted *cyclo*hexane ring. L. S. T.

Syntheses of ketones by means of mixtures of acids and acid anhydrides. I. F. Unger (Annalen, 1933, **504**, 267—286).—Examination of the action of various acids and anhydrides on PhOMe (I) and PhOEt (II) shows that org. acids resemble certain metallic halides and inorg. acids in their ability to activate the condensation of other org. acids with unsaturated compounds with production of ketones; one or both org. acids must be in the form of anhydride. If both acids are free, aromatic compounds do not react, whereas aliphatic and hydroaromatic unsaturated substances pass into the corresponding saturated esters. Production of ketones depends on the temp., particularly on the strength of the activating acid and the character of the unsaturated compound. An exact parallelism between the activation and the dissociation const. of the activating acid cannot be drawn. No generalisation can be made between the relative strengths of the activating and reacting acids and the rate of reaction, nor can it be foretold which acid will react, although in most cases the acyl of the acid with the smaller dissociation const. is introduced. The reverse is the case when *o*-substituted or inorg. acids are used.

In general, (I) or (II) is heated with acid and anhydride (mol. ratio 1 : 1 : 2) at 170—180°. The following p-*anisyl ketones* are described: *Me*, b.p. 133—134°/10 mm., 256—258°/755 mm., m.p. 38·5° (*semicarbazone*, m.p. 196·5°; p-*nitrophenylhydrazone*, m.p. 195—195·5°); *Et*, b.p. 148—149°/15 mm., m.p. 27° (*semicarbazone*, m.p. 172°; p-*nitrophenylhydrazone*, m.p. 149—150°); Pr^{β}, b.p. 152·5—153°/16 mm.; Bu^{β}, b.p. 158·5—159·5°/12 mm. (*semicarbazone*, m.p. 203·5°); CH_2Ph, b.p. 221—222°/11 mm., m.p. 77—78° (p-*nitrophenylhydrazone*, m.p. 157·5°); Pr^{α}, b.p. 152—153°/12 mm. (*semicarbazone*, m.p. 173·5°); n-*amyl*, b.p. 172—174°/14 mm. (*semicarbazone*, m.p. 142·5°); α-*ethylpropyl*, b.p. 168—170°/14 mm., and

α-*propyl*-n-*butyl*, b.p. 183—186°/13 mm., which do not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ or p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$; *pentadecyl*, m.p. 75°; Δ^9-*heptadecenyl*, m.p. 43°; *benzhydryl*, m.p. 130°, from (I), $CHPh_2{\cdot}CO_2H$, and $(CH_2Cl{\cdot}CO)_2O$ or (I), $CPh_2{:}CO$, and $CH_2Cl{\cdot}CO_2H$; CPh_3, m.p. 200·5°; Ph, m.p. 61—62° (p-*nitrophenylhydrazone*, m.p. 198—199°); o-C_6H_4Me, b.p. 202—204°/13 mm.; p-$C_6H_4{\cdot}OMe$, m.p. 146°; o-C_6H_4Br, b.p. 226—229°/10 mm., m.p. 96°; p-C_6H_4Br, m.p. 160—161°; o-C_6H_4Cl, b.p. 209—211°/9 mm., m.p. 84·5°; α-$C_{10}H_7$, m.p. 101·5—102°; 2 : 4 : 6-$C_6H_2Br_3$, m.p. 149—150°. (II), $CH_2(CO_2H)_2$, and Ac_2O at 120° and then at 150—160° afford p-*ethoxyphenyl Me ketone*, b.p. 145·4—145·8°/13 mm., 268—269°/758 mm., m.p. 37—38° (*semicarbazone*, m.p. 181·5°; p-*nitrophenylhydrazone*, m.p. 211°). (I), β-phenylpropionic acid, and $(CH_2Cl{\cdot}CO)_2O$ at 170° yield 1-hydrindone, b.p. 127—129°/20 mm., m.p. 41—42°, whilst ββγ-triphenylpropionic acid similarly affords p-anisyl CH_2Cl ketone and 3 : 3-*diphenyl*-1-*hydrindone*, m.p. 121° (p-*nitrophenylhydrazone*, m.p. 234°). (I), PhCHO, and $CH_2Cl{\cdot}CO_2H$ at 160° yield 4 : 4′-*dimethoxytriphenylmethane*, b.p. 242—246°/11 mm., m.p. 101·5°, whereas (I), benzhydrol, and $CH_2Cl{\cdot}CO_2H$ at 170—180° give 4-methoxytriphenylmethane, b.p. 235—236°/16 mm., m.p. 63°, and a *substance* $C_{38}H_{28}O$, m.p. 147—148°. H. W.

Synthesis of hydroxyphenyl α-bromoethyl ketones. C. Torres and J. Amargós (Anal. Fís. Quím., 1933, **31**, 37—47).—By heating the product obtained by fusing phenol and $AlCl_3$, with EtCOCl at 125—130°, and treatment with dil. HCl, a mixture of *o*- and *p*-hydroxypropiophenones (2 : 4-*dinitrophenylhydrazones*, m.p. 229° and 189°, respectively; *semicarbazone* of *o*-derivative, m.p. 221°) is obtained. Analogously, with CHMeBr·COBr, there are obtained o-, m.p. 32°, b.p. 143—147°/18 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 143—144°), and p-*hydroxyphenyl* α-*bromoethyl ketone*, m.p. 81° [2 : 4-*dinitrophenylhydrazone*, m.p. 147° (decomp.); *benzoate*, m.p. 87°]. Interaction of pyrocatechol, $POCl_3$, and $CHMeCl{\cdot}CO_2H$ or $CHMeBr{\cdot}CO_2H$ yields only small amounts of the α-halogenated 3 : 4-dihydroxypropiophenones. Pyrocatechol dipropionate, m.p. 25—26°, yields with Br in AcOH the di-α-bromopropionate, m.p. 62°, b.p. 220—227°/18 mm. An attempt to convert the latter into the α-bromoethyl ketone by treatment with $AlCl_3$ and pyrocatechol in $PhNO_2$ resulted in the formation of only a trace af ketone. 3 : 4-Dihydroxypropiophenone (2 : 4-*dinitrophenylhydrazone*, m.p. 226°) yields with Br in AcOH the α-Br-compound. R. K. C.

Reformatsky reaction with anisil. J. W. Cook and W. Lawson (J.C.S., 1933, 827—829).—Anisil, $CH_2Br{\cdot}CO_2Et$, and Zn give *Et* ββ′-*dihydroxy-dianisyladipate*, m.p. 153—154°, which on reduction (Hg–Zn) forms an *acid*, $C_{20}H_{22}O_6$, m.p. 248—249° (*Me* ester, m.p. 108—109°), and an *acid*, $C_{19}H_{22}O_4$, m.p. 160·5—161·5° (*Me* ester, m.p. 99—100°). The reaction also yields a resin, reduced to an *acid*, $C_{18}H_{20}O_4$, m.p. 167—168° (*Me* ester, m.p. 63—64°), due to the condensation of one CO group only of anisil. F. R. S.

Synthesis of isomeric unsymmetrical benzoins. S. S. Jenkins (J. Amer. Chem. Soc., 1933, **55**, 3048).—Ph p-methoxybenzyl ketone and Br in CCl_4 in light give desyl bromide, which with NaOEt yields *Ph* α-*hydroxy*-p-*methoxybenzyl ketone* (*anisbenzoin*), m.p. 89°, rearranged by KCN–EtOH to benzanisoin. R. S. C.

Preparation of ninhydrin (triketohydrindene hydrate). W. O. Teeters and R. L. Shriner (J. Amer. Chem. Soc., 1933, **55**, 3026—3028).—1 : 3-Diketohydrindene (I) (modified prep. from Et_2 phthalate and EtOAc) and SeO_2 in aq. dioxan give a 31—35% yield of ninhydrin (II). Aq. $Ce(SO_4)_2$ and (I) gave a resin. (I) with HNO_2 gives *triketohydrindene-2-oxime*, m.p. 200—201° (decomp.), resistant to hydrolysis, and condenses with p-$NO{\cdot}C_6H_4{\cdot}NMe_2$ to a product, whence (II) could not be obtained. R. S. C.

Resorcinol ketones and *C*-alkylresorcinols. K. W. Rosenmund, R. Buchwald, and T. Deligiannis (Arch. Pharm., 1933, **271**, 342—352).—5-Ethylresacetophenone, m.p. 117—118° (lit. 115°), is obtained from 4-ethylresorcinol diacetate (I) and $AlCl_3$ (slightly > 2 mols.) at 40—50° (47% yield) or from (I), 4-ethylresorcinol (II), and $AlCl_3$ in $PhNO_2$ first at room temp. and then at 50—60° (method *A*) (nearly quant. yield). 2 : 6-*Diacetyl*-4-*ethylresorcinol*, m.p. 74°, is prepared from (I) and $AlCl_3$ alone at 110° or in $PhNO_2$ at 60—70° (50% yield). Similarly are prepared 6-*propionyl*-, m.p. 67·5° (*phenylhydrazone*, m.p. 170°), -*butyryl*-, m.p. 100° (*phenylhydrazone*, m.p. 142·5°), -*valeryl*-, m.p. 92°, b.p. 220°/9 mm. (*phenylhydrazone*, m.p. 125—126°), -*hexoyl*-, b.p. 220—225°/10 mm., m.p. 93—94° (*phenylhydrazone*, an oil), -*benzoyl*-, m.p. about 63—64°, and 2 : 6-*dipropionyl*-, m.p. 81°, -4-*ethylresorcinol*, and 6-*acetyl*-, m.p. 108—109°, -*propionyl*-, m.p. 73—74°, b.p. 190—195°/9·5 mm. (*phenylhydrazone*, m.p. 143—144°), -*butyryl*-, m.p. 64°, b.p. 190°/9 mm. (*phenylhydrazone*, m.p. 139—140°), -*valeryl*-, b.p. 205°/9·5 mm., m.p. 85° (*phenylhydrazone*, an oil), -*hexoyl*-, m.p. 53°, b.p. 225—230°/9 mm. (*phenylhydrazone*, an oil), -*benzoyl*-, m.p. 138—140°, b.p. 240—245°/9 mm., and 2 : 6-*diacetyl*-, m.p. 64—65°, -4-*propylresorcinol*. Thence by Clemmensen or catalytic (Pd–$BaSO_4$) reduction are obtained: 4 : 6-diethylresorcinol; 4-*ethyl*-6-*propyl*-, m.p. 65°, b.p. 170—175°/11 mm., -6-*butyl*-, b.p. 220°/9 mm., -6-*amyl*-, b.p. 220°/11 mm., -6-*hexyl*-, b.p. 215°/11 mm., -2 : 6-*dipropyl*-, b.p. 195°/9 mm., 6-*benzyl*-4-*propyl*-*resorcinol*, b.p. 220°/9 mm.; 2 : 6-*diethyl*-4-*propyl*-, b.p. 195°/11 mm., 4-*propyl*-6-*butyl*-, b.p. 200°/13 mm., -6-*amyl*-, b.p. 195—200°/14 mm., -6-*hexyl*-, b.p. 210—215°/14 mm., and 6-*benzyl*-4-*ethyl*-, b.p. 230—235°/9 mm., -*resorcinol*. The appropriate diacylresorcinols and slightly > 2 mols. of $AlCl_3$ at 70—130° (not higher) give 2 : 4-*diacetyl*- (III), m.p. 88—89°, b.p. 170—172°/26 mm., -*dipropionyl*- (IV), m.p. 78—79°, b.p. 184—185°/24 mm., -*dibutyryl*-, b.p. 190°/20 mm., and -*divaleryl*-, b.p. 196°/20 mm., -*resorcinol*. Method *A* is generally better than the usual modification, in accordance with the view that the rearrangement is a bimol. process. Clemmensen reduction of (III) gives (II); catalytic reduction (Pd in AcOH at 3 atm.) gives

2-*acetyl*-4-*ethylresorcinol*, m.p. 127° (*phenylhydrazone*, m.p. 147), giving (II) by Clemmensen reduction. (IV) affords similarly 4-propylresorcinol and 2-*propionyl*-4-*propylresorcinol*, m.p. 92° (*phenylhydrazone*, m.p. 124°). R. S. C.

Constituents of *Filix mas*. I. Aspidinol. A. Robertson and W. F. Sandrock (J.C.S., 1933, 819—823).—2 : 6-*Dinitro*-4-*ethoxytoluene*, m.p. 108—109°, prepared by ethylation of 2 : 6-dinitro-*p*-cresol, is reduced ($SnCl_2$–HCl) to 6-*nitro*-4-*ethoxy*-o-*toluidine*, m.p. 89—90° (*Ac* derivative, m.p. 192—193°), which gives the corresponding *-cresol*, m.p. 117—118°, ethylated to 2-*nitro*-4 : 6-*diethoxytoluene*, m.p. 103°. This is reduced (Na_2S) to 4 : 6-*diethoxy*-o-*toluidine* (*Ac* derivative, m.p. 134—135°), the sulphate of which with $NaNO_2$–H_2SO_4 forms C-*methylphloroglucinol* α-*Et*$_2$ *ether*, m.p. 64—65°. The ether and *n*-butyronitrile condense to 2-*hydroxy*-4 : 6-*diethoxy*- (I), m.p. 103·5—104·5° (*acetate*, m.p. 82—83°), and 4-*hydroxy*-2 : 6-*diethoxy*-3-*methyl*-n-*butyrophenone*, m.p. 68°. (I) is identical with monoethylaspidinol, and with Ac_2O and NaOAc forms 5 : 7-*diethoxy*-2 : 8-*dimethyl*-3-*ethylchromone*, m.p. 140—141°.

Methylation of 6-nitro-4-ethoxy-*o*-cresol gives the *Me ether*, m.p. 89—90°, reduced to 6-*methoxy*-4-*ethoxy*-o-*toluidine* (*Ac* derivative, m.p. 132—133°), which forms the *-cresol* (+H_2O), m.p. 52°. The cresol condenses with *n*-butyronitrile to 2-*hydroxy*-4-*methoxy*-, m.p. 114—115° (*acetate*, m.p. 72—73°), and 4-*hydroxy*-2-*methoxy*-6-*ethoxy*-3-*methyl*-n-*butyrophenone*, m.p. 59°, the former giving 7-*methoxy*-5-*ethoxy*-2 : 8-*dimethyl*-3-*ethylchromone*, m.p. 132—133°, with Ac_2O and NaOAc. Aspidinol (2 : 6-dihydroxy-4-methoxy-3-methylbutyrophenone), m.p. 143° (*diacetate*, m.p. 68°), is obtained by condensation of methylphloroglucinol β-Me ether and *n*-butyronitrile, identical with a natural specimen. Methylation of *C*-methylphloro-*n*-butyrophenone with MeI–K_2CO_3 or CH_2N_2 gives 2-*hydroxy*-4 : 6-*dimethoxy*-3-*methyl*-n-*butyrophenone*, m.p. 111—112° (*acetate*, m.p. 61—62°), which cyclises to 5 : 7-*dimethoxy*-2 : 8-*dimethyl*-3-*ethylchromone*, m.p. 171—172°. F. R. S.

Anthraquinone derivatives. II. Chloroaminoanthraquinones. M. Hayashi and A. Nakayama (J. Soc. Chem. Ind. Japan, 1933, **36**, 202—204B).—Comparison of absorption spectra with those of 4- and 5-amino-2-benzoylbenzoic acids indicates that the NH_2-compounds, m.p. 192° and 225·5—226° (this vol., 612), are the 5- and 4-NH_2-derivatives, respectively. The corresponding 5-, m.p. 198°, and 4-NO_2-derivatives, m.p. 194—194·5°, are also obtained from the chloride (I) of 1-Me 4-nitrophthalate with PhCl and $AlCl_3$, together with (?) *nitro*-3 : 4-*di*-p-*chlorobenzoylbenzene*, m.p. 177·5—178·5°. (I) with conc. NH_3 gives 4-nitrophthaldiamide. A. A. L.

Scission of aloin. E. Léger (J. Pharm. Chim., 1933, [viii], **18**, 25—26).—A discussion (cf. Rosenthaler, A., 1932, 516). W. O. K.

Mechanism of the formation of α-terpineol from linalool. R. Horiuchi (J. Soc. Chem. Ind. Japan, 1933, **36**, 191—193B).—A study of the products of reaction of AcOH–H_2O, AcOH, and Ac_2O under various conditions with linalool, geraniol, and nerol leads to the conclusion that the first products in the above rearrangements are geraniol and nerol, the latter then forming terpineol. A. A. L.

Raman effect in terpenes. IV. Terpinenes and terpinolene. G. Dupont, J. Levy, and (Mlle.) Marot (Bull. Soc. chim., 1933, [iv], **53**, 393—406; cf. this vol., 337).—Terpineol and aq. $H_2C_2O_4$ (I) at 100° give cineole (II) (40%), dipentene (III), α- (IV), and γ- (V) -terpinene, terpinolene (VI), and constituents *T* and *U* (obtained also from pinene). With Al_2O_3 it gives (VI), (IV), limonene (VII), and (II) (trace), and with 80% HCO_2H (II) (40%), (VI), (III), (IV), *T*, and *Z*. Terpin and anhyd. (I) give (II) (11%), (IV), (III), *T*, and *Z*. α-Terpenyl acetate at 80—90° gives (IV), (VII), and possibly (VI). Dipentene hydrochloride and NH_2Ph give pure (III); terpinene dihydrochloride (VIII) gives (II) and nearly pure (IV). (VIII), from commercial terpinolene, gives (III), (IV), and traces of (VI). (II) and aq. (I) give slowly (IV), (V), and a little *T*. R. S. C.

Terpenes, sesquiterpenes, and related compounds. I. Silicon compounds of menthol and the refractivity of silicon. S. Uchida and T. Kondo (J. Soc. Chem. Ind. Japan, 1933, **36**, 190—191B).—$SiCl_4$ with the calc. amounts of menthol gives *monomenthoxysilicon trichloride*, b.p. 112—113°/9 mm., *dimenthoxysilicon dichloride*, b.p. 193°/8 mm., *trimenthoxysilicon monochloride*, b.p. 244—245°/10 mm., and *tetramenthoxysilicon*, m.p. 93°, b.p. 264°/7 mm. The at. refractivity of Si found from the three first of these is 5·114. A. A. L.

Picrocrocin, the terpene-glucoside of saffron, and the biogenesis of carotenoid carboxylic acids. R. Kuhn and A. Winterstein (Naturwiss., 1933, **28**, 527).—Picrocrocin (I), $C_{16}H_{26}O_7$, $[\alpha]_D$ −58° in H_2O [*Ac*$_4$ derivative, $C_{24}H_{34}O_{11}$, m.p. 143° (*semicarbazone*, $C_{25}H_{37}O_{11}N_3$, m.p. 105°)], is decomposed by acids or alkalis without addition of H_2O to glucose (1 mol.) and *safranal* (II), C_9H_{13}·CHO (1 mol.). (II) is monocyclic, with two double linkings; it is oxidised by $KMnO_4$ to [·CHMe·CO_2H]$_2$ and AcOH and by controlled catalytic hydrogenation yields β-*cyclo*citral. Autoxidation produces β-*cyclo*geranic acid. (II) is therefore a *dihydro*-β-cyclo*citral* ($\Delta^{1:5}$-m-*terpadien*-2-*al*). (I), which gives no CH_2O with $Pb(OAc)_4$, is considered to be 5-β-*glucosido*-Δ-1-m-*terpen*-2-*al*. As (I) is regarded as an oxidative degradation product of carotenoid carboxylic acids, the above ring structure is assumed to be present in the latter. R. N. C.

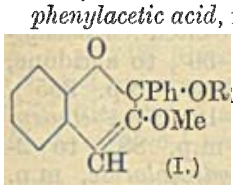
Stability of the tetrahydrofuran ring. I. Fission of the oxide linking in tetrahydrofurfuryl alcohol. Derivatives of αβε-trihydroxypentane. R. Paul (Bull. Soc. chim., 1933, [iv], **53**, 417—426).—Partly a detailed account of work already published (this vol., 397). Tetrahydrofurfuryl bromide and powdered KOH give 2-*methylenetetrahydrofuran*, b.p. 82—83°, immediately hydrolysed by 2*N*-H_2SO_4 to OH·[CH_2]$_3$·COMe, b.p. 115—117°/29 mm. (*semicarbazone*, m.p. 155—157°). R. S. C.

Orientation in the furan nucleus. VI. β-Substituted furans. H. Gilman and R. R. Burtner (J. Amer. Chem. Soc., 1933, **55**, 2903—2909; cf.

this vol., 505).—The prep. of Me coumalate, Me bromocoumalate, and furan-2 : 4-dicarboxylic acid (I) is described. (I) with Cu-bronze at 285° gives 3-furoic acid (II), identical with the natural product [*acid chloride* (III), b.p. 65°/47 mm., m.p. 29°; *amide*, m.p. 169°], the *Et* ester, b.p. 65—67°/14 mm., of which is nitrated (here, as below, by fuming HNO_3 in Ac_2O at —15°) to *Et* 2-*nitro*-4-*furoate*, m.p. 56°, hydrolysed to the corresponding *acid*, m.p. 138°, also obtained by nitration of (II). (II) and Br in $CHCl_3$ give 2-*bromo*-4-*furoic acid*, m.p. 130°, also obtained from (I) by way of the HgCl-compound. The Me_2 ester of (I) with Br at 160° gives an ester, hydrolysed to 5-*bromofuran*-2 : 4-*dicarboxylic acid*, m.p. 250°, reduced to (I) by Zn dust and hot, aq. NH_3, and giving by way of the HgCl-compound 2-*bromo*-3-*furoic acid*, m.p. 158°. Hydrogenation of (III) yields 3-*furfuraldehyde* (IV), b.p. 70—72°/43 mm., 144°/732 mm. (*phenylhydrazone*, m.p. 149·5°), nitrated to 2-*nitro*-4-*furfurylidene diacetate*, m.p. 87°. Nitration of the *diacetate*, m.p. 50°, b.p. 130°/15 mm., of (IV) gives an oil, hydrolysed by acid to 2-*nitro*-4-*furfuraldehyde*, m.p. 76°, the *hydrazone*, m.p. 122° (decomp.), of which affords (Wolff–Kishner) 3-methylfuran (2-*HgCl*-compound, m.p. 142°), nitrated to 2-nitro-3-methylfuran. These reactions allow formulation of the following rules for the substitution of β-substituted furans: if the group in the β-position is *o*-*p*-directing in the C_6H_6 series, the substituent enters the contiguous α-position; if it is *m*-directing, the more remote α-position is substituted.

R. S. C.

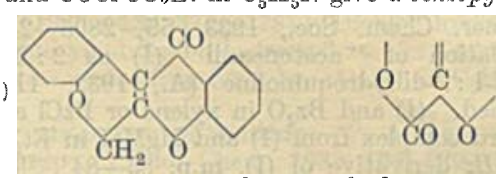
Pyrenium salts. XX. Oxidation of pyrenium salts. W. Dilthey and W. Hoschen (J. pr. Chem., 1933, [ii], **138**, 42—50; cf. A., 1931, 1305).—3-*Methoxyflavenium perchlorate*, m.p. 195—196° [from the chloride (modified prep.)], gives with MeOH or EtOH the *ethers* (I), R=*Me*, m.p. 117—118°, and *Et*, m.p. 126°, and with H_2O_2 in AcOH affords o-*benzoyloxyphenylacetic acid*, m.p. 142°, slightly bitter, hydrolysed to BzOH and *o*-hydroxyphenylacetic acid, bitter, and obtained also by oxidation of 3-*hydroxyflavenium perchlorate*, m.p. 226—227° (decomp.), which is prepared from *o*-$OH{\cdot}C_6H_4{\cdot}CHO$, $CH_2Bz{\cdot}OMe$, and HCl. 7-*Hydroxy*-3-*methoxyflavenium perchlorate*, m.p. 245—246°, gives, when oxidised, 4-*hydroxy*-2-*benzoyloxyphenylacetic acid*, m.p. 186—187°, but 7-*hydroxy*-3 : 4′-*dimethoxyflavenium picrate*, m.p. 249°, affords *Me* 4-*hydroxy*-2-*anisoyloxyphenylacetate*, m.p. 112—113°, hydrolysed to anisic acid. In the above oxidations H_2O_2 attacks first the 2-position. This and the results of nitration show that the charge on the pyrenium cation is isolated, if at all, on the 2-C atom.


(I.)

R. S. C.

Rotenone. XXV. Synthesis of tetrahydrotubanol and tetrahydrotubaic acid. H. L. Haller. **XXVI. Synthesis of the parent substances of some characteristic rotenone derivatives.** F. B. La Forge (J. Amer. Chem. Soc., 1933, **55**, 3032—3035, 3040—3048; cf. this vol., 163).—XXV. $MgBu^{\beta}Br$ and 2 : 6-dimethoxybenzonitrile (modified prep.) in Et_2O–PhMe give 2 : 6-*dimethoxyphenyl* Bu^{β} *ketone*, b.p. 136°/1 mm. (does not give an oxime or a semicarbazone), reduced (Clemmensen) to a *substance*, (?) δε-*di*-(2 : 6-*dimethoxyphenyl*)-βη-*dimethyloctane*, m.p. 188°, and 2 : 6-*dimethoxy*isoa*mylbenzene*, b.p. 102°/1 mm., demethylated by HI, or, better, $AlCl_3$ in PhMe, to tetrahydrotubanol.

XXVI. 2 : 2′-Dimethoxybenzoin and $SOCl_2$ give 2 : 2′-*dimethoxydesyl chloride*, m.p. 87°, reduced by Zn dust and KOH–EtOH–H_2O to 2 : 2′-*dimethoxydeoxybenzoin*, m.p. 57° (also obtained by a similar reduction of 2 : 2′-dimethoxybenzoin), which with HI and a little PhOH gives 2 : 2′-*dihydroxydeoxybenzoin anhydride* (I), m.p. 95—98°. Salicylaldehyde $OMe{\cdot}CH_2$ ether (modified prep.), b.p. 128—130°/11 mm., and KCN in aq. EtOH give 2 : 2′-*dimethoxybenzoin Me ether*, b.p. 200—210°/1 mm., hydrolysed to 2 : 2′-*dihydroxybenzoin*, m.p. 142—149°, which is reduced to 2 : 2′-*dihydroxydeoxybenzoin* (II), m.p. 104° [anhydride = (I)]. (I), NaOEt, and $CH_2Br{\cdot}CO_2Et$ give *anhydro*-2-*hydroxy*-2′-*carbomethoxydeoxybenzoin*, m.p. 170°; this is also obtained similarly from (II), but longer heating gives also α-*benzopyrano*-γ-*benzopyrone* (III), reduced (Zn dust, KOH) to 2′-*hydroxy*-2-*carbomethoxydeoxybenzoin*, m.p. 129°, which with hot KOH–H_2O_2 gives 2-carbomethoxyphenylacetic acid. (II) and $COCl{\cdot}CO_2Et$ in C_5H_5N give α-*benzopyrono*-γ-

(III.)  (IV.)

benzopyrone (IV), m.p. about 240° (decomp.), colourless. *Ethylene ethers* of the following were prepared: *disalicylaldehyde*, m.p. 130° (*oxime*, m.p. 170°), 2 : 2′-*dihydroxybenzoin*, m.p. 165° (5-*Ac* derivative, m.p. 165°), 2 : 2′-*dihydroxybenzil*, m.p. 200°, and 2 : 2′-*dihydroxydesyl chloride*, m.p. 105°.

R. S. C.

Calorimetric determination of simple and polynuclear derivatives of pyrrole. A. Stern and G. Klebs (Annalen, 1933, **504**, 287—297).—The heats of combustion of mono- and di-nuclear pyrroles can be calc. from the characteristics of the individual at. linkings. This is true for di-derivatives when the nuclei are formed in the 1- or 2-position as pyrromethanes, directly as in the diphenyl type or as pyrromethenes. Tetrapyrranes behave similarly. The thermochemical characteristics of $CH_2{\cdot}CN$ (β), C:N (β), $\cdot CH_2{\cdot}CH(CO_2Et)_2$ (β), C·O·H (β), :N·NH_2, CO·NH·C:O, C·NH·C (in ring), C·N:C (in ring), CO·O·CO, and C:N·OH (α) are 297·1, 30·0, 995·7, 4·7, 159·3, 77·0, 94·0, 90 0, 11·2, and 69·2 kg.-cal., respectively.

H. W.

Action of Grignard's reagent on *N*-methylpyrrolidone. Synthesis of substituted pyrrolines. R. Lukes (Chem. Listy, 1933, **27**, 97—100, 121—126).—1-Methylpyrrolid-2-one yields with MgRBr (R=alkyl) a mixture of dialkylpyrrolidine and alkylpyrroline, whilst with MgR′Br (R′=aryl) only pyrroline derivatives are obtained. The following compounds have been prepared by this reaction: 1 : 2-dimethyl-$\Delta^{2:3}$-pyrroline (*perchlorate*, m.p. 238°); 1 : 2 : 2-*trimethylpyrrolidine*, b.p. 130—135° [*picrate*, m.p. 250° (decomp.)]; 1-*methyl*-2-*ethyl*-$\Delta^{2:3}$-*pyrroline*,

b.p. 40—41°/10 mm. (*perchlorate*, m.p. 209°; *chloroaurate*, m.p. 115—117°); 1-*methyl*-2 : 2-*diethylpyrrolidine*, b.p. 168° [*picrate*, m.p. 233° (decomp.); *chloroaurate*, m.p. 159—163°]; 1-*methyl*-2-n-*propyl*-$\Delta^{2:3}$-*pyrroline*, b.p. 82°/30 mm.; 1-*methyl*-2 : 2-*di*-n-*propylpyrrolidine*, b.p. 206°/738 mm. (*picrate*, m.p. 130°); 2-*phenyl*-1-*methyl*-$\Delta^{2:3}$-*pyrroline*, b.p. 112°/13 mm. (*hydrochloride*, $+H_2O$, m.p. 96°; *perchlorate*, m.p. 117—118°; *chloroaurate*, m.p. 95—97°; *chloroplatinate*, m.p. 140—141°). R. T.

Cleavage of carbonyl compounds by alkalis. IX. Phenacylpyridinium salts. S. H. Babcock and R. C. Fuson (J. Amer. Chem. Soc., 1933, **55**, 2946—2948; cf. this vol., 74).—Phenacylpyridinium chloride with 20% NaOH gives BzOH and a solution, whence by alkaline $K_3Fe(CN)_6$, followed by Br, 3 : 5-dibromo-1-methylpyridone is obtained. p-*Bromo*-α-*methylphenacylpyridinium bromide*, m.p. 232—233° (from C_5H_5N and α : p-dibromopropiophenone), leads to p-$C_6H_4Br{\cdot}CO_2H$ and *N*-ethylpyridone, b.p. 124°/9 mm. (3 : 5-Br_2-compound, m.p. 109°), also prepared from C_5H_5N and Et_2SO_4. R. S. C.

Alleged formation of aliphatic keto-anils. J. T. Murray, W. F. Short, and R. Stansfield (J. Amer. Chem. Soc., 1933, **55**, 2805—2806).—Formulation of "acetoneanil" (I) as 2 : 2 : 4-trimethyl-1 : 2-dihydroquinoline (A., 1932, 1142) is confirmed. (I) and Bz_2O in xylene or BzCl and the Grignard complex from (I) and MgMeI in Et_2O give the N-*Bz* derivative of (I), m.p. 83—84°. The Ac derivative, m.p. 54°, b.p. 163—164°/15 mm., of (I) gives (I) on hydrolysis and 2 : 4-dimethylquinoline with dry HCl at 180°. The supposed benzyl derivative (A., 1930, 1571) is impure (I). R. S. C.

Derivatives of 8-aminoquinoline as antimalarials. I. Effect of alkyl [groups] in position 6 on the chemotherapeutic properties. O. J. Magidson and I. T. Strukov (Arch. Pharm., 1933, **271**, 359—369).—8-Nitro-6-methoxy- and -6-ethoxyquinoline (I) are prepared from *m*-nitro-*p*-acetanisidide and -phenetidide in 56·5 and 71% yield, respectively. These are reduced by $(NH_4)_2S$ in EtOH (79% yield) or other reagents to 8-amino-6-methoxy- and 8-*amino*-6-*ethoxy-quinoline* (II), b.p. 172—176°/2 mm., m.p. 60° [*picrate*, m.p. 195—196° (decomp.); *benzylidene* and *Ac* (III) derivatives, m.p. 113—114° and 144°, respectively]. (II) with NaOEt at 150—160°, followed by *iso*amyl bromide at 130—140°, gives 8-iso*amylamino*-6-*ethoxyquinoline* (IV), b.p. 207—210°/8 mm. (*hydrochloride*). 8-Aminoquinoline and $CH_2Cl{\cdot}CH_2{\cdot}NEt_2$,HCl at 120° give 8-δ-(diethylamino)ethylammoquinoline (V), b.p. 163—164°/4 mm. (II) gives similarly 8-β-(*diethylamino*)-*ethylamino*-6-*ethoxyquinoline* (VI), b.p. 235—238°/8—9 mm. [dihydrochloride, m.p. 210—212° (decomp.); *NO*-derivative, m.p. 127°]. (I) and H_2SO_4 (65% by wt.) at 120—140° give 8-*nitro*-6-*hydroxyquinoline* (VII), m.p. 230° (decomp.). (VI) and HBr at 145—155° give 8-δ-(*diethylamino*)*ethylamino*-6-*hydroxyquinoline hydrobromide*, $+2H_2O$, m.p. 108—114°. The Na or K salt of (VI) with the appropriate alkyl halide at 100° gives the following *ethers* of (VII): Pr^{β}, m.p. 70°; Pr^{α}, m.p. 89°; Bu^{α}, m.p. 90°; iso*amyl*, m.p. 83°; n-*octyl*, m.p. 61°; and *allyl*, m.p. 114·5°. These are reduced by $(NH_4)_2S$ in EtOH to the following 8-*amino*-6-*hydroxyquinoline ethers*: Pr^{β} (*dihydrochloride*); Pr^{α}, b.p. 188—189°/3·5 mm.; Bu^{α}, b.p. 197—202°/5 mm.; iso*amyl*, b.p. 195—197°/2—3 mm., m.p. 53°; n-*octyl*, b.p. 212—217°/1 mm. (*dihydrochloride*); and *allyl* (*dihydrochloride*). Thence were prepared the following 8-β-(*diethylamino*)*ethylamino*-6-*hydroxyquinoline ethers*: Pr^{β}, b.p. 205—208°/2 mm. (*dihydrochloride*, hygroscopic); Pr^{α}, b.p. 210—211°/2 mm. (*dihydrochloride*); Bu^{α}, b.p. 210—213°/? mm. (*dihydrochloride*); iso*amyl*, b.p. 238—245°/2—3 mm.; n-*octyl*, b.p. 255—262°/1 mm.; and *allyl* (*meconate*). The val. of the OR-derivatives of (VI) as antimalarials (canary tests) falls as R changes from H through Me to higher alkyl groups, being very low if R is Pr or Bu, and 0 if R is *n*-octyl or allyl. 8-Amino-6-methoxyquinoline and *N*-*iso*amyl and -di*iso*amyl derivatives are inactive. R. S. C.

Synthesis of quinoline derivatives. III. K. Dziewoński and J. Mayer (Rocz. Chem., 1933, **13**, 370—374).—$COPhPr^{\alpha}$ when heated at 240° for 4 hr. with PhNCS yields 4-*anilino*-2-*phenyl*-3-*methylquinoline*, m.p. 158° [*sulphate*, m.p. 180° (decomp.); *picrate*, m.p. 240° (decomp.); 4-N-*NO*-, m.p. 120°, 4-N-*Ac*, m.p. 170°, and 6-NO_2-derivative, m.p. 240° (*sulphate*, m.p. 296° decomp.)], converted by fusion with NaOH into the corresponding 4-OH-derivative. R. T.

Simplified preparation of acridones and 9-chloroacridines. W. Dirscherl and M. Theron (Annalen, 1933, **504**, 297—304).—Diphenylamine-*o*-carboxylic acids are converted by PCl_5 into the corresponding chlorides, which when heated alone or in solution pass into acridone hydrochlorides, from which HCl is removed at a higher temp. or by KOH–EtOH, yielding acridones. If the chloride is heated with the chlorides of P (mainly $POCl_3$), 9-chloroacridines result, 1 mol. of PCl_5 sufficing for the whole change. The following examples are cited: *diphenylamino*-o-*carboxyl chloride*, m.p. 48—50°, to acridone, m.p. 355° (*hydrochloride monohydrate*, m.p. 355°), and 9-chloroacridine, m.p. 119—120°; 4′-*ethoxydiphenylamine*-o-*carboxyl chloride*, m.p. 88°, to 2-*ethoxyacridone*, m.p. 258—259° [*hydrochloride*, m.p. 190° (decomp.), and its *monohydrate*, m.p. 225—226°], and 9-*chloro*-2-*ethoxyacridine*, m.p. 147—148°; 4′-*methyldiphenylamine*-o-*carboxyl chloride*, m.p. 66° (decomp.), to 2-*methylacridone*, m.p. 345° (*hydrochloride* and its *monohydrate*, m.p. 320°), and 9-*chloro*-2-*methylacridine*, m.p. 121—122°; 4-*nitro*-4′-*ethoxydiphenylamine*-2-*carboxylic acid*, m.p. 195°, to the *chloride*, m.p. 118—120°, decomp. 125—130°, and thence to 7-*nitro*-2-*ethoxyacridone*, m.p. 365° (*hydrochloride*), and 9-*chloro*-7-*nitro*-2-*ethoxyacridine*, m.p. 196°; 2-methyldiphenylamine-*o*-carboxylic acid to 4-*methylacridone hydrochloride* and 4-methylacridone, m.p. 343°. H. W.

Mechanism of the formation of acridones by condensation of *o*-nitrobenzaldehydes with aromatic hydrocarbons. III. I. Tanasescu and (Mme.) M. Macarovici. **IV. Reply to Lehmstedt.** I. Tanasescu (Bull. Soc. chim., 1933, [iv], **53**, 372—

380, 381—384; cf. A., 1932, 169).—III. 2 : 4-$CHO{\cdot}C_6H_3(NO_2)_2$, PhMe, and H_2SO_4 give the substance, m.p. 105° (*A*), and 3-*nitro*-6-*methylacridone*, m.p. > 300°, which with $POCl_3$ and $NPhMe_2$ gives (probably) impure 3-*nitro*-9-p-*dimethylanilino*-6-*methylacridine*, m.p. 200° after softening at 170°. PhCl gives similarly (*A*) and 6-*chloro*-3-*nitroacridone*, m.p. > 300°, which gives similarly 6-*chloro*-3-*nitro*-9-p-*dimethylanilinoacridine*, m.p. 235° after softening at 230°. Similarly were obtained 6-*bromo*-3-*nitro*-, m.p. > 300°, and 2-*chloro*-6-*methyl-acridone*, decomp. 200°, and 2-*chloro*-9-p-*dimethylanilino*-6-*methylacridine*, m.p. 261°. 5-Chloro-2-nitrobenzaldehyde, PhMe, and H_2SO_4 give 2-*chloro*-N-*oxy*-p-*tolylanthranil*, m.p. > 300°, a yellow *substance*, and (*A*).

IV. Polemical (cf. A., 1932, 754). R. S. C.

Heterocyclic ketones. I. β-Aminoketones and related pyrazolines derived from benzylidene- and furfurylidene-acetone. H. B. Nisbet and C. G. Gray (J.C.S., 1933, 839—840; cf. A., 1928, 301).—Furfurylideneacetone, $NHMe_2$,HCl and paraformaldehyde in EtOH give α-*dimethylamino*-ε-*furyl*-Δ^{α}-*penten*-γ-*one hydrochloride*, m.p. 170° (*phenylhydrazone*, m.p. 185°). The following are similarly obtained: α-*diethylamino*-, m.p. 125°, and α-*piperidino*-ε-*furyl*-Δ^{α}-*penten*-γ-*one hydrochloride*, m.p. 192° (darkens) [*phenylhydrazone* (I), m.p. 182°]. The phenylhydrazone of α-diethylamino-ε-phenyl-Δ^{α}-penten-γ-one is not a pyrazoline, since it gives NH_2Ph on reduction. The phenylhydrazone of the corresponding piperidino-compound in hot AcOH gives the *pyrazoline*, m.p. 60°. The *pyrazoline hydrochloride*, m.p. 158°, is similarly obtained from (I).

A. A. L.

Co-ordination compounds of oximes. III. Compounds of 4-oximino-1-phenyl-3-methyl-5-pyrazolone with the alkali metals, nickel, and thallium. O. L. Brady and (Miss) M. D. Porter (J.C.S., 1933, 840—842).—The prep. is described of *Li*, m.p. 203° (decomp.), *Na*, m.p. 230° (decomp.), *K*, m.p. 248° (decomp.), *Rb*, m.p. 233° (decomp.), and *Cs di*-4-*oximino*-1-*phenyl*-3-*methyl*-ο-*pyrazolone*, m.p. 209° (decomp.), and *Tl*, m.p. 219° (decomp.), and *Ni* 4-*oximino*-1-*phenyl*-3-*methyl*-ο-*pyrazolone*.

A. A. L.

Synthesis of 5-α-naphthyl-5-ethylhydantoin. De W. T. Keach (J. Amer. Chem. Soc., 1933, **55**, 2979—2981).—α-$C_{10}H_7{\cdot}COEt$, anhyd. HCN, and NH_3 in EtOH give α-*amino*-α-1-*naphthyl*-n-*butyronitrile* (*hydrochloride*), which with KCNO in AcOH gives α-*carbamido*-α-1-*naphthyl*-n-*butyronitrile*, m.p. 201—202°, hydrolysed by hot HCl to 5-α-*naphthyl*-5-*ethylhydantoin*, not hypnotic, m.p. 222—223°.

R. S. C.

Brazilin and hæmatoxylin. XIII. Phenoxycitramalic acids. P. Pfeiffer and H. Hoyer (J. pr. Chem., 1933, [ii], **138**, 69—80; cf. this vol., 832).—Et *m*-anisoxyacetylcyanoacetate, KCN, $(NH_4)_2CO_3$, and CO_2 (pressure) in EtOH at 80—90° give m-*anisoxyacetamide*, m.p. 110°. *Et* γ-m-*anisoxyacetoacetate*, b.p. 170—180°/0·5 mm. (*Cu* salt, m.p. 121°) (best obtained from Et *m*-anisoxyacetate, $CH_2Cl{\cdot}CO_2Et$, and Zn filings), similarly gives *Et* 5-m-*anisoxymethylhydantoin*-5-*acetate*, m.p. 133—134°, hydrolysed by cold aq. NH_3 to 5-m-*anisoxyhydantoin*-5-*acetamide*, m.p. 203—204°, and slowly by hot 25% KOH to α-m-*anisoxymethylasparagine*, m.p. about 170° (decomp.) (sinters from 153°) (*Ba* salt, $+H_2O$), which with HNO_2 gives γ-m-*anisoxycitramalic acid*, an oil (*Ba* salt, $+H_2O$). $OPh{\cdot}CH_2{\cdot}CO_2Et$, $CH_2Br{\cdot}CO_2Et$, and Zn give Et γ-phenoxyacetoacetate (not isolated pure), whence were prepared *Et* ο-*phenoxymethylhydantoin*-ο-*acetate*, $+H_2O$ (lost at 120°), m.p. (anhyd.) 157—158°, the corresponding *acid*, m.p. 238—239°, α-*phenoxymethylasparagine*, m.p. 230—240° (decomp.) (*Ba* salt, $+H_2O$), and γ-*phenoxycitramalic acid*, m.p. 173—174° (*Me_2* ester, m.p. 67—68°).

R. S. C.

Amino-acids and related compounds. VI. Electrolytic oxidation of glyoxalinylpropionic acid. Y. Takayama (Bull. Chem. Soc. Japan, 1933, **8**, 189—195; cf. this vol., 720).—Electrolytic oxidation of glyoxalinylpropionic acid in 2*N*-H_2SO_4 gives succinic acid (> 30·4%), the semi-aldehyde thereof, NH_3, and NH_2-compounds (12·5%), including carbamide (1·3%).

R. S. C.

2 : 5-Dihydroxy-3 : 4 : 5 : 6-tetrahydropyrimidine. J. S. Turski and P. Kazmierczak (Rocz. Chem., 1933, **13**, 375—378).—Dichlorohydrin and carbamide yield 2 : 5-*dihydroxy*-3 : 4 : 5 : 6-*tetrahydropyrimidine* on heating for 1 hr. at 135° in C_5H_5N.

R. T.

Ring structure of uridine. P. A. Levene and R. S. Tipson (J. Biol. Chem., 1933, **101**, 529—534).—Acetylation of uridine (I) affords *triacetyluridine* (cf. A., 1911, i, 96), catalytically reduced to triacetyldihydrouridine, the Me derivative of which on simultaneous hydrolysis and oxidation (Br–HBr) yields a mixture of trimethylribonolactone and its Me ester. The rotation of the lactone during hydrolysis indicates a γ-lactone, confirmed by formation of *dl*-dimethoxysuccinic acid on oxidation with HNO_3 under conditions which give trimethoxyglutaric acid from trimethyl-δ-ribonolactone (A., 1931, 1399). Hence (I) is a ribofuranoside.

F. O. H.

Pyrimidines. CXXXIII. Reactions and derivatives of ethyl 2-keto-4-phenyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate. K. Folkers and T. B. Johnson (J. Amer. Chem. Soc., 1933, **55**, 2886—2893; cf. this vol., 616).—Thiocarbamide, $CH_2Ac{\cdot}CO_2Et$, PhCHO, and a little HCl in EtOH give *Et* 2-*thio*-4-*phenyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate* (I), m.p. 207—208°. Methylcarbamide affords similarly *Et* 2-*keto*-4-*phenyl*-1 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 176—178°. MeNCO and Et β-aminocrotonate give α-(*N*-methylcarbamyl)-β-iminobutyrate. (I) with Br in $CHCl_3$ at 5° gives the 5 : 6-Br_2-compound, m.p. 180—181°, and with $POCl_3$ at 100° gives *Et* 2-*chloro*-4-*phenyl*-6-*methyl*-1 : 4-*dihydropyrimidine*-5-*carboxylate*, readily hydrolysed. This with cold NaOMe–MeOH–C_6H_6 gives *Et* 2-*keto*-4-*phenyl*-3 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 159—160° (unchanged by HCl–EtOH), and with NH_3 affords *Et* 2-*imino*-4-*phenyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 85—87°, decomposed slowly by

cold, and rapidly by hot, dil. HCl. All m.p. are corr. R. S. C.

Mechanism of the narcosis induced by hypnotics. I. Synthesis of coloured derivatives of phenobarbital. (Miss) M. Rising, J. H. Shroyer, and J. Stieglitz (J. Amer. Chem. Soc., 1933, **55**, 2817—2820).—Phenobarbital (5-phenyl-5-ethylbarbituric acid) gives the 5-m-*nitrophenyl*, m.p. 279—280°, and thence by hydrogenation (PtO_2) the 5-m-*aminophenyl*, m.p. 207·5—208·5°, derivatives. The diazotised base, coupled with β-naphthol, resorcinol, salicylic acid, and tyrosine, gives *dyes*, approx. m.p. 302°, 248—250°, 250—251°, and 200° (decomp. 216—222°), respectively, which are pharmacologically inactive. All m.p. are corr. R. S. C.

Spatial structure of the platinum-tetrammine salts. F. Rosenblatt and A. Schleede (Annalen, 1933, **505**, 51—58).—The optical activity observed by Reihlen is due to asymmetry of the substituents, and does not establish the tetrahedral configuration. Asymmetry of the complex salts is commensurate with the plane arrangement of the atoms united to Pt. Thus if the N atoms of $C_2H_4(NH_2)_2$ lie in the same plane as Pt, four arrangements are possible, viz. (i) with both $\cdot C_2H_4\cdot$ groups in the plane of Pt; (ii) with one above and one below the plane; (iii) with both above the plane; (iv) with one above and one in the plane of the Pt. If, as in Reihlen's compounds, the group $\cdot C_2H_4\cdot$ is unsymmetrically substituted, each of these types renders possible *cis*- and *trans*-isomerism and four of the eight sterically possible forms are asymmetric.

K_2PtCl_6 and 2 : 2′-dipyridyl (I) yield the *compound* $Pt(C_{10}H_8N_2)Cl_2$, into which NH_3, C_5H_5N, or a further mol. of (I) could not be introduced. The *salt* [Pb dip en]Cl_2 is converted into the corresponding bromocamphorsulphonate (II), which is not resolved by crystallisation from H_2O. (II) is converted into the *compounds* [Pt dip en]I_2,H_2O and Pt dip$(CN)_2$. H. W.

The viologen indicators. L. Michaelis and E. S. Hill (J. Gen. Physiol., 1933, **16**, 859—873).—Various viologen indicators (quaternary bases derived from 4 : 4′-dipyridyl) have been prepared and their oxidation–reduction (I) properties studied. They differ from other indicators of this type in that the colour is exhibited by the reduced form and also in that the (I) potential of these substances is independent of p_H. The (I) potential of a solution which causes coloration to the extent of A% of the max. colour is $E_0 - 0{\cdot}06 \log A/(100-A)$, where E_0 is the normal potential of the viologen used. Vals. for E_0 (at 30°) for methyl-, ethyl-, betaine-, and benzyl-viologens are given. Some properties of the last three compounds (NN′-*diethyl*-, NN′-*dibetaine*-, and -*dibenzyl*-4 : 4′-*dipyridylium dichloride*, respectively) are recorded. A. W.

Constitution of dimeric indoles. O. Schmitz-Dumont, K. Hamann, and K. H. Geller (Annalen, 1933, **504**, 1—19).—The quant. depolymerisation of di-indole (I) to indole, the presence in it of two active H, and the observation that only 1 NH can be acylated or caused to react with PhNCO indicate the structure $C_6H_4\langle^{CH}_{NR}\rangle C\cdot CH\langle^{CH_2}_{C_6H_4}\rangle NR'$ (*A*; R=R′=H) for (I), which is supported by the ability of skatole and 1- and the inability of 2-methylindole to dimerise. (I) is transformed by $NaNO_2$ and AcOH into *dinitroso-di-indole* (II), m.p. 160—162° (decomp.), converted by boiling EtOH into *nitrosodi-indole* (*A*; R=H, R′=NO), m.p. 121—122° after softening at 117°. *Nitrosoacetyldi-indole* (II) (*A*; R=NO, R′=Ac), m.p. 126—128° (decomp.), and *nitrosobenzoyldi-indole*, m.p. 150—151° (decomp.), are derived from the acyldi-indoles and $NaNO_2$ in AcOH. There are prepared analogously *dinitroso-* (III), m.p. 127—129° (decomp.), *nitroso-*, m.p. 170° (decomp.), and *nitrosoacetyl-*, m.p. 127—129° (decomp.), *-di-7-methylindole*, *dinitroso-*, m.p. 134° (decomp.), *nitroso-*, m.p. 145—146° (decomp.), and *nitrosoacetyl-*, m.p. 67—69° (decomp.), *-diskatole*. (IV) is converted by KOH–EtOH under N_2 at room temp. mainly into 2 : 3-*di-indolyl*, m.p. 206° (slight decomp.) after softening at 204°, the constitution of which follows from its transformation by $NaNO_2$ in AcOH–HCl into *oximino*-2 : 3-*di-indolyl* (V),

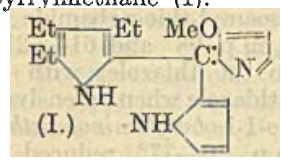
$C_6H_4\langle^{C(:N\cdot OH)}_{N}\rangle C\cdot C\langle^{CH}_{C_6H_4}\rangle NH$, m.p. 242—243° (decomp.) (obtained also as a secondary product of the above reaction) [Ac_2 derivative, m.p. 214—215° (decomp.), converted by conc. HCl into (VI); Bz_2 compound, m.p. 228—229° (decomp.)]. (V) is also obtained by oximation of indoxyl-red, into which it is converted by reduction by $Na_2S_2O_4$ to 3-*amino*-2 : 3-*di-indolyl*, not molten below 250°, and treatment of the *Ac* derivative, m.p. 200—201°, with $NaNO_2$. (II) and KOH–EtOH yield acetyldi-indole, m.p. 157—158°, and (V), whilst (III) and NaOEt afford 2 : 3-*di-7-methylindolyl*, m.p. 204—205° (decomp.), and *oximino*-2 : 3-*di-7-methylindolyl*, m.p. 244—245° (decomp.). H. W.

Isatin condensation products of pyrroles (pyrrole-blue). P. Pratesi (Annalen, 1933, **504**, 258—266).—Condensation does not occur between isatin (I) and 1-methyl-, 1-phenyl-, 1-ethyl-, 1-acetyl-, 2 : 5-dimethyl-, or 2 : 4 : 5-trimethyl-3-ethyl-pyrrole in AcOH or H_2SO_4. (I) condenses with 2 : 3-dimethyl-, 3-methyl-4-ethyl-, and 2 : 4-dimethyl-3-ethyl-pyrrole with loss of 1 H_2O and formation of the *substances* $C_{14}H_{12}ON_2$, $C_{15}H_{14}ON_2$, and $C_{16}H_{16}ON_2$, respectively, the mol. wt. of which could not be determined in PhOH, $PhNO_2$, or veratrole. The dyes could not be caused to react with Ac_2O and NaOAc or AcCl. Their absorption spectra are closely similar. They are therefore formulated NH$\langle^{C_6H_4}_{CO}\rangle C{:}C\langle^{CR{:}CR'}_{N=CR''}$ H. W.

Catalytic oxidation of cysteine with copper. K. A. C. Elliott (Biochem. Z., 1933, **263**, 230).—Andresen and Nielsen (this vol., 793) used an unsuitable respiration vessel and failed to prevent irregular diffusion of O_2. Hence their criticism of the author's work (A., 1930, 869) cannot be maintained. W. McC.

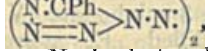
Constitution of prodigiosin. H. Raudnitz (Naturwiss., 1933, **21**, 518).—In opposition to the views of Wrede (A., 1932, 1043) prodigiosin is formu-

lated as 2 : 3 : 4-triethylpyrryl-(5)-3′-methoxy-(2′)-pyrryl-(2″)-pyrrylmethane (I).

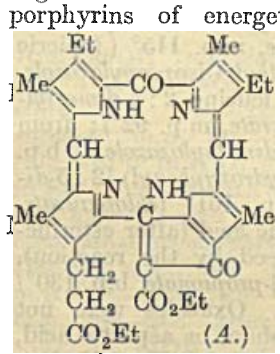


(I.)

W. O. K.

Derivatives of 1-aminotetrazole. R. Stolle [with A. Netz, O. Kramer, S. Rothschild, H. Erbe, and O. Schick] (J. pr. Chem., 1933, [ii], **138**, 1—17).—Benzylidenebenzhydrazide chloride, $CClPh{:}N{\cdot}N{:}CHPh$, and NaN_3, when heated in EtOH for 1 hr. only, give benzylidenebenzhydrazide azide, $N_3{\cdot}CPh{:}N{\cdot}N{:}CHPh$. 1-Amino-5-phenyltetrazole (*Ac*$_2$ derivative, m.p. 90°) gives with $COMe_2$ slowly the *isopropylidene* compound, m.p. 66°, and with Cl_2 and aq. $NaHCO_3$, or fresh aq. Cl_2, the N-*Cl*$_2$-derivative, highly explosive, which in HOCl or, better, aq. KI gives 1 : 1′-*azo*-(5-*phenyltetrazole*),  , deflagrates at 141°, explosive (gives N_2 in hot solvents). *p*-Tolylaldazine and Cl_2 in dry CCl_4 at 35° give p-*tolylidene*-p-*tolylhydrazide chloride*, m.p. 96°, which with NaN_3 yields 1-p-*tolylideneamino*-5-p-*tolyltetrazole*, m.p. 176°, whence by HCl 1-*amino*-5-p-*tolyltetrazole*, m.p. 141°, is obtained. This gives with HNO_2 5-*p*-tolyltetrazole and with HOCl the N-*Cl*$_2$-derivative, very unstable, whence 1 : 1′-*azo*-(5-p-*tolyltetrazole*), explosive (gives *p*-tolyltetrazole in hot AcOH), is obtained by KI. Similarly were prepared o-*chlorobenzylidene*-o-*chlorobenzhydrazide chloride*, m.p. 77°, 1-o-*chlorobenzylideneamino*-5-o-*chlorophenyltetrazole*, m.p. 140°, 1-*amino*-5-o-*chlorophenyltetrazole*, m.p. 173° (*Ac*$_2$ derivative, m.p. 106°; N-*Cl*$_2$-derivative), 1 : 1′-*azo*-(5-o-*chlorophenyltetrazole*), m.p. 112° (decomp.), 5-o-*chlorophenyltetrazole*, m.p. 177° (decomp.), p-*nitrobenzylidene*-p-*nitrobenzhydrazide chloride* (I) (prepared from the azine by Cl_2–I in C_2HCl_5), m.p. 164°, and *azide* (II), m.p. 244° (decomp.), 1-p-*nitrobenzylideneamino*-5-p-*nitrophenyltetrazole* [from (II) in hot AcOH or (I) and NaN_3 in hot xylene], m.p. 261° (decomp.), 1-*amino*-5-p-*nitrophenyltetrazole*, m.p. 154°, 5-p-*nitrophenyltetrazole*, m.p. 222° (*benzylidene* derivative, m.p. 240°), m-*nitrobenzylidene*-m-*nitrobenzhydrazide chloride*, m.p. 144°, and *azide*, m.p. 134° (decomp.), 1-m-*nitrobenzylideneamino*-5-m-*nitrophenyltetrazole*, m.p. 185° (decomp.), and *anisylideneanishydrazide chloride* (III), m.p. 150°. (III) with N_2H_4,H_2O gives *anisylideneanishydrazone hydrazide*, $OMe{\cdot}C_6H_4{\cdot}C(NH{\cdot}NH_2){:}N{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OMe$, m.p. 190—200° (decomp.), which with $OMe{\cdot}C_6H_4{\cdot}CHO$ in hot EtOH forms *dianisylideneanishydrazone hydrazide*, m.p. 149°. Benzanilideimide chloride and N_2H_4 in cold ligroin give triphenyltriazole and a little *benzanilideimide hydrazide*, m.p. 90°, which with HNO_2 give diphenyltetrazole. Benzoylphenylhydrazide chloride and N_2H_4 give anilinodiphenylpyrrodiazole. *p*-Tolylidine-*p*-toluoylhydrazide and Cl_2 give di-*p*-tolylfurodiazole. R. S. C.

***iso*Phæoporphyrin a_6.** H. Fischer and J. Riedmair (Annalen, 1933, **505**, 87—102).—Reduction of native phæophorbide *a* or methylphæophorbide *a* with AcOH–HI at low temp. leads to *isophæoporphyrin* a_6 (I) (previously considered to be *iso*phæoporphyrin a_5, which should be deleted from the lit.). Phæophorbide Sandoz gives a much smaller yield, since phylloerythrin, neophæoporphyrin a_6, and phæoporphyrin a_7 are also produced. Reduction in N_2 gives almost exclusively phæoporphyrin a_5 (II), whereas the highest yields of (I) are obtained in O_2, so that (I) is a secondary product. (I) is characterised by the *Me*$_2$ ester (II), m.p. 276°, which yields a *dioxime*, hydrolysed by 20% HCl to (III). (I) is unusually stable towards reducing agents, but is very readily oxidised. Energetic degradation with KOH–MeOH leads to the known porphyrins of energetic chlorophyll degradation, indicating the same skeleton in (I) and (II) and the probable position of the second CO between two pyrrole nuclei. The presence in (I) of the isocyclic ring characteristic of chlorophyll is established by hydrolysis to a *chloroporphyrin* e, the *Me*$_3$ ester, m.p. 270°, of which exhibits oxime displacement, does not add HCN, and is hydrolysed to (I), which is therefore *A*. (I) gives a *Bz* derivative, probably a mixed anhydride of (I) and BzOH. H. W.



(*A*.)

Constitution of cytochrome. II. K. Zeile and P. Piutti (Z. physiol. Chem., 1933, **218**, 52—64; cf. A., 1932, 627).—Treatment of hæmatoporphyrin hydrochloride with HBr–AcOH and digestion of the product with C_5H_5N gives 6 : 7-*di*-(β-*carboxyethyl*)-2(or 4)-α-*hydroxyethyl*-4(or 2)-α-*pyridinium hydrobromide*-1 : 3 : 5 : 8-*tetramethyl-ethylporphin* (I). By introduction of Fe and treatment with HBr–AcOH, hæmatoporphyrin is obtained. Protoporphyrin (II) forms a compound similar to (I) with 1 mol. of histidine Me ester. A series of compounds with *N* bases was obtained from the acid chlorides of porphyrins by combining the $\cdot CH_2{\cdot}CH_2{\cdot}CO_2H$ group with NH_2-acid esters as in peptide synthesis: *mesoporphyrindiamide*; 6 : 7-*di*(*propionyl*-N-*glycine Me ester*)-1 : 3 : 5 : 8-*tetramethyl*-2 : 4-*diethylporphin*, m.p. 261° (corr.) [Fe salt, m.p. 274° (corr.)]; dl-6 : 7-*di*(*propionyl*-N-*alanine Me ester*)-1 : 3 : 5 : 8-*tetramethyl*-2 : 5-*diethylporphin*, m.p. 276° (corr.); 6 : 7-*di*(*propionyl*-N-*glycine Me ester*)-1 : 3 : 5 : 8-*tetramethylporphin*, m.p. 289° (corr.); dl-6 : 7-*di*(*propionyl*-N-*leucine Me ester*)-1 : 3 : 5 : 8-*tetramethylporphin*, m.p. 285° (corr.) (free *acid*). All show spectra identical with that of the parent porphyrin. Hydrolysis of the HBr additive product of (II) gives *ethylhæmatoporphyrin*. With mesochlorohæmin ester in $CHCl_3$ glyoxaline affords *glyoxalinemesoesterhæmin*. Saturation of histidine in MeOH with NH_3 and treatment of the residue on evaporation with aq. HCl and $COMe_2$ gave *histidineamide dihydrochloride*, m.p. 259° (corr.). J. H. B.

Fluorescence of the porphyrins. I. H. Fink and W. Hoerburger (Z. physiol. Chem., 1933, **218**, 181—201).—The influence of various factors (concn., presence of salts, solubility) on the fluorescence of the porphyrins was studied. The p_H–fluorescence

curves are plotted for four isomeric copro- and three uro-porphyrins. They are reproducible and offer a suitable means of characterisation. J. H. B.

Preparation of oxazoles from α-amino-acids. F. WREDE and G. FEUERRIEGEL (Z. physiol. Chem., 1933, **218**, 129—141).—Oxazoles are produced by heating α-NH_2-acids with AcCl and AcOH, but better yields are obtained by addition of PCl_5 to the NH_2-acid after acetylation with Ac_2O and NaOAc. The following were prepared by this method: from glycine, 2 : 5-dimethyloxazole [*chloroaurate*, m.p. 152°; *chloroplatinate*; picrate, m.p. 124° (? picric acid)]; from alanine, 2 : 4 : 5-*trimethyloxazole*, b.p. 134° [*chloroaurate*, m.p. 93°; *picrate*, m.p. 115° (? picric acid)]; from valine, 2 : 5-*dimethyl*-4-iso*propyloxazole*, b.p. about 150° (*picrate*); from leucine, 2 : 5-*dimethyl*-4-iso*butyloxazole*, b.p. 180° (*picrate*, m.p. 92°); from phenylalanine, 4-*benzyl*-2 : 5-*dimethyloxazole*, b.p. 267°; from tyrosine, (4-*hydroxyphenyl*)-[2 : 5-*dimethyloxazolyl*-(4)]-*methane*, m.p. 161° (*chloroaurate*, m.p. 103—104°); from glutamic acid (after esterification of the CO_2H groups freed by the reaction), *Me* β-[2 : 5-*dimethyloxazolyl*-(4)]-*propionate*, b.p. 130°/12 mm. (*picrate*, m.p. 118°). Oxazoles were not obtained from cystine, tryptophan, or aspartic acid, although the last gave a *compound* $C_8H_{13}O_4N$, b.p. 205°/1 mm. J. H. B.

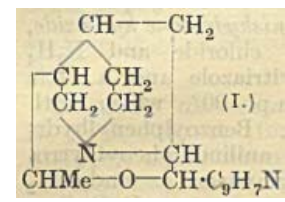
Local anæsthetics containing the morpholine ring. II. J. H. GARDNER, (MISS) D. V. CLARKE, and J. SEMB (J. Amer. Chem. Soc., 1933, **55**, 2999—3000; cf. A., 1931, 1075).—The following are prepared: the *hydrochlorides* of β-4-*morpholine-propyl cinnamate*, m.p. 189·6° (powdered) or 178° (large crystals), *phenylurethane*, m.p. 186·8°, and α-*naphthylurethane*, m.p. 170·7°, and of β-4-*morpholine-ethyl cinnamate*, m.p. 215·2°, and *phenylurethane*, m.p. 232·3°; β-4-*morpholine-ethyl* α-*naphthylurethane*, m.p. 96·5° (*hydrochloride*, hygroscopic). All are local anæsthetics of low toxicity. R. S. C.

Formation and stability of polybromide derivatives of heterocyclic compounds. II. Polybromide ion derivatives of alkylaminobenzthiazoles obtained from *s*-phenylalkylthiocarbamides and bromine, and a comparison of the ease of nuclear substitution by bromine in 1-alkylaminobenzthiazolium and 1-imino-2-alkyl-1 : 2-dihydrobenzthiazolium ions. M. O. FAROOQ, R. F. HUNTER, and S. T. H. JAFFERY (J. Indian Chem. Soc., 1933, **10**, 189—196).—NHPh·CS·NHEt with excess of Br in hot $CHCl_3$ affords 1-*ethylaminobenzthiazole hydrotetrabromide*, m.p. 90°, which contains a $Br_4^{\ominus}$ ion [also obtained from 1-*ethylaminobenzthiazole hydrobromide*, m.p. 219—220° (prepared from the base and HBr) and excess of Br in warm $CHCl_3$], converted by H_2SO_3 into 1-ethylaminobenzthiazole, m.p. 93—94° (lit., 87—88°), and by boiling EtOH–H_2O into 5-bromo-1-ethylaminobenzthiazole as a result of the high reactivity of the *p*-position to the ring N atom in the thiazolium ion (cf. A., 1930, 483). Similarly, NHPh·CS·NHPr$^{\alpha}$ (I) affords 1-n-*propylaminobenzthiazole hydropentabromide*, m.p. 57—59°, which loses Br over KOH to give the *hydrotribromide*, m.p. 57° [also obtained from (I) and a lower concn. of Br], further reduced by H_2SO_3 to the base. *s*-Phenyl-*iso*butyl- and -*iso*amyl-thiocarbamide and Br afford *hydrotribromides*, m.p. 98° and 61—62°, respectively, both reduced to the thiazoles with H_2SO_3. 1-*iso*-Butylaminobenzthiazole when extensively brominated affords 5-*bromo*-1-iso*butylaminobenzthiazole hydropentabromide*, m.p. 76—77°, reduced to 5-bromo-1-*iso*butylaminobenzthiazole (A., 1927, 263). *s*-Phenyl-*n*-hexylthiocarbamide, m.p. 110° (lit., 103—104°), affords an unstable *hydropentabromide*, m.p. 66—67°, reduced (H_2SO_3) to 1-*n*-hexylaminobenzthiazole, m.p. 67—68° (lit., 57°). The -*n*-heptylthiocarbamide, m.p. 78° (lit., 70—71°), gives an indefinite Br-additive *compound*, m.p. 73—74°, reduced to 1-*n*-heptylaminobenzthiazole, m.p. 61—62° (lit., 55°). J. L. D.

Synthesis of nornicotine and nicotine. L. C. CRAIG (J. Amer. Chem. Soc., 1933, **55**, 2854—2857).—The prep. of Na pyridine-3-sulphonate (V catalyst; 35—40% yield) is modified. Et γ-bromopropyl ether forms a Grignard reagent normally, which with β-picolinonitrile gives 3-*pyridyl* γ-*ethoxypropyl ketone*, b.p. 141—143°/5 mm., the oily oxime of which is reduced (EtOH–Fe–AcOH–Zn dust) to δ-3-*pyridyl*-δ-*amino*-n-*butyl alcohol*, b.p. 151—152°/5 mm. (*picrate* and *phenylthiourethane*, oils; *oxalate*, m.p. 155°), also obtained in poor yield from the oily phenylhydrazone by Zn and AcOH. This base with 48% HBr at 150—155° gives nornicotine, b.p. 139—140°/12 mm., and thence nicotine. R. S. C.

Polarimetric determination of quinine and its salts. C. LAPP (Ann. Chim. Analyt., 1933, [ii], **15**, 289—301).—[α] of quinine and some of its salts shows changes at p_H 4·5 and 6·5, being const. between these two vals., and corresponding with successive dissociation at the N atoms; the results are independent of the nature of the acid. The amount of quinine either alone or as the salt may be determined by measuring [α] between p_H 4·5 and 6·5. F. R. S.

Analogies between β-*iso*cinchonine (cinchonigine) and β-*iso*quinidine. A. KONOPNICKI, R. LUDWICZAKÓWNA, and J. SUSZKO (Rocz. Chem., 1933, **13**, 360—369).—β-*iso*Cinchonine [regarded as (I) (*methiodide*, m.p. 252°; *benzyliodide*, m.p. 216°; *oxide*, m.p. 192—193°)] yields when heated at 100° for 30 hr. with 25% AcOH β-*iso*cinchonicine [*hydriodide*, m.p. 149—150°; N-*Ac*, m.p. 121°, N-*NO*-, $+H_2O$, m.p. 101—103°, *Br*-, m.p. 60°, N-*Me*, m.p. 86° (*methiodide*, m.p. 231—232°; *hydriodide*, m.p. 282°; *Br*-derivative, m.p. 178—179°), N-*Et*, m.p. 85—86° (*hydriodide*, m.p. 232°), and N-*benzyl* derivative, an oil]. The behaviour of (I) towards various reagents is in every way analogous to that of β-*iso*quinidine (II) under similar conditions, and the [α] of the above compounds vary similarly to those of the corresponding derivatives of (II). R. T.



Attempts to prepare antimalarials. IV. Derivatives of cotarnine. G. S. AHLUWALIA, K. N. KAUL, and J. N. RÂY (J. Indian Chem. Soc., 1933,

10, 197—201; cf. A., 1932, 1047).—Cotarnine (I) and *o*-NO_2·C_6H_4·CHO in hot EtOH afford 1-*cotarnino-o-nitrophenyl ketone*, m.p. 154°, reduced ($SnCl_2$–HCl) during 10 hr. to the *amine*, m.p. 121°, which affords with $COMe_2$ in EtOH, *anhydrocotarnino-4-quinoline*, m.p. 133°. Similarly, (I) and 3 : 4-dimethoxy-6-nitrobenzaldehyde afford 1-*cotarnino-(3′ : 4′-dimethoxy-6′-nitrophenyl) ketone*, m.p. 165° (decomp.), which cannot be reduced to the amine. *Me* β-2 : 4-*dinitrophenylpropionate*, m.p. 40°, with (I) in MeOH containing piperidine affords a *compound*, m.p. 112—113°, not reduced to an anhydrocotarninoquinoline. Nitration of β-3 : 4-methylenedioxyphenylpropionic acid in AcOH at 0° affords the 6-NO_2-derivative, m.p. 152° (*Me* ester, m.p. 72°). Similarly, β-piperonylpropionamide affords the 6-NO_2-derivative, m.p. 186°. (I) with COPh·CH_2Br or COPh·CH_2·OMe in boiling EtOH affords *ω-ethoxy-ω-cotarninoacetophenone*, m.p. 120°. (I) in hot EtOH with ω-anilino-, ω-p-toluidino-, and ω-*m*-toluidino-acetophenone affords *anhydrocotarnino-anilino-*, m.p. 130° (decomp.), -p-*toluidino-*, m.p. 134°, and -m-*toluidino-acetophenone*, m.p. 116°, none of which can be cyclised to an indole. (I) in hot EtOH with β-aceto-α-naphthol, resacetophenone, and phenylcarbamide affords *products*, m.p. 146°, 191° (isolated as the hydrochloride), and 155°, respectively. J. L. D.

Preparation of hydrastinine from narcotine. K. Toptschiev (J. Appl. Chem. Russ., 1933, **6**, 529—535).—In large-scale repetition of Pyman and Remfry's synthesis (J.C.S., 1912, **101**, 1595) 53 kg. of narcotine yielded on oxidation 26 kg. of cotarnine, which with Zn and H_2SO_4 gave 20 kg. of hydrocotarnine, and this with Na in C_5H_{11}·OH yielded 8·17 kg. of hydrohydrastinine, which on oxidation with I gave 4 kg. of hydrastinine hydrochloride. R. T.

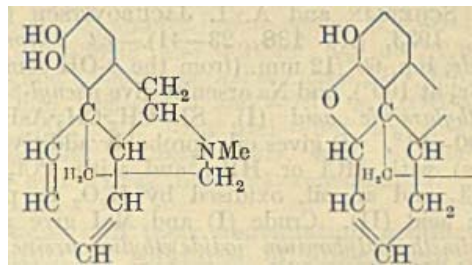
Camphorcarboxylates of the alkaloids. J. Bouillot and M. Leulier (J. Pharm. Chim., 1933, [viii], **18**, 49—59).—Camphorcarboxylic acid (I) (cf. A., 1903, i, 4) when anhyd. has m.p. 119°, $[\alpha]_D$ +10·82° in EtOH. (I) in hot $CHCl_3$ with strychnine and brucine affords *strychnine* (+4H_2O, m.p. 128°), and *brucine camphorcarboxylate*, m.p. 90°, $[\alpha]_D$ +6·65° in EtOH, respectively. (I) (Ba salt) and sparteine sulphate in H_2O afford the *neutral salt*, $[\alpha]_D$ +39·5° in H_2O, and the basic salt (+3H_2O, $[\alpha]_D$ +12·5° in H_2O). The camphorcarboxylates are easily hydrolysed or decomposed by heat. J. L. D.

Alkaloids of *Berberis heteropoda*. A. Orekhov (Arch. Pharm., 1933, **271**, 323—327).—This plant contains oxyacanthine+berbamine (2·7), berberine (3·85), palmatine (0·20), and jatrorrhizine + columbamine (0·25%). R. S. C.

M.p. and crystal forms of morphine. L. Kofler and A. Kofler (Arch. Pharm., 1933, **271**, 387—392).—Anhyd. morphine is obtained in stable, micro-m.p. 240° or 248° (decomp.) according to the rate of heating, and metastable, m.p. 197°, forms. Crystallographic data and photomicrographs of these and the hydrated form are given. R. S. C.

Deoxymorphines. L. F. Small and D. E. Morris (J. Amer. Chem. Soc., 1933, **55**, 2874—2885).—Deoxycodeine-*A* cannot be demethylated. α-Chloromorphide is resinified by Na and EtOH, or Zn dust and EtOH, but, when reduced electrolytically, gives *deoxymorphine*-A (I), m.p. 260—262°, $[\alpha]_D^{28}$ +106°

(I.)



10% AcOH [*salicylate*, m.p. 248—251° (decomp.), $[\alpha]_D$ +85° in MeOH; *benzoate*, m.p. 240—245° after sintering at 215—223°, $[\alpha]_D^{31}$ +82° in EtOH; *H sulphate*, m.p. 145—151° after softening at 130°, $[\alpha]_D$ +61·6° in H_2O], giving (as benzoate) with CH_2N_2 in Et_2O (but not with other reagents) deoxycodeine-*A*, and hydrogenated (as salicylate) (PtO_2) in EtOH to *tetrahydrodeoxymorphine* (II), unstable, sublimes at 150°/0·3 mm., $[\alpha]_D^{24}$ −77±5° in MeOAc [*salicylate*, m.p. 238—240°, $[\alpha]_D^{28}$ −31° in MeOH; *hydrochloride*, m.p. 260—262° after softening at 255—260°, $[\alpha]_D^{24}$ −47° in EtOH; *hydriodide*, m.p. 268—271°, $[\alpha]_D^{24}$ −32·7° in H_2O; *methiodide*, m.p. 269—271° (decomp.), $[\alpha]_D^{31}$ −31° in MeOH], also obtained from tetrahydrodeoxycodeine (IV) by HI and giving this base when treated as hydrochloride with an excess of CH_2N_2 in MeOH. Dihydromorphine hydrate, double m.p. 132° and 204—206°, and $SOCl_2$ give chlorodihydromorphide, m.p. 228—229° after sintering at 155°, $[\alpha]_D^{30}$ −145° in EtOH (*hydrochloride*, m.p. 323—326°, $[\alpha]_D^{28}$ −131° in H_2O), which is not reduced electrolytically or catalytically, with CH_2N_2 gives chlorodihydrocodide, and with Na and pure MeOH at 140° affords *deoxymorphine*-C (III), +0·5H_2O, m.p. 189—190° (slight sintering at 130°), $[\alpha]_D^1$ −155·7° in EtOH [*hydrochloride*, +1·5H_2O, decomp. 240—245° when fresh and 291—294° when kept, $[\alpha]_D^{30}$ −147° in H_2O; *hydriodide*, m.p. 292—294°, $[\alpha]_D^{32}$ −111° in H_2O; *methiodide*, softens at 155—160°, m.p. 260—264° (decomp. 265°), $[\alpha]_D^{32}$ −98° in MeOH], giving with CH_2N_2 in MeOH–Et_2O deoxycodeine-*C* [*tartrate*, m.p. about 161—165° (decomp. 170°)] and obtained therefrom by NaOMe–MeOH at 140°, and hydrogenated as hydrochloride in H_2O to (II) and in AcOH to a mixture of (II) and *dihydrodeoxymorphine*-D. The last base, when methylated, gives dihydrodeoxycodeine-*D*, m.p. 103—105° (*H tartrate*, +2H_2O, m.p. 124—125°, $[\alpha]_D^8$ −29·9° in H_2O, anhyd., m.p. 154—154·5°), and is also obtained by hydrogenation of deoxycodeine-*C* in AcOH. Tetrahydrodeoxycodeine exists in two anhyd. *forms*, m.p. 124—125° (unstable) and 156—157·5° (stable). The substance termed "deoxycodeine-*B*" (A., 1931, 1077) was deoxycodeine-*A*, anhyd. m.p. 159—161°, and +H_2O, two forms, m.p. 151—152° (decomp. 153°) and about 122—126°, respectively (both lose H_2O in the air), $[\alpha]_D$ −118·8° in EtOH (*salicylate*, m.p. 220·5—221°, $[\alpha]_D$ +104·4°; methiodide obtained cryst., m.p. 219—221°, $[\alpha]_D$ +95·7°), mixed with a tenaciously retained *substance*, m.p. about 115°, $[\alpha]_D^{26}$ +6·6° in 10% AcOH, which is hydrogenated to (IV). R. S. C.

Arsenic derivatives of organic sulphides. I. *sec.*-Phenyl-β-sulphidoalkylarsinic acids of the type, SR·C_2H_4·AsR'O·OH, and their derivatives. S. M. SCHERLIN and A. I. JACUBOVITSCH (J. pr. Chem., 1933, [ii], **138**, 23—41).—*Et* β-*bromoethyl sulphide*, b.p. 60°/12 mm. (from the β-OH-compound by PBr_3 at 100°), and Na arsenite give *phenyl*-β-(*ethylthiol*)*ethylarsinic acid* (I), SEt·CH_2·CH_2·$AsPhO_2H$, m.p. 90—91°. (I) gives oils (probably additive compounds) with HCl or HBr, and with PCl_3 gives $AsPhCl_2$ and an oil, oxidised by H_2O_2 to phenylarsinic acid (II). Crude (I) and MeI give *phenyl*-β-(*ethylmethylsulphonium iodide*)*ethyliodoarsine* (III), SEtMeI·CH_2·CH_2·AsPhI, m.p. 105—106°, but pure (I) gives *phenyl*-β-(*ethylsulphonium iodide*)*ethylarsinic acid*, m.p. 97—100°, which with HCl liberates I and with HI gives (III). (I) with Br, followed by NaOH, gives (II), and with 1·5 or 3% H_2O_2 affords *phenyl*-β-(*ethylsulphone*)*ethylarsinic acid*, $SO_2Et·CH_2·CH_2·AsPhO_2H$, m.p. 177°, which with HCl, H_2S, and a little I gives *phenyl*-β-(*ethylsulphone*)-*ethylchloroarsine*, $SO_2Et·CH_2·CH_2·AsPhCl$, m.p. 66°. C_5H_{11}·SK and $CH_2Cl·CH_2·OH$ give iso*amyl* β-*hydroxyethyl sulphide*, b.p. 110—111°/13 mm., whence iso*amyl* β-*bromoethyl sulphide*, b.p. 102°/13 mm., and the crude *iso*amyl analogue of (I) were obtained; the last with H_2O_2 gives *phenyl*-β-(iso*amylsulphone*)-*ethylarsinic acid*, m.p. 139·5—140·5°. Similarly were obtained *ethyl*-β-(*ethylsulphone*)*ethylarsinic acid*, m.p. 164—165°, *Ph* β-*bromoethyl sulphide* (from the β-OH-compound and PBr_3), *phenyl*-β-(*phenylsulphone*)*ethylarsinic acid* (IV), m.p. 192—193° (decomp.), and *phenyl*-β-(*phenylthiol*)*ethylarsinic acid* (V), m.p. 85—86° (*Ca* salt). (V) gives an oil with HCl and with PCl_3 an oily chloride which decomposes when distilled to $AsPhCl_2$. (IV) and PCl_3 give *phenyl*-β-(*phenylsulphonyl*)*ethylchloroarsine*, m.p. 90—91°. The C·As''' linking is weakened by the SR group, and the ease of oxidation of the S atom is greatly increased by the presence of As in the mol. R. S. C.

Hydrochlorides and perchlorates of *p*-aminophenylarsinic acid. J. PRAT (Compt. rend., 1933, **197**, 67—69).—The *dihydrochloride* (+1H_2O) (I), and the *perchlorates* $NH_2·C_6H_4·AsO_3H_2,HClO_4$ and $2NH_2·C_6H_4·AsO_3H_2,HClO_4$ are described. At 100° in dry air (I) loses 1 H_2O and 1 HCl, but the hydrochloride of the Ac derivative is stable, whence it is concluded that the residue after heating (I) is the arsonium chloride. H. A. P.

Tetra-arylarsonium halides. F. F. BLICKE and C. MARZANO (J. Amer. Chem. Soc., 1933, **55**, 3056).—Addition of halogen acid to the product of reaction of MgPhBr and $AsPh_3O$ gives *tetraphenylarsonium chloride*, m.p. 272—274°, *bromide*, m.p. 273—275°, and *iodide*, m.p. 292—293°, the halogen of which is fairly stable to NaOH–EtOH and Ag. R. S. C.

Phosphorus derivatives of triphenylmethane. H. H. HATT (J.C.S., 1933, 776—786).—Triphenylmethylhydrogenphosphinic acid (I), m.p. 245—248° (decomp. 255—260°) [improved prep.; *Ag* salt; *Me* ester, m.p. 163—164°; *Et* ester, m.p. 118—121·5°. (I) is regenerated from the esters with I-free HI in AcOH], with I in AcOH, or alkaline $KMnO_4$, gives triphenylmethylphosphinic acid (II) [Me ester, m.p. 154·5—155·5° (no second form; cf. A., 1924, 832); additive *compound* with $POCl_3$], and with PCl_3 in presence of N_2 gives *triphenylmethyldichlorophosphine* (III), m.p. 138—140° (decomp. 240°). (III) is converted by NaOH into (I), by NaOEt–EtOH into $CHPh_3$ (IV), by H_2SO_4 into $CPh_3·OH$ (V), by O_2 in Et_2O or C_6H_6 into PhOH, $COPh_2$, $[CPh_3·O·]_2$ (VI), and triphenylmethylphosphinyl dichloride (VII), and by I in $NaHCO_3$ in $CHCl_3$ into (V) and (VI). (VII) is also obtained from $CPh_3·OK$ with PCl_3, is stable to Cl_2, Br, or I in $CHCl_3$, and is converted by EtOH-free NaOEt according to the conditions mainly into the Et (VIII), or Et H (IX) ester of (II), or into Et triphenylmethylchlorophosphinate (X), m.p. 140—141°, which is converted by H_2SO_4 into (V), and by HI in AcOH into triphenylmethylchlorophosphinic acid (XI), m.p. 229—230°. (XI) is also obtained from (II) with PCl_5 in C_6H_6, whilst PCl_5 alone with (XI) or (VII) gives CPh_3Cl. PCl_5 in C_6H_6 converts (IX) into (X) [isolated as (XI)], and a little (II) and (IV). (V) with $PCl_5·OEt$ gives (X) and a little (XI). (XI) with Et_2SO_4 and K_2CO_3 in xylene gives (X) and *Et triphenylmethylchloropyrophosphinate*, m.p. 221—222·5°, also obtained by the action of Et_2SO_4 in xylene on a mixture of (VII) and (XI), and converted by H_2SO_4 into (V). The mechanism of the formation of the pyro-ester is discussed. (VIII) with PCl_5 in C_6H_6 gives *Et triphenylmethylpyrophosphinate* (mixture of stereoisomerides, α-, m.p. 222—223°, and β-, m.p. 228—231°), hydrolysed by HI in AcOH, or by HCl at 195—200° to the *acid*, m.p. 267—270° (decomp. 280°) [mixture of *Me* esters, m.p. 227—233°, similarly obtained from the Me ester of (II), and not separated; *Ag* salt], which is an individual giving the same mixtures on re-esterification. The asymmetry of the pyro-acid is considered to be destroyed by ionisation or tautomeric shift of the H atoms of the OH groups. The constitutions of (VII) and related compounds are discussed and reasons are given for preferring its formulation as a phosphinyl dichloride rather than as triphenylmethoxyphosphorus dichloride (cf. A., 1929, 1470). A. A. L.

Decomposition and reactions of carbamide. III. Reactions of carbamide with amines and amino-acids. J. M. DAS-GUPTA (J. Indian Chem. Soc., 1933, **10**, 169—175).—Interaction of aromatic amines and varying proportions of $CO(NH_2)_2$ give results substantially in agreement with previous work (cf. A., 1923, i, 902) and indicate the probable absence of *s*-diphenylcarbamide-4 : 4-distibinic acid (A., 1931, 751) in "urea stibamine" (I). Alkaline hydrolysis of (I) affords no carbamide derivative, but *p*-stibanilic acid, which appears to be the principal constituent of (I). J. L. D.

Interaction of the boron sextet with adjacent groups. D. L. YABROFF, G. E. K. BRANCH, and H. J. ALMQUIST (J. Amer. Chem. Soc., 1933, **55**, 2935—2941).—Combination formulæ for $B(OH)_3$ involving the tautomeric effect are in better accord than other formulæ with the nature of its additive compounds, the substitution of aromatic B compounds, and the fact that it is a weaker acid than phenylboric acid ($\alpha=1·9\times10^{-9}$ at 20°). R. S. C.

Mercury derivatives of camphor. I. Constitution of Reychler's acid. J. D. LOUDON (J.C.S., 1933, 823—825).—Camphor-10-sulphinic acid (I) with $HgCl_2$ in EtOH gives *camphor*-10-*mercuri-chloride* (II), m.p. 166°, converted by alkaline $SnCl_2$ into *biscamphor*-10-*mercury* (III), m.p. 255—256° [reconverted into (I) by $HgCl_2$], and by Br in KBr at room temp. into *camphor*-10-*mercuribromide*, m.p. 156° [also obtained from (I) and (III) with $HgBr_2$, or from (III) together with 10-bromocamphor by bromination], or at 70° into 10-bromocamphor (*oxime*, m.p. 156°), which is identical with β-bromocamphor. Similar reactions are described for *camphor*-10-*mercuri-iodide*, m.p. 146°, and for 10-*iodocamphor*, m.p. 75° (*oxime*, m.p. 158°) [best prepared by the action of I in C_6H_6 on (II)]. (III) with $(SCN)_2$ in $CHCl_3$ gives camphor-10-thiocyanate (not isolated), reduced to camphor-10-thiol (and a little camphor), which is also obtained from (I), or from camphorchlorosulphoxide. The composition of the above compounds, and hence of Reychler's acid, follows from the known 10-position of the S atom in the last-named compound. A. A. L.

Abnormal reactions of magnesium benzyl chloride. II. Mechanism of the *o*-tolyl rearrangement. J. R. JOHNSON (J. Amer. Chem. Soc., 1933, **55**, 3029—3032; cf. A., 1932, 385).—The abnormal reactions of $CH_2Ph{\cdot}MgBr$ are explained, without assuming rearrangement of free CH_2Ph ions or radicals, on the assumption of the formation of primary additive complexes leading, through chelation and ring opening, to abnormal products. R. S. C.

Reactions of magnesium triphenylmethyl bromide. II. W. E. BACHMANN and R. F. COCKERILL (J. Amer. Chem. Soc., 1933, **55**, 2932—2934; cf. A., 1931, 1058).—$CPh_3{\cdot}MgBr$ with dry air gives after decomp. by dil. acid $(CPh_3{\cdot}O{\cdot})_2$ (10%) and $CPh_3{\cdot}OH$ (54%). With the reagents stated (first name) it gives the following products in > 66% yield: MeI, CPh_3Me; EtBr, CPh_3Et; $Pr^{\alpha}Br$, CPh_3Pr^{α} (41% yield); $Bu^{\gamma}Br$, $CHPh_3$; allyl bromide, *δδδ-triphenyl-Δ$^{\alpha}$-butene*, m.p. 69·5—70·5° (hydrogenated to ααα-triphenylbutane); CH_2PhCl, $CPh_3{\cdot}CH_2Ph$; $ClCO_2Me$ (or Et), $CPh_3{\cdot}CO_2Me$ (or Et); $CH_2Cl{\cdot}OMe$, $CPh_3{\cdot}CH_2{\cdot}OMe$; $HgBr_2$, CPh_3; S, $CPh_3{\cdot}SH$; PhOBz, CPh_3Bz (46% yield); PhNCS, $CPh_3{\cdot}CS{\cdot}NHPh$. R. S. C.

Organic lead compounds. V. Asymmetric derivatives. P. R. AUSTIN (J. Amer. Chem. Soc., 1933, **55**, 2948—2953; cf. A., 1932, 1148).—Attempts to resolve asymmetric Pb compounds containing four covalent linkings failed. $PbPh_3Cl$ and $MgPr^{\alpha}Br$ in Et_2O–C_6H_6 give *Pb triphenyl* n-*propyl*, m.p. 69—70°, which with HCl gives *Pb diphenyl* n-*propyl chloride*, m.p. 141° (decomp.), or *Pb phenyl* n-*propyl dichloride* (I), m.p. 123° (decomp.), according to the conditions. (I) with *o*-$C_6H_4Me{\cdot}MgBr$ or Pb di-*o*-tolyl chloride with $MgPr^{\alpha}Br$ affords *Pb di*-o-*tolyl phenyl* n-*propyl*, m.p. 49—50°, which with HCl gives *Pb* o-*tolyl phenyl* n-*propyl chloride* (II), m.p. variable, max. 122—123° (decomp.); this with d- or l-p-*lithiumphenyl* sec.-*octyl ether* (III) gives *Pb phenyl* p-sec.-*octyloxyphenyl* o-*tolyl* n-*propyl*, $C_6H_{13}{\cdot}CHMe{\cdot}O{\cdot}C_6H_4{\cdot}PbPhPr^{\alpha}{\cdot}C_6H_4Me$, an oil, $[\alpha]_D^{25}$ +2·4° or −3·2° in $CHCl_3$, which could not be separated into isomerides and gave (II) with HCl. Similarly were prepared: *Pb triphenyl* n-*amyl*, m.p. 16—17°; and *Pb diphenyl* n-*amyl chloride*, m.p. 123° (decomp.). *d*- and *l*-β-Bromo-octane, b.p. 80—81°/18 mm., $[\alpha]_D$ +36·36° and −37·46°, and *p*-$C_6H_4Br{\cdot}ONa$ give d- and l-p-*bromophenyl* sec.-*octyl ether*, b.p. 141—144°/2 mm., $[\alpha]^{25}$ +8·10° and −7·72° in EtOH, whence d- and l-(III), $[\alpha]_D^{25}$ +8·3° and −9·8°, and d- and l-p-*carboxyphenyl* sec.-*octyl ether*, m.p. 63—64°, $[\alpha]_D^{23}$ +9·64° and −10·42° in EtOH, were obtained. R. S. C.

Proteins and their degradation products. I. Liberation of mixtures of amino-acid esters from mixtures of their hydrochlorides. S. UCHIDA and S. AI (J. Soc. Chem. Ind. Japan, 1933, **36**, 221—222B).—The use of Ag_2O in Et_2O–EtOH is recommended. A. A. L.

Clupein. VII. K. FELIX, R. HIROHATA, and K. DIRR (Z. physiol. Chem., 1933, **218**, 269—279; cf. this vol., 80).—After hydrolysis of clupein Me ester hydrochloride (I) with 2*N*-HCl for 16 hr. the N pptd. by phosphotungstic acid corresponds with the arginine (II) content and the N not pptd. with the NH_2-acid content. Thus the linkings between mono-NH_2-acid (III) and (II) are completely hydrolysed. (II) and arginylarginine (IV) (*dipicrolonate*, decomp. 290°) were obtained from the reaction products. After 8 hr. hydrolysis of (I) with *N*-HCl the product gave the biuret reaction. In addition to (II) a protone (*picrolonate*, m.p. 190°, decomp 220°) containing 2 mols. of (II) and 1 mol. of (III) (having 5 C atoms, not identified) was isolated, also *triarginylarginine* (V) (*picrolonate*, decomp. 190°, blackens 230°; *picrate*, sinters 190°, decomp. 220°). The clupein mol. yields two kinds of protone differing only in the linking of (III), which is attached in the one case through CO_2H, and in the other through NH_2 to (IV). These protones are arranged alternately in the chain and can thus give rise to (V). J. H. B.

Simultaneous determination of nitrogen and the halogens in organic substances. D. BUTTESCU (Bul. Chim. Soc. Romane, 1933, **34**, 105—110).—The substance is mixed with Ag powder (made by reducing Ag_2O with H_2) and heated gently in a current of H_2, the gases evolved and the H_2 passing over Ni–quartz to convert the N in the substance into NH_3, which is absorbed in H_2SO_4 and determined volumetrically. The halogen is retained by the Ag in the boat and the Ag halide is extracted from this mixture by treatment with aq. NH_3 (for Cl or Br) or $Na_2S_2O_3$ (for I) and converted into AgCl for weighing. A. R. P.

Analysis of propylene and *cyclo*propane in mixtures containing both. S. Z. ROGINSKI and F. H. RATHMANN (J. Amer. Chem. Soc., 1933, **55**, 2800—2805).—Mixtures of propylene (I) and *cyclo*propane (II) may be analysed by aq. I–Br, which reacts very rapidly with (I), but very slowly with (II). Other methods are inaccurate or tedious. The reagent also removes traces of (I) from nearly pure (II). The small amount of I used acts catalytically for the reaction of (I) with Br only. (II) reacts more rapidly with conc. H_2SO_4 than does (I), and is

rapidly attacked by cold aq. $KMnO_4$. Preliminary experiments on the isomerisation of (II) to (I) by Pt-asbestos at 600—650° are described. R. S. C.

Reactions of organic sulphur compounds. L. BERMEJO and J. J. HERRERA (Anal. Fís. Quím., 1933, **31**, 48—49).—Me, Et, Pr, Bu, and amyl sulphides give violet colorations with Na nitroprusside in feebly alkaline solution, but Ph_2S, PhSH, and $(CH_2Ph)_2S$ do not. R. K. C.

Identification of organic compounds. XII. Carboxylic acid principle and its importance for the detection of organic acids. L. ROSENTHALER (Arch. Pharm., 1933, **271**, 328—337).—Org. acids give reactions similar to the substances derived formally from them by loss of CO_2, *e.g.*, $CCl_3{\cdot}CO_2H$ resembles $CHCl_3$ rather than AcOH; when isomerism exists, the resemblance is the greater the easier is the loss of CO_2. This is called the "carboxylic acid principle." Examples are quoted. R. S. C.

Determination of oxalacetic acid. P. OSTERN (Z. physiol. Chem., 1933, **218**, 160—163).—The CO_2 quantitatively developed with NH_2Ph by Wohl's reaction (A., 1901, i, 365) is measured manometrically. $CH_2Ac{\cdot}CO_2H$ interferes, but as it reacts much more slowly than oxalacetic acid, the correct val. for the latter may be found by extrapolation. J. H. B.

Identification of the acyl group in certain esters. C. F. KOELSCH and D. TENENBAUM (J. Amer. Chem. Soc., 1933, **55**, 3049—3050).—MgEtBr and *p*-$C_6H_4Me{\cdot}NH_2$ in Et_2O give $C_6H_4Me{\cdot}NH{\cdot}MgBr$, which reacts with a no. of esters to give the *p*-toluidides. Et β-chlorolactate gives β-*chlorolacto*-p-*toluidide*, m.p. 164—165°, and the p-*toluidide*, m.p. 168—169°, of *N*-*p*-tolylserine. The method fails with esters of several dibasic acids. R. S. C.

Hydrazines. II. *p*-Tolylhydrazine as a reagent for the identification of aldehydes and ketones. P. P. T. SAH and H. H. LEI. **III. *p*-Chlorophenylhydrazine as a reagent for the identification of aldehydes and ketones.** P. P. T. SAH, H. H. LEI, and T. SHEN (Sci. Rep. Nat. Tsing Hua Univ., 1933, **2**, 1—5, 7—12).—II. *p*-Tolylhydrazine (improved prep.) gives p-*tolylhydrazones* of the following: *m*-, m.p. 154—155°, and *p*-nitrobenzaldehyde, m.p. 164—165°, furfuraldehyde, m.p. 105—106°, 2-furfurylideneacetone, m.p. 187—188° (sinters 181°), COPhMe, m.p. 126—127°, $COPh_2$, m.p. 84—85°, $CH_2Ac{\cdot}CO_2Et$, m.p. 87—88°, Et lævulate, m.p. 117—119°, Et oxalacetate, m.p. 105—106°, benzylideneacetone, m.p. 179—180° (sinters 171°).

III. *p*-Chlorophenylhydrazone (improved prep.) gives the following: *acetaldehyde*-, m.p. 98—99°, benzaldehyde-, m.p. 134—135°, salicylaldehyde-, m.p. 177—178°, *cinnamaldehyde*-, m.p. 138—139°, *m*-, m.p. 158—159°, and p-*nitrobenzaldehyde*-, m.p. 162—163°, *furfuraldehyde*-, m.p. 97—98°, *furfurylideneacetone*-, m.p. 179—180°, *acetophenone*-, m.p. 108—109°, *benzophenone*-, m.p. 121—122°, *Et acetoacetate*-, m.p. 115—116°, *Et lævulate*-, m.p. 112—113° *Et oxalacetate*-, m.p. 119—120°, *benzylideneacetone*-, m.p. 179—180°, and p-*nitrobenzylideneacetone*-p-*chlorophenylhydrazone*, m.p. 218—219°. All m.p. are corr. A. A. L.

2 : 4-Dinitrophenylhydrazine in determination of carbonyl compounds. C. TORRES and S BROSA (Anal. Fís. Quím., 1933, **31**, 34—36; cf. A., 1932, 411).—Δ^6-*m*-Menthen-5-one (Δ^6-1-methyl-3-*iso*propyl*cyclo*hexen-5-one, "hexetone") forms a 2 : 4-*dinitrophenylhydrazone*, m.p. 104°, which is pptd. quantitatively from aq.-alcoholic H_2SO_4. R. K. C.

Cuprometric determination of sugars in the presence of ammonia. L. BEY, R. BEY, and G. VALENSI (Bull. Soc. chim., 1933, [iv], **53**, 407—416).—Directions are given for the determination of glucose, fructose, invert sugar, lactose, and maltose by ammoniacal Cu tartrate. The effects of various factors are studied. R. S. C.

Shaffer–Somogyi reagent [for determination of sugar]. V. J. HARDING and C. E. DOWNS (J. Biol. Chem., 1933, **101**, 487—492).—The Somogyi reagent (A., 1927, 69) is made up in two parts which are kept separate until used. The influence of varying p_H on the reduction vals. of different sugars is studied, the results providing a method of sugar differentiation. The presence of NH_3 influences the determination of sugars; it is removed by MgO and KH_2PO_4. H. D.

Microchemical reaction for cholesterol. C. VAN ZYP (Pharm. Weekblad, 1933, **70**, 775—776).—Cholesterol (I) gives characteristic bluish-black, strongly dichroic crystals when treated in the dark with vapours of conc. HI containing I. The reaction fails with ergosterol and phytosterol (II) or with mixtures of (I) containing 5% of (II). Animal fats which have been adulterated with vegetable fats also fail to give the reaction. The latter should be useful in examining cod-liver oil. S. C.

Polarographic studies with the dropping mercury cathode. XXXIII. Micro-determination of cysteine and cystine in the hydrolysates of proteins, and the course of protein decomposition. R. BRDICKA (Coll. Czech. Chem. Comm., 1933, **5**, 238—252).—Cystine (I) (and cysteine) is determined in the products of hydrolysis of proteins (II) by comparison of the polarographic curves in the presence of $CoCl_2$ with those of solutions of (I) of known concn., the optimum concn. being 1·2—24 mg. per litre (this vol., 619, 681). The method is accurate to about 5%. The hydrolysis products from glutathione give high results. Albumins contain approx. twice as much (I) as globulins. A similar method using $Co[NH_3]_6Cl_3$ is applied to (II), and an equation derived which is shown to describe approx. the course of hydrolysis of (II). A. A. L.

Compounds which give a Beilstein reaction yet contain no halogen. J. VAN ALPHEN (Rec. trav. chim., 1933, **52**, 567—568).—Many derivatives of 1 : 3 : 4 : 6-Δ^2-trimidine, which contain no halogen, give a positive Beilstein test. J. L. D.

Reactions of purine bases with copper sulphate and alkali. R. KLIMEK and J. K. PARNAS (Z. physiol. Chem., 1933, **218**, 30—32).—The purine bases unsubstituted in position 7 (adenine, guanine,

hypoxanthine, xanthine, trichloropurine, theophylline) give alkali-sol. complexes with $Cu^{"}$; 7-methyladenine, theobromine, caffeine, and 2 : 6-dichloro-7-methylpurine give no such complex. The alkali-sol. Cu complex given by one of the adenine nucleotides is a property of the carbohydrate group, not of the glyoxaline ring. J. A. B.

Erythroquinine reaction : its realisation, technique, and specificity. M. R. MONNET (J. Pharm. Chim., 1933, [viii], **18**, 59—65).—Factors influencing the reaction are investigated. J. L. D.

Selenium in the determination of phosphorus and nitrogen in phospholipins. F. E. KURTZ (Ind. Eng. Chem. [Anal.], 1933, **5**, 260).—Using Se as catalyst, digestion is more rapid than with Cu or Hg, and is more convenient than using a H_2SO_4–HNO_3 mixture. N and P can be determined in the same digest. E. S. H.

Biochemistry.

Apparatus for maintaining artificial respiration in laboratory animals. W. R. BOND Science, 1933, **77**, 515—516). L. S. T.

Oxidation of hæmocyanin. J. B. CONANT, B. F. CHOW, and E. B. SCHOENBACH (J. Biol. Chem., 1933, **101**, 463—473).—Hæmocyanin from *Limulus polyphemus* is oxidised by K cyanomolybdate or $KMnO_4$ in absence of O_2 to methæmocyanin (I) and in presence of O_2 to oxymethæmocyanin (II). Reduction of the partial pressure of O_2 above aq. (II) produces deoxygenation; hence (I), unlike methæmoglobin, combines reversibly with O_2. (I) and (II), which are $Cu^{"}$ compounds, are readily reduced, especially by $K_4Fe(CN)_6$ and 1 : 4-naphthoquinol when the reduction can be followed electrometrically or, with the latter reagent, titrimetrically using phenol-indophenol as indicator. F. O. H.

Mol. wt. of erythrocruorin. T. SVEDBERG and I. B. ERIKSSON (J. Amer. Chem. Soc., 1933, **55**, 2834—2840).—The term "erythrocruorin" for the red blood-pigment of invertebrates is revived. The erythrocruorins of *Arenicola marina* and *Lumbricus terrestris* are stable at p_H 2·6—8 and 2·6—10, have sedimentation const. 57·4 and $60·9\times10^{-13}$, mol. wt. 2,850,000 and 2,730,000, and isoelectric point 4·56 and 5·3, respectively, thus differing from hæmocyanins. The pigments from *Spirographis spallanzanii* and *Pomatoceros triqueter* also have mol. wt. of the order of millions. R. S. C.

Position of the bands in the spectrum of oxyhæmoglobin. A. KRUPSKI and F. ALMASY (Nature, 1933, **132**, 242).—A marked shift of the band maxima towards the ultra-violet occurs with a decrease in concn. of oxyhæmoglobin. L. S. T.

Specific gravity, dry substance, and nitrogen content of leucocytes. H. SCHLOSSMANN and M. GRUTER (Arch. exp. Path. Pharm., 1933, **171**, 317—318).—The following data were obtained with rabbit polymorphonuclear leucocytes and lymphocytes, respectively: sp. gr. $1·061\pm0·007$, $1·065\pm0·0045$; residue on drying in vac. over H_2SO_4, $20·40\pm0·87$, $21·04\pm0·64\%$ of the vol., $19·24\pm0·81$, $19·75\pm0·56\%$ of the wet wt.; N content on dry substance, $15·76+0·53$, $15·99\pm0·27\%$. F. O. H.

Separation and zinc content of the nucleus [of blood-corpuscles]. N. MIYAKE (Keijo J. Med., 1933, **4**, 247—260).—The nuclei of hen's blood-corpuscles, separated by freezing in presence of 0·9% NaCl or NH_4Cl, have a Zn content > that of the cytoplasm or plasma; the Fe content is very low. F. O. H.

Distribution of calcium between blood-plasma and erythrocytes. R. G. THOMAS (Austral. J. Exp. Biol., 1933, **11**, 109—118).—Blood-corpuscles (I) of the pig and man are devoid of Ca, whilst those of the ox contain 6·1 mg. Ca per 100 c.c. of (I). (I) of sheep, ox, and man are impermeable to $Ca^{"}$. H. G. R.

Bromine of blood. F. L. HAHN (Klin. Woch., 1933, **12**, 390).—Crit. of the method of Roman and Pincussen for the determination of blood-Br. NUTR. ABS. (*b*)

Determination of "normal" bromine content of blood. I. A. BIER and W. ROMAN (Klin. Woch., 1933, **12**, 391). **II.** H. FLEISCHHACKER and G. SCHEIDERER (Klin. Woch., 1933, **12**, 392).—I. The Pincussen method for the determination of blood-Br gives accurate results.

II. Crit. of the Pincussen method. NUTR. ABS. (*b*)

Determination of the iron content of the blood in children. I. P. SOBEL and I. J. DREKTER (Amer. J. Dis. Children, 1933, **45**, 486—497).—The venous blood of normal children contained 40—52 mg. Fe per 100 c.c. (average of 43·9 mg.). In various pathological conditions, the Fe content ranged from 18·2 to 74 mg. per 100 c.c. NUTR. ABS. (*b*)

Sulphur content of arterial and venous blood of the pancreas. S. KUMANI (J. Biochem. Japan, 1933, **17**, 423—432).—In fasting and normal dogs the total S content of the venous blood of the pancreas is > that of the arterial blood. The difference is enhanced by feeding or by stimulation of the vagus, but not of the splanchnic, and is at least partly due to insulin secreted into the blood. F. O. H.

Mineral composition of the haemolymph of the crayfish. A. BERNARD (Compt. rend. Soc. Biol., 1933, **112**, 880—882).—The ash content of crayfish hæmolymph is remarkably const., but the org. matter shows wide variations. The Na and Mg contents are similar to those previously reported, but the K and Ca contents differ. NUTR. ABS. (*b*).

Amino-acid-nitrogen in blood and its determination. I. S. DANIELSON (J. Biol. Chem., 1933, **101**, 505—522).—The Folin method for the determination of α-NH_2-acid-N (I) (A., 1922, ii, 540) is modified. NH_3 should be removed before analysis of the filtrates. Determinations of (I) in filtrates from laked and unlaked samples of blood show considerably higher vals. in the case of laked samples. In opposition to the findings of Simon (A., 1931,

1082) repeated washing of the corpuscles failed to give higher vals. The calc. distribution ratios of NH_2-acids between corpuscles and plasma was decreased by addition of (II) when the determination was made on laked blood filtrates, whilst when unlaked filtrates were used the ratio remained approx. the same. The same results were obtained by intravenous injection of (II) into dogs. It is concluded that the red blood-cells contain indiffusible substances capable of reacting with the reagents used. H. D.

Physico-chemical study of the flocculation of serum-albumin by resorcinol. A. Boutaric, M. Pietre, and M. Roy (Compt. rend., 1933, **197**, 357—358).—Flocculation is due to adsorption, solubility decreasing with the amount adsorbed and becoming zero at the saturation point. R. S. C.

Total pigment and bilirubin in normal human blood-serum. J. R. Peter (Biochem. Z., 1933, **262**, 432—460).—A method for spectrophotometric determination of normal human serum-pigments is described. Serum-pigment vals. of whole blood or serum, on keeping in the dark at a low temp., remain const. or only very slowly decrease. A method of prep. of azo-solutions is described. The absorption curves of the extracts from the serum of healthy fasting subjects resemble those of Na bilirubin, but show deviations due to the lipochrome content. The absorption curves of the corresponding azo-solutions resemble, above 560 mμ, the curves for azobilirubin, but below this the absorption shows differences due to the absorption of a yellow pigment formed on treatment with diazo-reagent. The normal bilirubin val. for the serum of fasting subjects is 0·3—0·6 mg. per 100 c.c., the serum-pigment val. being always higher. A correction of the results of the Van den Bergh method is given. P. W. C.

Keto-acids in blood-serum. H. Westerkamp (Biochem. Z., 1933, **263**, 239—244).—Using Warburg's carboxylase method, $AcCO_2H$ (I) was detected in fifteen human serum samples in amounts of 0·59—2·09 mg. per 100 c.c. Pig's serum contained 5—10 mg. per 100 c.c. The method detected not only (I), but also α-keto-butyric, -*iso*valeric, -hexoic, and -glutaric and oxalacetic acids. The keto-acid fraction of the serum is not solely (I), since treatment with 2 : 4-dinitrophenylhydrazine, although yielding the hydrazone of (I), gave this in small amounts and not in every case. P. W. C.

Lactic acid determination in blood. W. Müller-Parcham (Z. physiol. Chem., 1933, **218**, 209—217).—Minor modifications of the Lehnartz technique (A., 1929, 48) are advocated, chiefly in respect of the titration of the $NaHSO_3$. The compound with MeCHO is decomposed by Na_2HPO_4 in presence of excess of I and the unused I is titrated with Na_2HAsO_3. J. H. B.

Fluctuations of blood-sugar *in vitro*. I. S. Kleiner and R. Halpern (J. Biol. Chem., 1933, **101**, 535—545).—Hyperglycæmic blood, whether diabetic or artificially produced, when dialysed for a short time against Ringer's solution exhibits marked variations in its sugar content on removal from the dialysis chamber. Similar variations, however, are noticed in undialysed blood. H. D.

Comparative determinations of the blood-sugar of the ox. M. Demmel (Biochem. Z., 1933, **262**, 294—299).—Fujita and Iwatake's method (I) with ox serum gives blood-sugar vals. 8—36% < those given by the Hagedorn–Jensen method (II), and their modification of (II) has an error of ±2%. With glucose, the error of Herzfeld's methylene-blue method (III) is ±10% and of the osazone test (IV) −25%. With serum, (III) gives the same vals. as (I), whereas (IV) gives even lower vals. than with glucose. P. W. C.

[H·] of the blood. W. Bladergroen (Chem. Weekblad, 1933, **30**, 526—532).—A crit. review of methods indicates that only the electrometric method of Michaelis is trustworthy; the quinhydrone electrode method is not recommended. For a given individual the varies between very close limits, except under markedly abnormal conditions (diabetic coma etc.). Determinations of blood-p_H are not usually as important as determination of alkali reserve and free CO_2. H. F. G.

Relationship between the structure of antigens and the specificity of antibodies. H. Erlenmeyer, E. Berger, and N. Leo.—See this vol., 834.

Modification of antibodies by formaldehyde. S. Mudd and E. W. Joffe (J. Gen. Physiol., 1933, **16**, 947—960).—The isoelectric point of certain bacteria maximally sensitised with sp. antisera is shifted to the acid side to the extent of 0·6—0·8 of a p_H unit by the action of CH_2O. The properties of the sensitising films are the same whether CH_2O has been allowed to act on the antibody (I) before or after the combination of (I) and antigen (II). These results, together with the observations of other authors, suggest that the union of (II) and (I) does not involve, to any appreciable extent, the CH_2O-combining basic groups of the (I). A. W.

Embryo-chemistry of Amphibia. I. M. Tomita and H. Fujiwara. **II. Perivitelline fluid of salamander eggs.** H. Fujiwara and S. Tsunoo. **III. Inorganic constituents during incubation of salamander eggs.** T. Iseki and T. Kumon. **IV. Nitrogenous substances during incubation of salamander eggs.** T. Iseki, T. Kumon, I. Takahashi, and F. Yamasaki. **V. Carbohydrate metabolism during incubation of salamander eggs.** E. Kataoka and S. Tsunoo. **VI. Fatty substances during incubation of salamander eggs.** E. Kataoka and I. Takahashi (J. Biochem. Japan, 1933, **17**, 401—405, 407—408, 409—411, 413—415, 417—418, 419—422).—I. Following incubation for 1—4 weeks, the eggs of the salamander (*Chryptobranchus japonicus*) consist approx. of 75% perivitelline fluid (I), 21% gelatinous layer, and 4% yolk. The eggs or young embryos contain only traces of creatine, creatinine, and glucose, whilst the content of fat is inversely proportional to that of H_2O.

II. During 4 weeks' development, (I) changed in p_H from 7·1 to 6·9, whilst d remained practically = that of H_2O.

III. The ash and inorg. PO_4 increase.

IV. Whilst the total N tends to decrease, the residual N increases, especially during the fourth week.

V. The glycogen content decreases slowly.

VI. During the fourth week the free fatty acids and cholesteryl esters increase, whilst the saponification val. and the free and total cholesterol decrease. F. O. H.

Lipins of human placenta. K. KLAUS (Zentr. Gynakol., 1933, **57**, 558—561).—The unsaponifiable fraction of placenta, its free, combined, and total cholesterol, and the fatty acid content and its I val. are tabulated. NUTR. ABS. (*b*)

Sulphur-containing lipin of brain cerebronsulphuric acid. G. BLIX (Z. physiol. Chem., 1933, **219**, 82—98).—A lipin isolated from human brain is probably the K salt of *cerebronsulphuric acid*, m.p. 209—210°, since it yields on hydrolysis, in addition to H_2SO_4, the constituents of cerebron, viz., cerebronic acid, sphingosine, and galactose. Probably 20—25% of the cerebrosides of brain are esterified with H_2SO_4. J. H. B.

Lipins of mammalian liver. V. Nature of the "unsaponifiable fraction" of mammalian liver. E. FRÄNKEL and G. LÖHR (Z. physiol. Chem., 1933, **218**, 218—222; cf. this vol., 846).—From the unsaponifiable fraction of liver, after removal of cholesterol, an oil was obtained, which, when esterified with butanetetracarboxylic anhydride, yielded an *oil*, b.p. 152—158°/0·03 mm., C 80·5, H 12·3%, I val. 104, distilling without decomp. and not pptd. by digitonin. Fractionation of the unsaponifiable fraction with aq. EtOH gave a neutral saturated *substance*, m.p. 96—97°, of similar composition to, but differing in properties from, sphingosine. J. H. B.

Determination of uric acid. Uric acid content of normal and diseased liver. O. FÜRTH and E. EDEL (Biochem. Z., 1933, **263**, 9—23).—The material (*e.g.*, minced liver ground with sand) is extracted with hot 0·01% aq. Li_2CO_3, the extract is deproteinised with uranyl acetate, excess U is removed with Na_2HPO_4, and the uric acid in the filtrate is determined colorimetrically by Folin's method or by the method of Ludwig and Salkowski. Decomp. products of nucleic acid do not interfere, nor are the results affected if brief autolysis precedes the working up of the material, but hot dil. H_2SO_4 destroys much of the uric acid in a few hr. The normal uric acid content (I) (8—12 mg. per 100 g.) of rat's liver is reduced by fasting or by diet of pure protein, but increased by diet rich in purines. Administration of phenylquinolinecarboxylic acid (atophan) reduces (I) to $\lesssim$ 3—5 mg. per 100 g. The (I) of normal or only slightly parenchymatous human liver is 7—10 mg., that of the liver of cirrhosis patients 2—5 mg. per 100 g. W. McC.

Spectrographic investigation of the metallic content of the liver in childhood. H. RAMAGE, J. H. SHELDON, and W. SHELDON (Proc. Roy. Soc., 1933, **B**, **113**, 308—327).—Data are given for 111 children's and 14 fœtal livers, analysed spectrographically (A., 1929, 527). Fe and Cu are stored in the fœtal liver. The concns. of Fe, Cu, and Mn fall during nursing, and increase during childhood on a mixed diet. Mn and Rb are not stored in the fœtal liver. There is a parallelism between the amounts of Fe, Cu, and Ca, and between those of Rb and K in children's livers. The results are discussed in relation to the diseases causing death. A. C.

Iron and copper in liver extracts. H. G. REES (Analyst, 1933, **58**, 384—388).—Fresh ox-liver contains 80 mg. of Fe and 24 mg. of Cu per kg. H_2O at 50° extracts 31·5 mg. of Fe and 1·75 mg. of Cu per kg. Part of the Fe is associated with coagulable protein, so that extraction at higher temp. is less effective than at 50°. E. C. S.

Affinity between lung-proteins and lung-tissue. P. MASCHERPA (Arch. exp. Path. Pharm., 1933, **171**, 119—124).—Subcutaneous injection into rabbits of Co admixed with press-juice from rabbit's lung is followed by deposition of Co in the lung tissue; this deposition does not occur when Co is administered with serum. Hence confirmation is afforded for the affinity between various tissues and their constituent proteins (this vol., 423). F. O. H.

Preparation and properties of thyroglobulin. M. HEIDELBERGER and W. W. PALMER (J. Biol. Chem., 1933, **101**, 433—439).—Minced washed thyroid glands (pig) are pressed out, re-extracted with 1% NaOAc, the combined juices freed from fat, adjusted to p_H 4·8—5·0, and the pptd. nucleoprotein is separated. The residual fluid is half-saturated with Na_2SO_4 at 35°, the ppt. dissolved in H_2O, and the pptn. with Na_2SO_4 repeated, yielding thyroglobulin (I), $[\alpha]_D$ −56° to −59°, 0·58% I, 15·8% N, which could not be further fractionated by varying concns. of aq. Na_2SO_4. Exposure of (I) to dil. AcOH at $<$ 4·8 even at low temp. results in partial denaturation. F. O. H.

Chemical analysis of muscles of marine invertebrates. O. RIESSER and A. HANSEN (Z. physiol. Chem., 1933, **219**, 62—71).—Creatine- (I), arginine- (II), pyro- (III), hexose- (IV) -phosphoric acids and glycogen were determined in the muscles of marine invertebrates. (I) was present in all cases, but in smaller amount than (II). (III), (IV), and (V) were also found, (IV) and (V) sometimes in considerable quantity. The total acid-sol. PO_4''' varied from 0·45% P_2O_5 in the cephalopods to 0·1% in representatives of the Echinoderms. J. H. B.

Phosphorus nucleus of ichthulin of the pike. S. POSTERNAK and T. POSTERNAK (Compt. rend., 1933, **197**, 429—430).—Ichthulin, a vitellin of pike spawn, affords ichthiotyrin" (I), a glucosidic polypeptide containing 12·6% P, similar in properties to the ovotyrins (A., 1927, 1100). Hydrolysis (35% H_2SO_4) of (I) yields H_3PO_4 (II) 39·2, NH_3 2·3, $AcCO_2H$ (III) 6·4, arginine 4·6, and *l*-serine (IV) 26·1%, respectively, NH_3 and (III) arising from deamination of (IV). Hydrolysis of (I) with 15% H_2SO_4 yields a polypeptide (N : P=1·05—1·3) which is further hydrolysed to mainly (II) and (IV) and deamination products of (IV). (I) is composed of serine-phosphoric acid chains in which H_3PO_4 is linked with the OH of (IV). A. C.

Succinic acid in shellfish. K. AOKI (J. Agric. Chem. Soc. Japan, 1932, **8**, 867—868).—Vals. are: *Corbicula atrata*, Prime, 6·4117; ligament of *Pecten yessoensis*, Jay, 0·3700; *Tapes philippinarum* 0·3300;

Cytherea meretrix, L., 0·1420; *Arca pectunculus*, 0·1010; *Turbo cornutus* 0·0720; *Ostrea talienwahnensis*, Cross, 0·0520; *Mactra sulcatoria* 0·0270; *Habliotis tuberculata* 0·0250%. CH. ABS.

Chemistry of bioluminescence. I. Determination of luciferin. R. S. ANDERSON (J. Cell. Comp. Physiol., 1933, **3**, 45—59).—A photo-electric cell with appropriate recording instruments is utilised to follow the course of the luminescent reaction. The ratio of total light emitted to luciferin originally present was const. at p_H 6·8 over the experimental range of concns. of luciferin and luciferase. The ratio is influenced by temp., p_H, buffer and salt concns. A. G. P.

Discordant behaviour of accelerators, *e.g.*, of the darkening [of pigment precursors]. HANS SCHMALFUSS, HELENE SCHMALFUSS, I. HEISE, R. KASLER, and H. HAEUSSLER (Biochem. Z., 1933, **263**, 278—294).—The ability of various accelerators (I) prepared from the bloods of seven species of Orthoptera, Coleoptera, Hymenoptera, and Lepidoptera in various dilutions to cause and accelerate the darkening of sixteen pigment precursors (II) containing 1 or 2 OH groups attached to Ph nucleus is investigated. The activity of a particular (I) is different for different (II), and the series of (II) darkened by a particular (I) is different for the various (I). Dilution of (I) decreases and concn. increases the no. of (II) darkened. P. W. C.

Darkening of the skin. III. P. MULZER and H. SCHMALFUSS. **Free *l*-tyrosine from human skin, a pigment precursor.** H. SCHMALFUSS, A. HEIDER, and K. WINKELMANN (Biochem. Z., 1933, **263**, 371—374).—A H_2O extraction method is described for the separation of *l*-tyrosine from the skin of corpses (2 kg. of skin gave 18 mg. of tyrosine). P. W. C.

Distribution of inorganic salts in birds. I, II. Inorganic salts in *Vanellus vanellus*, L. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1933, **262**, 380—386, 387—389).—I. Tables summarise the total inorg. salt content in fourteen types of tissue, both fresh and after drying at 40°, and their H_2O content in thirteen birds of different orders. The % salt contents of the fresh and dried organs and breast muscle were very const., but those of leg muscle showed large variations.

II. Tables show the H_2O, salt, total H_2O-sol. and acid-sol. PO_4, Cl, Ca, and Mg contents of eleven tissues, both fresh and after drying at 40°, of *V. vanellus*. P. W. C.

Mineral composition of the skeletons of some recent *Echinodermata*. K. F. TERENTEVA (Trav. lab. biogéochim. acad. sci. U.R.S.S., 1932, **2**, 45—62). —Different parts of the same skeleton of *Echinoidea*, *Ophiuroidea*, and *Asteroidea* differ in composition. The distribution of $MgCO_3$ is regular. CH. ABS.

Composition of insects during metamorphosis. G. G. BERGMAN (Trav. lab. biogéochim. acad. sci. U.R.S.S., 1932, **2**, 31—42).—*Rhagium indogator* contained H_2O 29·70—40·60, C 15·60—21·06, H 8·90—10·10, N 1·88—3·52, ash 3·18—4·17%. *Pieris brassicæ* and *Polistis gallica* gave analogous vals. The most marked change in composition takes place when the insect changes from pupa to adult. CH. ABS.

Chemical changes during the life cycle of the tent caterpillar (*Malacosoma americana*). V. W. RUDOLFS (J. N.Y. Entomol. Soc., 1932, **40**, 481—488).—Analyses are recorded. CH. ABS.

Carbon content of the bodies of certain species of *Acridiidæ*. K. G. KUNASHEVA (Trav. lab. biogeochem. acad. sci. U.R.S.S., 1932, **2**, 27—30).—Comparative vals. for male and female insects are recorded. CH. ABS.

Distribution of fixed mineral matter in mammalian spermatozoa. A. POLICARD (Compt. rend., 1933, **197**, 427—429).—Microscopical examination of incinerated rat and human spermatozoa shows that the neck and posterior part of the head are rich, whilst the tail and anterior part of the head are poor, in ash. The latter parts are more readily incinerated. In the rat the total spermatozoal ash is > in man. A. C.

Digestive enzymes of *Bombyx mori*. K. YAMAFUGI (J. Agric. Chem. Soc. Japan, 1933, **9**, 152—159).—A sucrose-hydrolysing enzyme with optimum p_H 9·5 and max. at 45° occurs in a glycerol extract of the fresh digestive ducts of *B. mori*. The diastatic activity of the extract varies with the species. CH. ABS.

Reaction of Rivalta. S. KOZAWA, R. IWATSURU, and T. ADACHI (J. Biochem. Japan, 1933, **17**, 375—383).—The % of constituent NH_2-acids and the isoelectric points (I) of the proteins of transudates, exudates, and other œdematous fluids are almost equal [p_H 4·4 for (I)], whilst the albumin/globulin ratio is approx. 1 for each protein mixture. The Rivalta reaction fails with a protein content of < 1%; the salt concn., however, also influences the reaction (cf. A., 1924, i, 243). F. O. H.

Secretion of phosphorus in the saliva of sheep. R. H. WATSON (Austral. J. Exp. Biol., 1933, **11**, 67—74).—P of the saliva (I) is mainly inorg. and is of the order 20—60 mg. per 100 c.c. The ratio of P in (I) to that of the blood is between 5 : 1 and 8 : 1. 2·4—7·7 g. of P are secreted daily in (I). H. G. R.

Bile acids from fistulary bile of rabbits. S. SHIBUYA and T. TANAKA (J. Biochem. Japan, 1933, **17**, 391—393).—When fed with Na dehydrocholate, the bile of rabbits with biliary fistulæ contains glycocholeic acid, m.p. 186°, $[\alpha]^{20}$ +48·56° in EtOH (cf. A., 1931, 1179), deoxycholic acid, m.p. 172°, $[\alpha]_D^{20}$ +57·14° in EtOH, and $NH_2 \cdot CH_2 \cdot CO_2Et$. F. O. H.

Tests of gastric function. I. Studies of gastric juice by means of a protein-peptone solution. HECKMANN (Z. ges. exp. Med., 1933, **87**, 506—528).—A test meal containing 20% of ovalbumin and 2% of Witte's peptone is to be preferred to one containing coffee or EtOH, particularly in the investigation of cases of hypoacidity. NUTR. ABS. (*b*)

Thiocyanate content of gastric juice in children. E. RIECKE (Z. Kinderheilk., 1933, **54**, 408—412).—The CNS' content of gastric juice was lower in prematures than in full-term infants. It rose

rapidly as age increased to 5 months, then more slowly to 5—10 years, after which there was a slight decline. In dyspepsia the content was greatly reduced, in dystrophy only slightly. NUTR. ABS. (*b*)

Clinical micropyknometry. I. E. OLIVA and F. GONZALEZ NUNEZ. **II. Mikropyknometry of milk and determination of dietetic value.** F. GONZALEZ NUNEZ and E. OLIVA (Anal. Fís. Quím., 1933, **31**, 68—70, 71—73).—I. 0·5 c.c. of liquid in a graduated pyknometer is used and d is obtained with an accuracy of 0·05%.

II. Total N, lactose, fat, and d are determined in an 8-c.c. sample of human milk. R. K. C.

Effect of diet on calcium and phosphorus content of human milk. B. HERZ (Z. Kinderheilk., 1933, **54**, 413—420).—With change in diet of nursing women any changes in the Ca and P content of the milk (I) were in the same direction. The difference in the Ca content of (I) when the diet was changed from Ca-poor to Ca-rich was of the order of 8—15%, but the addition of salts such as Ca citrate or malonate caused no definite increase in the (I)-Ca. With the Ca-poor diets the total Ca secreted in (I) was > the Ca intake in the food. NUTR. ABS. (*b*)

Chemical changes produced in caseinogen by boiling. K. BALLOWITZ (Biochem. Z., 1933, **263**, 119—127; cf. this vol., 177).—When milk, or a solution containing caseinogen, is boiled, the chemical change which the protein undergoes is accompanied by appreciable binding of Ca by caseinogen, a two-phase process, similar to coagulation with rennin, taking place. The extent of pptn. increases as [$Ca^{\cdot\cdot}$] increases. An explanation is provided for the decreased nutrient val. of boiled as compared with unboiled milk. W. McC.

Effect of boiling on the coagulation by rennin of caseinogen. K. BALLOWITZ (Biochem. Z., 1933, **263**, 128—134).—Coagulation with rennin sets in later in boiled than in unboiled solutions of caseinogen prepared by Marui's method (A., 1926, 866) and the type of coagulation is altered by the boiling. The difference is due to the action of the $CaCl_2$. W. McC.

Antirachitic potency of the milk of human mothers fed previously on "vitamin-*D* milk" of the cow. J. W. M. BUNKER, R. S. HARRIS, and R. S. EUSTIS (New Engl. J. Med., 933, **208**, 313—315).—The antirachitic potency is increased. CH. ABS.

Lability of the reducing factor (vitamin-*C* ?) in milk. S. K. KON (Nature, 1933, **132**, 64).—The amount of the substance in milk which reduces chlorophenol-indophenol reagent varies to a marked and irregular extent. L. S. T.

Methylene-blue reductase test [in milk]. C. S. MILES (J. Min. Agric., 1933, **40**, 414—419).—The reductase test is unsuitable for the examination of milk of low bacterial count. There is better correlation between the plate count and the keeping quality (I) of milk than between the reduction time and (I). E. C. S.

Bromothymol-blue reaction in freshly drawn milk. C. S. BRYAN (Amer. J. Pub. Health, 1933, **23**, 721—724).—The determination of p_H of fresh milk cannot be used alone to detect mastitis (I), since positive reactions are obtained with animals free from (I) and *vice versa*. The test is of val. only in determining the relative disease or freedom from (I) in a herd. A. L.

Glycerol as a preservative for milk to be examined for hæmolytic streptococci. R. GILBERT and M. E. CLARK (Amer. J. Pub. Health, 1933, **23**, 720).—Addition to milk of $\frac{1}{3}$ vol. of glycerol preserves it for hæmolytic streptococci examination for several days. A. L.

Yeast extract medium for determining the bacterial content of milk by the plate method. E. D. DEVEREUX and J. L. ETCHELLS (Amer. J. Pub. Health, 1933, **23**, 149—151; cf. *ibid.*, 1932, **22**, 1291, 1293).—Milk samples plated out on yeast extract agar give counts after 24 hr. incubation 18% >, after 48 hr. 45% >, on plain agar. E. C. S.

Accuracy of clinical methods of determining urinary protein. M. HORI (J. Biochem. Japan, 1933, **17**, 367—373).—Of the methods of Esbach, Tsuchiya, and Sueyoshi, the last is the most accurate. The accuracy of all three methods is increased by application of the centrifuge technique of Inoue (A., 1930, 1610). F. O. H.

Influence of foodstuffs on rate of urinary acid excretion. C. E. BRUNTON (J. Physiol., 1933, **78**, 65—97).—A standard breakfast was taken at 8 a.m. and the test foodstuff was taken at noon. If no meal was taken at noon, the acid excretion per min. increased 2½ hr. afterwards. Ingestion of raisins and prunes caused increase of the acid output. Ingestion of potato caused a decrease of 0·2 c.c. of 0·1*N*-acid. per min. with max. fall at 2½ hr. Ingestion of beet and banana also caused decrease. Meals of beans, rice, bread, grape fruit, and meat caused little change. NUTR. ABS. (*b*)

Excretion of cholesterol during the action of therapeutic substances on the intestine. F. PENDL and G. BERGER (Arch. exp. Path. Pharm., 1933, **171**, 319—328).—The fæcal excretion of cholesterol (I) was investigated in two dogs fed approx. 0·2 g. (I) per day and a standard diet supplemented with mineral salts, cellulose (II), or an anthraquinone derivative. The excretion of (I) with the standard diet alone was fairly const. (II), however, produced marked increases in the wts. of fæces and (I) excreted. The other two diets gave results varying with the dog used. F. O. H.

Physical characteristics of residues from the small intestine. H. LANDT and K. DAUM (Arch. Int. Med., 1933, **52**, 96—104).—Residues (I) obtained from an ileal fistula varied in colour and consistency with the food (II). H_2O varied from 92 to 97%, N was approx. const. and independent of (II). The wt. of (I) varied with (II) and only slightly with the amount fed. No fæcal odour was noted. H. G. R.

Mode of occurrence of acidosis. S. M. NEUSCHLOSZ (Z. ges. exp. Med., 1933, **87**, 161—177).—During development of both renal and extra-renal acidosis the formation of NH_3 was delayed, indicating that

there was a loss of fixed base from the body for neutralising purposes in the urine. Hence acidosis is in large part due to the abs. or relative inefficiency of the kidneys to form NH_3. In liver disease there was an increased amount of urinary NH_3 due to imperfect synthesis of urea. In cases of liver deficiency acidosis was present with high val. of Q (acid–base quotient), indicating that the NH_3 which formed as a result of defective urea formation had less neutralising power than the NH_3 formed by the kidneys. NUTR. ABS. (*b*)

Nutritional anæmia of the rat. VII. Parentally administered iron. M. W. EVELETH, F. C. BING, and V. C. MYERS. **VIII. Determination of hæmoglobin and erythrocytes on a single sample of blood.** R. W. HEINLE and F. C. BING (J. Biol. Chem., 1933, **101**, 359—368, 369—372).—VII. Intraperitoneal injection of Fe into young rats made anæmic by restriction to a diet of raw milk containing an average of 0·34 mg. Cu per litre, produced a rapid increase in growth, hæmoglobin (I) concn., and blood count. Doses of $>$ 0·025 mg. Fe produced a polycythæmia with low (I) concn. Injection of both Cu and Fe gives the same effects as Fe alone.

VIII. Blood is diluted in a hæmocytometer with 0·9% NaCl. A drop is used for the count and the residue expelled on to a watch-glass, from which 0·1 c.c. is taken for the benzidine–H_2O_2 determination of (I). H. D.

Hæmoglobin production factors in the human liver. I. Normal, infection, and intoxication. III. Anæmias. G. H. WHIPPLE and F. S. ROBSCHEIT-ROBBINS. **II. Liver degeneration, cancer, cirrhosis, and hepatic insufficiency.** F. S. ROBSCHEIT-ROBBINS and G. H. WHIPPLE (J. Exp. Med., 1933, **57**, 637—651, 671—677, 653, 670). CH. ABS.

Hæmopoietic factor in marmite. L. WILLS (Lancet, 1933, **224**, 1283—1286).—Clinical trials of preps. containing vitamins-B_1, -B_2, and -B_4 failed to show that these vitamins have hæmopoietic properties in tropical macrocytic anæmias. Marmite was active curatively in these cases. Its hæmopoietic factor is sol. in H_2O and 80% EtOH, and is heat-stable. L. S. T.

Metabolism of phenol and indole. I, II. Latent phenol–indole poisoning and arteriosclerosis. M. BIEBL (Z. ges. exp. Med., 1933, **87**, 416—435, 436—472).—I. A technique for the study of the relationship of PhOH–indole intestinal intoxication and various pathological conditions in rabbits is described.

II. Arteriosclerosis (I) produced by PhOH or indole administration was partly or completely prevented by doses of olive oil or Ca. The lesion is different from cholesterol-(I). NUTR. ABS. (*b*)

Calcinosis universalis. B. J. HEIN (Arch. Surg., 1933, **26**, 389—396).—Heliotherapy produced gradual disappearance of diffuse Ca deposition in fascias. CH. ABS.

Experimental production of malignant tumours. J. A. MURRAY (Proc. Roy. Soc., 1933, B, **113**, 268—292).—A discussion (see also Nature, 1933, **132**, 156—158). A. C.

Relation of carcinogenicity of mineral oils to certain physical and chemical characteristics of these oils. R. LYTH (J. Ind. Hygiene, 1933, **15**, 226—237).—In a large series of oil samples the carcinogenic activity (I) runs parallel to the refractivity $[(n-1)/d]$, but certain exceptions occur. Similarly, amongst samples of crude oil the I vals. and (I) show a direct correlation, but with refined oils this was less marked. The $KMnO_4$ val. did not indicate (I). W. O. K.

Composition of the lipins of normal and diseased organs. V. Lipins of carcinomatous, sarcomatous, and tuberculous human lymph glands. VI. Lipins of human melanotic carcinoma and sarcoma. B. LUSTIG and E. MANDLER (Biochem. Z., 1933, **263**, 50—57, 58—62; cf. this vol., 736).—V. The carcinomatous (I) glands contain more lipins than do sarcomatous (II) or tuberculous (III). (II) contain normal, (I) and (III) reduced, amounts of phosphatides (IV), and in (I) the P content of (IV) is greatly reduced, whilst the N content is increased. In all cases the amount of unsaponifiable matter (V) is high, the cholesterol (VI) content of (V) being 45—70% for (I) and 90% for (II) and (III). In (III) also one third of (VI) is esterified. The liquid fatty acids of the lipins of (I) contain one double linking; those of the lipins of (II) and (III) are to a great extent highly unsaturated.

VI. The composition of the lipins (I) of melanotic carcinoma (II) (from human liver) is the same as that of the (I) of melanotic sarcoma (III), but differs from that of the (I) of normal or carcinomatous liver. (II) and (III) have high contents of free fatty acid and low contents of phosphatide precipitable by $COMe_2$. W. McC.

Proteolysis in organ- and cancer-cells. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, **218**, 142—152; cf. this vol., 628, 636).—The liver, spleen, and kidneys of carcinomatous and sarcomatous mice and hens contain much more cathepsin than the tumours; further, the organ-cathepsin shows a greater degree of activation. Thus proteolysis is or may be greater in the organ-cells than in cancer-cells. J. H. B.

Action of radium on cancer cells. I. Effects of hydrocyanic acid, iodoacetic acid, and sodium fluoride on metabolism and transplantability of cancer cells. II. Factors determining susceptibility of cancer cells to radium. H. G. CRABTREE and W. CRAMER (Proc. Roy. Soc., 1933, B, **113**, 226—238, 238—250).—(I) HCN ($M/1000$—$M/500$) causes 85—95% inhibition of tumour tissue respiration (I) and an increase of aerobic glycolysis (II) to approx. the anaerobic val. The effects, after treatment for 1 hr., are reversible up to a HCN concn. of $M/20$, the tumour being transplantable. $CH_2I{\cdot}CO_2H$ (III) (3×10^{-5} to $10^{-3}M$) causes gradually increasing inhibition of (I) and a greater inhibition of (II). At the lower concn. recovery is complete after treatment for 1 hr., but at $10^{-3}M$ the cells are killed and the tumour is not transplantable. NaF is similar

in action to (III), but at higher concns. Recovery occurs at $M/100$, but not at $M/20$.

(II) The sensitivity to Ra of tumour cells, the respiration of which has been reversibly checked *in vitro*, has been determined in terms of transplantability after irradiation. Anaerobiosis diminishes, and HCN ($M/1000$) and low temp. (0°) increase, the sensitivity, which is not affected by $CH_2I{\cdot}CO_2H$ or NaF. A. C.

Effect of inhibiting factor from normal tissues on spontaneous tumours of mice. J. B. Murphy and E. Sturm (Science, 1933, **77**, 631—632).—Extracts from mouse placenta and embryo skin known to reduce the growth of transplanted cancer have an inhibiting effect on natural or spontaneous cancer. L. S. T.

Serum-proteins in diabetic acidosis. J. P. Peters, D. M. Kydd, and A. J. Eisenman (J. Clin. Invest., 1933, **12**, 355—376).—During severe acidosis the proteins were generally within or above normal limits owing to hæmo-concn. (I), falling during recovery to below the normal min. The initial loss of serum-H_2O was due in part to passage of fluid into the tissues, and restoration of serum vol. seemed to be largely independent of restoration of tissue fluids. Shock due to (I) is at least an aggravating factor of diabetic coma. Nutr. Abs. (*b*)

Nature of diabetic acidosis. J. P. Peters, D. M. Kydd, A. J. Eisenman, and P. M. Hald (J. Clin. Invest., 1933, **12**, 377—392).—Although great variation was found in the concns. of the various blood constituents, the results suggest the following processes: (*a*) displacement of CO_2 by keto-acids (I); (*b*) urinary elimination of a proportion of (I), free or neutralised by NH_3; (*c*) neutralisation of some of (I) by fixed base followed by excretion in the urine; (*d*) reduction of electrolyte concn. of body-fluids and consequent loss of H_2O. The base lost in combination with ketones is generally much < that excreted as Cl′. The actual deficiency of body-Cl′ is far > would appear from analyses of the serum if there is associated loss of body-fluid; there is a much greater decrease of base united with Cl′ than of base united with CO_2+ org. acids. Nutr. Abs. (*b*)

Diabetic acidosis. Electrolyte balances following the withdrawal and re-establishment of insulin therapy. D. W. Atchley, R. F. Loeb, D. W. Richards, jun., E. M. Benedict, and M. E. Driscoll (J. Clin. Invest., 1933, **12**, 297—326). Nutr. Abs. (*b*)

Utilisation of galactose in physiological and pathological conditions. II. Utilisation of galactose in diabetes mellitus. Galactose as substituent carbohydrate. III. Behaviour of galactose in the depancreatised dog during complete and partial insulin deprivation. IV. Galactose assimilation in the liver. H. Kosterlitz and H. W. Wedler (Z. ges. exp. Med., 1933, **87**, 397—404, 405—410, 411—415).—II. After oral administration of galactose (I) to diabetics the blood-sugar was lower than after an equal amount of glucose (II); less sugar was found in the urine. When frequent small doses (10—20 g.) of (I) were given, practically no galactosuria occurred. Addition of (I) to a measured diet over a long period caused less glycosuria than a corresponding amount of (II). (I) had a definite antiketogenic and protein-sparing effect.

III. (I) given *per os* to depancreatised dogs was not utilised, being completely recovered in the urine as (II). When insulin was given, (I) was not more utilised than (II).

IV. Oral administration of (I) to rats led to a rise in blood-(I), little change in -(II), and no evidence of (I) storage in the liver. (I) must, therefore, be changed into glycogen or some unknown substance. Nutr. Abs. (*b*)

Ketonic substance production and destruction in certain tissues of diabetic dogs. W. Goldfarb and H. E. Himwich (J. Biol. Chem., 1933, **101**, 441—448; cf. A., 1932, 80).—The concn. of ketones in arterial blood varies with time. Analysis of the efferent and afferent blood from and to the heart, striated muscle, brain, and testis shows a correlation between the striated muscle, the gastro-intestinal tract, and the heart in the production of these substances. H. D.

Hyperinsulinism. E. Ziskind (Arch. Int. Med., 1933, **52**, 76—85).—In a case of spontaneous hypoglycæmia, no improvement resulted from thyroid therapy. No abnormality was noted in the pancreas or in the endocrine glands. H. G. R.

Hypoglycæmia. C. Sippe and J. Bostock (Med. J. Austral., 1933, **1**, 207—218).—Hypoglycæmia in non-diabetic patients occurs as a symptom complex often associated with other disorders. Nutr. Abs. (*b*)

Glycine synthesis in pseudohypertrophic muscular dystrophy. I. K. Freiberg and E. S. West (J. Biol. Chem., 1933, **101**, 449—451).—In this disease the capacity to produce glycine in response to administration of BzOH is not different from that of the normal. H. D.

Etiology of gallstones. IV. Is cholesterol excreted by the gall-bladder mucosa? E. Andrews, L. E. Dostal, and L. Hrdina (Arch. Surg., 1933, **26**, 382—388).—Cholesterol, although excreted by the infected gall bladder, is not secreted in appreciable quantities by the mucosa of the normal gall bladder (I). Ca is excreted by (I) in large amounts. Ch. Abs.

Hypoproteinæmia. E. Moschcowitz (J. Amer. Med. Assoc., 1933, **100**, 1086—1092).—Review and description of illustrative cases. Nutr. Abs. (*b*)

Function of the liver. Modified glucose tolerance test. H. T. Ricketts (Arch. Int. Med., 1933, **52**, 147—157).—The test (A., 1930, 1470) is not a satisfactory measure of the metabolic function of the liver. H. G. R.

Non-protein-nitrogen of blood in health and in hepatic disease. M. T. Tindal (Arch. Dis. Children, 1933, **8**, 17—24).—After a dose of 15 g. of urea in 150 c.c. of H_2O, convalescent children showed a rise of blood-non-protein-N for the first hr. and a fall during the second hr. Children with diseased livers showed a higher fasting level, a slower rise, and a continued rise over the whole 2 hr. Nutr. Abs. (*b*)

Experimental hepatic insufficiency. Coefficient of Maillard and blood-nitrogen in the normal guinea-pig. F. MEERSSEMAN and J. DORCHE (Compt. rend. Soc. Biol., 1933, **112**, 903—905).—In the normal guinea-pig, the NH_3 coeff. of the urine was < 1. The ratio of the urea-N of the blood to the total non-protein-N averaged 0·63. NUTR. ABS. (*b*)

Experimental hepatic insufficiency. Coefficient of Maillard and blood-nitrogen in the guinea-pig during acute and subacute phosphorus poisoning. F. MEERSSEMAN, J. DORCHE, and F. MORELON (Compt. rend. Soc. Biol., 1933, **112**, 905—907).—Guinea-pigs poisoned with 4 drops *per diem* of 1% P in oil died in about 6 days. On the fifth day in three animals of six, the NH_3 coeff. of the urine was > 13. In one animal the blood-urea-N increased and in three animals the ratio of urea-N to total non-protein-N was 0·32—0·54. NUTR. ABS. (*b*)

[Absence of] pressor substance in the blood in essential hypertension. G. E. WAKERLIN and H. D. BRUNER (Arch. Int. Med., 1933, **52**, 57—65). H. G. R.

Hysteria in dogs. H. D. WALSTON (Nature, 1933, **132**, 243).—Canine hysteria appears to be connected with vitamin-*A* deficiency coupled with a substance ("*E*-substance") occurring in dog biscuits and other cereal foods. L. S. T.

Methods of increasing the defensive power of the peritoneum: behaviour of the serous membrane with increased defences in the course of acute bacterial infections. M. TABANELLI (Arch. Ist. Biochim. Ital., 1933, **5**, 155—174).—Guinea-pigs were injected intraperitoneally with different quantities of colloidal Ag, arsenobenzene (I), and $MgCl_2$, at varying periods both before and after intraperitoneal inoculation with the min. lethal dose of *B. coli*. In general, animals treated with Ag survived, with (I) to a smaller degree, whilst $MgCl_2$ retarded death. R. N. C.

Calcium content of blood-serum in leprosy. A. G. BADENOCH and F. E. BYRON (Trans. Roy. Soc. Trop. Med. Hyg., 1932, **26**, 253—258).—When the lepra reaction was positive the serum-Ca was definitely subnormal (average 8·9 mg. per 100 c.c.); in most other cases the Ca was, or approached, normal. Clinical improvement was usually associated with a rise in Ca in both "reaction" and "non-reaction" cases. A few patients showed an abnormally high serum-Ca which appeared to be correlated with rapid advance of the leprotic process. NUTR. ABS. (*b*)

Plasma-protein and plasma-colloid osmotic pressure in pathological conditions with special reference to the occurrence of œdema. E. MUNTWYLER, C. T. WAY, D. BINNS, and V. C. MYERS (J. Clin. Invest., 1933, **12**, 495—504).—Nephritic œdema is usually accompanied by lowering of plasma-protein and -colloid osmotic pressure (normally 29—36 cm. of plasma). CH. ABS.

Calcium. VII. Calcium effects on thoracic lymph flow of dogs. A. L. LIEBERMAN. **VIII. Therapeutic effects of calcium gluconate on thrombophlebitic œdema.** A. L. LIEBERMAN and L. M. ZIMMERMAN (J. Pharm. Exp. Ther., 1933, **48**, 293—299, 301—304).—VII. Ca, when rapidly injected, tends to retard the lymph flow in dogs, possibly by lowering cell permeability.

VIII. Subcutaneous and, to a smaller extent, oral administration of Ca gluconate and parathyroid extract hastens the disappearance of experimental thrombophlebitic œdema in dogs. J. H. B.

Galactose (?) in the blood of pregnant women. S. BATTISTINI, L. HERLITZKA, and B. COSSU (Biochem. Z., 1933, **263**, 24—32).—In women, towards the end of pregnancy, the glucose content and total reducing power of the blood decrease, although the content of reducing non-sugars remains normal. Methods are described by which it is shown that there is also present another reducing substance (I) which does not occur in normal blood. (I), which is not adsorbed by yeast and is found in the filtrate after deproteinisation by Somogyi's method, is probably galactose. W. McC.

Relationship of iodine to the basal metabolic rate and to the changes in the thyroid gland in pregnant rabbits. J. D. STEWART and F. R. MENNE (Endocrinol., 1933, **17**, 93—102).—Pregnant rabbits fed with I (0·001—0·003 mg. per kg. per day) showed a smaller increase in metabolic rate and thyroid activity, presumably through protection of the thyroid against over-function. NUTR. ABS. (*b*)

Gas exchange in new-born and premature infants. A. SCHLOSSMANN and H. MURSCHHAUSER (Z. Kinderheilk., 1933, **54**, 301—316).—In the normal infant the O_2 consumption averaged 27·9 c.c. per min. and the R.Q. was 0·828; in the premature the O_2 consumption was 6·2—12·7 c.c. and the R.Q. 0·852—0·891. The low val. for premature infants is attributed to very low body-temp. NUTR. ABS. (*b*)

Diastase content of saliva of premature infants. G. HENSEL (Z. Kinderheilk., 1933, **54**, 367—376).—The amylase (I) content (determined by the Wohlgemuth–Michaelis–Pechstein method) of the saliva of premature infants was considerable, falling within the same limits as in full-term infants; in children it was 2·5 times and in adults 5 times as great. The (I) content varied irregularly in any one infant and could not be raised by the use of food rich in starch. NUTR. ABS. (*b*)

Mineral and water metabolism of premature infants. H. PAFFRATH and J. MASSART (Z. Kinderheilk., 1933, **54**, 343—366).—In premature infants receiving breast- (I) or butter-milk (II) or mixtures of these, the mineral retention increased with increase in intake. Ca may be retained without any H_2O, but alkali retention was always associated with corresponding increase in H_2O storage. With a subcaloric diet there appeared to be a dry retention of alkali, but this was due to endogenous formation of H_2O resulting especially from fat catabolism. When the diet was changed from the mineral-rich (II) to the mineral-poor (I) both H_2O and alkali were excreted in excess. The H_2O and alkali metabolism appear to be the same as in œdematous adults. NUTR. ABS. (*b*).

Creatinuria in premature infants. H. PAFFRATH and W. OHM (Z. Kinderheilk., 1933, **54**, 377—

379).—The creatinine (I) coeff. [(I)-N in 24 hr./body-wt. in kg.] was 4·4—6·5 in premature and 4·2—7·8 in full-term infants. In the first 3 weeks of life the prematures excreted very little or no creatine (II); from 4 to 7 months they excreted 10% of the total (I) as (II), so that prematures excrete less (II) than full-term infants of the same age. The reduced (II) excretion is attributed to the lower muscular activity in the prematures. NUTR. ABS. (*b*)

Bromine of blood in manic depressive psychoses. J. M. SACRISTAN and M. PERAITA (Klin. Woch., 1933, **12**, 469—470).—Cases of manic depressive psychosis show diminished vals. of blood-Br. Cases of post-encephalitis show normal or high vals. NUTR. ABS. (*b*)

Blood-urea clearance test. G. S. ORTIZ (Semana Med., 1933, i, 865—874).—In renal insufficiency the val. is $\not> 50\%$; addition of NaCl to the diet causes a decrease. Vals. $> 75\%$ are normal. CH. ABS.

Blood-phosphate fractions in experimental rickets. E. JACOBSEN (Biochem. Z., 1933, **263**, 313—315).—The decrease of total acid-sol. PO_4 in red blood-cells in experimental rickets is due chiefly to a decrease in the pyrophosphate fraction. Since the inorg. PO_4 fraction is equally decreased, there appears to be an equilibrium between ortho- and pyro-phosphate in blood, such that decrease of ortho- results in corresponding decrease of pyro-phosphate. P. W. C.

Behaviour of cholesterol in saturnism. U. BASSI and G. CASTROVILLI (Arch. Ist. Biochim. Ital., 1933, **5**, 119—154).—Cholesterol (I) tests were carried out on 56 cases of saturnism (II). Blood-(I) increased in chronic (II), but was normal in pre-(II), whilst during saturnine colic it was decreased. The intradermic reaction with colloidal (I) was positive in (II), strongly positive during colic. Serum flocculation by colloidal (I) was positive in chronic cases in general, but was negative during colic, tending, however, to become positive after it. In cases where (II) was accompanied by other diseases, results were discordant. R. N. C.

Incidental hyperguanidæmia in dogs in parathyroid tetany. W. R. BRYAN and A. S. MINOT (Proc. Soc. Exp. Biol. Med., 1933, **30**, 595—597).—Only 50% of animals had an increased blood-guanidine after parathyroidectomy and the concn. was not proportional to the symptoms of tetany. A disturbance of Ca metabolism is probably the main cause of tetany. NUTR. ABS. (*b*)

Substances in thymus and urine producing tetany. II. Occurrence of tetanising substances in urine of children and adults. H. SELZER (Z. Kinderheilk., 1933, **54**, 421—434).—Convulsions and 30% lowering of serum-Ca were found in two children with tetany and three children and five adults with conditions associated with tissue destruction. In five patients the findings were only partly positive, whilst in sixteen, including three infants with tetany, they were negative. NUTR. ABS. (*b*)

Thyroxine content of blood during hyperthyroidism. U. S. VON EULER and A. G. HOLMQUIST (Arch. exp. Path. Pharm., 1933, **171**, 201—205).—Hyperthyroidism in man is accompanied by an increase in the thyroxine content of the peripheral venous blood, the increase with non-febrile patients being logarithmically related to that in the basal metabolism. F. O. H.

Blood-cholesterol in thyroid disease. II. Effect of treatment. L. M. HURXTHAL (Arch. Int. Med., 1933, **52**, 86—95).—Blood-cholesterol (I) is low in toxic thyroid states. Determination of (I) is of distinct but limited val. in diagnosis of hyperthyroidism. H. G. R.

Lipase content of the urine and blood-serum in kidney tuberculosis. R. YASUDA (Tohoku J. Exp. Med., 1933, **20**, 265—274).—Normal urine contains 0·0007 and blood-serum 0·0039 [unit ?] of lipase; in tuberculosis without kidney involvement the vals. are 0·0009 and 0·0040, respectively. When one kidney is involved the lipase in the urine secreted by that kidney may be much $>$ or $<$ that in urine secreted by the other kidney. CH. ABS.

Tuberculosis and the deficiency of vitamin-*A* in the diets of young children in India. N. K. BASU (Z. Vitaminforsch., 1933, **2**, 190—193).—A protective action of vitamin-*A* against tuberculosis is indicated. E. B. H.

Enzyme content of human pancreas [in disease]. J. BALÓ and L. LOVAS (Virchow's Arch., 1933, **288**, 326—332).—There is generally a parallelism between the contents of lipase, trypsin, and diastase in the pancreas of persons who have died of various diseases; an exception, however, occurs with septic diseases, when the tryptic action is very much decreased. All three enzymes are diminished in quantity in cases where the diseases have led to cachexia, especially in tuberculosis. In two cases of fat necrosis there was an increase in lipase. NUTR. ABS. (*b*)

Liver-glycogen content. IV. Glycogen and fat content of liver in toxic states in infancy. H. C. GLOTZ. **V. Glycogen content of liver in meningitis and brain injuries.** L. BECK (Z. Kinderheilk., 1933, **54**, 394—403, 404—407).—IV. The vals. found for the glycogen (I) content of the livers of infants who died with toxæmic symptoms by Dische and Popper's method varied between 1·4 and 4·0%, *i.e.*, were relatively high in comparison with those found in infants dying of other diseases. The slightly lower vals. than those reported in infants without disease are attributed to partial inanition. The fat content of the livers of the toxæmic infants was relatively low. The toxæmia of infants is not a primary disturbance of carbohydrate metabolism.

V. In cases of meningitis with and without convulsions the % of liver-(I) was high, whilst in convulsions due to epilepsy, cerebral hæmorrhage, and icterus gravis it was lower. NUTR. ABS. (*b*)

Oxidation-reduction potential of retina. M. NAKASHIMA and K. HAYASHI (J. Biochem. Japan, 1933, **17**, 315—341).—The oxidation-reduction potential (I) of suspensions or extracts of frog's retina in physiological saline or Ringer's solution rises when the prep. is exposed to light and falls again when the

light is removed. The effect is influenced by the duration of exposure to darkness and by the p_H and concn. of the medium. Fe^{***} but not Cu^{**} augments the action of light, whilst KCN decreases (I) to the initial val. Addition of PhMe is followed after 24 hr. by a diminution in (I). The bearing of the results on vision is discussed. F. O. H.

Sensitivity of tissue respiration to action of cyanide. B. KISCH (Biochem. Z., 1933, **263**, 75—97; cf. this vol., 305).—Tissues (kidney, liver, diaphragm, heart, retina, Jensen rat sarcoma) differ greatly in regard to the extent to which their respiration (I) in Ringer solution containing no org. matter is checked by 0·01*N*-NaCN. The extent to which (I) resists the action of NaCN increases with the age of the tissue and is usually greater in "phosphate Ringer" than in "carbonate Ringer." When KCN replaces NaCN an additional effect due to $K^{\cdot}$ is observed. The increased (I) caused by adding org. matter (glucose, NH_2-acids, lactate, pyruvate, sarcosine) is checked by NaCN to extents which differ according to the substance added and to the tissue concerned. Although 0·02*N*-pyruvate checks the (I) of ox-kidney, it increases the extent to which (I) resists the action of NaCN. These results are best explained by supposing the existence of various respiratory catalysts. W. McC.

Chlorophyll. XX. Transformation of chlorophyll in the animal organism. L. MARCHLEWSKI and W. URBANCZYK (Biochem. Z., 1933, **263**, 166—172).—Spectroscopic and other examination shows that anhydro-β-phyllotaonin from the fæces of the silk-worm is probably identical with Conant's phæopurpurin-18 (A., 1930, 1299) and closely related to Fischer and Hendschel's phyllobombycin (A., 1932, 659). All these substances are closely related to phyllocyanin, which itself is very similar to chlorophyll. Structural formulæ are suggested. There is no evidence that chlorophyll serves as a source of blood-pigments in the animal body. W. McC.

Fate of dehydrocholic acid in the toad. S. SHIBUYA (J. Biochem. Japan, 1933, **17**, 385—390).—Following subcutaneous injection of Na dehydrocholate and glycine into toads, the urine contains a diketohydroxycholanic acid, *isoreductodehydrocholic acid*, m.p. 258°, $[\alpha]_D^{20}$ +28·7° in $COMe_2$ [*Me* ester, m.p. 126° ($1H_2O$), 136° (anhyd.), $[\alpha]_D^{20}$ +28·44° in MeOH (*dioxime*, m.p. 248°, $[\alpha]_D^{20}$ +24·59° in MeOH)]. It appears to be an isomeride of reductodehydrocholic acid (A., 1922, i, 1158). F. O. H.

Pigment deposits in intestinal muscle coats and their relation to diet factors. E. NACHTNEBEL (Amer. J. Pathol., 1933, **9**, 261—269).—The muscle coats of the intestinal tracts of dogs previously fed on liver diets showed brown or buff-coloured pigmentation. The pigment was found to bear some similarity to that observed in human hæmochromatosis (hæmofuscin) and in old age, and may be due to the absorption of some constituent of liver.

NUTR. ABS. (*b*)

Effect of dietary and environmental factors on the p_H of intestinal tract. F. E. MUSSEHL, M. U. BLISH, and C. W. ACKERSON (Poultry Sci., 1933, **12**, 120—123).—There was no marked difference in the p_H vals. of the contents of different parts of the alimentary canal of young cockerels receiving diets high in various substances, such as $NaHCO_3$, NH_4Cl, and different carbohydrates, or of birds with rickets and healing rickets. NUTR. ABS. (*b*)

Fat absorption. G. FARKAS and L. VON THANHOFFER (Z. Biol., 1933, **93**, 560—565).—Feeding of olive oil (I) to frogs is followed by an intensive absorption, (I) penetrating to the centre of the alimentary canal cells and leaving the cell-membrane free from (I). No absorption occurs when milk or (I), emulsified with bile, is directly injected into the intestine under conditions whereby hydrolysis is inhibited. Bile is not essential to fat absorption, whilst no difference could be detected between the rates of absorption at p_H 9—10 and 4—5. The intracellular re-synthesis of fat and the mechanism of absorption are discussed. F. O. H.

Decomposition of fat infused directly into the animal body. III. Formation of sugar and ketonic substances from infused fat. T. BABAA (Tohoku J. Exp. Med., 1933, **20**, 452—470).—Intravenous infusion into depancreatised dogs of highly dispersed fat emulsions, in amounts which could produce considerable lowering of the R.Q., did not bring about either increase of blood-sugar or increased excretion of sugar in the urine, but caused an increase of both blood- and urinary ketones. Injection of ketonic substances caused hyperglycæmia as determined by the Hagedorn–Jensen method, but this is not necessarily the result of their conversion into sugar. NUTR. ABS. (*b*)

Relationship of muscle metabolism to formation of ketones. C. BRENTANO (Deut. med. Woch., 1933, **59**, 448—451).—Creatinuria (I) always accompanies the breakdown of muscle- (but not of liver-)glycogen, and also diabetic and other severe ketoses. In all cases of (I) an increased formation of ketonic substances takes place from both exogenous and endogenous sources. This may be an indication of increased conversion of fat into carbohydrate associated with the destruction of muscle-glycogen.

NUTR. ABS. (*b*)

Relation between mitochondria and glucose–glycogen equilibrium in the liver. E. M. HALL and E. M. MACKAY (Amer. J. Pathol., 1933, **9**, 205—220).—Histological examination of the liver mitochondria in rabbits, dieted so as to give varying liver-glycogen (I) contents, revealed marked changes in these structures relative to the (I) content.

NUTR. ABS. (*b*)

Rate of absorption of glucose from the intestinal tract. E. M. MACKAY and H. C. BERGMAN (J. Biol. Chem., 1933, **101**, 453—462).—The coeff. of intestinal absorption (I) of glucose (II) was determined in rats by feeding variable amounts of (II) and subsequent determination of that remaining in the intestine after killing. (I) is raised by increasing the concn. or amount of (II) fed; it decreases with time after feeding. H. D.

Action of the parenteral administration of sugars on the hydrogen-ion concentration of

normal and malignant tissues in living animals. C. VOEGTLIN, H. KAHLER, and R. H. FITCH (Science, 1933, 77, 568).—Injection of pure natural sugars into the voluntary muscle of rats, and into various standard sarcomata, forces the production of lactic acid to such an extent that [H·] is increased. Acid–base equilibrium is therefore a function of carbohydrate metabolism. L. S. T.

Behaviour of the alkaline reserve of rats after feeding with glucose and fructose. R. STOHR (Z. physiol. Chem., 1933, 218, 263—268).—0·2 g. of glucose per 100 g. of body-wt. fed to fasting rats lowered the alkaline reserve after 15—30 min., but it became normal after 1 hr.; fructose had no effect. J. H. B.

Influence of various organic acids on the ability of the rat's liver to store carbohydrate. E. H. MAJER and H. REISNER (Biochem. Z., 1933, 263, 340—352).—The total carbohydrate (I) of rat's liver can be determined by combining the methods of Dische and Popper (A., 1926, 1282) with the reduction method of Bertrand. By feeding rats with a carbohydrate-poor diet only transient changes of (I) occur, and by adding the Na salts of succinic, malic, and citric acids, only in exceptional cases were any considerable increases in (I) obtained. After 24 hr. fasting, the mean (I) val. of rat's liver was 0·4%. After administration to these starved animals of the Na salts of AcOH, $EtCO_2H$, butyric, valeric, hexoic, *dl*-lactic, succinic, malic, and citric acids, (I) vals. were increased only by $EtCO_2H$, lactic, and succinic acids, and then became 2 or 3 times the normal fasting val. P. W. C.

Duration of recovery period following strenuous muscular exercise. O. M. SOLANDT and J. H. RIDOUT (Proc. Roy. Soc., 1933, B, 113, 327—344).—Recovery from 30—45 sec. of strenuous exercise, *i.e.*, a permanent return of CO_2 production and O_2 intake to within the normal range of basal control vals., was complete in $< 1·5$ hr. in three subjects. A prolonged slight increase in O_2 intake in two of the subjects is regarded as not due to the recovery process. A. C.

Effect of long-continued muscular exercise on the chemical composition of the muscles and other tissues of beef cattle. H. H. MITCHELL and T. S. HAMILTON (J. Agric. Res., 1933, 46, 917—941).—Exercise had no effect on the H_2O, Fe, hæmoglobin, or red cell content of the blood or on the Fe or hæmoglobin of the tissues except in the case of the Fe content of the bone-marrow, which was considerably reduced. The Et_2O-sol. matter of all tissues tended to decrease with muscular work, but decisive effects were evident only in the liver. The H_2O content of the liver, heart, and skeletal muscle was also reduced, but no evidence of changes in the proportion of free and bound H_2O was obtained. Light work reduced the N content of the liver, the result being intensified and extended to muscular tissue with heavier work. This N change results from a decrease in N extractives and an increase in glycogen and lipins not extractable by Et_2O. The creatine content and the % of collagen-N in total N of the muscle are reduced. Ash contents of tissues are not appreciably altered by work. A. G. P.

Soya-bean (vegetable) milk in infant feeding. F. R. RITTINGER and L. H. DEMBO (Amer. J. Dis. Children, 1932, 44, 1221—1238).—The fat, protein, and vitamin contents are approx. equal to those of cow's milk. CH. ABS.

Infant nutrition. VII. Lactic acid milk. J. R. GERSTLEY (Amer. J. Dis. Children, 1933, 45, 538—554).—Lactic acid milk is less effective in reducing the alkalinity of infants' intestinal contents than cow's milk+lactose. CH. ABS.

Feeding experiments with decomposition products of proteins. III. S. MAYEDA (Proc. Imp. Acad. Tokyo, 1933, 9, 277—279; cf. A., 1932, 643, 1060).—A cryst. substance, m.p. 220° (decomp.), necessary for the growth of rats fed on a basal diet of pure NH_2-acids, starch, butter, yeast extract, and salts, has been isolated from the mono-NH_2-mono-CO_2H fraction of the acid hydrolysate of fish-meat protein. The C, N, and H contents agree with the formula for aminohydroxyvaleric acid. E. C. S.

Loss of nitrogen during protein inanition. A. ROCHE (Compt. rend., 1933, 197, 279—280).—Rats which died of protein inanition had a ratio of loss of tissue-N/loss in body-wt. 0·5—1·5, whilst when death was due to total inanition the ratio was 0·5, which indicates partial disintegration of muscular protein in the former case. R. S. C.

Comparative chemical composition of normal animal muscle and after death due to total or protein inanition. A. ROCHE (Compt. rend., 1933, 197, 431—432).—Total fasting (I) diminishes, and protein fasting (II) increases, nucleic P in fat- and ash-free rat muscle. The ratio NH_2-N : $(NH_2)_2$-N is the same in normal rats and (I), but is considerably higher in (II). (I) causes only slight variations from the normal in the content of individual NH_2-acids. The effect of (II) is irregular; histidine is unchanged, tryptophan, tyrosine, lysine, and, to a smaller extent, arginine diminish, whilst cystine increases slightly, as in (I). The results are explained by partial degradation of muscle-protein to provide necessary NH_2-acids for maintenance. A. C.

Influence of nutrition on the mechanical properties of [sheep's] hairs. W. SPOTTEL (Bied. Zentr. [Tierernahr.], 1933, B, 5, 13—64).—Protein-rich feeding-stuffs tend to increase the breaking strength and extensibility of hairs, but the effect is not uniform among hairs of different fineness. Deficiency of protein affects the quality especially of the finest and coarsest hairs. In general, dietary changes influence the extensibility more than the breaking strain. A. G. P.

Some aspects of intermediary protein metabolism. E. BRAND and M. M. HARRIS (Science, 1933, 77, 589—590). L. S. T.

Metabolism of *d*- and *l*-methionine. R. W. JACKSON and R. J. BLOCK (Proc. Soc. Exp. Biol. Med., 1933, 30, 587—588).—Growth in rats was stimulated equally effectively by *d*-, *l*-, and *l*-formyl-methionine, but the *d*-formyl derivative was without action. NUTR. ABS. (*b*)

Degradation of amino-acids in the animal body. H. A. KREBS (Z. physiol. Chem., 1933, **218**, 157—159; cf. this vol., 856).—In the oxidative deamination of aspartic (I) or glutamic (II) acid by the kidney of the rabbit, guinea-pig, or dog, the primary keto-acid products undergo further reaction unless the cells are poisoned with 0·001*M*-H_3AsO_3, when the keto-acids may be isolated. (I) affords oxalacetic acid (yielding $AcCO_2H$ and CO_2), (II) gives α-ketoglutaric acid (2 : 4-*dinitrophenylhydrazone*, m.p. 222°). J. H. B.

Embryochemical investigations with the injection method. VI. Behaviour of creatine or creatinine in the hen's egg on amino-acid injection. I. TAKAHASHI (Z. physiol. Chem., 1933, **219**, 31—33; cf. A., 1932, 298).—Eggs were incubated for 17 days after injection with various NH_2-acids. Only arginine and creatine produced a definite increase in the creatinine content. J. H. B.

Formation of urea in vertebrates. H. MANDERSCHEID (Biochem. Z., 1933, **263**, 245—249).—In the liver of amphibians (*Rana esculenta*) and of reptiles (*Testudo graeca*) synthesis of urea is strongly accelerated by addition of ornithine as in mammalian liver. Formation of urea in the whole of the vertebrates occurs always by way of citrulline and arginine. P. W. C.

Energy of urea synthesis. H. BORSOOK and G. KEIGHLEY (Proc. Nat. Acad. Sci., 1933, **19**, 626—631).—The respiration of rat-liver slices has been studied. An increased O_2 consumption accompanies the synthesis of urea from NH_4HCO_3 in Ringer's solution, and it is considered that this process is probably responsible for part (⩾ 20%) of the sp. dynamic action of proteins. A. W.

Chemical structure and physiological response. IV. Conjugation of salicylic acid with glycine and its action on uric acid excretion. A. J. QUICK (J. Biol. Chem., 1933, **101**, 475—485; cf. A., 1932, 1277).—The formol titration method (A., 1926, 539) for hippuric acid was applied to the determination of salicyluric acid (I) and an adaptation of the Day and Taggard bromination method (cf. A., 1932, 1061) for total salicylic acid (II) was used. (I) is obtained from the urine after a diet of fruit and vegetables and administration of Na salicylate (III) by acidifying and extraction with Et_2O and leaching the residue, after the removal of Et_2O, with toluene and $CHCl_3$. Acetylsalicylic acid is determined in the Et_2O extract of urine by Br titration before and after hydrolysis with 5% aq. NaOH. The excretion of (I) after doses of (III) is uninfluenced by exogenous glycine (IV). The excretion of (II) is not rapid, only 50% excretion occurring after feeding 2 g. in 24 hr. Whilst 5 g. of (IV) has practically no effect on the excretion of uric acid, 1·5 g. when given with 2 g. of (II) produces a large augmentation; (IV) also shortens the period of stimulation of excretion due to (II). A crit. concn. of (II) in the body exists below which no stimulation occurs. H. D.

Phosphorus metabolism in embryonic life. III. Phosphagen in avian development. E. BALDWIN and D. M. NEEDHAM (J. Exp. Biol., 1933, **10**, 105—112).—The inorg. P of the chick embryo as % of the body-wt. rose gradually from the 70th to the 240th hr. of incubation, when there was a sudden and enormous increase due to ossification of bone. Creatine phosphate was present at the earliest stage investigated. As a % of the body-wt. it rose up to the 4th day and then slowly fell. At the 4th day there was also a max. in the phosphagen considered as a % of the inorg.+labile P. NUTR. ABS. (*b*)

Effect of pasteurisation of milk on the utilisation of its calcium for growth in the rat. M. ELLIS and H. H. MITCHELL (Amer. J. Physiol., 1933, **104**, 1—9).—Rats were fed for 30 days by the paired feeding method on a low-Ca ration supplemented by raw or pasteurised milk. The milk supplement provided 57% of the total Ca intake, which was restricted to about half that normally retained during the period of rapid growth. All rats gained in wt. (4·4—5·4 g. daily), with a slight difference in favour of raw milk. Analysis of the carcases showed no consistent differences between pair mates as regards % of H_2O, fat, and ash, but the % of Ca in the ash was higher for the rats on raw milk. The pasteurisation of milk thus lowered by 12·3% the availability of its Ca for the growing rat. Under conditions of severely restricted Ca intake, the Ca retention was as high as 98% for the rats on raw milk and 92% for those on pasteurised milk. NUTR. ABS. (*b*)

Behaviour of the lungs in intermediate chlorine metabolism. T. MAKI (Biochem. Z., 1933, **263**, 410—420).—The lungs normally retain blood-Cl and give it back again to the blood in fasting and hypochloræmic conditions and in periods of high and low temp. P. W. C.

Mineral metabolism—copper and iron. S. W. KLETZIEN, K. W. BUCHWALD, and L. HUDSON (Proc. Soc. Exp. Biol. Med., 1933, **30**, 645—647).—Rats given 5·43 mg. Cu daily, as $CuSO_4$, with a diet containing 2 mg. Fe and 0·033 mg. Cu daily, for 12 weeks, showed small increases over controls in the Fe content of all the tissues analysed. There was a definite decrease in the Cu content of the spleen. NUTR. ABS. (*b*)

Development and functional activities of the albino rat as affected by diets deficient in iron. T. B. KEITH and R. C. MILLER (J. Agric. Res., 1933, **46**, 943—961).—Normal growth was obtained with a daily intake of 0·06 mg. of Fe supplied in skim-milk powder, but reproduction was less successful, especially in the second generation, than when adequate Fe was given. A. G. P.

Resorption of iron of food as ferrous iron. W. LINTZEL (Biochem. Z., 1933, **263**, 173—186).—In growing rats prolonged oral administration of 2 : 2′-dipyridyl (I) causes reduction of Fe assimilation and of hæmoglobin production and checks growth, but (I) given parenterally has no such effect. Part of (I) given orally or parenterally is excreted unchanged in the urine. The Fe compound of (I) is not resorbed, but is excreted quantitatively in the fæces when given orally and is partly retained, partly excreted in the urine, when given parenterally. Since (I) forms a complex with $Fe^{\cdot\cdot}$ but not with $Fe^{\cdot\cdot\cdot}$, it follows that the symptoms mentioned are due to the

fixing of Fe" by (I) in the stomach and intestine and that the Fe of food is resorbed as Fe". Since (I) given orally and parenterally does not cause excretion of the complex in the urine it follows that Fe" probably plays no part in the intermediate Fe metabolism. W. McC.

Oxidation within the tissues and hot carbon dioxide baths. A. MOUGEOT and V. AUBERTOT (Compt. rend., 1933, **197**, 282—283).—Emanation (I) enters the body through the skin; this is accompanied by increased respiratory activity, absorption of O_2, and reabsorption of CO_2. No (I) is absorbed from a radioactive bath in absence of excess of CO_2, nor is there increased absorption of O_2 in presence of excess of CO_2, but in absence of (I). C. A. S.

Stimulation of tissue respiration by small amounts of cyanide. B. KISCH (Biochem. Z., 1933, **263**, 187—194).—The respiration of fresh and old tissues from the organs of mammals in " carbonate " and " phosphate " Ringer solution in the presence or absence of org. nutrient matter is increased (up to 60%) by addition of low concn. (0·0005—0·000002*N*) of NaCN, the extent of the increase and the optimum concn. being different for different tissues. W. McC.

Effect of administration of cyanides on the thyroid gland of chickens. A. W. SPENCE (J. Pharm. Exp. Ther., 1933, **48**, 327—331).—Chickens are extremely resistant to injections of MeCN both as regards thyroid reaction and toxic effect. This is due to their lack of power to liberate the CN group of MeCN; the fæces contain only 0·1% of the CN injected as CNS′, although with allyl, K, and benzyl cyanides the vals. are 4·5%, 20—30%, and 24·4%, respectively. J. H. B.

Administration of bilirubin to herbivorous animals under normal and pathological conditions. F. HEIMANN (Biochem. Z., 1933, **263**, 316—322).—The serum of rabbits on a normal diet (alkaline) does not contain a determinable amount of bilirubin (I) until the amount injected is 20 mg. and on an acid diet is 7·5 mg. After P poisoning the serum on injection of 10 mg. of (I) contains considerable amounts of (I). After keeping the animals under reduced pressure and injecting large amounts of (I), none was detectable in the serum. After establishing a condition of hæmolytic jaundice (prsodin poisoning) and injecting (I), the serum on an alkaline diet did not, but on an acid diet did, contain a determinable amount of (I). Results with guinea-pigs are also recorded. P. W. C.

Fate of " cardiazol " in man. A. ESSER and A. KÜHN (Arch. exp. Path. Pharm., 1933, **171**, 284—288).—Ingestion of 100 c.c. of 10% " cardiazol " (I) produced convulsions and death in 1 hr. Analysis of the intestinal contents indicated that 7·4 g. were absorbed from the stomach, but the greater part of this could not be found. The (I) actually detected occurred mainly in the liver and blood. F. O. H.

Pharmacological activity of ethyl nitrite, U.S.P. M. R. THOMPSON, M. J. ANDREWS, and C. T. ICHNIOWSKI (J. Amer. Pharm. Assoc., 1933, **22**, 487—495).—The action of fresh and deteriorated preps. of $EtNO_2$ was investigated. The main action is on the circulation, whilst diuresis is not produced. Deterioration, which is accompanied by a change in p_H, produces no toxic substance. A high EtOH content enhances the stability of the prep. F. O. H.

Alteration of the blood-[H·] and mineral metabolism during narcosis. II. Blood-[H·]. J. BEČKA (Arch. exp. Path. Pharm., 1933, **171**, 244—249; cf. this vol., 744).—Rabbits narcotised for short periods (with one of fifteen narcotics tested) experienced a decrease in blood-p_H. A max. decrease occurred with $CHCl_3$ (0·14—0·24) and with veronal (0·20). The decrease persisted for some time after recovery excepting with amylene and chloral hydrates. Morphia, however, produced hyperpnœa and alkalosis, the p_H increasing 0·40—0·49. F. O. H.

Post-operative hyperglycæmia. F. LEFÈVRE (Rev. belge Sci. méd., 1933, **5**, 5—20).—The post-operative hyperglycæmia, produced when a mixture of scurocaine and adrenaline is used as local anæsthetic, is absent when either is used alone. NUTR. ABS. (*b*)

Local anæsthetic action of *p*-aminobenzoates of diethylaminoethoxy-alcohols. W. H. HORNE and R. L. SHRINER (J. Pharm. Exp. Ther., 1933, **48**, 371—374).—The compounds $NEt_2{\cdot}[CH_2{\cdot}CH_2{\cdot}O]_n{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, where $n=1$—4, were prepared (A., 1932, 935), converted into the *p*-nitrobenzoate hydrochlorides (oils), and reduced to *p*-aminobenzoates (oils). When $n=1$, the compound has low toxicity and high anæsthetising power, the ether linking producing surface as well as injection anæsthesia. The higher homologues are too irritating for use. J. H. B.

Hæmaturia from handling 5-chloro-*o*-toluidine. A. N. CURRIE (J. Ind. Hygiene, 1933, **15**, 205—213). W. O. K.

Hæmolysis by Australian snake venoms. I, II. C. H. KELLAWAY and F. E. WILLIAMS (Austral. J. Exp. Biol., 1933, **11**, 75—80, 81—94).

Comparison of the action of sapotoxin, strophanthin, and certain snake-venoms on the heart. J. W. C. GUNN and D. EPSTEIN (Quart. J. Pharm., 1933, **6**, 182—186).—The high tolerance of the toad to digitalis (I) and the absence of tolerance to sapotoxin are suggested as a biological test for distinguishing these. Two cobra venoms (*Naia flava* and *N. nigricollis*) have (I)-like action. H. G. R.

Standardised preparation of digitalin for injection. J. C. GAGE (Quart. J. Pharm., 1933, **6**, 161—168).—Assay of digitalin (I) by the frog and the guinea-pig methods gives results which do not differ significantly. The Knudson–Dresbach colorimetric method does not agree with the biological methods, but the results are of the same order. H. G. R.

Paraldehyde in digitalis standardisation by the cat method. D. EPSTEIN (Quart. J. Pharm., 1933, **6**, 169—173).—Paraldehyde is recommended for anæthesia in the assay of digitalis by the cat method. H. G. R.

Solanine poisoning. S. G. WILLIMOTT (Analyst, 1933, **58**, 431—438).—An extract in AcOH is evapor-

ated at alkaline reaction and extracted with 95% EtOH, and the solanine pptd. with aq. NH_3 and purified by dissolution in AcOH and repptn. Amounts found per 100 g. were 2·7—9·1 mg. in Irish and Cyprus potato tubers, and 27—49 mg. in the shoots, the lowest vals. being obtained for plants from high altitudes. Cases of poisoning are cited. Solanine sets to a firm jelly in hot EtOH or C_5H_{11}·OH and (like solanidine) produces a red colour with Na_2SeO_4 in H_2SO_4; reddish-yellow changing to reddish-brown with Frohde's reagent; orange-yellow changing to violet with NH_4VO_3 in H_2SO_4; pink to red with warm H_2SO_4 in EtOH (2 : 3); reddish-brown with conc. HNO_3; and deep red with the $SbCl_3$ vitamin reagent. J. G.

Action and rate of elimination of atropine and genatropine. M. Haferkorn and L. Lendle (Arch. exp. Path. Pharm., 1933, **171**, 276—283).—That genatropine (I) has a lower toxity than atropine (II) is confirmed (cf. A., 1926, 82). The action of (II) on the cat's vagus, however, is 4—5 times as strong as that of (I); the therapeutic indices of (I) and (II) are therefore approx. equal. The min. rates of continuous effective injection indicate that, when allowance is made for the difference in the single effective dose, the rates of elimination of (I) and (II) are practically equal. F. O. H.

Morphine and enzymes. II. E. Keeser (Arch. exp. Path. Pharm., 1933, **171**, 311—316; cf. A., 1932, 1167).—The action of lecithinase (I), phosphatase, urease, or tyrosinase is modified by the presence of small amounts of morphine (II), heroin, and codeine. Thus subcutaneous injection of low concns. of (II) into man activates the blood-(I) and produces decomp. of lecithin with liberation of choline and methylguanidine. These substances are probably concerned with the symptoms of abstinence in (I) addicts. F. O. H.

Comparison of the toxicity of nicotine and anabasine. W. A. Gersdorff (J. Amer. Chem. Soc., 1933, **55**, 2941—2945).—The theoretical thresholds of toxicity for rotenone, nicotine, and anabasine towards goldfish are 0·012, 8·0, and 9·5 mg. per litre, and the rate of increase of the theoretical velocity of fatality with increase in concn. 90, 5·6, and 5·2 c.c. per mg. per min., respectively. R. S. C.

Physico-chemical properties of some new choline derivatives in relation to their chemical constitution and pharmacological action. W. F. von Oettingen and R. O. Bowman (J. Pharm. Exp. Ther., 1933, **48**, 333—340).—Choline hydrochloride, $NMe_3Cl{\cdot}CH_2{\cdot}CH_2Cl$, $[{\cdot}CH_2{\cdot}NMe_3Cl]_2$, $NMe_3Cl{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, and $NMe_3Cl{\cdot}CH_2{\cdot}CH_2{\cdot}NHMe$ in 0·01*M* concn. do not affect surface tension, are not sol. in oil, do not ppt. serum and lecithin emulsions, and do not affect rate of sedimentation of erythrocytes. The velocity of diffusion through living frog-skin is in inverse ratio to their pharmacological action. J. H. B.

Aminohydroxy-compounds which show the biuret reaction. IX. Fate of some ω-amino-hydroxy-acids in phloridzin glycosuria and phosphorus poisoning. T. Kawada (Z. physiol. Chem., 1933, **219**, 34—37; cf. A., 1932, 1118).—In passage through phloridzinised dogs *iso*serine, but not γ-amino-β-hydroxybutyric acid (I), is converted into glucose. In dogs poisoned with P, a substance (*chloroaurate*, m.p. 182°; *chloroplatinate*, m.p. 225°), probably γ-butyrobetaine, was isolated from the urine. About ¼ of the (I) was recovered unchanged. J. H. B.

Permeability and variation of permeability. Influence of surface-active and hydrotropic substances on the permeability of acids and of sucrose. A. N. Rao (Biochem. Z., 1933, **262**, 332—350).—The permeability is investigated of aq. solutions of $H_2C_2O_4$, tartaric and lactic acids, and sugar solutions through membranes of collodion, parchment, rubber, collagen, pig's bladder, and intestine with and without addition of saponin (I), $PhSO_3Na$ (II), a series of alcohols, etc. (I) generally (except with a rubber membrane) causes increased permeability to sugar solutions, the effect being greatest with medium to small concns. of (I). Surface-active substances also cause increased permeability. Na salicylate and (II) increase the permeability to acids, especially of biological membranes. P. W. C.

Electrical potential difference across living frog skin. H. B. Steinbach (J. Cell. Comp. Physiol., 1933, **3**, 1—26).—The skin is mounted as a diaphragm between two neutral salt solutions and the p.d. across the skin is equal to the sum of the "partial" p.d. from skin to solution on either side. Addition of KCl to either solution lowers the p.d. between skin and solution irrespective of the nature of the dissolved salt. $CaCl_2$ lowers the p.d. between skin and both solutions when applied to the outside but not when applied to the inside of the skin. The skin has a low sensitivity to changes in electrolyte concn. of the inside solution, but responds quickly to small changes in the outside medium. The curve relating p.d. and log [NaCl] shows a max. corresponding with 0·006*M*-NaCl. A. G. P.

Actual reaction of the skin, in normal, morbid, and different experimental conditions. E. Rastelli (Arch. Ist. Biochim. Ital., 1933, **5**, 175—208).—The skin-p_H has been measured by intradermic injection of vital indicators. In the normal condition it is neutral. Gangrene is accompanied by a fall in p_H in direct relation with the extent of the gangrenous lesion, and probably also with its duration. In ordinary cutaneous inflammation p_H is normal, but tends to fall if suppurative exudations occur. Experimental arterio-venous stasis induces a fall of p_H for the duration of the stasis; venous stasis has no effect. Injection of adrenaline and histamine produces short periods of acidosis, that for adrenaline being double the length of that for histamine. The time for re-establishment of neutral conditions after intradermic injection of solutions of known p_H varies for each subject with the difference between the p_H of the solution used and neutral p_H, on either side of neutrality. R. N. C.

Measurement of polarisation in skin. H. Schaefer (Z. Biol., 1933, **93**, 570—577).—The nature of the polarisation produced by application of a const. current to human skin indicates a marked sensitivity to electrical currents. The phenomena associated

with the resistance and polarisation capacity of the skin are discussed. F. O. H.

Neuromuscular excitability in relation to the biochemistry of minerals. II. Influence of change of Ca/P and Na/K ratio in the diet. L. SEEKLES and B. SJOLLEMA (Biochem. Z., 1933, **262**, 367—379).—Using the same technique (this vol., 532), the authors further investigate the changes of AS/AO (I) ratio with changes of diet. Increase of P relative to Ca in the rabbit's diet led to a condition of latent tetany characterised by increased (I). Using the normal salt ratio, excitability was low, (I) being usually < 1, whereas abnormal ratios of Na/K=1/542 and Ca/P=1/8·4, and still more diets combining both of these ratios, led to considerable increase in (I). P. W. C.

Effect of sensory stimulation on the blood-sugar content of rabbits, splanchnicotomised or suprarenalectomised. F. OHMI (Tohoku J. Exp. Med., 1933, **20**, 498—505).—Whilst double splanchnicotomy considerably diminishes the hyperglycæmia due to sensory stimulation in rabbits, double adrenalectomy has little effect. NUTR. ABS. (*b*)

Stimulation by mineral and fatty acids in the barnacle, *Balanus balanoides*. W. H. COLE and J. B. ALLISON (J. Gen. Physiol., 1933, **16**, 895—903).—Stimulation of *B. balanoides* by HCl, H_2SO_4, HNO_3, and the first seven members of the normal fatty acids has been measured by recording the % closure over a range of $[H^{\cdot}]$ from $3{\cdot}2\times10^{-8}$ to $5{\cdot}889\times10^{-6}$. The intensity of stimulation is proportional to the effects of two forces, one related to the change in $[H^{\cdot}]$ and the other to the field of force around the anion of the acid added. The order of stimulating activity is $HCl>H_2SO_4>HNO_3$ and for the fatty acid series heptoic > hexoic > valeric acid > $PrCO_2H$ = AcOH > $EtCO_2H$ = HCO_2H. A. W.

Storage of halogens in hens' eggs and therapeutic application of halogenised eggs. I. L. BERKESY and K. GONCZI (Arch. exp. Path. Pharm., 1933, **171**, 260—268).—The greater part of the I of hens' eggs is organically combined, the yolk being richer in I than the white. Intravenous injection of 1·25% aq. $NaIO_3$ into hens produces a marked increase in the I content of the eggs. The feeding of such eggs to persons with thyroid diseases results in an increase in the blood-I. F. O. H.

Daily administration of inorganic iodine in Dutch tap-water. J. F. REITH (Biochem. Z., 1933, **263**, 395—399).—A method is described for the determination of various I fractions (EtOH-insol, EtOH-sol., etc.) in drinking H_2O. In spite of the high I content, those who drink this H_2O show no ill effects. P. W. C.

Case of chronic lead poisoning. H. E. MONK (Analyst, 1933, **58**, 397).—The liver, brain, kidney, and right tibia of a stereotyper dying 4 years after the last exposure to Pb contained 35, 8, 8, and 27 p.p.m. of Pb. E. C. S.

Experimental variation of the distribution and excretion of medicinal preparations. F. SERIO and R. INDOVINA (Biochem. Z., 1933, **262**, 308—320).—A series of complex Au and As compounds is injected into rabbits and the distribution of Au and As investigated by analysis of the organs and tissues. The effect on this distribution of a preliminary injection of substances which accelerate (I) or inhibit (II) blood coagulation is then determined. (I) facilitate the storage of these compounds, especially in the liver, and (II) accelerate their elimination. P. W. C.

Variations in blood-cholesterol immediately after a single irradiation with rays intermediate between ultra-violet and *X*-rays. S. MALCZYNSKI (Compt. rend. Soc. Biol., 1933, **112**, 925—927).—Irradiation of the shaved skins of two dogs at 10 cm. distance for 15 min. produced transient falls of 4% and 7% in blood-cholesterol. After 10 min. at 8 cm. there were temporary increases of 18% and 22%. Such rays are less potent than *X*-rays. NUTR. ABS. (*b*)

Variations in mineral elements of blood as affected by irradiation with rays intermediate between ultra-violet and *X*-rays. S. MALCZYNSKI (Compt. rend. Soc. Biol., 1933, **112**, 928—931).—Irradiation for 15 min. at 10 cm. distance produced temporary increases of about 25% in K and 28—29% in Ca content, the effect being most permanent in the latter case. The Na content also increased immediately after irradiation, this being followed by a fall. The effect on P content was indefinite. NUTR. ABS. (*b*)

Quinones as enzyme models. X. Activation by salts of bivalent cations of the catalysis of oxidative deamination of amino-acids. B. KISCH. **XI. Role of the anions in this process.** B. KISCH and K. SCHUWIRTH (Biochem. Z., 1933, **263**, 98—104, 195—197; cf. this vol., 634).—X. The oxidative deamination of glycine in presence of hydroxyquinol or resorcinol [as measured by yield (I) of NH_3] is not affected by NaCl, KCl, LiCl, or TlCl and only very slightly affected by $BaCl_2$. The other alkaline-earth metals (II) greatly (up to 200%) increase (I); in this connexion they form the series Ba<Sr<Mg<Ca. The optimum concns. for $MgCl_2$ and $CaCl_2$ are 0·001M and 0·002M, respectively, and the optimum p_H for $SrCl_2$, $MgCl_2$, and $CaCl_2$ is 9—11. Colloidal factors are not involved in the process, but the ability of the halides of (II) to combine with NH_3 may play a part.

XI. The activity of $Mg^{\cdot\cdot}$ and $Ca^{\cdot\cdot}$ is not affected by the anions (Cl', Br', I', NO_3', SO_4'', formate, acetate, lactate) with which they are combined. W. McC.

Yellow oxidation enzyme. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1933, **263**, 228—229; cf. this vol., 753).—The dye $C_{13}H_{12}O_2N_4$ (I), when heated at 100° with 0·2N-$Ba(OH)_2$ in an indifferent atm., gave a pale yellow cryst. *substance* (II), $C_9H_{10}O_2N_2$, m.p. 210—211°. The absorption spectrum of (II) resembles that of (I), having three bands, but these are shifted in (II) towards the ultra-violet. (II) is not decolorised by $Na_2S_2O_4$. W. McC.

Role of phosphate in oxidations. I. Activity of catalase in phosphate solutions. II. Peroxidase activity in phosphate solutions. A.

MALKOV (Biochem. Z., 1933, **263**, 268—273, 274—277).—I. The activity of yeast-catalase (I) is inhibited by PO_4'''. Added Fe inhibits (I), but PO_4''' removes this effect.

II. The activity of yeast-peroxidase (II) is decreased by PO_4''' most strongly at first. Added Fe increases the activity of (II). P. W. C.

Oxidation-reduction potential of peroxidase preparations. M. PADOA and N. NEROZZI (Biochem. Z., 1933, **263**, 375—386).—The r_H vals. of peroxidase preps. do not support the view that active O is present, the latter in presence of peroxides never being detected. On the contrary, the greater is the activity of the enzyme prep., the more strongly reducing is the medium. P. W. C.

Potentiometric study of the Schardinger reaction. J. TOYAMA (J. Biochem. Japan, 1933, **17**, 433—439).—Using a Au or Pt electrode, the oxidation–reduction potential of a system containing the Schardinger enzyme (I) is not influenced by the addition of MeCHO, salicylaldehyde, or PhCHO, whilst methylene-blue produces an abrupt change to a reduction potential (cf. A., 1926, 1175). With a Pt but not with a Au electrode, CH_2O produces a small reducing effect which is increased by presence of (I). F. O. H.

Coupled reactions in biological systems. H. F. SCHOTT and H. BORSOOK (Science, 1933, **77**, 589).—In (i) the reduction of pyruvate to lactate by means of the energy of the anaerobic oxidation of formate to H carbonate and (ii) the reduction of fumarate to succinate through the anaerobic oxidation of lactate to pyruvate intermediary substances, methylene-violet for (i) and methylene-blue for (ii) were necessary for reaction to occur. PhMe-treated *B. coli*, the enzyme system for (i) and (ii), contain no mediators or energy carriers capable of serving these two systems. L. S. T.

Coupled redox potential of the lactate–enzyme–pyruvate system. J. P. BAUMBERGER, J. J. JURGENSEN, and K. BARDWELL (J. Gen. Physiol., 1933, **16**, 961—976).—The term " coupled redox potential " (I) is defined as the potential at which an irreversible system comes into equilibrium with a reversible system when a suitable catalyst is present. The system lactate–pyruvate is reversible in the presence of lactic acid dehydrogenase. Thermodynamic calculations have been made to determine the free energy of the reaction lactic ion $\longrightarrow$ pyruvic ion and an approximation for the standard free energy of formation of $AcCO_2H$. The importance of (I) as a factor in the regulation of the equilibrium of metabolites is indicated. A. W.

Eleutoamylase, an anti-sistoamylase. T. CHRZASZCZ and J. JANICKI (Biochem. Z., 1933, **263**, 250—261).—Amylase (I) is normally accompanied by sistoamylase (II), which combines with and inactivates (I). Witte's peptone and other protein degradation products act as an eleutoamylase antagonistic to (II). These peptones inhibit the union of (I) and (II), they can liberate active (I) from the inactive compound of (I) and (II), and they show a protective action against the inactivation of (I) by shaking. P. W. C.

Glycolytic co-enzymes. H. MATSUZAKI (J. Biochem. Japan, 1933, **17**, 457—481).—Whilst the degradation of glucose by various tissues [rabbit sarcoma (I), mouse tumour, mouse diaphragm (II), and guinea-pig cerebral cortex] is marked, that of hexose diphosphate (III) is very slight: the reverse is true, however, for rabbit red-muscle (IV) and mouse liver (V). The glycolytic co-enzyme from (I) (A., 1928, 1274) accelerates the decomp. of glucose by (I), (II), and kidney, but not that by (IV) and (V); acceleration by the co-enzyme from baker's yeast (A., 1927, 590) or by extract of adrenal cortex occurs with (IV), but not with the tumour tissues. (IV) has a high content of both phosphatase and phosphatese, whilst the tumour tissues are poor in the latter. Oxidation of (III) by (IV), but not that of glucose by tumour tissue, is attended by a marked H-activation. The tissues decompose AcCHO and, to a smaller extent, dihydroxyacetone and glyceraldehyde. F. O. H.

Action of iodine on glycolytic metabolic processes, especially fermentation by yeast. Effect of iodoacetic acid. A. STURM and J. SCHULZ (Biochem. Z., 1933, **263**, 198—218; cf. A., 1931, 761).—The fermentation (I) of surviving liver and (I) by yeast or yeast extract is increased by low (0·0001—0·01*M*) concn. of I′. With yeast the extent of the effect depends on the concn. of I′, the species of yeast, the p_H, and (in particular) on the stage of (I) at which the I′ is added. The optimum conditions are: baker's yeast at p_H 7·2, I′ in 0·001*M* concn. added as (I) sets in. The I′ affects the phosphorylation of the sugar and its action is inhibited if $CH_2I{\cdot}CO_2H$ (II) is present. The inhibiting action of (II) on the (I) of yeast decreases and vanishes (*e.g.*, with baker's yeast buffered with phosphate at p_H 6·9) as the p_H increases; under certain conditions (II) even accelerates (I). (II) also inhibits co-enzyme action, (I) of hexose diphosphate, and (I) of $AcCO_2H$ only at $p_H < 6{\cdot}5$. Possibly (II) acts by combining with NH_2-compounds which accelerate (I). There is parallelism between changes in the I content of the animal organism and changes in its metabolism. W. McC.

Thiocyanate formation in the animal body. II. K. LANG (Biochem. Z., 1933, **263**, 262—267).—The author's previous work (this vol., 637) on the synthesis of thiocyanate under the action of an enzyme rhodanese widely spread through the animal body is confirmed in the perfusion of cat's liver and kidney preps. with mixtures of cyanide and thiosulphate. The formation of CNS′ from mustard oil and thiocyanate esters is also demonstrated. Investigation of the CNS′ balance in man shows that CN′ is a regular product of intermediate metabolism. P. W. C.

Stability and separation of phosphatases. E. JACOBSEN (Biochem. Z., 1933, **263**, 302—312).—The destruction of the non-sp. phosphatases (I) of kidney, bone, and liver at different p_H are investigated. Whereas (I) are destroyed by heating for a short time in feebly acid reaction in presence of NH_4Cl, the sp. adenylpyrophosphatase (II) is much more stable, and a separation by differential heat inactivation is described. (II) so purified attacks only that

PO_4 which is readily hydrolysed by acid. The optimum p_H is 7·2. Sp. (II) is detected in most tissues. P. W. C.

Influence of electrolytes on mono- and pyrophosphatase. S. MUNEMURA (J. Biochem. Japan, 1933, **17**, 343—366).—Monophosphatases with p_H optima at 3, 5·6, and 9 and pyrophosphatases with p_H optima at 4, 5—6, and 9 were prepared from pig's kidney and rice bran (A., 1932, 305) and freed from proteins and electrolytes by autolysis and dialysis. The acceleration of some of the enzymes by $Mg^{\cdot\cdot}$ is noteworthy. $Ca^{\cdot\cdot}$ has no action, whilst in some cases F' has an inhibiting effect. AsO_4''' inhibits all types, whilst PO_4''' has a similar but less marked effect. The bearing of the results on glycolysis is discussed. F. O. H.

Lipases in the animal organism. I. A. I. VIRTANEN and P. SUOMALAINEN (Z. physiol. Chem., 1933, **219**, 1—21).—The lipase (I) contents of various organs of guinea-pigs and rabbits show wide individual and seasonal variations. The liver contains most (I), next come pancreas, lungs, and kidneys in that order. Intravenous injection of (I) from pig's pancreas into rabbits almost doubled the (I) content of the liver; moreover, the extract showed the characteristics of liver (I) (inhibition by atoxyl, no action on olive oil), not of pancreatic (I). Pancreas (I) and liver (I) are probably identical, the differences being due to concomitants. J. H. B.

Determination of lipase. H. STEUDEL (Biochem. Z., 1933, **263**, 231—238).—The hydrolysis of olive oil by pancreatic lipase, using preps. from three different pigs and from the mixed sample from twenty pigs, as determined by Willstatter's method, gives very different curves for the various preps., and the curve for the mixed sample is not the mean of those for the individual samples. P. W. C.

Esterase action. IV. E. A. SYM (Biochem. Z., 1933, **262**, 406—424).—The influence on the reaction velocity of increasing the concn. of the substrates in enzymic and acid–base catalysis is investigated. Increasing the concn. of alcohol, acid, and ester had almost the same effects on the reaction velocities in the synthetic and hydrolytic reactions with esterase of pig's pancreas as in the corresponding acid–base-catalysed reactions. H_2O, on the other hand, accelerated both the hydrolytic and synthetic enzyme reactions, but inhibited both reactions when catalysed by HCl. The reaction products also inhibited the reaction when catalysed by esterase, by HCl, and by picric acid, the inhibition with acid–base being $<$ with enzymic catalysis. The sp. character of the pancreatic, liver, and gastric esterases is also investigated in comparison with the acid–base catalysis. P. W. C.

Biochemical synthesis of fatty esters of *cyclo*hexanols. L. VELLUZ and P. SAULEAU (Compt. rend., 1933, **197**, 277—279).—The enzyme from *Ricinus* seeds (modified prep.) forms the following % of esters from oleic acid and the alcohol in 2 days at 16—18°: *cyclo*hexanol (I) 33 (63 in 12 days), *cyclo*hexane-1 : 2- and -1 : 4-diol, 26 and 35, respectively. It forms 30% of the hexoate of (I) and 12% of that of glycerol in 2 days. Esterification is hindered sterically ($o>p>m$), as shown by the methyl- and dimethyl-*cyclo*hexanols. R. S. C.

A product of the action of pepsin on glycine. A. BLANCHETIÈRE (Compt. rend., 1933, **196**, 1926—1927).—From the residues after isolation of diketopiperazines (I) in the product of the hydrolysis of glycine (II) with pepsin (A., 1931, 1090) is isolated unchanged (II) (total recovery 50%) and a *substance* which does not give Abderhalden and Komm's reaction (A., 1924, i, 1361) and is pptd. from aq. solution by careful addition of dil. alkali or alkali carbonate, but its solution in excess of *N*-NaOH cannot be pptd. by neutralisation after 24 hr., the solution then dissolving $Cu(OH)_2$ like an NH_2-acid. Hence the substance is probably the enolic form of (I). J. W. B.

Influence of reducing and oxidising treatment on the function of organ cathepsins. P. RONDONI and L. POZZI (Z. physiol. Chem., 1933, **219**, 22—30).—Cysteine promotes autoproteolysis of extracts of rabbit liver and mouse carcinoma, as measured by pptn. of residual protein with $CCl_3{\cdot}CO_2H$. Fe^{II} salts increase and glycogen inhibits the action. Oxidising agents (H_2O_2 or a stream of O_2) and increase of p_H inhibit proteolysis and in some cases produce an increase in the amount of protein pptd. J. H. B.

Autolysis of muscle. I. Influence of temperature on the distribution of nitrogen in ox flesh. I. A. SMORODINCEV, N. V. SCHIROKOV, and P. V. ZYGANOVA (Biochem. Z., 1933, **262**, 425—431).—During autolysis of flesh, the changes in the protein fraction both at room temp. (17—18°) and at 4° and 25—37° are followed by means of determinations of total, NH_2- and residual N of the flesh extract, and the results tabulated. Only small differences of total N were obtained at the different temp. The highest NH_2-N vals. were obtained at all temp. after 6 hr. autolysis and the curve for residual N at 17—25° followed, but lay $>$ that at 4—8°. P. W. C.

Nuclein metabolism. XXXI. Enzymic depolymerisation of animal nucleic acid. W. KLEIN. **XXXII. Ribodeoseguanylic acid.** W. KLEIN and S. J. THANNHAUSER (Z. physiol. Chem., 1933, **218**, 164—172, 173—180; cf. A., 1932, 776, 1167).—XXXI. Nucleophosphatase from intestinal mucosa contains two enzymes: thymonucleinase (I), which depolymerises thymus-nucleic acid to the mononucleotide (II), and a sp. phosphatase (III), which eliminates H_3PO_4 from (II). The action of (III) is suppressed by the addition of Na_2HAsO_4, thus permitting the isolation of (II). Yeast-nucleic acid is not attacked by (I). Hydrolysis of glycerophosphate and hexose diphosphate by (III) is only slightly suppressed by AsO_4'''.

XXXII. (II) was obtained in the manner indicated from thymus-nucleic acid and isolated as the cryst. *dibrucine* salt. This was converted into the unstable cryst. *ribodeoseguanylic acid* by way of the sec. *Ba* salt (IV), browns at 200°. (III) eliminates H_3PO_4 from (IV) yielding guaninedeoxyriboside. J. H. B.

Conversion of the intermediate term of the permanganate oxidation of uric acid into allan-

toic acid in the presence of soya enzymes and potassium cyanide. R. FOSSE, P. DE GRAEVE, and P. E. THOMAS (Compt. rend., 1933, **197**, 370—374).—Allantoic acid (I) is produced by the action of soya-bean extract on hydroxyacetylenediureincarboxylic acid (II) (A., 1932, 864), confirming the view (Schuler and Reindel, this vol., 427) that (II) is the intermediate compound between uric acid and (I) in enzymic uricolysis. A. C.

Tannase. H. DYCKERHOFF and R. ARMBRUSTER (Z. physiol. Chem., 1933, **219**, 38—56).—Extracts of the mycelium of *Aspergillus niger* contain at least two enzymes catalysing the hydrolysis of esters, tannase (I) hydrolysing Me gallate (III) and mould-esterase (II) hydrolysing PhOAc. (II) is destroyed by warming at p_H 8·9 at 40°, (I) being mostly unchanged. In order to undergo fission by (I) the acid component of the ester must contain two phenolic OH groups. The esterified CO_2H must be attached directly to the oxidised Ph ring and must not be in the *o*-position to an OH. The specificity of (II) is probably coincident with that of liver-esterase. The hydrolysis of (III) by (I) is unimol., optimum p_H 5—6. J. H. B.

Mechanism of enzyme action. XII. Cryolysis and the absorption of gases by lyophile colloids. II. F. F. NORD and G. WEISS (Biochem. Z., 1933, **263**, 353—365).—In continuation of previous work (A., 1932, 337, 909, 1203) curves show the changes of surface tension of various lyophile colloids (gum-arabic, saponin, and metacholesterol sols) in the unfrozen condition and after freezing for 2 hr. at −18° and −79° and also after treatment with C_2H_4, C_2H_2, and N_2O. Using the results of such methods, the enhanced activity of a cell-free lyophile-colloidal zymase solution after freezing and thawing is explained in terms of increased surface of the enzyme carriers. P. W. C.

Separation from yeast of an alcohol-dehydrogenase. D. MÜLLER (Biochem. Z., 1933, **262**, 239—247).—Lebedev's maceration extract of bottom yeast contains an alcohol-dehydrogenase, obtained as a dry prep. by pptn. with EtOH–Et_2O. The enzyme, which is destroyed by heating at 90° for 30 min., oxidises $Pr^{\beta}OH$ to $COMe_2$. In this reaction, O_2 and methylene-blue do, but benzoquinone does not, act as a H_2 acceptor, the latter strongly inhibiting the reaction. Addition of cytochrome-*C* and of indophenoloxidase has no effect on the formation of $COMe_2$. P. W. C.

Action of yeast on glycerophosphoric acid. C. NEUBERG and M. KOBEL (Biochem. Z., 1933, **263**, 219—227; cf. this vol., 637).—*l*-Glycerophosphoric acid (I), prepared from the Ba H salt by a modification of Nilsson's method (A., 1930, 641), is converted by yeast into $AcCO_2H$. Concurrently a decarboxylation reaction (II) occurs. At appropriate p_H, if sufficient yeast is present, (II) becomes the main reaction. If dry yeast or yeast extract is used, the fermentation of (I) yields CO_2, MeCHO, and acetoin. W. McC.

Influence of organic dyes on cell and organ function. IV. Absorption by living cells (yeast). F. AXMACHER (Arch. exp. Path. Pharm., 1933, **171**, 289—310; cf. this vol., 751).—$NHPh_2$ and, to a smaller extent, $CHPh_3$ dyes are absorbed by living and, to a greater extent, by dead top-yeast cells. Certain azo-dyes are absorbed only by dead cells. Cells rendered lipin-free by $COMe_2$, Et_2O, or $CHCl_3$ absorb to practically the same extent as normal cells. The mol. dimensions and surface activity of the dyes used indicate that a process of adsorption occurs. F. O. H.

Pantothenic acid, a growth determinant of universal biological occurrence. R. J. WILLIAMS, C. M. LYMAN, G. H. GOODYEAR, J. H. TRUESDAIL, and D. HOLIDAY (J. Amer. Chem. Soc., 1933, **55**, 2912—2927).—Extracts (usually prepared by 80% MeOH) of rice bran, beef liver, eggs of *Cancer productus* and of *Strongylocentrotus purpuratus*, oysters, earthworms, planarian worms, *Physarum polycephalum*, *B. subtilis*, *Aspergillus niger*, *Spyrogyra*, *Oscillatoria*, milk, and egg-white stimulate the growth of yeast. Fractional electrolysis, diffusion, and other tests lead to the belief that all the extracts contain the same *pantothenic acid*, a polyhydroxylic acid, mol. wt. about 150, stable at 119° at p_H 5 or 7, but not at p_H 9. It is destroyed by N_2O_3, but can be esterified to an inactive ester and recovered in partly active form by acid or very dil. alkaline hydrolysis. It has no amphoteric properties, does not contain a reducible (hydrogenation) or carbohydrate (Ag_2O) group, and is closely related to vitamin-B_6. It is probably accompanied in the extracts by toxic substances. R. S. C.

Inhibition of growth by heparin. A. FISCHER and P. NYSTRÖM (Biochem. Z., 1933, **262**, 364—366).—Crude liver extracts and pure samples of heparin inhibit the growth of yeast. P. W. C.

Oxidisability and rate of growth [of fungi]. A. ARTUNDO and E. AUBEL (Compt. rend. Soc. Biol., 1932, **108**, 1111—1112; Chem. Zentr., 1932, ii, 3904).—The growth of *Aspergillus niger* in solutions of glucose, citric and succinic acids is affected by changes in p_H in the same sense as the oxidisability of the nutrient at the active C. L. S. T.

Utilisation of aliphatic acids by moulds. O. FÜRTH and E. H. MAJER (Biochem. Z., 1933, **263**, 332—339).—The dry wts. of mycelium obtained under comparable conditions by growing *Aspergillus niger*, *Penicillium glaucum*, and *Mucor mucedo* on a medium containing a series of Na salts of aliphatic acids and on sugars as the source of C are given. Of the acids, lactic and acetic are most readily utilised, then butyric, succinic, malic, and citric acids, and lastly HCO_2H, $EtCO_2H$, valeric and hexoic acids. Sugars are still more readily available, pentoses (arabinose are xylose) and hexoses (glucose, fructose) being equally readily utilised. P. W. C.

Biochemical transformation of formic acid by moulds. Chemistry of the process. T. CHRZASZCZ and M. ZAKOMORNY (Biochem. Z., 1933, **263**, 105—118; cf. this vol., 536, 749).—Moulds attack formates much more easily and rapidly than oxalates. The biochemical transformation of sugar by moulds normally proceeds thus: sugar $\longrightarrow$ AcOH $\longrightarrow$ fumaric acid $\longrightarrow$ glyoxylic acid $\longrightarrow$ $HCO_2H \longrightarrow CO_2 + H_2$, but there are also other stages.

$H_2C_2O_4$ is a secondary product. The variations which the process undergoes may be due to the presence of "sisto" and "eleuto" substances. W. McC.

Acid formation by moulds. R. Falck, W. Schoeller, and S. Michael (Biochem. Z., 1933, **262**, 280—293).—Whereas *Aspergillus niger* converts mono- and di-saccharides into a mixture of gluconic, citric, and oxalic acids, with starch only citric and oxalic acids are detected. The quotient CO_2/O_2 is 1 in neutral and feebly acid medium so long as the process is aerobic, but becomes > 1 when anaerobic processes occur. P. W. C.

Action of iron on formation of kojic acid by means of *Aspergillus flavus*. A. Di Capua (Gazzetta, 1933, **63**, 296—302).—Fe promotes the growth of *A. flavus*, and within certain limits accelerates and increases the formation of kojic acid (I) from sucrose or from glucose. It also promotes growth of the mould on Ca salts of fatty acids, but no (I) is formed from these. E. W. W.

Biochemistry of micro-organisms. XXIX. 2 : 5-Dihydroxybenzoic acid (gentisic acid), a new product of the metabolism of glucose by *Penicillium griseo-fulvum*, Dierckx. H. Raistrick and P. Simonart. **XXX, XXXI. Molecular constitution of the metabolic products of *P. brevi-compactum*, Dierckx, and related species. (I.) Acids $C_{10}H_{10}O_5$, $C_{10}H_{10}O_6$, and $C_{10}H_{10}O_7$.** A. E. Oxford and H. Raistrick. **(II.) Mycophenolic acid.** P. W. Clutterbuck and H. Raistrick.—See this vol., 949.

Nutrition of trypanosomes. M. Lwoff (Ann. Inst. Pasteur, 1933, **51**, 55—116).—Trypanosomes (I) require for growth and reproduction proteoses and polypeptides. *Strigomonas oncopelti* is the only (I) requiring only peptones; the others need blood in small amounts [1 : 20,000 for *S. fasciculata*, 1 : 5000 for *Leptomonas pyrrhocoris* (Zotta), 1 : 500 for *L. ctenocephali*]. The active portion of blood is hæmatin; it can be replaced by animal catalase or vegetable peroxidases. The nutrition of (I), like that of the hæmophilic bacteria, is characterised by the need for active Fe, with which is linked a deficiency in respiratory enzyme. J. H. B.

***Pseudomonas Lindneri*–*Kluyver* (*Termobacterium mobile*, Lindner). Aerobic and anaerobic fermentation. Acid formation.** K. Schreder, R. Brunner, and R. Hampe (Woch. Brau., 1933, **50**, 233—237, 243—245; cf. this vol., 428).—Under aerobic (I) and anaerobic (II) conditions the bacterium produces CO_2, lactic acid (III), AcOH (IV), and a small amount of succinic acid from glucose in presence of inorg. nutrients. MeCHO and fusel oil are also produced with (I) and glycerol and esters with (I) and (II). The total acid formation remains approx. const. with increase of initial sugar concn. The production of (IV) is much stronger than that of (III) with (I) and (II), but the difference is not so great with (II). Similar products are obtained by using wort as nutrient, when malic acid is also produced. R. H. H.

Preparation of diacetyl by fermentation. R. Heublyum, M. Barlas, M. Klyachko, and A. Zevalina-Blokh (Masloboino-Zhir. Delo, 1932, No. 4—5, 54—60).—The best yields (400—500 mg. per litre) of Ac_2 were obtained by fermenting a 2% sugar solution, to which 0·1% of MeCHO was added, with a mixture of yeast and *B. bulgaricus* at 32° for 18 hr. CHMeAc·OH was oxidised to Ac_2 by $FeCl_3$. Ch. Abs.

Action of *Staphylococcus* on oxalated plasma and on fibrinogen. O. Gengou (Ann. Inst. Pasteur, 1933, **51**, 14—31).—The coagulation of oxalated plasma by *Staphylococcus* and the lysis of the clot are due to a single substance secreted by the organism even in media not containing fibrinogen (I), *e.g.*, bouillon. Pure (I) shows a short and incomplete coagulation followed by rapid digestion; the active substance is a fibrinolytic agent, coagulation being merely a stage in the process. Antilytic substances in plasma and inactivated serum have a retarding effect; serum-globulins and to a much greater extent -albumins show this inhibitory action. The lytic agent is resistant to ageing, drying, and heat and cannot be dialysed or filtered. J. H. B.

Nitrogen metabolism of *Bacillus mycoides*. VI. Utilisation of various sources of nitrogen. E. Glinka-Tschernorutzky (Biochem. Z., 1933, **263**, 144—148; cf. A., 1929, 608).—Provided that K_2HPO_4 (0·2%) is present, *B. mycoides* grows satisfactorily in a mineral nutrient medium containing NH_4 salts as N source (I) and glucose as C source. Sol. NH_2-acids also serve as (I), but growth is then not so satisfactory as when NH_4 salts are used, whilst, in both cases, it is less satisfactory than when peptone is the medium. Mixtures of NH_2-acids (15), however, provide a medium not less satisfactory than peptone. Except with glycine and *d*-lysine hydrochloride K_2HPO_4 has no effect on the efficiency of NH_2-acids as (I). W. McC.

Chemistry of bacteria. V. Fat and phosphatide of diphtheria bacteria. E. Chargaff (Z. physiol. Chem., 1933, **218**, 223—240; cf. this vol., 867).—The fat consists mainly of free fatty acids; from the esterified portion no glycerol or insol. carbohydrates were isolated on hydrolysis, but a $COMe_2$-sol. amorphous substance. The unsaponifiable portion contained highly unsaturated substances (I val. 140). Sterols were not detected. The solid saturated fatty acid (about $\frac{1}{3}$ of total) was palmitic exclusively. The chief constituent of the liquid unsaturated acids was *Δ^9-hexadecenoic acid* (*Me* ester, b.p. 110°/0·01 mm.), since it was catalytically hydrogenated to palmitic acid and gave on oxidation with $KMnO_4$ in alkaline solution *9:10-dihydroxypalmitic acid*, m.p. 130° (corr.), and with $KMnO_4$ in $COMe_2$, azelaic and *n*-heptoic acids. 1% of the fatty acids consisted of an *acid*, $C_{14}H_{26}O_2$. The higher unsaturated acids form a complex mixture from which *diphtheric acid*, probably $C_{20}H_{68}O_2$, m.p. 35—36°, $[\alpha]_D^{23}$ +2·6° in $CHCl_3$, was isolated.

Acid hydrolysis of the phosphatide gave aldohexoses, fatty acids, and a high-mol. compound and traces of a base. The solid fatty acid was exclusively palmitic acid; the liquid acids contained a substance *corynin*, probably $C_{50}H_{100}O_4$, m.p. 70—71° (corr.), b.p. 220°/0·005 mm. [cryst. *Ac* (? Ac_2) derivative,

m.p. 75—76° (corr.)], having 1 CO_2H and 2 OH groups. J. H. B.

Neutralisation of diphtheria toxin by heterocyclic compounds. L. VELLUZ (Compt. rend., 1933, **197**, 359—361).—10 mg. of ninhydrin neutralise 2000 lethal doses of diphtheria toxin in 24 hr. at 39°; an indigo-blue solution is formed, indicating the protein nature of the toxin. 5 mg. of rotenic acid or 10 mg. of *l*-dihydrorotenic acid neutralise 2000 doses in 4—5 days at 39°, as also does 0·5 mg. of *iodorotenic acid*, m.p. 239° (prepared by I and HgO), in 15 days. R. S. C.

Non-specific flocculation of diphtheria antitoxin, toxin, and toxoid and its bearing on the *Lf* titre. J. F. ANDERSON, G. F. LEONARD, and A. HOLM (Amer. J. Pub. Health, 1933, **23**, 681—686).—The Ramon flocculation test of diphtheria toxin and antitoxin is not always a measure of antigenic val., and may be influenced by bacillary proteins, phosphates, and pyrophosphates which increase the flocculation val. and decrease the time of flocculation. The reaction may therefore consist of a combination of the reactions occurring between inorg. constituents of toxin and serum, bacillary proteins and serum precipitins, and toxin and antitoxin. A. L.

Immunisation of human beings against diphtheria with purified diphtheria anatoxin and aluminium hydroxide. A. SCHMIDT (Dansk Tidsskr. Farm., 1933, **7**, 123—133).—Tests on rabbits showed that Ramon's anatoxin is much more effective when mixed with 10% of $Al(OH)_3$. R. P. B.

Lipins of tubercle bacilli. XXXIII. Isolation of trehalose from acetone-soluble fat of human tubercle bacillus. R. J. ANDERSON and M. S. NEWMAN (J. Biol. Chem., 1933, **101**, 499—504).—The fat (A., 1927, 1114) was saponified, unsaponifiable matter and fatty acids were separated, and the aq. residue was neutralised with KOH and conc. in vac. to dryness. The residue consisted of KCl and a syrup which on purification with neutral and basic Pb acetates yielded trehalose. The neutral $COMe_2$-sol. fat from human tubercle bacilli therefore appears to be not a glyceride but a complex ester of fatty acids with trehalose. F. O. H.

Absence of α-cellulose in tubercle bacilli. O. BINDER (Compt. rend., 1933, **197**, 197—198). F. R. S.

Examination of immune-serum lipins for complement-fixing antibodies of tuberculosis. A. HAMBLETON (Canad. J. Res., 1933, **8**, 553—562).—The antibodies are not removed from the protein fraction of immune serum by extraction with lipin solvents before or after digestion with trypsin or by desorption. They are therefore not lipoidal. R. S. C.

Mechanicism, vitalism, and the growth of bacteria. J. M. SHERMAN and G. M. CAMERON (Science, 1933, **77**, 537—538).—Abrupt environmental changes within the range of growth of *Bacterium coli* result in high mortality among the young cells. L. S. T.

Effect of carbon dioxide on bacterial growth. F. P. COYNE (Proc. Roy. Soc., 1933, **B**, **113**, 196—217; cf. B., 1932, 749).—The inhibition of the growth of several types of *Achromobacter*, and other bacteria isolated from fish, by CO_2 increases as the $[CO_2]$ is increased and the temp. is lowered from 37° to 0°. Growth of bacteria responsible for deterioration of fish is completely inhibited at 0° in an atm. containing 20% of CO_2. The inhibition is not due to a change of p_H in the agar culture medium, but is probably due to an intracellular p_H change and/or an effect of CO_2 on cellular enzyme systems. A. C.

Phenomenon of Charrin and Roger (serum agglutination of bacteria). P. LASSEUR, A. DUPAIX, and J. G. MARCHAL (Compt. rend., 1933, **196**, 1930—1932).—The limits of agglutination of the plastids (I) of *B. caryocyaneus* have been studied to explain the presence of free (I) in an agglutinating system containing an excess of antibodies (II). With high concn. of agglutinin all the (I) are coagulated, but a portion of the (II) remains free, whereas in medium or small concn. all the (II) are fixed, but some of the (I) remain free. J. W. B.

Significance of the colloidal carrier for the stability of the virus of foot-and-mouth disease. G. PYL (Z. physiol. Chem., 1933, **218**, 249—262).—The virus (I) has two stability max. at p_H 3·0 and 7·6 with a min. at 6·0—6·5. Although active (I) solutions at the alkaline p_H can be acidified to 3·0 without entirely losing activity, when the p_H is increased from 3·0 to 7·6 the solution becomes inactive. The isoelectric point is at p_H 3·5—3·9, and at 3·9 there is a pptn. optimum, but these properties are probably due to the colloidal carrier, which markedly increases the stability of (I). (I) has two carriers, one for each stability max., acidification or alkalisation being accompanied by exchange of carrier. Each exchange damages (I). The stability min. corresponds with the isoelectric point of the free (I). The ampholyte nature of (I) indicates its protein character. J. H. B.

Influence of monoiodoacetic acid on the bacterial and enzymic hydrolysis of glucosides. K. MEYER (Biochem. Z., 1933, **262**, 329—331).—$CH_2I{\cdot}CO_2H$ has the same sp. inhibitory action on the hydrolysis of β-glucosides (I) by lactic acid streptococci as on lactic acid formation from glucose. The inhibitory action of the acid on the hydrolysis of (I) by emulsin is 500 times feebler, the bacterial β-glucosidase being different from that of emulsin. P. W. C.

Antiseptic and trypanocidal properties of some anil and styryl derivatives of 4-aminoquinaldine. J. N. ASHLEY, C. H. BROWNING, J. B. COHEN, and R. GULBRANSEN (Proc. Roy. Soc., 1933, **B**, **113**, 293—299; cf. A., 1929, 1109).—4-Chloro-2-methylquinoline is converted by NH_3 or suitable amines into 4-amino- [*methosulphate*; *methiodide*, decomp. 270°; *Ac* derivative, m.p. 176—178° (*methosulphate*; *methiodide*, decomp. 274—275°)], 4-*dimethylamino*-, an oil (*methiodide*, decomp. 290—295°), 4-*diethylamino*-, an oil (*methiodide*, m.p. 157—159°), and 4-β-*diethylaminoethylamino*-2-*methylquinoline*, an oil (*dimethiodide*, decomp. 279°). Condensation of these with *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$, *p*-$CHO{\cdot}C_6H_4{\cdot}NMe_2$, or *p*-$CHO{\cdot}C_6H_4{\cdot}NEt_2$ affords *methiodides* of the correspond-

ing 2-(*p*-dimethylaminoanil), 2-(*p*-dimethylaminostyryl), and 2-(*p*-diethylaminostyryl) derivatives. The antiseptic action of the anils on *B. coli* is weak. Some of the styryl derivatives of the *tert.* aminoquinolines are active towards *S. aureus*. None of the above is curative to mice infected with *T. brucei*.

A. C.

Antiseptic and trypanocidal action of some benzamidoquinoline anil and styryl compounds. C. H. Browning, J. B. Cohen, K. E. Cooper, S. Ellingworth, and R. Gulbransen (Proc. Roy. Soc., 1933, B, **113**, 300—307; cf. A., 1932, 522, 623).—6-Amino-2-methylquinoline and *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ afford 6-(p-*nitrobenzamido*)-, m.p. 266—267° (*methoacetate*), which is reduced to 6-(p-*aminobenzamido*)-2-*methylquinoline* (I) m.p. 197—199° [*methosulphate*; *methochloride*; *Ac* derivative, m.p. > 300° (*methochloride*)]. (I) and Me_2SO_4, followed by treatment with NaCl or KI, yield 6-(p-*dimethylaminobenzamido*)-2-*methylquinoline methochloride* and *methiodide*, respectively. The appropriate methochloride condenses with *p*-substituted benzaldehydes or *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$, yielding the following styryl and anil derivatives, respectively, methoacetates being prepared from methochlorides by treatment with AgOAc; 2-(p-*acetamidostyryl*)-6-(p-*aminobenzamido*)*quinoline methoacetate* and -6-(p-*dimethylaminobenzamido*)*quinoline methochloride*; 2-(p-*dimethylaminostyryl*)-6-(p-*aminobenzamido*)- and -6-(p-*acetamidobenzamido*)-*quinoline methochlorides*; 2-(p-*aminostyryl*)-6-(p-*acetamidobenzamido*)*quinoline methoacetate*; the *methochlorides* of 2-(p-*dimethylaminoanil*)-6-(p-*acetamidobenzamido*)- and -6-(p-*aminobenzamido*)-*quinoline*. The anils and, to a smaller extent, some of the styryl derivatives are antiseptic towards *B. coli* and *S. aureus*. Slight to marked trypanocidal action is shown by the anil and styryl derivatives, with the exception of the 2-(*p*-dimethylaminostyryl) compounds, which are inactive.

A. C.

Ketogenic diet. Nature of bactericidal agent. A. T. Fuller (Lancet, 1933, **224**, 855—856).—Specimens of urine from patients on ketogenic diets were inoculated with an emulsion of *B. coli* and subcultured on agar, immediately, after 5, and after 20 hr. Urine containing 100 mg. of $CH_2Ac{\cdot}CO_2H$ per 100 c.c. showed bacteriostatic power at 5 hr., with 200 mg. per 100 c.c. frequently inhibition of growth after 20 hr. *l*-β-Hydroxybutyric acid was identified as the bacteriostatic substance. Acid urines showed greater bacteriostasis than alkaline urines of the same concn.

Nutr. Abs. (*b*)

Influence of parenterally introduced liver-cell constituents on the amount of urobilin in the urine. I. Effect on normal excretion of urobilin. II. Effect on experimental urobilinuria due to injection of hæmolysed blood. III. Effect on experimental urobilinuria due to injection of urobilin. R. Watarai (Japan. J. Exp. Med., 1932, **10**, 325—345, 347—358, 359—371).—In normal rabbits intraperitoneal injection of an emulsion of rabbit's liver (0·05 g. per kg.) decreases or (0·5—1·0 g.) increases the urinary urobilin. The smaller dose decreased urobilinuria induced by intramuscular injection of hæmolysed blood or subcutaneous injection of urobilin. Emulsions of other tissues (except kidney; occasional decrease) had no effect. The effects are due to the action of a hepatic autohormone on the liver. Ch. Abs.

Specific effect on the stomach of the secretions of the fundic glands. II. Influence of the parenteral injection of emulsions of gastric mucosa on the secretory activity of the Pavlov pouch. I. Sugishima (Japan. J. Exp. Med., 1932, **10**, 177—201, 303—323).—Stimulation observed with optimal small doses is due to the sp. action of an auto-hormone.

Ch. Abs.

Effect of insulin on amino-acid- and urea-nitrogen in laked and unlaked blood. H. H. Powers and F. Reis (J. Biol. Chem., 1933, **101**, 523—527).—Injection into rabbits of 1 unit of insulin (I) and analysis of the blood before and after injection shows a decrease in NH_2-acid-N (II) uninfluenced by the method of preparing the filtrate, indicating that the diffusible portion of the (II) alone is affected by (I). No significant change in the blood-urea-N was observed. H. D.

Effect of hormones on enzyme action. I. Effect of insulin on blood- and liver-amylase. A. Utevski, S. Epstein, and V. Osinskaja (Klin. Woch., 1933, **12**, 388—389).—Insulin (I) has no activating action on blood-amylase (II) *in vitro*. Injected into rabbits, (I) produces an increase in the amount of (II), probably owing to transference of the enzyme from the tissues. Nutr. Abs. (*b*)

Effect of subcutaneous injections of trypsin on the blood-sugar and on insulin action. O. B. Buckley (Brit. J. Exp. Path., 1933, **14**, 57—62).—Subcutaneous injection of trypsin resulted in a rise of blood-sugar in the rabbit and an inhibition of the action of insulin subsequently administered.

Nutr. Abs. (*b*)

Distribution of carbohydrate in tissues and organs during insulin- and synthalin-hypoglycæmia, hunger, and liver-storage. K. Matsuura (J. Biochem. Japan, 1933, **17**, 441—455).—Insulin (I) and synthalin (II), injected into rabbits, produce a decrease in the true sugar (III) and glycogen (IV) levels of the lung, muscle, and kidney, whilst the non-glucose sugar (V) remains fairly const. With (I) but not with (II), the (III) and total reducing substances of the liver are increased. When the liver is damaged by P or CCl_4, all the tissues excepting the brain show normal vals. for (V), whilst (III) and (IV) decrease, the fall in (IV) with (II) being > with (I). Starvation for 8—12 days is followed by a steady fall in the levels of (III), (IV), and (V), that of (IV) becoming practically zero. (I), (II), and starvation have entirely different effects on carbohydrate metabolism. F. O. H.

Accuracy of insulin assay on white mice. II. A. M. Hemmingsen (Quart. J. Pharm., 1933, **6**, 187—218).—The convulsion rates plotted on a probability scale against the logarithm of the dose give a straight line. A method of injection has been devised to eliminate errors due to changes in sensitivity; in calculating the average of the results of single tests, the logarithms of the results should be

averaged. For mice with low body-wt. the sensitivity is greater in the evening. H. G. R.

Anti-insulin principle occurring in the pancreas. I. Presence in external secretion of the pancreas of non-diabetic and diabetic persons. W. WOHLENBERG and K. MULLER (Arch. exp. Path. Pharm., 1933, **171**, 340—345).—The ultra-filtrate (free from diastase) of 2·5—8·0 c.c. of pancreatic secretion (from the duodenum) of non-diabetic and, to a greater extent, of diabetic persons has a marked hyperglycæmic action when intravenously injected into rabbits (cf. A., 1929, 103). F. O. H.

Determination of adrenaline and thyroxine in blood. U. S. VON EULER (Arch. exp. Path. Pharm., 1933, **171**, 186—200).—Normal human serum in concns. $\leq$ 1 : 200—1 : 400 accelerates the oxidation by finely-divided muscle as measured by the methylene-blue technique (cf. A., 1929, 474). A similar action by rabbit's serum is inhibited by adrenalectomy of the animal, by alkalis, and by ergotamine, and hence is due to adrenaline, the normal level of which is $10^{-12\cdot5}$ to 10^{-13} g. per c.c. in man and rabbit. A similar but transient action is produced by thyroxine, the level of which in the blood is approx. 10^{-15} g. per c.c. F. O. H.

Calorigenic action of thyroxine polypeptide. W. T. SALTER, J. LERMAN, and J. H. MEANS (J. Clin. Invest., 1933, **12**, 327—334).—The calorigenic effect of thyroxine polypeptide (40% I) administered orally is equal to that when administered intravenously. The polypeptide is as active as an equiv. amount of thyroxine. CH. ABS.

Determination of functional activity of the thyroid by urine or serum. II. Influence of Ca, K, Na, and Mg. M. KOH (Keijo J. Med., 1933, **4**, 291—299).—The ability of the urine or serum to inhibit the mydriatic action of atropine when incubated together at 37° for 2 hr. affords a criterion of the thyroid activity (I) of the animal. Intravenous injection into rabbits of 2·5% aq. $CaCl_2$ or NaCl increases, whilst that of KCl or $MgCl_2$ inhibits, (I). F. O. H.

Pituitary and thyroid. VIII. Action of extract of the anterior pituitary lobe on the weight of the thyroid. B. A. HOUSSAY, A. BIASOTTI, and P. MAZZOCCO. **XV. Thyroidectomy and the thyroid-exciting action of the anterior pituitary of diverse species.** B. A. HOUSSAY, A. NOVELLI, and R. SAMMARTINO. **XVI. Action of extract of the anterior pituitary on the blood-iodine of animals with thyroid or pituitary removed.** B. A. HOUSSAY, A. BIASOTTI, and P. MAZZOCCO (Rev. soc. argentina biol., 1932, **8**, 122—129, 514—522, 554—555).—XVI. The extract elevates the blood-I in normal or hypophysectomised dogs and lowers it in thyroidectomised dogs. CH. ABS.

Factors influencing the functional development of the male gonad. J. M. ROBSON and H. TAYLOR (Proc. Roy. Soc., 1933, **B**, **113**, 251—267).—An account is given of the effects of anterior pituitary substance (I), gonadotropic urine of pregnancy (II), suprarenal extracts (III), and rabbit's heart muscle (IV) on the growth of testes (V) and spermatogenesis (VI) in rats. Inhibition of (V) is caused by (I), (III), and (IV), and an increase by (II). (VI) is inhibited by (I) and not affected by (II) and (IV). A. C.

Mucification of the vaginal epithelium of immature mice following injections of follicular fluid. S. B. D. ABERLE (Science, 1933, **78**, 17—18).—Follicular fluid from the ovary of the sow may cause mucification for approx. 60 hr. of the vaginal epithelium in the normal immature mouse. L. S. T.

Fat-soluble vitamins. XXXVI. Carotene and vitamin-*A* content of butter. XXXVII. Stability of carotene solutions. C. A. BAUMANN and H. STEENBOCK (J. Biol. Chem., 1933, **101**, 547—560, 561—572).—XXXVI. Carotene (I) was determined in butter-fat (II) by comparison of the absorption vals. of ultra-violet light of λ 460 and 480 mμ with a solution of pure (I) in refined cottonseed oil (III). Vitamin-*A* (IV) was determined by photographing the intensity of the 328 mμ band of the unsaponifiable matter purified by cooling at −72° in MeOH, filtering, and washing with cold MeOH. (I) accounts for only 15% of the total (IV)-activity of (II), amounting to $2\cdot0\times10^{-3}$ and $8\cdot6\times10^{-3}$ g. per g. of April and July (II), respectively. (IV) vals. ranged from 9×10^{-3} to 20×10^{-3} g. per g. of April and June (II), respectively. Neither storage for 6 months at 0° nor ultra-violet radiation influences the content of either component.

XXXVII. Solutions of (I) in (III), sesame, olive, maize, wheat-germ, and coconut oils stored at 4° in the dark for 5 months lost 8, 15, 38, 45, 62, and 25% of their activity, respectively. The losses were uninfluenced by the presence of quinol (V). In (III) the stability of (I) is influenced unfavourably by exposure to air, daylight, and room temp.; (V) did not influence the effects of these factors. Addition of Et_2O to solutions of (I) in (III), or the use of rancid (III), was without effect on the stability of (I). In C_6H_6 and light petroleum losses up to 46% were sustained and in Et_2O, $CHCl_3$, *cyclo*hexane, $COMe_2$, PhMe, and C_5H_5N > 75% losses in activity occurred, which, however, were considerably reduced by addition of (V). (I) was very unstable in the Et esters of stearic, lauric, lævulic, and malonic acids, and in the di- and tri-acetates of glycerol. In EtOAc and Et succinate (I) was comparatively stable. H. D.

Vitamin-*A* in the livers of native mine labourers. F. W. FOX (Lancet, 1933, **224**, 953—955).—Abnormally low vitamin-*A* reserves (I) have been found in apparently healthy individuals. Persons dying from pneumonia tend to have low (I) in the liver. L. S. T.

Determination of vitamin-*A* expressed in international units. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1933, **263**, 444—453).—The difficulties of obtaining standardised animals in the biological assay of vitamin-*A* are discussed and a new procedure is described. The limiting dose is that amount which fed to a group of 10 rats over 35 days is sufficient to keep $\leq$ 8 alive and cure or prevent xerophthalmia. P. W. C.

Stability of international standard carotene in solution in oil. A. SCHEUNERT and M. SCHIEBLICH

(Biochem. Z., 1933, **263**, 454—457).—International standard carotene (1% in sesame oil) if kept cool and in the dark retains its activity without loss for 18 months. P. W. C.

Separation of forms of vitamin-*A* based on the antimony trichloride reaction. M. VAN EEKELEN, A. EMMERIE, H. W. JULIUS, and L. K. WOLFF (Nature, 1933, **132**, 171).—Fuller's earth has been used previously to $Ca(OH)_2$ (this vol., 805) for the separation of vitamin-*A* into two fractions. L. S. T.

Sterols of rice embryo. K. TANAKA (J. Biochem. Japan, 1933, **17**, 483—494).—Fractionation of the sterols gave a *myricyl alcohol*, $C_{30}H_{62}O$, m.p. 86—87° (*acetate*, m.p. 71—72°; *benzoate*, m.p. 70°) (cf. B., 1926, 713), and dihydrositosterol (I) (A., 1924, i, 1153, 1217). Following the removal of (I), the residue was acetylated, the product fractionated by EtOH, and the fractions brominated to yield tetrabromostigmasteryl and dibromo-α-sitosteryl acetates. Debromination and repeated crystallisation from EtOH then gave *β-sitosteryl acetate*, m.p. 127—128°, $[\alpha]_D$ −39·0° in $CHCl_3$, and *γ-sitosteryl acetate*, m.p. 142—143°, $[\alpha]_D$ −46·09° in $CHCl_3$. *β-Sitosterol*, m.p. 139—140°, $[\alpha]_D^{20}$ −37·7° in $CHCl_3$, and *dihydro-β-sitosterol*, m.p. 139—140°, $[\alpha]_D^{20}$ +24·0° in $CHCl_3$ (*acetate*, m.p. 137—138°, $[\alpha]_D^{0}$ +13·57°), were also prepared. F. O. H.

Antimony trichloride reaction with compounds containing 5-membered monoheterocyclic rings. V. E. LEVINE and E. RICHMAN (J. Biol. Chem., 1933, **101**, 373—390).—With $SbCl_3$ in $CHCl_3$, pyrrole, thiophen, furan, and their derivatives give characteristic colour reactions which are intensified and often modified by addition of Ac_2O (cf. A., 1931, 988). The intensity and rapidity of development of the colour are, to a certain extent, governed by the substituents in the mol. The non-specificity of the reaction for vitamin-*A* (I) is confirmed. Vegetable and animal oils contain a chromogenic substance [other than (I)] which gives a more intense reaction when oxidised. That oxidation readily destroys the colour response of (I) indicates an alcohol or aldehyde. F. O. H.

Effects of cod-liver oil concentrate injections. B. GORDON and R. J. TITHERINGTON (Amer. Rev. Tuberc., 1933, **27**, 368—374).—In animals signs of vitamin-*A* deficiency decreased. There was no evidence of a sp. effect on tuberculous lesions. CH. ABS.

Alleged toxic action of cod-liver oil and concentrates of vitamin-*A*. M. E. BELL, E. GREGORY, and J. C. DRUMMOND (Z. Vitaminforsch., 1933, **2**, 161—182).—A disturbance of growth of rats occurs when their diet contains 15% of cod-liver oil (I) and sufficient "vitamin-*B* complex" (II) for a diet containing 2% of (I). This disturbance may be alleviated by increasing the amount of (II). The apparent toxic effect was not caused by vitamin-*A* itself, by nitrogenous bases in fish-liver oils, by an oxidation product of (I), or by an over-dosage of vitamin-*D*, and could not be produced by ingestion of large amounts of provitamin-*A* (carotene). No evidence that rats "overdosed" with (I) failed to assimilate it, or that it affected the normal reaction of the gastric and intestinal contents, was obtained. E. B. H.

Is there a vitamin-*A*-hypervitaminosis? G. ROSSI (Z. Vitaminforsch., 1933, **2**, 194—207).—Rabbits and guinea-pigs showed no unfavourable effects with large doses of vitamin-*A*, but in white rats this treatment resulted in diarrhœa. Large doses of vitamin-*A* together with an over-dose of -*D* retarded growth of rabbits. E. B. H.

Ascorbic acid (vitamin-*C*). A. SZENT-GYORGYI (Bull. Soc. Chim. biol., 1933, **15**, 694—705).—A lecture.

Antiscorbutic property of suprarenal cortex. R. DEOTTO (Z. Vitaminforsch., 1933, **2**, 182—190).—Aq. extracts of suprarenal cortex (acidulated with citric acid 1 : 3) has an antiscorbutic power, whilst similar extracts from liver have no such property, and neither has adrenaline. E. B. H.

Experimental scurvy. XVI. Effect of irradiated narcotine. J. SHIMADA (J. Biochem. Japan, 1933, **17**, 395—400).—The cryst. product, m.p. 173°, from ultra-violet-irradiated narcotine has no antiscorbutic properties (cf. A., 1932, 310). F. O. H.

Absorption spectrum of the vitamin-*E* fraction of wheat-germ oil. F. P. BOWDEN and T. MOORE (Nature, 1933, **132**, 204—205).—The pigment of wheat-germ oil (I) gives an absorption spectrum practically identical with that of xanthophyll. The absorption of the vitamin-*E* fraction of (I) is due to > one kind of mol. The visible absorption is due to xanthophyll (II), which can be removed by charcoal. (II) is probably not the vitamin, since treatment with HCl and by catalytic hydrogenation both destroy the visible bands but not biological activity. The ultra-violet absorption between 2850 and 2400 Å. cannot always be correlated with this activity, but that between 3200 and 2850 Å. closely follows it, since both are destroyed by Ac_2O and irradiation, and both resist the action of HCl, hydrogenation, and oxidation. At liquid air temp. this absorption shows a structure. It is probable that the vitamin-*E* mol. has a high resistance to hydrogenation. L. S. T.

Auxins. F. KOGL (Angew. Chem., 1933, **46**, 469—473).—A lecture. Previous work (this vol., 435, 612) is summarised, and hypotheses of the structure of auxin *a*, based on oxidation experiments, are discussed. *Auxin* b, $C_{18}H_{30}O_4$, m.p. 183°, a keto-acid, has been isolated from maize oil and malt. Experiments on the diurnal variation in the potency of auxin indicate the existence of an atmospheric-electrical influence. R. K. C.

Growth-promoting substance and illumination. A. E. NAVEZ (Proc. Nat. Acad. Sci., 1933, **19**, 636—638).—The growth-promoting substance, auxin (I), is formed more abundantly in apical portions of seedlings of *Lupinus albus* when these are exposed to light. The relative amounts of (I) produced in illuminated and dark-grown seedlings are of the order of 2 to 1, as measured by the angle of curvature induced in decapitated coleoptiles of *Avena*. A. W.

Oxidising power of chondriome. P. JOYET-LAVERGNE (Compt. rend., 1933, **197**, 184—185).—The oxidising power of the chondriome of *Elodea canadensis* on leuco-derivatives has been examined. F. R. S.

Carbohydrate changes in shelled green peas. Z. I. KERTESZ (New York [Geneva] Agric. Exp. Sta. Bull., 1933, No. 622, 14 pp.).—Carbohydrates (I) in shelled peas are consumed during respiratory changes. Other products than (I) contribute to the increase in solid contents of stored peas. Starch formation from sugars was not apparent, but increased proportions of other acid-hydrolysable higher (I) and matter insol. in 80% EtOH are recorded. A. G. P.

Transport of carbohydrates in the cotton plant. III. Polar distribution of sugar in the foliage leaf. E. PHILLIS and T. G. MASON (Ann. Bot., 1933, **47**, 585—634; cf. A., 1928, 1061).—Sugars present in leaves include glucose, fructose, sucrose (I), and a polyglucoside (sol. in H_2O and 80% EtOH; reducing power approx. doubled on hydrolysis). (I) is the principal form in which carbohydrates travel from assimilating cells to the phloem of the bundle ends and longitudinally through the phloem to the stem etc. Concn. gradients of (I) in various tissues are determined and the influence of external conditions on its movement is examined. A. G. P.

Growth processes in oats during water shortage and in early-sown winter wheat. IV. H. WAGNER (Z. Pflanz. Düng, 1933, **30**, A, 208—232; cf. B., 1932, 696).—H_2O-deficiency results in a temporary heavy decrease in H_2O content of the leaves of oats and a relative increase in that of the straw. With the beginning of drought there is a transition of K from straw to leaves, but no movement of minerals from roots back to the soil. Changes in the N, P, K, and Ca of stems, leaves, and panicles with high and with low supplies of H_2O are recorded. Winter wheat sown in May produces much vegetative growth, but no ears, and the straw has a high N content. The plant-K was high, but the high Ca of the young plants declined rapidly. Relationships are indicated between Ca content and sugar formation and between K and polysaccharide production. The wilting of plants during drought is ascribed to high concn. of dissolved substances, among which K and N compounds are of prime importance. A. G. P.

Course of growth of potato plants. V. H. WAGNER (Z. Pflanz. Düng., 1933, **30**, A, 232—249).—The process of transition of mineral nutrients from aerial parts to the tubers is examined and the interrelationships between Ca and K contents on the one hand and sugar and starch accumulation on the other are discussed. A. G. P.

Chemistry of tobacco. I. P. KOENIG and W. DÖRR (Biochem. Z., 1933, **263**, 295—301).—The methods for the isolation from natural nicotine-free tobacco of chlorogenic acid, m.p. 206°, and quinic acid (Cu salt, m.p. 226°) are described. P. W. C.

Effects of chlorine, bromine, and fluorine on the tobacco plant. L. B. WILSON (J. Agric. Res., 1933, **46**, 889—899).—Thickening of leaves caused by cell enlargement results from applications of Cl′, Br′, or F′ to tobacco plants, Cl′ producing the greatest effect. This action is correlated with increased osmotic pressure in the cell sap. Plants receiving excessive amounts of Cl′ or Br′ have less bound H_2O in leaves than plants deficient in mineral nutrients. Treatment with NaF causes a transition of free to bound H_2O. Under field conditions, the sap of Cl′-injured plants has a lower osmotic pressure and % bound H_2O than those of plants receiving complete fertiliser. A. G. P.

Catabolism of the non-volatile organic acids of tobacco leaves during curing. G. W. PUCHER and H. B. VICKERY (Proc. Nat. Acad. Sci., 1933, **19**, 623—626).—Modified methods (to be described elsewhere) have been used to determine the changes which occur to the non-volatile org. acids of tobacco leaves (I) during curing. The polybasic org. acids were pptd. as Ba salts, these decomposed with H_2SO_4, and the liberated acids extracted with Et_2O. The acids were then esterified and the esters distilled. The bulk of the distillate was Et_2 malate, and this ester + Et_3 citrate account for 90% of the esters derived from the partly and fully cured (I). Another procedure is necessary for the determination of $H_2C_2O_4$. The curing of (I) is accompanied by very little change in the amounts of oxalic and malic acids, but there is a very marked increase in the amount of citric acid. Other analyses seem to suggest that the extra citric acid is derived from unknown polybasic acids and as a result of carbohydrate metabolism. A. W.

Reactions of *Valonia* and of *Halicystis*: (*a*) to colloids; (*b*) to injections of certain proteins. E. M. EAST and B. WHITE (J. Gen. Physiol., 1933, **16**, 925—935, 937—945).—(*a*) *Valonia* (I) and *Halicystis* (II) cells have a high tolerance for ovalbumin (III), animal peptone, and animal proteoses ("bacto-protone"). Yeast nucleic acid (dissolved in sea-H_2O containing NaOH) has an injurious effect, more pronounced on (I). (II) has a very high, and (I) a very low, tolerance towards diphtheria toxin, and the converse applies for edestin. (III) does not pass through the membrane to any significant extent, but it is possible, particularly in the case of the proteose of the scarlet-runner bean, that there is some passage of the proteins with smaller mols.

(*b*) Cryst. (III), animal peptone, animal proteose, and diphtheria toxin have been injected into (I) and (II) cells to determine the tolerance of these algæ to the presence of foreign proteins in the vacuole, and to determine whether antibodies are formed. (I) cells injected twice with (III) show no change in susceptibility to its effects, and neither species of algæ gives evidence of having formed antibodies against the antigens used. A. W.

Carbon dioxide narcosis. I. Specific effects of carbon dioxide on protoplasmic streaming and consistency in *Nitella* and on the life of the cell. II. Effect of carbon dioxide compared with that of the hydrogen ion. Threshold of tolerance in *Nitella* to carbon dioxide and to the hydrogen ion. D. L. FOX (J. Cell. Comp. Physiol.,

1933, **3**, 75—88, 89—100).—I. Typical narcotic effects were produced by CO_2 in unbuffered aq. solutions on *N. clavata*.

II. The action of CO_2 is not due to the [H·] produced. A. G. P.

Permeability of living cells. XV. Penetration into *Valonia ventricosa* of oxidation-reduction indicators including *m*-bromophenol-indophenol and guaiacol-indophenol. M. M. Brooks (J. Cell. Comp. Physiol., 1933, **3**, 61—73).—Guaiacol-indophenol penetrates in the reduced form into the sap of *Valonia*, and its redox potential probably approximates to that representing the limit of the ability of the plant to reduce. A. G. P.

Relation between cell volume and penetration of a solute from an isosmotic solution. M. H. Jacobs (J. Cell. Comp. Physiol., 1933, **3**, 29—43).—Mathematical discussion. A. G. P.

Accumulation of ions by living cells. S. C. Brooks (Nature, 1933, **132**, 97—98). G. E. Briggs (*ibid.*, 98).—Polemical. L. S. T.

Physiological factors influencing the production of flax fibre cells. B. B. Robinson (J. Amer. Soc. Agron., 1933, **25**, 312—328).—In field trials, fertiliser combinations containing N produced the longest stems in seedlings, but at maturity these were equalled or exceeded by those receiving P and K. In H_2O cultures, media high in P and moderately high in K produced the best yields of fibre in cu.mm. per stem. A. G. P.

Influence of length of day on the response of plants to boron. K. Warington (Ann. Bot., 1933, **47**, 429—457).—The delayed appearance of B deficiency in plants during spring and autumn results from the shortened day rather than lowered temp. B is an important factor in meristematic activity, but in no other respect was evidence obtained of relationship between B supply and flower production. A. G. P.

Evolution of ammonia by the nodules of the roots of *Leguminosæ*. S. Winogradsky (Compt. rend., 1933, **197**, 209—212).—The nodules on or detached from the roots of peas liberate NH_3. Poisons, *e.g.*, $CHCl_3$, and drying at 40—50° do not stop this action. Roots freed from nodules and roots of maize etc. do not evolve NH_3. R. S. C.

Phytochemistry of *Gillenia stipulata*. L. L. Manchey (J. Amer. Pharm. Assoc., 1933, **22**, 520—528).—Analysis of commercial preps. of the root indicates the presence of a terpene-rich volatile oil, glucose, tannin, protocatechuic and benzoic acids, a wax associated with a phytosterol, $C_{26}H_{44}O$, m.p. 135° (acetate, m.p. 121°), an *alcohol*, $C_{30}H_{62}O$, m.p. 78° (*acetate*, m.p. 63—63·5°), stearic and palmitic acids, a trihydric *alcohol*, $C_{38}H_{70}O_5$ (*triacetate*, m.p. 162°), myristic acid, and an EtOH-sol. substance, m.p. 237—241° (decomp.). No glucoside or alkaloid could be detected. F. O. H.

Unsaponifiable fraction from spinach fat. II. F. W. Heyl and D. Larsen (J. Amer. Pharm. Assoc., 1933, **22**, 510—513).—Purification of the alcohol, m.p. 87—88°, previously described (A., 1929, 855) yields an alcohol, $C_{26}H_{54}O_2$, m.p. 103·5°. The predominant paraffin alcohol is *n*-tetracosanol (A., 1932, 204), whilst *n*-hexacosanol, *n*-tetracosoic acid, m.p. 82·5—83°, and *n*-hexacosoic acid were isolated. From the sterols pptd. by digitonin was separated *β-spinasterol*, $C_{27}H_{46}O$, m.p. 145—148°, $[\alpha]_{546}$ +7·65° (*acetate*, m.p. 150—154°, $[\alpha]_{546}$ +7·2°), which on reduction yields the same spinastanol as spinasterol. F. O. H.

Fat from the seeds of *Vateria indica*, Linn. S. V. Puntambekar and S. Krishna (J. Indian Chem. Soc., 1933, **10**, 203—211).—The fat contains the glycerides of myristic, stearic, lignoceric, elaidic (? *iso*oleic), and oleic acids together with sitosterol, m.p. 133—134°. Contrary to Jones (cf. B., 1932, 354), no palmitic or arachidic acid can be isolated. J. L. D.

Fat from the seeds of *Picrammia Sow.* A. Steger and J. van Loon (Rec. trav. chim., 1933, **52**, 593—600).—Light petroleum extracts 58·6% of the seeds, the extract consisting mainly (89·8%) of stearolic acid (I). (I) affords adipic acid and lauric acid with O_3, ζη-diketostearic acid with $KMnO_4$, and a ζη-dibromide with Br in Et_2O at —10°. J. L. D.

Chlorophyll content of leaves of barley mutants. H. von Euler, H. Hellstrom, and D. Burstrom (Z. physiol. Chem., 1933, **218**, 241—248).—The deviations from the mean of a no. of determinations of chlorophyll (I) in barley mutants under const. conditions follow the normal mathematical curve. Normal (green) mutants form the same amount of (I) as an ordinary strain. The (I) ratio between deficient and normal mutants varies from 1 : 4 to 1 : 30. There is a linear relation between the (I) content at various points in the leaf from base to tip and the position of the sample. J. H. B.

Primitive cellulose and lignin in the wood-forming plant-saps as chemical builders of the wood substance. H. Wislicenus (Papier-Fabr., 1933, **31**, Fest- u. Auslands-heft, 65—77).—An account is given of the mechanism of tree growth and the accompanying physical and chemical changes. Theories of the formation of cellulose (I) and lignin (II) together with recent developments of work in this field are discussed, and the collection and examination of the sap of the cambium, which is the source of primitive (I) and (II), in attempts to build up (II) from it, are described. D. A. C.

Hemicelluloses of mesquite wood. L. Sands and W. Y. Gary (J. Biol. Chem., 1933, **101**, 573—581).—The hemicelluloses were prepared from the fat- and pectin-free wood by extraction with 5% NaOH, acidification, and addition of $COMe_2$. The two fractions thus obtained were purified by repeated pptn. from alkaline solution with EtOH. By further fractionation with EtOH the existence of two distinct hemicelluloses was shown, differing in the amount of xylose in the mols. The relation of these hemicelluloses to mesquite gum is slight. H. D.

Floridoside, trehalose, and glycogen in red, fresh-water algæ (*Lemanea, Sacheria*). H. Colin and J. Augier (Compt. rend., 1933, **197**, 423—425; cf. this vol., 652).—Extraction of sugar- and gum-free *L. nodosa*, or spores thereof, with 5% aq. KOH

leads to the isolation of a glycogenic substance, $[\alpha]_D$ +105°, giving a violet I reaction. This property is lost under the action of pancreatin, and further hydrolysis by dil. H_2SO_4 yields glucose. A. C.

Presence of maltose in fresh tubercles of *Lathyrus tuberosus*, L. A. MEUNIER (Compt. rend., 1933, **197**, 98—100).—Maltose is isolated from an aq. extract of the tubercles by pptn. with $Ba(OH)_2$ after treatment with invertase. H. A. P.

Non-fermentable reducing sugar in koji extract. II. F. HEMMI and N. TSUKITARI (J. Agric. Chem. Soc. Japan, 1933, **9**, 179—185).—Treatment with 90% EtOH+Et_2O at the end of the fermentation afforded a sugar resembling *iso*maltose [phenylosazone, m.p. 160—161°, $[\alpha]_D^{20.5}$ +22·53° (in 95% EtOH), +23·26° (in MeOH); Ac derivative, m.p. 72—78°, $[\alpha]_D$ +135·97° in $CHCl_3$]. CH. ABS.

***i*-Inositol in citrus fruits.** E. K. NELSON and G. L. KEENAN (Science, 1933, **77**, 561).—The residue insol. in MeOH obtained in the isolation of ascorbic acid from citrus fruits is *i*-inositol. L. S. T.

Minor constituents of the sweet potato. I. I. OSE (J. Agric. Chem. Soc. Japan, 1933, **9**, 165—179).—Maltose, and two monoaminophosphatides, each containing glucose and probably of the lecithin and cephalin types, respectively, are present. CH. ABS.

Organic acids of grape-juice. L. SEMICHON and M. FLANZY (Compt. rend., 1933, **197**, 198—201).—The juice contains tartaric, malic, glyoxylic, and other aldehydic acids. F. R. S.

Alkaloids of fumaraceous plants. VII. *Dicentra eximia* (Ker), Torr. R. H. F. MANSKE (Canad. J. Res., 1933, **8**, 592—599; cf. this vol., 841).—The base, previously (A., 1930, 122) called eximine is *d*-dicentrine (I). The roots of *D. eximia* contain (I) (0·41), glaucine (II) (0·03), protopine (0·45), *eximine* (III) (0·30), *eximidine* (IV) (0·04), and an *alkaloid* δ (V) (0·01%). (III), +MeOH, m.p. 116—117° (decomp.), and anhyd. m.p. 142° [*hydrobromide*, m.p. 270° (decomp. from 248°); *methiodide*, +$2H_2O$, m.p. 212° (decomp.)], and (IV), m.p. 133° (*methiodide*, decomp. 218° after darkening at 190—195°), both phenolic, $C_{17}H_{14}ON(OMe)_3$, are probably aporphine bases. (V) has m.p. 239° (decomp. from 235°) (*hydrochloride*, decomp. 237—238°, commencing at 234°). (I) gives a *methine*, m.p. 158—159° [*hydrochloride*, m.p. 302° (decomp.)], the *methiodide*, cryst., of which with aq. KOH gives NMe_3 and a cryst. substance. (II) affords N-*carbethoxy*-2 : 3 : 5 : 6-*tetramethoxy*-8-β-*methylaminoethylphenanthrene*, m.p. 115°. R. S. C.

Organic bases in germinated soya beans. K. SASAKI (J. Agric. Chem. Soc. Japan, 1933, **9**, 115—119).—The mother-liquor after removal of asparagine from an aq. extract of soya beans germinated in the dark afforded (per kg. from two species): adenine 0·52, 0·42; guanine 0·12, 0·08; histidine 1·60, 2·01; arginine 3·33, 3·09; choline 1·44, 1·71; cadaverine 1·22, 1·16 (g. ?). CH. ABS.

Presence of allantoic acid in fungi. R. FOSSE and A. BRUNEL (Compt. rend., 1933, **197**, 288—290).—Twenty-two varieties of fungi (dried) contain 0·014—0·672% of allantoic acid, the amount increasing greatly with development of the plant. R. S. C.

Chemical composition and grades of barley and oat varieties. D. D. HILL (J. Amer. Soc. Agron., 1933, **25**, 301—311).—Analytical data of numerous samples are recorded. Relationships between nutrient contents and the official system of grading are discussed. A. G. P.

Toxic substance in mulberry leaves damaged by tobacco. Toxic action of nicotine and trimethylamine on silkworms. T. YABUTA and T. KOZU (J. Agric. Chem. Soc. Japan, 1932, **8**, 770—775).—The toxic substance in damaged mulberry leaves appears to be nicotine. CH. ABS.

Enzymic activity of the plant organism and some phenomena of physiological immunity. K. SUCHORUKOV (Z. Opytn. Agron. Jugo-Vostoka, 1930, **8**, 237).—Peroxidase activity is related to resistance to rust in *Helianthus*, *Artemisia*, and *Xanthium*, being lowest in immune parts and individuals; catalase and the albumin enzymes play no part in the establishment of immunity. Alteration of the soil acidity affects peroxidase activity in the roots of sunflowers, the greatest depression of activity being obtained with neutral soils. The presence of antioxidases could not be detected. CH. ABS.

Effect of decay caused by white rot fungi on the chemical composition of wood. J. WIERTELAK (Bull. Acad. Polonaise, 1932, **B**, 19—36).—Decomp. of pine and fir wood by *Trametes pini* (I) and *Polystictus hirsutus* (II) results in the more rapid destruction of lignin than of cellulose. (II) attacks cellulose more rapidly than does (I). Neither organism could be grown on pure lignin. A. G. P.

Biological applications of semi-conducting photo-electric cells. T. KOFMAN (Bull. Soc. Chim. biol., 1933, **15**, 623—636).—The application of the Cu_2O–Cu and Se photo-electric cells to nephelometry and blood colorimetry is described. F. O. H.

Colorimetric calibration of micro-pipettes. F. C. BING (J. Lab. Clin. Med., 1933, **18**, 531—534).—Pipettes delivering 0·0005—1·0 c.c. are calibrated by colorimetric determination of the hæmoglobin content of dilutions of the blood delivered. CH. ABS.

Pipette electrode for determining the p_H of biological fluids. H. E. GORESLINE (J. Bact., 1933, **25**, 435—438).—A Au-plated Pt electrode is sealed into a bulb blown into the stem of a small pipette. The electrode vessel has a total capacity of 1·5—2·0 c.c. A. G. P.

Determination of thiocyanate in biological material. K. LANG (Biochem. Z., 1933, **262**, 14—19; cf. this vol., 637).—After removal of protein the CNS′ is pptd. as AgCNS, the ppt. is decomposed with H_2S, and the liberated CNS′ converted into the Cu–C_5H_5N–CNS complex, which is then determined, after extraction with PhBr, by means of a step photometer. Blood (30 c.c. used) contains 0·1—0·2 mg. of HCNS per 100 c.c. Methods previously used are untrustworthy. W. McC.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1933.

General, Physical, and Inorganic Chemistry.

Emission spectrum of molecular hydrogen in the extreme ultra-violet. C. R. JEPPESEN (Physical Rev., 1933, [ii], 44, 165—184).—Using a new grazing-incidence vac. spectrograph, > 2200 lines in the emission spectrum of H_2 in the range 1375—810 Å. were photographed. The known spectrum was extended about 200 Å. towards shorter wave-lengths, and 1400 new lines were found. Full data, analyses, and mol. and rotational consts. are given. N. M. B.

Photo-excitation of Balmer series of hydrogen canal rays in relation to conditions of the discharge. F. ZIMMER (Ann. Physik, 1933, [v], 17, 553—580).—The intensities of the β, γ, and δ Balmer lines of H canal rays have been studied at different discharge potentials and different pressures; the variation of the intensities under different conditions is discussed and the data are compared with theoretical predictions. W. R. A.

Attempt to extend the helium spectrum by exciting both electrons. A. H. ROSENTHAL (Z. Physik, 1933, 84, 794—798).—The result is doubtful. A. B. D. C.

Wave-lengths of the vacuum spark spectrum of carbon, nitrogen, and oxygen. B. EDLEN (Z. Physik, 1933, 85, 85—106).—The region tabulated is from 104 to 1923 Å. A. B. D. C.

Term tables of the atomic spectra of carbon, nitrogen, and oxygen. B. EDLEN (Z. Physik, 1933, 84, 746—766).—Tables of spectral terms are given for C I to C IV, N II to N V, and C II to C VI, including the extreme ultra-violet. A. B. D. C.

Second positive group of the nitrogen spectrum. D. COSTER, F. BRONS, and A. VAN DER ZIEL (Z. Physik, 1933, 84, 304—334).—Rotation lines are analysed, and from intensity perturbations and predissociation mol. terms are shown to dissociate thus: $X^1\Sigma$ to $^4S+^4S$, 9, $a\ ^1\Pi$ to $^2D+^2D$, 5·2, $A^3\Sigma$ to $^4S+^2D$, 3·56, $B^3\Pi$ to $^2D+^2P$, 5·95, and $C^3\Pi$ to $^2D+^2P$, 2·30 volts. Ths isotope effect gives a mass 15 assuming the normal atom to be 14. A. B. D. C.

Rotation structure and Zeeman effect of NH bands. H. BATSCH (Ann. Physik, 1933, [v], 18, 81—96).—Numerous weak lines were found in the NH spectrum between 3360 and 3370 Å., in addition to the strong triplets. The effect of a magnetic field showed that these were partly lines of the (1,1) band, and partly lines of the subsidiary transition. In a magnetic field the lines between the intensity max. of the Q branch undergo the greatest change. With the principal lines no splitting was observed, but only a change in the triplet distance which varied with the square of the field strength. Subsidiary lines show a widening proportional to field strength as demanded by theory. A. J. M.

Hyperfine structure in the arc spectrum of fluorine. J. S. CAMPBELL (Z. Physik, 1933, 84, 393—401).—The nuclear moment of F is . A. B. D. C.

Fine structure and natural width of spectral lines by self-absorption. E. LAU, O. REICHENHEIM, and J. JOHANNESSON (Ann. Physik, 1933, [v], 18, 97—106; cf. A., 1932, 208).—The asymmetry of the reversed lines of Ne is due to the difference in temp. of the emitting and absorbing gas, and also to the isotopic nature of Ne. The natural half-width of the lines is obtained. There are two groups of lines of which the natural half-widths are in the ratio 1 : 2, the lines of the first group being derived from a non-metastable, and those of the second from a metastable, ground term. The Hg line 5461 Å. shows three non-absorbed satellites, and the Hg line 4358 Å. one. The principal line of Hg 5769 is not simple. A. J. M.

Spectrum of doubly-ionised neon in the extreme ultra-violet. V. VON KEUSSLER (Z. Physik, 1933, 85, 1—3). A. B. D. C.

Optical determination of the diffusion constant for sodium. L. A. GINSEL and L. S. ORNSTEIN (Z. Physik, 1933, 84, 276—281).—Intensity measurements in a Na flame gave a diffusion const. corresponding with a gas kinetic radius of 2·4 Å. for the atom. A. B. D. C.

New band systems of aluminium hydride. W. HOLST (Nature, 1933, 132, 207—208).—Details of a new band system at 3800 Å. are recorded and a new system at 3600 Å. is reported. L. S. T.

Variation with temperature of the continuous absorption spectrum of diatomic molecules. I. Experimental; absorption spectrum of chlorine. II. Theoretical. G. E. GIBSON and N. S. BAYLISS. G. E. GIBSON, O. K. RICE, and N. S. BAYLISS (Physical Rev., 1933, [ii], 44, 188—192, 193—200).—I. A photographic method used in the temp. range 18—765° showed that rise of temp. decreased the absorption coeff. at the max., and broadened the region of continuous absorption. Analysis of results gave the contributions of individual vibrational levels to the total absorption.

II. The absorption from a single vibrational level is practically independent of temp.; the temp. effect is due to the changing distribution of the absorbing mols. among the various levels. The electric moment corresponding with the absorption from the lower state for Cl_2 corresponds with the displacement of one electronic charge through 0·016 Å. N. M. B.

Wavy emission continuum of potassium hydride. T. HORI (Japan. J. Physics, 1933, **8**, 151—163; cf. this vol., 660).—The spectrum of an arc between K electrodes in H_2 shows, besides the $^1\Sigma$—$^1\Sigma$ band structure, a wavy continuum, which can also be attributed to the KH mol. It is interpreted as due to transition from the unstable $^1\Pi$ state to the stable $^1\Sigma$ ground-state. NaH shows a similar but feebler continuum, whilst no analogue is observed with LiH. J. W. S.

Fine structure and predissociation in the spectrum of calcium hydride. B. GRUNDSTRÖM and E. HULTHEN (Nature, 1933, **132**, 241—242). L. S. T.

Hyperfine structure of the resonance lines of Sr II. H. SCHÜLER and H. WESTMEYER (Naturwiss., 1933, **21**, 561—562).—The hyperfine structure of the resonance lines of Sr^{87} provides another example of inverted terms. The nuclear moment is $> 0·5$. Sr^{87} is an isotope of odd at. wt. and even at. no., whilst isotopes of odd at. wt. and odd at. no. possess regular terms. Sr^{87} is an isobar of Rb^{87}, but for the latter the terms are regular. A. J. M.

Band spectrum of barium hydride. G. FUNKE (Z. Physik, 1933, **84**, 610—628).—An investigation between 5950 and 7500 Å. is described. A. B. D. C.

Arc spectrum of rhenium between 2500 and 2320 Å. at normal pressure. S. PINA DE RUBIES and J. DORRONSORO (Anal. Fís. Quím., 1933, **31**, 412—415).—200 lines between 2500 and 2320 Å. are recorded (± 0·01 Å.); 14 are visible with 5×10^{-4} g. of Re, and 3 with 5×10^{-5} g., whilst a line at 2428·58 Å. is visible with 10^{-5} g. H. F. G.

Principal series $^1S_0$—m^1P_1 and $^1S_0$—m^3P_1 of the mercury arc spectrum (Hg I). Perturbation term $^1P_1(5d)^9(6s)^26p$. H. BEUTLER (Z. Physik, 1933, **84**, 289—303). A. B. D. C.

Abnormal increase in intensity of the mercury triplet 5461, 4358, 4057, in highly dried hydrogen and other gases. A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1933, **84**, 402—411).—The intensity ratio of green : yellow increases rapidly with exciting electron velocity and gas pressure for H_2, less rapidly for N_2 and A, and not at all for He and Ne. A. B. D. C.

Magnetic transition of the hyperfine structure of mercury. D. R. INGLIS (Z. Physik, 1933, **84**, 466—473).—Theoretical investigation of the Paschen–Back effect in hyperfine structure. A. B. D. C.

Band spectra superimposed on the continuous spectra of mercury in the visible region. J. OKUBO and E. MATUYAMA (Sci. Rep. Tôhoku, 1933, **22**, 383—392).—The spectrum of Hg vapour excited by a high-frequency current of 3×10^7 cycles in a tube of the reflux condensation type shows two bands, at 4340—4078 and at 4047—3650 Å. A. R. P.

Polarisation of fluorescence of mercury vapour. A. KASTLER (Compt. rend., 1933, **197**, 442—444).—The deduction that when Hg vapour is illuminated by a beam of light containing the lines 2537 and 4358 Å., the fluorescence lines 4358 and 4046, when observed perpendicularly to the incident beam, should be polarised rectilinearly perpendicular to each other is the more nearly satisfied the narrower and more accurately parallel is the incident beam, the lower the temp., and the more fully compensated the terrestrial magnetic field. C. A. S.

Prohibited lines due to nuclear spin. R. EINAUDI (Atti R. Accad. Lincei, 1933, [vi], **17**, 552—557).—Theoretical. The intensities of the lines $^1S_0\longrightarrow{}^3P_2$ and $^1S_0\longrightarrow{}^3P_0$ for a bivalent element are calc., and applied to the calculation of the 2270 and 2655 lines of Hg. O. J. W.

Possibility of the introduction of very high potentials in discharge tubes. M. SITNIKOV (Z. tech. Physik., 1932, **13**, 460—464; Chem. Zentr., 1933, i, 825). L. S. T.

Positive column in the Hittorf dark space. A. GUNTHER-SCHULZE and H. BETZ (Z. Physik, 1933, **84**, 740—745). A. B. D. C.

Electrical clean-up of gases. W. VON MEYEREN (Z. Physik, 1933, **84**, 531—540).—The clean-up of air and H_2 between 10^{-4} and 10^{-6} mm. was studied with a discharge tube designed to give high electron densities. A. B. D. C.

Re-striking of the electric arc as a discharge in highly ionised gases. G. TIMOSHENKO (Z. Physik, 1933, **84**, 783—793). A. B. D. C.

Temperature of the beginning of grey glow radiation of metals, oxides, and sulphides. G. TAMMANN and W. BOEHME (Ann. Physik, 1933, [v], **17**, 863—868; cf. this vol., 117).—The temp. at which grey glow appears for metals, salts, and oxides is lowered by pulverisation, not from diminution of the particle size, but because of cold-working. The effect disappears after the powders have been heated for some time. J. W. S.

Interpretation of nova spectra. D. H. MENZEL and C. H. PAYNE (Proc. Nat. Acad. Sci., 1933, **19**, 641—648).—The bright-line spectra of novæ are interpreted in terms chiefly of rapidly rising temp., rapidly falling pressure, and rapidly increasing dilution of radiation. C. W. G.

Electrostatic theory of the plasma. D. GABOR (Z. Physik, 1933, **84**, 474—508).—Electrostatic forces between ions are taken into account in determining the condition of plasma. A. B. D. C.

Vacuum discharges with internal high-voltage sources. W. KOSSEL and A. ECKARDT (Ann. Physik, 1933, [v], **17**, 543—552).—Description of necessary apparatus. W. R. A.

Precision of the measurement of the Lo Surdo–Stark effect patterns. Y. ISHIDA and T. TAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 158—177).—The main difficulty of the Lo Surdo

method is attributed to inaccuracy due to the inclination and chromatic variation; methods for correcting these are suggested. The effect of variation of the field strength with the cathode distance is discussed, and errors introduced by the method are compared critically with the probable error of reading. J. W. S.

Stark effect by the perturbation theory. W. VON KOPPENFELS (Z. Physik, 1933, **84**, 694—700).—The relevant equation is solved for first-order perturbations. A. B. D. C.

Absolute determination of scattering intensity of Cu α radiation in argon. G. HERZOG (Naturwiss., 1933, **21**, 607—608).—The apparatus is described. The observed scattering in A at 2 atm. and at angle 40° was $2{\cdot}88\times10^{-7}\pm5\%$, agreeing with the Hartree at. model. A. J. M.

Atom factor determination in the region of anomalous dispersion. R. GLOCKER and K. SCHAFER (Naturwiss., 1933, **21**, 559—560).—The determination of the at. factor on the short-wave side of the *K*-absorption edge of Fe gives anomalous results. A. J. M.

Effect of lattice binding forces on the fine structure of the carbon *K*α line. R. GLOCKER and H. KIESSIG (Naturwiss., 1933, **21**, 593—594).—Photographs have been obtained showing the difference between the C *K*α lines from graphite (I) and diamond (II), and consequently the effect of lattice forces on the lines. The components of the (I) line lie on the short-wave side of the max. in contrast to those of (II). SiC shows a fine structure similar to that of (II). A. J. M.

***X*-Ray line intensities and cathode-ray retardation in thick targets of Ag.** D. L. WEBSTER, W. W. HANSEN, and F. B. DUVENECK (Physical Rev., 1933, [ii], **44**, 258—264).—Measurements of *K* lin intensities for voltages up to 180 kv. and emergence angles 1—25° were made in order to determine the voltage for max. efficiency of line emission at any emergence angle, and to extend quant. relations on cathode-ray retardation. N. M. B.

Structure of *X*-ray *K* absorption limits of the elements manganese to zinc. A. H. BARNES (Physical Rev., 1933, [ii], **44**, 141—145).—The main absorption edges of Mn, Fe, Co, Ni, Cu, but not Zn, and of Mn_2O_3, Fe_2O_3, Co_2O_3, Ni_2O_3, CuO, but not ZnO, showed definite structure. The oxide edges were all displaced towards shorter wave-length. The observed width of the edges varied from 15 volts for Zn to 23 volts for Fe. N. M. B.

Relative intensities and transition probabilities of the *K*-series lines of the elements 24—52 by the ionisation chamber method. J. H. WILLIAMS (Physical Rev., 1933, [ii], **44**, 146—154).—The ionisation current ratios produced by *X*-ray lines of wave-lengths 2·29, 1·93, and 1·66 Å. entering a double ionisation chamber filled with MeI, MeBr, A, air, and SO_2 were practically const. The method was applied to measurement of the relative intensities of the *K*-series of 20 elements from Cr (24) to Te (52). Results, transition probabilities, and the absorption coeffs. of mica, cellophane, MeBr, and MeI are given. N. M. B.

Structure of *K* lines of light atoms. M. MORAND aud A. HAUTOT (Compt. rend., 1933, **197**, 520—522).—The *K* line of O, 23·6 Å., is 0·1—0·15 Å. wide (cf. A., 1930, 1502; this vol., 548); that of N, $31{\cdot}8\pm0{\cdot}2$ Å., is wider. The components of *K* of C are 44·5, 44·1, and 43·5 Å.; the width of that of B is 2·5 Å., and its max. intensity at 66·55—67·55; *K* of Be is 9 Å. wide, sharp edge towards short λ at 112·6 Å. Results agree with theory (cf. this vol., 201, 440, 760). C. A. S.

Intensity of the linear *X*-ray spectrum of tungsten. L. PINCHERLE (Atti R. Accad. Lincei, 1933, [vi], **17**, 560—564).—Theoretical. The intensities of the *K* and *L* lines of W are calc. O. J. W.

Excitation of *X*-ray lines of the second kind. D. COSTER and W. J. THIJSSEN (Z. Physik, 1933, **84**, 686—693).—Excitation of the $K\alpha_3\alpha_4$ line of S is described. A. B. D. C.

Magnitude of the *L*-absorption discontinuities. I. BACKHURST (Phil. Mag., 1933, [vii], **16**, 310—312).—Review of existing data suggests that the only relationship between absorption coeffs. which can be regarded as established is $J(L_3/M_1)=2^{-1/2}(E_3/E)$, where E_3 and E are the vals. of the L_3 and M_1 energy levels, respectively. J. W. S.

Removal potential and atomic separation. W. DISTLER and G. MONCH (Z. Physik, 1933, **84**, 271—275).—The potential required to remove an electron from glowing Ni, 4·63 volts, agrees with Schottky's formula (*ibid.*, 1923, **14**, 73), whilst that for Fe, 4·04 volts, does not. A. B. D. C.

Ionisation potential and formation of the hydrogen molecule. J. SAVARD (Compt. rend., 1933, **197**, 397—399).—Comparison of the total energies of H_2^+ and H_2 as calc. by Hylleraas (cf. A., 1931, 1206) with the ionisation potentials as determined shows that the energy of formation of the normal mol. from normal atoms is double the difference between the ionisation potentials of the mol. and atom. C. A. S.

Effect of temperature on the emission of electron field currents from tungsten and molybdenum. A. J. AHEARN (Physical Rev., 1933, [ii], **44**, 277—286).—Thermionic emission measurements were made for fields of range 5×10^5 to 1×10^6 volt per cm., and temp. range 300—2000° abs. Down to about 1600° abs. the thermionic currents masked the field currents. Below 1600° abs. thermionic emission vals. were obtained by extrapolation. Field currents were independent of temp. to within 5% in the range 300—1400° abs., above which data indicate that the current consists of a thermionic current plus a current which is independent of temp. N. M. B.

Gravitational field of an electron. J. GHOSH (Nature, 1933, **132**, 170, and Z. Physik, 1933, **85**, 511—513). L. S. T.

Electrostatic deviation and specific charge of positive electron. J. THIBAUD (Compt. rend., 1933, **197**, 447—448).—Examination of the magnetic

spectrum (field 10,000 gauss) given by Ra in a Ag tube or of Ra-Th in Pb shows a strong emission of positive electrons. Such electrons are unaffected by interposition of 0·04 mm. of Ag, but greatly absorbed by 0·5 mm. of Al, and almost entirely by 1·0 mm. Superimposition of an electric field shows that the mass of the positive is at least approx. identical with that of the negative electron. C. A. S.

Electron-microscopic images with secondary electrons. M. KNOLL and G. LUBSZYNSKI (Physikal. Z., 1933, **34**, 671—674).—By means of a new form of electrical electron lens it is possible to obtain images of metallic nets with secondary electrons. The apparatus will permit quant. determinations of secondary emission from metals and insulators. A. J. M.

Mott's polarisation effect for the scattering of electrons at atoms. F. SAUTER (Ann. Physik, 1933, [v], **18**, 61—80; cf. A., 1929, 861; 1932, 441).—Mott's results can be derived in a simpler and more general manner by the use of the Born–Dirac collision method. A. J. M.

Effect of exchange on the scattering of slow electrons from atoms. P. M. MORSE and W. P. ALLIS (Physical Rev., 1933, [ii], **44**, 269—276).—Mathematical. The treatment of states involving one or more unbound electrons scattered by an atom is developed. N. M. B.

Diffraction of slow electrons at single crystals of tungsten. R. VON MEIBOM and E. RUPP (Ann. Physik, 1933, [v], **18**, 107—120).—The electrons were of velocities 25—600 volts. The apparatus is described, and the inner potentials corresponding with the various reflexion max. are obtained. 127 max. were measured, of which 87 can be assigned integral order nos. A. J. M.

Anomalies in mirror reflexion and diffraction of molecular rays at crystal cleavage surfaces. I. R. FRISCH and O. STERN. **II.** R. FRISCH (Z. Physik, 1933, **84**, 430—442, 443—447).—I. Reflexion and diffraction curves for H_2 and He by LiF and NaF show characteristic min. (saddles) in the Maxwell distribution curve, probably due to adsorption of the mol. ray by the crystal.

II. The characteristic min. of the intensity curves are shown to occur when the reflected or diffracted rays have definite components of momentum relative to the crystal axes; for these momenta the rays are most readily adsorbed by the doubly periodic force field of the crystal surface. A. B. D. C.

Mobility of positive ions in gases. T. EDQVIST (Physikal. Z., 1933, **34**, 618—623).—The mobility of positive ions in a gas is calc. on Lenard's formula with respect to pressure, temp., and field strength; conclusions agree with experiment. A. J. M.

Electrical diffusion of ions in gases of bipolar charge. N. VOLODKEVITSCH (Z. Physik, 1933, **84**, 593—609).—An extension of Townsend's equation for the time distribution of charge density around an ion in a gas containing ions of one charge and one mobility to that of an ion in a gas with positive or negative ions of various mobilities. A. B. D. C.

Determination of mobilities of ions in gases. A. STEPANOVA and T. TZAREVA (J. Exp. Theor. Phys., Russia, 1932, **2**, No. 5—6, 339—352).—Vals. in air and saturated vapours of HCO_2H, AcOH, $EtCO_2H$, $PrCO_2H$, $Bu^{\alpha}CO_2H$, camphor, and Et_2O are recorded. CH. ABS.

Fundamental at. wts. XII. Revision of at. wt. of potassium. Analysis of potassium chloride and potassium bromide. O. HONIGSCHMID and R. SACHTLEBEN (Z. anorg. Chem., 1933, **213**, 365—376).—From the ratios KCl : Ag, KCl : AgCl, KBr : Ag, and KBr : AgBr vals. of 39·096, 39·097, 39·097, and 39·094, respectively, were obtained. The mean of 39 determinations was 39·096. H. J. E.

Revision of at. wt. of potassium. G. P. BAXTER and W. M. MACNEVIN (J. Amer. Chem. Soc., 1933, **55**, 3185—3190).—From determinations of the ratio KCl : Ag with K from various sources the at. wt. of K is 39·094, which accords with Richards' vals., but is 0·01 unit < that recorded by Honigschmid and Goubeau (A., 1929, 370). J. G. A. G.

At. wt. of less volatile potassium prepared by Hevesy. G. P. BAXTER and C. M. ALTER (J. Amer. Chem. Soc., 1933, **55**, 3270—3271).—From determinations of the ratio KCl : Ag, the at. wts. of ordinary K and heavy K conc. by ideal distillation (cf. A., 1928, 684) are 39·096 and 39·109, respectively; the heavy K contains 7·3% K^{41} (cf. A., 1929, 370). J. G. A. G.

Relative abundance of hydrogen isotopes. W. BLEAKNEY and A. J. GOULD (Physical Rev., 1933, [ii], **44**, 265—268).—The abundance ratio $H^2 : H^1$ determined by the mass-spectrograph for H_2 liberated in the electrolysis of ram-H_2O varied between 1 : 4500 and 1 : 6500. N. M. B.

Isotopes of cobalt by the magneto-optic method. T. R. BULL and S. S. COOPER (J. Amer. Chem. Soc., 1933, **55**, 3207—3210).—Two new isotopes of Co, probably of masses 57 and 58, have been discovered. Co^{59} is by far the most abundant, followed in order by 57 and 58, in keeping with the at. wt. 58·94. Earlier data (A., 1930, 1541) are revised. J. G. A. G.

Mass ratio of the lithium isotopes from the spectrum of Li_2. A. MCKELLAR (Physical Rev., 1933, [ii], **44**, 155—164).—Wave nos. of all the lines of the blue-green absorption bands of the Li^7Li^7 and Li^6Li^7 systems are given. Vibrational, rotational, and electronic consts. are calc. N. M. B.

Packing effect. A. SOMMERFELD (Conv. Fis. nucl., 1932, **1**, 155—157; Chem. Zentr., 1933, i, 1078).—Aston's and Stefan Meyer's curves do not differ essentially. The bifurcation of Aston's curve has no physical basis. The packing effect exhibits a periodicity parallel with that of the outer at. shell. A. A. E.

Energy levels of radium-C′. G. BECK (Conv. Fis. nucl., 1932, **1**, 167—172; Chem. Zentr., 1933, i, 1079).

Artificial transformation of magnesium with polonium α-rays. W. BOTHE and H. KLARMANN (Naturwiss., 1933, **21**, 639—640).—The Rutherford–

Geiger counter was used in the investigation of nuclear transformation of Mg with Po α-rays of various ranges. The absorption curves of protons were obtained. For the longer ranges (3·87 cm.) there are four distinct proton groups, but this no. decreases with the range until for ranges $< 2{\cdot}84$ cm. there is only one group. Some of the proton groups possess a narrow excitation interval with regard to α-ray range. A. J. M.

Nuclear radii and atomic disintegration efficiency for heavy elements. G. KIRSCH (Naturwiss., 1933, **21**, 640).—For Ra-*C* absorption, elements with odd at. no., especially In and Sb, show, contrary to expectation, concave absorption curves; even elements, *e.g.*, Te, Sn, and Cd, show a step in the absorption curve. α-Particles within a certain velocity range were not reflected. A no. of experiments give results apparently incompatible with the Gamow nuclear model. A. J. M.

α-Particles, artificial nuclear transformation and excitation, isotopes. W. BOTHE (Conv. Fis. nucl., 1932, **1**, 83—106; Chem. Zentr., 1933, i, 1078—1079).

Theory of β-emission. K. SITTE (Physikal. Z., 1933, **34**, 627—630).—Dirac's theory is applied to β-emission. A. J. M.

β-Radiation of radium-*E* and of active deposit of actinium. M. LECOIN (Compt. rend., 1933, **197**, 405—407).—$H\rho$ for 600 β-rays from active deposit of Ac, 250 from Ac″, and 400 from Ra-*E* have been measured. The (no. of rays)–$H\rho$ curves are: for Ac″ bell-shaped, max. at about 3000 $H\rho$, ending at about 6500; and for Ac-*B* max. about 1000, ending at 3000—3500. That for Ra-*E* seems to end or change direction at about 5800. Ra-*E* emits < 1 positive electron per 2000 β-rays. C. A. S.

Energy law and reversibility of elementary processes. G. BECK (Z. Physik, 1933, **84**, 811—813).—The relation of the energy law to reversibility is discussed for elementary processes, particularly for β-ray disintegration. A. B. D. C.

Radioactivity of potassium. D. BOCCIARELLI (Atti R. Accad. Lincei, 1933, [vi], **17**, 830—836).—Absorption measurements show that the radiation from K is made up of (*a*) a relatively soft β component forming 60% of the total intensity with a velocity 0·83 *c*, (*b*) a harder β component (nearly 40%) with velocity 0·93 *c*, and (*c*) a very hard γ-radiation forming 1·08% of the total. O. J. W.

β- and γ-rays. C. D. ELLIS (Conv. Fis. nucl., 1932, **1**, 107—117; Chem. Zentr., 1933, i, 1079—1080).—A discussion. A. A. E.

Inner photo-effect with γ-rays. L. MEITNER and K. C. WANG (Naturwiss., 1933, **21**, 594).—The intensity of β-ray groups emitted from Th-*B*+*C*+*C*″ was determined in a magnetic field by a Geiger–Müller counter. Agreement is shown between the results of this method and the photographic method of Ellis. A. J. M.

Internal conversion [of γ-rays]. J. SOLOMON (Compt. rend., 1933, **197**, 401—403; cf. this vol., 110, 111).—Mathematical; the probability of the occurrence of these transitions is calc. C. A. S.

Absorption of very penetrating γ-rays. W. GENTNER (Compt. rend., 1933, **197**, 403—405).—The absorption of γ-rays of great energy is attributed to (*a*) Compton effect, (*b*) photo-electric absorption, (*c*) nuclear diffusion, and (*d*) excitation of positive electrons. (*a*) obeys Klein and Nishina's formula; (*b*) is determinable by Gray's method. The coeff. of absorption of Pb for γ-rays of λ 4·7—9·3 X experimentally determined, compared with the coeff. deduced from (*a*) and (*b*), gives by difference the effect due to (*c*). Its effect begins at $\lambda=12$ X, and increases as λ diminishes (cf. A., 1932, 671, 791). C. A. S.

Passage of penetrating corpuscular rays through a ferromagnetic. C. F. VON WEIZSACKER (Ann. Physik, 1933, [v], **17**, 869—896).—Theoretical. J. W. S.

Spin and statistics of the neutron. T. SEXL (Nature, 1933, **132**, 174). L. S. T.

Existence of a neutron of mass 2. H. WALKE (Nature, 1933, **132**, 242—243).—Certain anomalies in recent measurements in disintegration experiments can be explained by assuming the existence of a neutron of mass 2 with an energy of 16×10^6 electron volts. L. S. T.

Theory of the neutron. J. J. PLACINTEANU (Z. Physik, 1933, **84**, 370—379).—The model consisting of a proton and an electron of negative kinetic energy fits known empirical data for the neutron (cf. this vol., 660). A. B. D. C.

Constitution of neutrons, positive electrons, and protons: existence of negative protons. J. J. PLACINTEANU (Compt. rend., 1933, **197**, 549—552; cf. this vol., 660, 683, and preceding abstract).—It is shown that photons of energies $\lessgtr 10^6$ and 10^9 ev. should be decomposable into a negative and a positive electron, and a negative and a positive proton, respectively; non-detection of the negative proton is probably due to the great energy required C. A. S.

Interaction of neutrons and protons. G. C. WICK (Z. Physik, 1933, **84**, 799—800).—Heisenberg's hypothesis of neutron and proton interchange (A., 1932, 1074) is applied to scattering of these particles. A. B. D. C.

Theory of atomic nuclei. IV, V. E. N. GAPON (Z. Physik, 1933, **84**, 509—519, 520—530).—IV. Mass defects are determined for nuclear protons, neutrons, and α-aggregates; binding energies for nuclei of α-particles and neutrons and the diameter of the α-particle are also calc.

V. A scheme is given representing the transformation of light nuclei by α-particles, neutrons, and proton, and the α- and β-disintegration of radioactive elements. A. B. D. C.

Ultra-corpuscular radiation. W. BOTHE (Conv. Fis. nucl., 1932, i, 153—154; Chem. Zentr., 1933, i, 1080).

Disintegration of various substances by ultra-radiation. E. G. STEINKE, A. GASTELL, and H. NIE (Naturwiss., 1933, **21**, 560; cf. A., 1932, 556,

791).—With some exceptions, there is proportionality between collision impact and normal ionisation. There is comparatively high collision frequency with Fe and Al compared with Pb. A. J. M.

Interaction between cosmic rays and matter. B. Rossi (Nature, 1933, **132**, 173—174).—The showers of secondary particles produced when cosmic rays pass through matter occur more frequently in elements of high at. no. For Pb, Fe, and Al, the ratio is 4 : 2 : 1. The radiation which causes the showers has a mean range of a few cm. in Pb and cannot be identical with the primary cosmic rays. The shower-producing rays are more readily absorbed by elements of high at. no. Absorption of secondary rays by an element and the no. of showers produced depend similarly on at. no. L. S. T.

Diminution of cosmic-ray intensity by transmission through various materials. E. G. Steinke and H. Tielsch (Z. Physik, 1933, **84**, 425—429).—Comparison of absorption by Pb, Fe, and Al indicates that only orbital electrons reduce the intensity of the beam. A. B. D. C.

Secondary and tertiary particles produced by cosmic rays. J. H. Sawyer, jun. (Physical Rev., 1933, [ii], **44**, 241—245).—Counts of triple coincidences by means of Geiger counters, as a function of the thickness of plates of Pb, Sn, and Al as scatterers, give curves which can be explained by assuming that the effect is due to tertiary particles generated in the metal by light element secondaries produced in the regions above the scatterers. N. M. B.

Mechanism of the Geiger-Müller counter. W. Christoph and W. Hanle (Physikal. Z., 1933, **34**, 641—645).—The normal form of the charge in the Geiger-Müller counter is a photon charge. The no-potential characteristics are explained. A. J. M.

Application of the FP-54 pliotron to atomic disintegration studies. L. R. Hafstad (Physical Rev., 1933, [ii], **44**, 201—213).—Investigation of the resonance disintegration of Al gave 20 protons of range 30—50 cm. per 10^8 α-particles. Evidence of groups of ranges 30 and 60 cm., and a strong group 45—50 cm., was obtained. N. M. B.

Quantum theoretical treatment of radiation problems. L. Rosenfeld (Conv. Fis. nucl., 1932, **1**, 131—135; Chem. Zentr., 1933, i, 1075—1076).—A review. A. A. E.

Subdivision of the series of transition elements. W. Biltz and W. Klemm (Z. Elektrochem., 1933, **39**, 597—598; cf. this vol., 110).—A discussion of the electron arrangement in the elements between Ca and Zn. H. J. E.

Charge distributions in fluorine and neon. F. W. Brown (Physical Rev., 1933, [ii], **44**, 214—223).—Mathematical. Energy parameters of electrons are calc. by a modified Hartree field method. N. M. B.

Dissociation of diatomic molecules with p–p binding. H. Lessheim and R. Samuel (Z. Physik, 1933, **84**, 637—656).—By comparison of electron configurations of mol. terms and of the energies of bound and separated atoms, the influence of the electrons of the individual atoms on the strength of the linking is deduced. The results are applied to BeO, NO, PO, BeF, MgF, CaF, SrF, AlO, PbO, and SnCl. A. B. D. C.

Theory of the nucleus. G. Wataghin (Atti R. Accad. Lincei, 1933, [vi], **17**, 645—647).—Certain aspects of Heisenberg's theory of the at. nuclear structure are discussed in the light of the discovery of the positive electron. O. J. W.

Frequency of the elements and constitution of the nucleus of atoms. II. Twenty years in the history of an observation and of a hypothesis. G. Oddo (Gazzetta, 1933, **63**, 355—380; cf. A., 1914, ii, 239).—The development of the theory that the nuclei of all atoms contain He atoms is discussed. O. J. W.

Quantum theory of nuclear structure. G. Gamow (Conv. Fis. nucl., 1932, **1**, 65—81; Chem. Zentr., 1933, i, 1077).—Units of nuclear structure are distinguished as (*a*) heavy (protons and agglomerations, *e.g.*, α-particles) and (*b*) light (electrons). Processes involving (*a*) which can be treated by non-relativistic quantum mechanics are considered. A. A. E.

Theoretical optics of the hydrogen molecule. B. Mrowka (Z. Physik, 1933, **84**, 448—465).—The mean polarisability of the mol., taking into account zero point vibration of the nuclei, is calc., and used to determine intensity of Raman lines, degree of depolarisation, and variation of refractive index with wave-length. A. B. D. C.

Charge distributions for the normal atoms from boron to neon. F. W. Brown, J. H. Bartlett, jun., and C. G. Dunn (Physical Rev., 1933, [ii], **44**, 296—299).—Mathematical. N. M. B.

Stability of the atom and the laws of conservation. N. Bohr (Conv. Fis. nucl., 1932, **1**, 119—130; Chem. Zentr., 1933, i, 1077).—A discussion. A. A. E.

Magnetic moment of the proton. I. Estermann, R. Frisch, and O. Stern (Nature, 1933, **132**, 169—170).—Deflexion experiments with para-H at room temp. give a rotational moment of 0·8—0·9 nuclear magneton per unit quantum no. This result together with deflexion experiments with ortho-H gives a val. of 2·5 nuclear magnetons, and not 1, as would be expected, for the moment of the proton. L. S. T.

Magnetic deviation of hydrogen molecules and the magnetic moment of the proton. I. R. Frisch and O. Stern. **II.** I. Estermann and O. Stern (Z. Physik, 1933, **85**, 4—16, 17—24).—I. Para-H gave deviations corresponding with approx. one nuclear magneton (1/1840 Bohr magneton) per rotational quantum. Ortho-H gave the magnetic moment of the proton between 2 and 3 nuclear magnetons.

II. More accurate measurements gave the moment of the proton as 2·5 nuclear magnetons, with a possible error $< 10\%$, and the rotational moment as 0·8—0·9 nuclear magneton per rotational quantum. A. B. D. C.

Magnetic moment of a rotating hydrogen molecule. G. C. WICK (Z. Physik, 1933, **85**, 25—28).—Introduction of circulation of the electronic cloud around the nuclei due to rotation of the mol. gives 0·36 and 0·925 as the limits of the magnetic rotational moment in nuclear magnetons (cf. preceding abstract). A. B. D. C.

Impulse corona in water. Y. TORIYAMA and U. SHINOHARA (Nature, 1933, **132**, 240). L. S. T.

Colour of precipitated cadmium sulphide. W. J. MULLER and G. LOFFLER (Angew. Chem., 1933, **46**, 538—539).—*X*-Ray examination shows that the variation in colour of CdS pptd. by H_2S from solutions containing differing amounts of H_2SO_4 is due solely to the differing size of the crystals. H. W.

Colour centres of alkali halide crystals. E. MOLLWO (Z. Physik, 1933, **85**, 56—67).—Quant. investigation of the production of centres by heating in presence of metal vapours shows that for each temp. there is a definite concn. of centres, and the v.p. of the cation metal at any temp. gives the lower limit of this concn. The principal optical properties of the centres were also determined, and show the width of the absorption band and its max. to depend on the thermal energy of the lattice. A. B. D. C.

New type of diffuse molecular spectrum. Optical absorption and photochemical decomposition of chromyl chloride vapour. R. DE L. KRONIG, A. SCHAAFSMA, and P. K. PEERLKAMP (Z. physikal. Chem., 1933, **B**, **22**, 323—332).—In the absorption spectrum of CrO_2Cl_2 five diffuse absorption bands without edges are repeated some 15 times at a const. interval of 136 cm.$^{-1}$ from 6000 Å. towards the violet. Light absorption is accompanied by dissociation, probably into CrO_2 and Cl_2, a dust appearing. Assuming this dissociation to correspond with passage of the mol. into an electronic state in which the interaction of the two groups of atoms is described by a repulsion curve, the spectrum may be interpreted as a Condon diffraction band. R. C.

Extension of ultra-violet absorption spectrum of ozone towards greater wave-lengths. D. CHALONGE and (MME.) L. LEFEBVRE (Compt. rend., 1933, **197**, 444—447).—An arrangement enabling a tube 245×3·5 cm. to be filled with O_2 containing 22% O_3 is described. The absorption spectrum of O_3 has been examined from λ 3385 to 3660, and the bands at 3439, 3515, and 3575 are shown to be due to O_3 (cf. A., 1925, ii, 998). C. A. S.

New band system of beryllium oxide and the structure of the BeO molecule. L. HERZBERG (Z. Physik, 1933, **84**, 571—592).—The electron configurations, dissociation energies, and other mol. consts. are deduced for various electron levels. A. B. D. C.

New bands in the spectrum of vanadium monoxide. G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], **17**, 836—838).—Twelve visible new bands of VO are recorded. O. J. W.

Spectrum of molybdic anhydride. G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], **17**, 654—656).—The light emitted when MoO_3 is heated in the Bunsen and O_2–H_2 flames gives a continuous spectrum between 6600 and 4840 Å., with intensity max. at 5520 and 6300 Å. The arc spectrum between Ag electrodes is almost wholly linear, but shows a few weak bands at 6100—6500 Å. The continuous spectrum may represent a new type of pre-dissociation spectrum, due to the group MoO. O. J. W.

3600 Å. doublet band of the carbon dioxide spectrum. R. SCHMID (Z. Physik, 1933, **84**, 732—739). A. B. D. C.

Influence of halides on the extinction coefficients, and its bearing on the constitution, of silver halides in fusion. G. S. FORBES and H. B. ELKINS (J. Amer. Chem. Soc., 1933, **55**, 3272—3276).—The extinction coeffs., *K*, of molten AgCl and AgBr at λ 5460 Å. are greatly diminished by small quantities of the chlorides and bromides, respectively, of Li, K, Rb, Ba, Sr, and Pb. The data are consistent with the presence of the complex cation Ag_2Cl^+ in equilibrium with AgCl, of which the dissociation const. is 3×10^{-4}. With mixtures of Ag halides, log *K* is almost a linear function of the mol. fraction of one constituent. J. G. A. G.

Spectrophotometry of short-lived intermediate products. H. SCHMID and E. GASTINGER (Z. Elektrochem., 1933, **39**, 573—576; cf. A., 1930, 1395).—Aq. $Na_2S_2O_3$ and aq. HCl were mixed by a continuous-flow method in an absorption cell, and the extinction coeff. of the unstable HS_2O_3' ion between 2800 and 2300 Å. was measured. H. J. E.

Absorption spectra of the samarium ion in solids. III. Absorption of $Sm(BrO_3)_3,9H_2O$ and a partial energy level diagram for the Sm^{+++} ion as it exists in crystalline $Sm(BrO_3)_3,9H_2O$. F. H. SPEDDING and R. S. BEAR (Physical Rev., 1933, [ii], **44**, 287—295; cf. A., 1932, 1188).—Data on the energy levels were obtained from a study of the absorption spectra in the temp. range 20—298° abs. Low-temp. splitting may be due either to actual removal of degeneracy or to development of two types of Sm^{+++} ion, differing in crystal environments, either effect being caused by small changes of crystal dimension and symmetry. N. M. B.

Ultra-violet absorption of the amino-group and other groups in simple gaseous molecules. G. HERZBERG and R. KÖLSCH (Z. Elektrochem., 1933, **39**, 572—573).—NH_2Me, NH_2Et, and NH_2Pr vapours show absorption bands between 2500 and 2100 Å. resembling those of NH_3. The band spacings for the amines and for NH_3 are approx. 650, 900 cm.$^{-1}$, respectively, interpreted as a vibration frequency of the excited NH_2 group. For $NHMe_2$, NMe_3, and $NHEt_2$ similarly placed but diffuse bands occur. NH_2Ph also has an absorption band at 2400 Å. $HCO{\cdot}NH_2$ vapour shows neither bands due to C:O nor those of NH_2. H. J. E.

Absorption spectra of mixed fatty acids from cod-liver oil. W. J. DANN and T. MOORE (Biochem. J., 1933, **27**, 1166—1169).—The mixed fatty acids (I) obtained by brief hydrolysis (aq. EtOH–KOH)

of cod-liver oil show only relatively low absorption (ultra-violet region) without fine structure. The acids obtained by more prolonged hydrolysis [or by further treatment of (I) with EtOH–KOH] show much more intense absorption, and definite signs of fine structure are evident. The absorption spectra of stearic and oleic acids are unaffected by treatment with KOH; the absorption of linoleic acid (II) increased about fourfold. There is no significant change in the degree of unsaturation (I vals.) of (I) or (II), indicating that increased absorption may be related to an isomeric change involving the double linkings of the more highly unsaturated acids. H. B.

Low-temperature absorption spectrum of pepsin. G. I. Lavin, J. H. Northrop, and H. S. Taylor (J. Amer. Chem. Soc., 1933, **55**, 3497—3498).—The absorption band of pepsin at 2600—2900 Å. is resolved into sharp narrow bands by cooling to −100°. Serum- and ov-albumin have narrow bands at low temp. J. G. A. G.

Infra-red radiations from small particles. A. H. Pfund (J. Opt. Soc. Amer., 1933, **23**, 270—272; cf. A., 1932, 212).—Powder films of quartz, $BaSO_4$, and K_2CO_3, the particle size of which is small compared with the wave-length, show pronounced emission max. within the region of selective absorption. The behaviour of quartz powder is the inverse of that of a polished plate. N. M. B.

Influence of H′ and OH′ ions in concentrated acids and alkalis on the infra-red absorption spectrum of water. R. Suhrmann (Z. Elektrochem., 1933, **39**, 642; cf. A., 1932, 1188).—Aq. H_2SO_4 (2·80, 1·40*N*), HCl (5·50, 2·75*N*), and KOH (10·9, 5·47, 2·73*N*) show a lowering of the normal absorption max. of H_2O at 0·98, 1·20, and 1·96 μ, respectively. The absorption on the long wave-length side of the band at 1·45 μ is increased. This result is attributed to association of H_2O mols. with the ions. H. J. E.

Infra-red dispersion of carbon dioxide. A. Parts and A. Tudeberg (Anal. Fís. Quím., 1933, **31**, 319—324).—A dispersion formula is derived which yields a val. of $1·00 \times 10^{-18}$ for the dipole moment of the C:O linking. H. F. G.

Resolution of the two difference bands of CO_2 near 10 μ. E. F. Barker and A. Adel (Physical Rev., 1933, [ii], **44**, 185—187).—The rotational structure of the two absorption bands at 9·4 and 10·4 μ is completely resolved; both bands have positive and negative, but no zero, branches. The moment of inertia is $70·6 \times 10^{-40}$ g.-cm.^{2} N. M. B.

Measurements of the rotation spectrum of water vapour. J. Kühne (Z. Physik, 1933, **84**, 722—731).—A vac. grating spectrometer was used to investigate this spectrum between 30 and 90 μ. A. B. D. C.

Rotation-vibration bands of ammonia. E. Fermi (Nuovo Cim., 1932, [ii], **9**, 277—283; Chem. Zentr., 1933, i, 1244—1245).—Theoretical. A. A. E.

Vibration structure of the carbon tetrachloride spectrum. J. Horiuti (Z. Physik, 1933, **84**, 380—392).—Resonance of the combination tone (315+457) cm.$^{-1}$ and the fundamental 774 cm.$^{-1}$ is investigated, and fits the empirical vibration spectrum. A. B. D. C.

Raman effect and its application to mineral chemistry. H. Volkringer (Bull. Soc. chim., 1933, [iv], **53**, 445—468).—A lecture.

Applications of the Raman effect to organic chemistry. M. Bourguel (Bull. Soc. chim., 1933, [iv], **53**, 469—505).—A lecture.

Rotation Raman spectrum of O_2 at high pressures. B. Trumpy (Z. Physik, 1933, **84**, 282—288).—The rotation Raman spectrum of O_2 showed lines up to 60 atm. pressures; at 15 atm. the intensity of the lines agreed with theory. A. B. D. C.

Relation between the Raman spectra of different halides. O. Redlich (Z. Elektrochem., 1933, **39**, 571; cf. this vol., 113).—For H_2SnBr_6, 5 lines were observed; only 3 were expected. H. J. E.

Existence of $NaHSO_3$ in solution. P. Fadda (Nuovo Cim., 1932, **9**, 227—230; Chem. Zentr., 1932, ii, 3838).—In the Raman spectra of solutions of $NaHSO_3$ only S_2O_5'' and not HSO_3' frequencies occur, showing that $NaHSO_3$ does not exist in solution. The lines 571 and 1054 ascribed to S_2O_5'' belong to HSO_4'. L. S. T.

Nuclear vibration spectrum of acetylacetone. K. W. F. Kohlrausch [with A. Pongratz and J. Koppl] (Anal. Fis. Quim., 1933, **31**, 315—318).—The oscillation frequencies of the CO group in a no. of aldehydes, ketones, acids, and esters are recorded; for each class of compound the variations from the mean are small. In symmetrical compounds containing 2 CO groups only 1 line due to CO appears (in the range < 2000 cm.$^{-1}$), and its frequency is increased by conjugation of the CO groups. In unsymmetrical mols. 2 lines appear; *e.g.*, $AcCO_2H$ exhibits the lines characteristic of ketones and of acids. CH_2Ac_2 exhibits the ketone line (1719 cm.$^{-1}$), and 2 lines (1593 and 1655 cm.$^{-1}$) characteristic of the C:C linking. The substance therefore exists as a tautomeric mixture of 1 keto- and 2 enol forms. H. F. G.

Raman spectra of *cis*- and *trans*-1 : 2-dimethyl*cyclo*hexanes. O. Miller and L. Piaux (Compt. rend., 1933, **197**, 412—414).—The Raman spectra of the isomerides (cf. this vol., 815) are radically different, having out of 24 lines measured between 315 and 2975 cm.$^{-1}$ only 5 the same; substances previously obtained were probably mixtures (cf. A., 1932, 213, 1240). C. A. S.

Predissociation in fluorescence emission spectra: fluorescence of acetone vapour. H. G. Crone and R. G. W. Norrish (Nature, 1933, **132**, 241).—With the Hg line 3340 Å. as excitant, visible fluorescence of $COMe_2$ is accompanied by considerable emission in the ultra-violet extending down to the exciting line. The visible fluorescence consists of diffuse bands, whilst the ultra-violet fluorescence consists of a series of fine, sharp lines. This is the first example of predissociation associated with fluorescence, and represents a transition from an

upper excited level to a lower metastable level. Predicted absorption in the near infra-red and a region of discrete structure in the ultra-violet absorption have been verified. L. S. T.

Conservation of kinetic moment and the rules of polarisation in spectroscopy. Application to the diffusion of light and to fluorescence. A. KASTLER (J. Phys. Radium, 1933, [vii], 4, 406—420).—Mathematical. N. M. B.

Polarisation of fluorescent light. (MLLE.) J. CAHEN (J. Chim. phys., 1933, 30, 420—428).—The degree of polarisation, p, of light emitted by solutions of fluorescent org. compounds in H_2O and in aq. and anhyd. glycerol, increases with increasing viscosity of the solvent, approaching a limiting val. for each substance as $\eta \longrightarrow \infty$. This val. varies considerably with the wave-length of the exciting light, each absorption band giving a different val. of p. D. R. D.

Destruction of zinc sulphide phosphors by α-rays. II. P. M. WOLF and N. RIEHL (Ann. Physik, 1933, [v], 17, 581—586).—The mechanism of the change in ZnS phosphors by α-rays is explained and the relation between the change in the phosphor and the part played by impurities is considered. W. R. A.

Temperature dependence of scintillation processes and the destruction of phosphors. N. RIEHL (Ann. Physik, 1933, [v], 17, 587—592).—The relation between the brightness of the scintillation of ZnS and the temp. has been investigated between −252° and 600°. Above 200° (but not below) the luminescence on exposure to α-rays diminishes gradually to 500°, where it disappears. Similar behaviour results from photo-excitation and by breaking the crystals. None of the known inorg. phosphors is luminescent above 500°; α-rays, therefore, increase or decrease the luminescence according to the temp. W. R. A.

Mechanisms of luminescence phenomena in the burning of combustible gases in air. PIETTRE (Ann. Office nat. Combust. liq., 1932, 7, 699—719; Chem. Zentr., 1933, i, 1260).—A summary and discussion. A. A. E.

Solarisation of luminiferous calcite. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 220—231; cf. this vol., 661).—Theoretical relations, confirmed by experiment, are developed for the rate of growth of the radiator of photoluminescence during excitation and for the rate of its decay after cessation of excitation. J. W. S.

Stopping layer of rectifiers. W. JUSE (Nature, 1933, 132, 242).—Rectification depends on the thickness of the contact layer between a semi-conductor and a metal within narrow limits (10^{-5} to 10^{-6} cm.). L. S. T.

Crystal photo-effect. A. JOFFÉ and A. F. JOFFÉ (Nature, 1933, 132, 168—169).—The assumption that the equilibrium of electrons in an illuminated crystal is dynamic, and consists of a continuous circulation of electrons between the bright and dark parts of a crystal, agrees with experimental facts. L. S. T.

Influence of metal surface on the position of selectivity of the external photo-electric effect. F. HLUCKA (Z. Physik, 1933, 84, 364—366).—The condition of the metal surface, although determining the long wave-length limit of sensitivity, does not displace the selective max. A. B. D. C.

Selectivity of the external photo-electric effect of alloys. F. HLUCKA (Z. Physik, 1933, 84, 367—369).—Spectral selectivity for alloys is additive of the constituent metals. A. B. D. C.

Internal photo-electric effect in amorphous substances. D. N. NASLEDOV, L. M. NEMENOV, and P. V. SHARAVSKI (J. Exp. Theor. Phys., Russia, 1932, 2, 97—101). CH. ABS.

Photo-electric effect with the carborundum detector. P. SPECHT (Physikal. Z., 1933, 34, 640).—The SiC detector shows a photo-potential with small contact pressures. For instantaneous currents, the photo-active places exhibit towards others a strong rectifying action. There was direct proportionality between photo-potential and unipolar conductivity. Experiments on the dependence of the photo-effect on the radiated energy gave no linear current curve. The potential and current reach saturation vals. A. J. M.

External photo-electric effect of alkali halide crystals. R. FLEISCHMANN (Z. Physik, 1933, 84, 717—721).—The dependence of photo-electric effect sensitivity on wave-length is examined for KBr; for the alkali halides, particularly KBr, illumination with short-wave ultra-violet light gives a new absorption region which is photo-electrically effective. A. B. D. C.

Thermal and photo-electric emission of cæsium–cæsium oxide cathodes, and the effect of cæsium atoms in the dielectric. P. GÖRLICH (Z. Physik, 1933, 85, 128—130).—An alternative method for getting Cs atoms in the dielectric is described (cf. de Boer and Teves, this vol., 887). A. B. D. C.

Behaviour of electrons and "holes" in cuprous oxide. A. JOFFÉ, D. NASLEDOV, and L. NEMENOV (Nature, 1933, 132, 239—240). L. S. T.

Photo-electric effect in the contact layer under the action of ultra-violet light. D. N. NASLEDOV and L. M. NEMENOV (J. Exp. Theor. Phys., Russia, 1932, 2, 179—182).—In Cu_2O–Zn, ultra-violet light drives the electrons from Cu_2O to Zn. CH. ABS.

Photo-electric effect in single crystals of cuprite. G. MÖNCH and R. STÜHLER (Z. Physik, 1933, 85, 131—134).—Polemical, against Deaglio (this vol., 554). A. B. D. C.

Electrical conduction in solids with high field strengths. A. VON HIPPEL (Z. Elektrochem., 1933, 39, 506—512; cf. A., 1932, 565).—The field strengths necessary for the passage of a spark through crystals of halides of Li, Na, K, and Rb were measured. Vals. between 3·2 and $0{\cdot}4 \times 10^6$ volt per cm. were observed, decreasing for a given halide in the order Li⟶Rb, and for a given alkali metal in the order F⟶I. For NaCl breakdown took place most easily along the [110] plane. Results are correlated with lattice structure. H. J. E.

Dependence of transport characteristics on temperature and the mechanism of the reverse voltage in solid ionic conductors. A. SMEKAL (Z. Elektrochem., 1933, **39**, 542—543).—A discussion. H. J. E.

Electron and lattice disarrangement in crystalline polar compounds as basis for electronic and ionic conduction. C. WAGNER (Z. Elektrochem., 1933, **39**, 543—545).—The changes in conductivity of ZnO, CdO, Cu_2O, NiO, and CuO between 500° and 1000° with the O_2 pressure of the surrounding atm. are correlated with changes in electron distribution and lattice structure in the solids. H. J. E.

Transport of matter in solid bodies. G. VON HEVESY (Z. Elektrochem., 1933, **39**, 490—500).—A survey of recent work on conduction and diffusion in solids. H. J. E.

Electrical conduction and diffusion in non-metallic solids. C. TUBANDT (Z. Elektrochem., 1933, **39**, 500—506).—A summary. H. J. E.

Dependence of electrical conductivity and self-diffusion in crystals on the crystallographic direction. W. SEITH (Z. Elektrochem., 1933, **39**, 538—542; cf. A., 1929, 1136).—The conductivity of solid PbI_2 was measured parallel and perpendicular to the *c* axis at temp. between 200° and 400°. The contribution of the Pb and I ions in the two cases is discussed. The self-diffusion of Pb in PbI_2, measured with Th-*B* as radioactive indicator, was independent of the crystallographic direction. For Bi, with Th-*C* indicator, the val. parallel to the *c* axis was very small, but, perpendicular, it had an abnormally high temp. coeff. H. J. E.

Relation between the electrical conductivity of glass and the strain. E. G. BACKER (Z. Elektrochem., 1933, **39**, 554—555).—The electrical conductivity of glass may be used to measure the strain of heat-treatment. H. J. E.

Electrical conduction in zeolites. E. RABINOWITSCH and W. C. WOOD (Z. Elektrochem., 1933, **39**, 562—566).—Natural zeolites had sp. resistances between approx. 0·1 and 100 ($\times 10^8$) ohms. The val. for chabasite (I) increased with progressive dehydration. Treatment of the partly dehydrated material with NH_3 lowered the resistance. In the electrolysis of (I), H_2 is liberated according to Faraday's law. The resistance of (I) falls rapidly on raising the temp. The mechanism of electrolysis is discussed. H. J. E.

Electrical conductivity of Cu_3Pd and Cu_3Pt alloys at low temperatures with disordered and ordered atomic distributions. H. J. SEEMAN (Z. Physik, 1933, **84**, 557—564).—Unlike Cu_3Au, Cu_3Pd and Cu_3Pt show only small increases in the resistance drop due to a fall in temp. when ordered replaces disordered at. distributions. *X*-Rays reveal no differences in these alloys, but magnetic measurements suggest that the difference between the Au and Pd or Pt alloys is due to a difference in behaviour of the valency electrons. A. B. D. C.

Electrical conductivity of cuprous oxide. V. ZHUSE and B. KURCHATOV (J. Exp. Theor. Phys., Russia, 1932, **2**, No. 5—6, 309—318).—The electrical conductivity of Cu_2O increases with the O content; that of pure Cu_2O at 12° is $2{\cdot}7\times10$ mho per cm. The computed work of dissociation of the electron is 0·72 volt. The work of dissociation in well-conducting samples is 0·134—0·129 volt. CH. ABS.

Electrical and optical behaviour of semiconductors. IX. Mechanism and origin of the "dark" current and the electrical conductivity of cuprous oxide. E. ENGELHARD (Ann. Physik, 1933, [v], **17**, 501—542).—The influence of heat-treatment in O_2 and in vac. on the electrical conductivity and the Hall const. of Cu_2O has been investigated between —70° and room temp. W. R. A.

Transitions in solidified gases. K. CLUSIUS (Z. Elektrochem., 1933, **39**, 598—601; cf. A., 1930, 1103).—Theoretical. In gases with high dipole moment (*e.g.*, HF, H_2O, NH_3) free rotation in the solid state is hindered, and transition points are not observed. With lower dipole moments (HCl, HBr, HI, H_2S, PH_3), and when the dispersion effect is more marked, transition points occur. H. J. E.

Dielectric constant of Volkenroda. H. LOWY (Physikal. Z., 1933, **34**, 674—676).—The dielectric const. of minerals in the Volkenroda potash mines is < normal. This supports the view that such decrease in dielectric const. is due to the presence of mineral oil. A. J. M.

Calculation of dielectric constant of a salt from a single determination with a salt mixture. D. A. G. BRUGGEMAN (Naturwiss., 1933, **21**, 577—578).—A formula derived for the dielectric const. of a pure salt from that of an isotropic mixture is tested with $Pb(NO_3)_2$. This can exist in octa- or tetrahedral crystals, and otherwise fulfils the conditions, satisfactory agreement being obtained. A. J. M.

Variation of the dielectric constants of bromine and iodine chloride vapours with temperature and pressure. K. F. LUFT (Z. Physik, 1933, **84**, 767—782).—Br has zero moment, ICl $0{\cdot}5\times10^{-18}$ e.s.u. A. B. D. C.

Dipole moment and association. G. BERGER (Z. physikal. Chem., 1933, **B**, **22**, 283—297).—B.-p. elevation measurements with C_6H_6 solutions of various aromatic compounds have shown that there is no general parallelism between dipole moment and association. Probably the latter is determined by group moments of substituents, as well as by the total moment. With position isomerides of disubstituted C_6H_6 derivatives and with various monosubstituted compounds the association is approx. proportional to the dipole moment. In some instances the latent dipoles of the C_6H_6 and $C_{10}H_8$ nuclei probably contribute to association. The association of phenols, anilines, alcohols, and acids is abnormally high, which is attributed to the moment of the polar group increasing with concn. R. C.

Dielectric constants and water of crystallisation of alums. [J.] ERRERA and H. BRASSEUR (Compt. rend., 1933, **197**, 480—482; cf. this vol., 663).—The dielectric const., ε, of the Al alums of

Cs, Rb, NH_4, K, and Tl^I, and the NH_4 alums of Cr and Fe (respectively 5·2, 5·7, 6·0, 6·6, 7·1, 7·0, and 7·9) increases approx. with decreasing at. vol. of the metal and m.p. of the alum. Only NH_4 Fe alum shows dispersion of ε at room temp.; ε increases slightly with temp. between 20° and the m.p., more so for greater wave-lengths. It is thus smaller the more strongly the H_2O is bound, and its relation to at. vol. suggests that the metal atoms are in the neutral rather than the ionic state. C. A. S.

Association of some salicylic esters and deformation of their molecules deduced from their dipole moments. C. Hrynakowski and C. Kalinowski (Compt. rend., 1933, **197**, 483—484).—The dipole moments of Ph, Et, and Me salicylate are respectively 3·15, 2·88, and $2·41 \times 10^{-18}$ e.s.u.; the association (at 40·2°) is respectively 71·56, 62·37, and 51·70% (55·86 at 13·2°). The unusually large difference between the moments of the Et and Me esters is due to the greater length of the former mol. and its deformation due to the OH group in the *o*-position. C. A. S.

Measurements of dielectric losses in castor oil. J. L. Snoek (Physica, 1932, **12**, 234—238; Chem. Zentr., 1932, ii, 3841).—Dielectric losses in relation to frequency and viscosity have been determined from 20° to 90°. The results agree with Debye's theory. The dielectric const. of castor oil Me ester is only slightly > that of the oil itself, and the losses are smaller owing to the smaller viscosity. L. S. T.

Refractive index. III. A. M. Taylor and (Miss) D. A. Durfee (J. Opt. Soc. Amer., 1933, **23**, 263—269; cf. this vol., 765).—The distance of penetration of light into the second medium at total reflexion was measured interferometrically, and the intensity of the superficial wave relative to the state of polarisation was obtained. Discrepancies in the laws of reflexion, as found with saturated aq. $KMnO_4$, are explained in terms of adsorbed surface layers. N. M. B.

Abbé's number and the constitution of liquid organic compounds. W. Bielenberg (Physikal. Z., 1933, **34**, 632).—Abbé's no., $\nu=(n_D-1)/(n_F-n_C)$ for dispersion, is a constitutive property. Rules for its use in the case of hydrocarbons are given. The no. can be derived from Drude's formula involving the characteristic frequencies of atoms and groups. A. J. M.

Dispersion measurements for potassium bromide and iodide in the infra-red. K. Korth (Z. Physik, 1933, **84**, 677—685).—Refractive indices for KI are given between 14 and 21 and for KBr between 14 and 20 μ. The method of prep. of these crystals artificially is given. A. B. D. C.

Rotatory dispersion of organic compounds. XXII. Borotartrates and bromomalates. B. Jones (J.C.S., 1933, 951—955).—The prep. of *NH₄, K Et*, and *K Me borotartrates*, and *K boromalate* (I) is described. The rotatory dispersion of solutions of each compound has been measured for 20 different wave-lengths, ranging from λ 6708 to 3590. Crystallographic data are given for (I). E. S. H.

Magnetic rotatory power of gases and vapours. P. Gabiano (Ann. Physique, 1933, [x], **20**, 68—131).—Using a special magneto-polarimeter, data are obtained for 24 gases and vapours, and are compared for the gaseous and liquid states. Verdet consts. and sp. at. rotations are calc. N. M. B.

Kerr effect with isomeric benzene derivatives. G. Otterbein (Physikal. Z., 1933, **34**, 645—646; cf. A., 1931, 669).—It is possible to calculate the Kerr const. of substitution products of C_6H_6 knowing the increments due to the substituting groups. PhCl and the three $C_6H_4Cl_2$ are taken as examples. A. J. M.

Two different states of liquid carbon disulphide. M. Wolfke and J. Mazur (Acta phys. Polonica, 1932, **1**, 63—69; Chem. Zentr., 1932, ii, 3828). L. S. T.

Structure of ammines of platinous chloride. F. W. Pinkard, H. Saenger, and W. Wardlaw (J.C.S., 1933, 1056—1060).—The prep. of the following compounds is described: *α-chloroamminodipyridino-* and *α-chlorodiamminopyridino-platinous chloride*, *β-chloroamminodipyridinoplatinous chloroplatinite*, *α-hydroxylamino-amminodipyridinoplatinous chloride* and *-tripyridinoplatinous chloroplatinite*, *α-dihydroxylaminodipyridinoplatinous chloride*, and *-amminopyridinoplatinous chloride*. A study of the decomp. of these compounds by HCl and of the action of $C_2H_4(NH_2)_2$ on α-platinous diammines suggests that the α-diammines have a *trans*-planar configuration, and that amine groups in *trans* positions are always eliminated by HCl from the tetrammines. It is suggested that the theoretical basis for Werner's hypothesis of *trans* elimination may be *trans* pairing when Pt has a covalency of 4. E. S. H.

Stereochemistry of crystal compounds. XI. Structural formulæ of crystal compounds, especially of silicates. P. Niggli (Z. Krist., 1933, **86**, 121—144).—Various methods of formulating silicates are discussed, with special reference to possible replacements of an element by one of another valency. Constitutional formulæ are suggested to show linkings between atoms. Graphical formulæ are proposed, somewhat similar to those of Rheinhold (cf. A., 1931, 1217), to indicate co-ordination nos. and the *X*-ray structure of the unit cell. C. A. S.

Stereochemistry of crystal compounds. X. Molecular and crystalline configuration. P. Niggli and W. Nowacki (Z. Krist., 1933, **86**, 65—99).—A discussion on the connexion between the possibilities of formation of a mol. and of a crystal lattice by the resultant mols., with special reference to the combining and co-ordination nos. of the constituent atoms. C. A. S.

General formula for lattice energy of crystals of any structure. A. Kapustinski (Z. physikal. Chem., 1933, **B**, **22**, 257—260).—The equation $U-256·1\Sigma n\eta_1\eta_2/(r_K+r_A)$ has been deduced for the energy, *U*, of any heteropolar lattice, where Σn is the no. of ions in the mol., and *r* and η are the effective ionic radii and valencies. R. C.

Crystal lattice energies and the Born–Haber cycle. A. Kapustinski and B. Veselovski (Z.

physikal. Chem., 1933, **B**, **22**, 261—266).—The energies calc. by Kapustinski's formula (cf. preceding abstract) agree with the vals. derived from experimental data by the cycle process as well as do those calc. by Born's formula. R. C.

Diamagnetism of thin films of bismuth. A. GOETZ (Nature, 1933, **132**, 206—207).—An explanation of the discrepancy between the results of Lane (this vol., 114) and those of other workers is advanced. L. S. T.

Diamagnetism of thin films of bismuth. S. R. RAO (Nature, 1933, **132**, 207; cf. preceding abstract).—A criticism (cf. this vol., 114). L. S. T.

Variation with temperature of the diamagnetic constant of water. B. CABRERA and H. FAHLENBRACH (Anal. Fís. Quím., 1933, **31**, 401—411).—The susceptibilities of H_2O and ice, respectively, at 0° are $-7{\cdot}177\times10^{-4}$ and $-7{\cdot}019\times10^{-7}$. For both the susceptibility varies linearly with temp. (between 0° and 100°, and 0° and −60°, respectively). The results are discussed in relation to the association of H_2O. H. F. G.

Diamagnetism and temperature. B. CABRERA and H. FAHLENBRACH (Compt. rend., 1933, **197**, 379—381).—The deviations from the law of additivity of mol. susceptibility are due to structural deformations in the outer portions of the atoms. χ is approx. independent of temp. in the solid and in the liquid state, but shows a sudden change on fusion, due to deformations caused by the cryst. forces. C. A. S.

Magnetic investigation of single electron linkings in compounds of the type tellurium dimethyl dihalide. S. S. BHATNAGAR and T. K. LAHIRI (Z. Physik, 1933, **84**, 671—675).—Investigation of the susceptibility of $TeMe_2X_2$ (X=Cl, Br, I, or NO_3) indicates that the single electron linking assumed by Lowry and Gilbert (A., 1929, 127) is not established. A. B. D. C.

Paramagnetism of salts. C. J. GORTER (Physica, 1931, **11**, 171—181; Chem. Zentr., 1933, i, 1256).—A discussion. A. A. E.

Paramagnetism and the molecular field of neodymium. P. W. SELWOOD (J. Amer. Chem. Soc., 1933, **55**, 3161—3177; cf. A., 1931, 788).—Magnetic susceptibility data in the range −190° to 100° are recorded for NdF_3, $Nd(NO_3)_3$, $Nd(ClO_4)_3$, $Nd_2(SO_4)_3$, $Nd_2(SO_4)_3{,}8H_2O$, 0·5—41 wt.-% $Nd(NO_3)_3$ in 90% EtOH, $H_2C_2O_4$, Pyrex glass, Nd_2O_3, La_2O_3, and mixtures of 2—50 wt.-% of Nd_2O_3 with La_2O_3. Although the results are in general accord with Van Vleck's quantum mechanical theory of paramagnetism, important discrepancies exist. The prep. of *anhyd.* $Nd(ClO_4)_3$ is described. J. G. A. G.

Susceptibilities of paramagnetic solutions. E. VOGT (Physikal. Z., 1933, **34**, 687—688).—Criticisms of the papers by Gorter (this vol., 664) and Fahlenbrach (this vol., 340). A. J. M.

Molecular volumes of ammonium phosphates. W. BILTZ and L. LE BOUCHER (Anal. Fís. Quím., 1933, **31**, 427—433).—Anhyd. $(NH_4)_3PO_4$ is prepared by treating dehydrated (over H_2SO_4) $(NH_4)_2HPO_4$ with liquid NH_3 under pressure for several days; it has d^{-78} 1·480. If $(NH_4)_2HPO_4{,}3H_2O$ is used the ratio $NH_4 : PO_4$ in the product is $> 2{\cdot}6$. The densities of $(NH_4)_3PO_4$, $(NH_4)_2HPO_4$, $(NH_4)H_2PO_4$, NH_4PO_3, and $(NH_4)_4P_2O_7$ at temp. down to −195° are recorded. The calc. zero vols. of the anions are normal, but < those for the free acids; for HPO_4'' and H_2PO_4' the zero vols. lie between those of PO_4''' and H_3PO_4. H. F. G.

Determination of the parachor by the drop-weight method. I. G. SEMERANO. **II.** G. SEMERANO and G. FABBRANI (Atti Accad. Veneto-Trentino-Istriana, 1932, **23**, 17—32, 33—44; Chem. Zentr., 1933, i, 1915).—I. A discussion.

II. Vals. have been determined for methylsuccinimide in C_5H_5N and $PhNO_2$, and for succinimide and pyruvimide in C_5H_5N and H_2O. The linear relation describing the contribution of the solvent and solute to the parachor of a solution is strictly valid only when the components have the sam surface tension. A. A. E.

Liquid drops on the surface of the same liquid. L. D. MAHAJAN (Z. Physik, 1933, **84**, 676; cf. this vol., 223).—Further observations show that between the drop and the surface there exists a layer of air or equiv. surrounding medium. A. B. D. C.

Surface tension of molten metals and alloys. IV. Alteration with time of the surface tensions and the drop method of measurement at high temperatures. F. SAUERWALD and B. SCHMIDT (Z. anorg. Chem., 1933, **213**, 310—318).—The surface tension of Hg in high vac. lies between the initial and end vals. in air. The val. for Sn is independent of the time under a pressure of 5×10^{-5} mm., whereas that for Tl increases with time at 10^{-5} to 10^{-4} mm. A. R. P.

Capillary ascent or depression of liquids in cylindrical tubes. A. W. PORTER (Trans. Faraday Soc., 1933, **29**, 702—707).—Tables for the capillary correction h_0 are given supplementing those of Cawood and Patterson (this vol., 367). J. S. A.

Dependence of focussing effect obtained with curved crystals in *X*-ray spectroscopes on the bending mechanism of the crystal. E. CARLSSON (Z. Physik, 1933, **84**, 801—810). A. B. D. C.

Non-crystallographic point-groups. W. NOWACKI (Z. Krist., 1933, **86**, 19—31). C. A. S.

Crystal lattice and spontaneous striction. A. PERRIER (Helv. phys. Acta, 1932, **5**, 306—310; Chem. Zentr., 1933, i, 742).—The extent to which a lattice-like arrangement of magnetic dipoles brings about a spontaneous striction is discussed. L. S. T.

Scattering of *X*-rays from powdered crystals at low temperatures. G. E. M. JAUNCEY and F. PENNELL (Physical Rev., 1933, [ii], **44**, 138—140).—Indication of a slight change (cf. this vol., 115, 558) in the true atom form factor was found by scattering at 295° and 103° abs. for KCl, but not for NaF. N. M. B.

Diffuse scattering of *X*-rays from sylvine. IV. Scattering at high temperatures. G. G. HARVEY (Physical Rev., 1933, [ii], **44**, 133—137; cf. this vol., 666).—Intensity measurements at 630° and

1020° abs. are in good agreement with the general expression previously found. N. M. B.

Vicinal faces and the work of Parker. G. KALB (Z. Krist., 1933, **86**, 1—7; cf. A., 1932, 682). C. A. S.

Effect of temperature and use of monochromatic radiation in the scattering of X-rays in carbon tetrachloride vapour. W. VAN DER GRINTEN (Physikal. Z., 1933, **34**, 609—618).—Apparatus for the investigation of scattering of *X*-rays by gases at high temp. is described, and is applied in the determination of the scattering curves of CCl_4 vapour at 100° and 350°. The effect of at. oscillations on *X*-ray interference in gases and crystals is compared. The use of monochromatic radiation gives for CCl_4 satisfactory agreement with theory. A. J. M.

Liquid metal single crystals. I. E. DONAT and O. STIERSTADT (Ann. Physik, 1933, [v], **17**, 897—914).—An improved method of preparing single Bi crystals is described. When such a crystal is heated to $\geqslant$ 10° above its m.p. it shows the same orientation after re-solidifying, suggesting that the melt itself is cryst. No asymmetry is observed in the conductivity of the melt, but this has no significance, as the passage of current disturbs the orientation of the melt. A method for expressing the anisotropy of any physical property of crystals is developed. J. W. S.

***X*-Ray examination of electrolytic chromium deposits.** G. R. LEVI and M. TABET (Atti R. Accad. Lincei, 1933, [vi], **17**. 647—653).—From *X*-ray measurements data are obtained regarding the size of the particles in Cr deposits prepared by the electrolysis of solutions of $Cr_2(SO_4)_3$, CrO_3, and NH_4 chromioxalate, respectively, and also of Cr obtained by thermal reduction. O. J. W.

Amorphous–crystalline transformation of arsenic and of antimony. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1933, [vi], **17**, 565—569).—*X*-Ray measurements show that the change of amorphous As to the cryst. form is accelerated by various catalysts, particularly by conc. HI. There is no definite transition point, and the change may occur as low as 180°. Amorphous Sb can be obtained in presence of $SbCl_3$. Reduction of Sb compounds in the absence of $SbCl_3$ gives cryst. Sb. The change of amorphous to cryst. Sb may take a few min. to several hr. in the temp. range 250—100° and does not require a catalyst. No amorphous preps. of Bi could be obtained. O. J. W.

Crystal structure of $LaSn_3$ and $LaPb_3$. A. ROSSI (Atti R. Accad. Lincei, 1933, [vi], **17**, 839—846).—The following data are obtained by the powder method: $LaSn_3$, a 4·77 Å., d 7·15—7·20 $d_{calc.}$ 7·516; $LaPb_3$, a 4·893, d 10·50, $d_{calc.}$ 10·71. O. J. W.

***X*-Ray proof of [existence of] ZrW_2.** A. CLAASSEN and W. G. BURGERS (Z. Krist., 1933, **86**, 100—105).—*X*-Ray examination of a W wire on which, when incandescent, Zr had been deposited from its vapour showed the presence of a face-centred cubic *compound*, ZrW_2, with a 7·61 Å., 8 mols. in unit cell, Zr—W=3·15 Å., $d_{calc.}$ 13·78. The structure resembles that of $MgCu_2$ (cf. A., 1928, 109). ZrW_2 was prepared by volatilising Zr on to W and heating for 20 hr. at 1800°; it contained a slight excess of Zr, and had d 12—13·5, m.p. > 2200°. C. A. S.

Constitution of anodically deposited Ta_2O_5 layers. P. O. SCHUPP (Z. Physik, 1933, **84**, 412—424).—Study of the formation of Ta in non-aq. solutions indicates that the high potential across the Ta_2O_5 layer is due to work required to remove electrons from the layer to the electrolyte, and not to electrical resistance of the layer (cf. Günther-Schulze and Betz, A., 1932, 214); during formation the layer is first porous and finally non-porous. A. B. D. C.

Crystal structure of rhombic chromium carbide. K. HELLBOM and A. WESTGREN (Svensk Kem. Tidskr., 1933, **45**, 141—150; cf. A., 1927, 279).—Rotation and powder diagrams of Cr_3C_2 were obtained. The space-group is V_h^{16}. The crystal probably consists of parallel long-chain mols. R. P. B.

Crystal structure of nitrides and phosphides of bivalent metals. M. VON STACKELBERG and R. PAULUS (Z. physikal. Chem., 1933, **B**, **22**, 305—322).—Crystals of Mg_3P_2 have a cubic structure with 16 mols. in the unit cell and the space-group T_h^7. The P atoms form a somewhat deformed closest-packed cubic lattice, and the Mg atoms occupy three quarters of the tetrahedral interstices. Be_3P_2, Be_3N_2, Mg_3N_2, and α-Ca_3N_2 have the same structure. The lattices of a second form of Ca_3N_2, Sr and Ba nitrides, and Ca, Sr, and Ba phosphides are not cubic. Zn_3P_2, Cd_3P_2, and Zn_3As_2 crystallise in the cubic system, but not with the Mg_3P_2 lattice, and have 16 mols. in the unit cell; they are metallic in character. R. C.

Crystal structure of zinc hydroxide. R. B. COREY and R. W. G. WYCKOFF (Z. Krist., 1933, **86**, 8—18; cf. A., 1928, 350; 1932, 214).—$Zn(OH)_2$ cryst. from aq. NH_3 (cf. A., 1927, 731) is orthorhombic with a 5·16, b 8·53, c 4·92 Å., and 4 mols. in the unit cell, space-group V^4. Each Zn is surrounded by 4 OH forming a distorted tetrahedron in which Zn—O=1·95 Å., and OH—OH is > 3 Å.; in adjacent tetrahedra OH—OH=2·83 Å. C. A. S.

Structure and polymorphism of the hydrogen halides. G. NATTA (Gazzetta, 1933, **63**, 425—439).—The existence of a face-centred cubic form of solid HBr is confirmed, with 4 mols. per unit cell, a 5·76—5·78 Å., v 191—193$\times10^{-24}$ c.c., $d_{calc.}$ 2·76—2·80. The form of HBr stable below 100° abs. is face-centred rhombic, with 4 mols. per unit cell, a 5·555, b 5·64, c 6·063$\pm$0·01 Å., v 190$\times10^{-24}$ c.c., $d_{calc.}$ 2·81, space-group V^7 or V_h^{23}. The cubic form of HCl, stable above 98° abs., has a 5·46 Å., v 162·8$\times10^{-24}$ c.c., $d_{calc.}$ 1·48. The face-centred rhombic form of HCl, stable below 98° abs., has 4 mols. per unit cell, a 5·03, b 5·35, c 5·71$\pm$0·02 Å., v 154·7$\times10^{-24}$ c.c., $d_{calc.}$ 1·55, space-group V^7 or V_h^{23}. O. J. W.

Crystal structure of anhydrous magnesium and calcium iodides. H. BLUM (Z. physikal. Chem., 1933, **B**, **22**, 298—304).—These compounds are isomorphous with CdI_2 (type $C6$). MgI_2 has a_0 4·14$\pm$0·02, c_0 6·88$\pm$0·03 Å., and CaI_2 has a_0 4·48$\pm$0·02, c_0 6·96$\pm$0·03 Å. R. C.

Crystal structure of cadmium iodide. O. HASSEL (Z. physikal. Chem., 1933, **B**, **22**, 333—334).—A modification of Bozorth's structure (A., 1922, ii, 851) is proposed. R. C.

Structure and polymorphism of silver cyanide. G. NATTA and O. VECCHIA (Gazzetta, 1933, **63**, 439—448).—The stable form of AgCN is rhombohedral, with 2 mols. per unit cell, a 5·99±0·01 Å., c/a 0·877, mol. vol. 46·8, $d_{calc.}$ 4·72, space-group C_{3v}^6. The cubic form, observed only as a solid solution in AgBr, has 4 mols. per unit cell, a 5·69±0·03 Å., mol. vol. 46·0, $d_{calc.}$ 4·80, space-group T' or Td'. The physical properties of AgCN and of the Ag halides, especially the solubility, are related to the apparent contraction of the anion due to the polarising action of the cation. O. J. W.

Crystal structure of boron phosphate and boron arsenate. G. E. R. SCHULZE (Naturwiss., 1933, **21**, 562).—The crystal structures of BPO_4 and $BAsO_4$ are similar, being of the SiO_2 type, with O arranged tetrahedrally around P, As, and B, each O atom belonging to two tetrahedra. The space-group is S_4^2. The unitary cells contain 2 mols. and have respectively a 4·334±0·008, 4·459±0·006; c 6·636±0·008, 6·796±0·006 Å.; c/a 1·534, 1·524. A. J. M.

Crystal structure of carbonatotetrammino-cobaltic sulphate. L. W. STROCK (Z. Krist., 1933, **86**, 42—52).—$[Co(NH_3)_4CO_3]SO_4,3H_2O$, prepared according to Jorgensen's method (cf. A., 1898, ii, 592), is monoclinic, $a:b:c$=1·1132 : 1 : 0·7030, β 98° 39′, d^{22} 1·8816 (Jaeger's orthorhombic substance, d 1·807, appears to have been another substance, or at least another modification), n_α 1·5973, n_β 1·6210, n_γ—n_α 0·248, for λ 6702 Å. X-Ray examination: unit cell with a 11·80, b 10·60, c 7·42 Å., β 98° 39′, containing 2 mols., space-group C_s^1. C. A. S.

Crystal structure of hydrohalides of ephedrine and *l*-ephedrine. B. GOSSNER and H. NEFF (Z. Krist., 1933, **86**, 32—41; cf. this vol., 892).—The following data are given for d, a, b, c (in Å.), β (if not 90°), no. of mols. in unit cell, and space-group: *d*-ψ-ephedrine hydrochloride 1·198, 25·49, 6·48, 6·91, 4, V^4; hydrobromide 1·410, 24·68, 6·93, 6·78, 4, V^4; hydriodide, 1·581, 11·39, 6·83, 15·62, 4, V^4; all three are rhombic disphenoidal; *l*-ephedrine hydrochloride 1·208, 12·64, 6·15, 7·34, 102° 6′, 2, C_s^2; hydrobromide 1·399, 12·74, 6·20, 7·62, 100° 48′, 2, C_2^2, both are monoclinic sphenoidal; hydriodide 1·607, 25·66, 7·33, 19·14, 12, V^3, rhombic disphenoidal. The relationships with the corresponding *r*-compounds are discussed. C. A. S.

Structure of edingtonite. W. H. TAYLOR and R. JACKSON (Z. Krist., 1933, **86**, 53—64).—Edingtonite, $BaAl_2Si_3O_5,4H_2O$, although apparently tetragonal, is probably orthorhombic; its unit cell has (approx.) a 9·7, c 6·6 Å., and contains 2 mols. The framework is identical with that of natrolite (cf. this vol., 451), the $Ba^{\cdot\cdot}$ ions and H_2O mols. being situated in the channels between the strings of (AlO_4) and (SiO_4) tetrahedra. C. A. S.

New type of transformation in alkali salts of higher fatty acids. P. A. THIESSEN and E. EHRLICH (Z. physikal. Chem., 1933, **165**, 453—463; cf. this vol., 116).—Near the m.p. of the free acid the vol.–temp. curve of Na palmitate and stearate changes in slope and there is a halt on the cooling curve. X-Ray fibre diagrams show that two kinds of change occur, one beginning near the m.p. of the fatty acid, and that these salts exist in two stable forms which have different temp. limits, are able to co-exist over a wide temp. interval, and are present in approx. equal amounts at the m.p. of the corresponding fatty acid. The suggested explanation is that the chains rotate about their long axis at comparatively low temp., and this rotation, which initiates a transformation, is followed by a directed oscillation of the chains, which sets in near the m.p. of the acid. R. C.

Crystal structure of a new type of molecular compound. E. HERTEL and G. H. ROMER (Z. physikal. Chem., 1933, **B**, **22**, 280—282).—The mol. compound of 2 : 4 : 6-$C_6H_2Cl(NO_2)_3$ (I) with 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ (II) has a pseudorhombic lattice with I_a 40·5, I_b 6·19, I_c 15·2 Å. and space-group C_{2h}^6. The lattice is equiv. to that of (II) with every second mol. replaced by a mol. of (I). R. C.

Fine structure of trinitrobenzene derivatives. E. HERTEL and G. H. ROMER (Z. physikal. Chem., 1933, **B**, **22**, 267—279).—The X-ray analysis of the crystal structure of various monosubstituted derivatives is reported. R. C.

Crystallography of the hydrates of phenylmethylethyl and phenylmethylpropyl betaine. (MME.) GUAISNET-PILAUD (Compt. rend., 1933, **197**, 419—420).—Mono- and di-hydrated phenylmethylethyl betaine (cf. this vol., 387) are doubtful and monoclinic, respectively, and both have n_α 1·549, n_β 1·585; the latter after melting at 79·5° resolidifies, remelts at 100°, and decomposes at 145—150°. The mono- and di-hydrates of phenylmethylpropyl betaine (cf. this vol., 948) are respectively probably orthorhombic and doubtful; both have n_α 1·555 and n_β 1·595. C. A. S.

Crystal structure of fibrin. J. R. KATZ and A. DE ROOY (Naturwiss., 1933, **21**, 559).—Fibrin spun into threads shows cryst. structure when examined with X-rays. The identity period along the thread axis is 6·7 Å. There are two NH_2-acid residues in this direction in the elementary cell. The polypeptide cell is almost straight, with slight crumpling and twisting. Fibrin agrees almost completely with stretched keratin (β-keratin), although the two consist of different NH_2-acids. A. J. M.

Contact potential differences between different faces of copper single crystals. H. E. FARNSWORTH and B. A. ROSE (Proc. Nat. Acad. Sci., 1933, **19**, 777—780).—A p.d. exists between the (111) and (100) faces of a Cu crystal, the (111) face being positive when the crystal is outgassed at high temp. The p.d. is increased by outgassing and has a max. val. of 0·463 volt. E. S. H.

Absolute saturation of cubic cobalt. R. I. ALLEN and F. W. CONSTANT (Physical Rev., 1933, [ii], **44**, 228—233).—Magnetisation for given temp. but increasing field strengths was measured, and

calc. for infinite field. Extrapolation gave the saturation intensity. The important influence of crystal structure is indicated. N. M. B.

Magnetic after-effects. P. C. HERMANN (Z. Physik, 1933, **84**, 565—570).—Magnetic after-effects investigated for soft Fe show a limit between eddy current and hysteresis effects. A. B. D. C.

Properties of gelatin in an electric field. (MLLE.) S. VEIL (J. Phys. Radium, 1933, [vii], **4**, 362—367).—Under the influence of an electric field gelatin underwent a complex mechanical deformation and the conductivity decreased, the substance becoming approx. a dielectric; Ohm's law was obeyed only for weak fields. Deformations were observed by impregnation with coloured indicators. Changes of $[H^{\cdot}]$ in the zones of deformation were observed. Similar results were obtained for agar-agar. N. M. B.

Crystal cohesion and crystal plasticity. A. SMEKAL (Physikal. Z., 1933, **34**, 633—639).—Experiments on the deformation of synthetic rock-salt are described. There can be no deformation by ideal slipping along crystallographic slip planes. The deformed crystal is converted into a conglomerate of crystallites. Self-diffusion of crystals is considered. A. J. M.

Plasticity in single crystals. W. G. BURGERS (Physikal. Z., 1933, **34**, 623—624).—A criticism of Schlechtweg's theory (this vol., 667). A. J. M.

Plasticity in single crystals. H. SCHLECHTWEG (Physikal. Z., 1933, **34**, 624).—A reply to Burgers (see above). A. J. M.

Optical crystallography of acetaldehyde-2 : 4-dinitrophenylhydrazone. W. M. D. BRYANT (J. Amer. Chem. Soc., 1933, **55**, 3201—3207; cf. A., 1932, 1109).—The stable modification obtained by crystallisation yields, on cooling the melt, a metastable form which exhibits crossed axial-plane dispersion. Both modifications are pleochroic; refractive indices are recorded. J. G. A. G.

Effect of water on the rigidity of rock-salt. N. N. DAVIDENKOV and M. V. KLASSEN-NEKLUDOVA (J. Exp. Theor. Phys., Russia, 1932, **2**, No. 5—6, 412—420).—H_2O does not penetrate into the crystal. Solidity occasioned by surface dissolution disappears on drying. CH. ABS.

Remanence of single iron crystals. S. KAYA (Z. Physik, 1933, 705—716).—The remanence is inversely proportional to the sum of the direction cosines of the direction of the field with respect to the cubic edges. A. B. D. C.

Fixed and variable electrical resistances of graphite. J. GUZMAN (Anal. Fís. Quím., 1933, **31**, 169—171).—The variable resistance described resembles the liquid type; one of the conducting wires moves up or down in a uralite tube containing finely-divided graphite. For high max. resistance the graphite is mixed with SiO_2. Fixed resistances may be constructed in a similar manner. H. F. G.

Self-consistent field for bound electrons; superconductivity. L. BRILLOUIN (J. Phys. Radium, 1933, [vii], **4**, 333—361).—Mathematical. Hartree's self-consistent field is applied to bound electrons in various metal crystal lattice structures. The energy curves for the face-centred cubic lattice permit the formation of electron groupings metastable at very low temp., and having a permanent current; this indicates a possible explanation of superconductivity. N. M. B.

Explanation of the discontinuity of superconductivity. U. DEHLINGER (Naturwiss., 1933, **21**, 607).—The reason for the sudden occurrence of superconductivity as temp. is lowered is considered from the point of view of lattices of alloys. A. J. M.

Frequency dependence of superconductivity and ferromagnetism. R. SANGER (Physical Rev., 1933, [ii], **44**, 302—307).—Mathematical. An explanation of the frequency dependence as a further consequence of the skin effect, assuming the existence of a surface layer which shows neither superconductive nor ferromagnetic properties, is proposed. N. M. B.

Effect of pressure on the electrical resistance of single metal crystals at low temperatures. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1933, **68**, 95—123).—Zn, Cd, Sn, Bi, Sb, As, and Te were examined. Vals. in different directions were determined. CH. ABS.

Heat capacity curves of the simpler gases. III. Heat capacity, entropy, and free energy of neutral OH from near 0° abs. to 5000° abs. H. L. JOHNSTON and D. H. DAWSON (J. Amer. Chem. Soc., 1933, **55**, 2744—2753).—The heat capacity curve of OH in the ideal gas state is computed from spectroscopic data to have a sharp max. at 0·06° abs., and a broad max. at 90° abs. The vibrational component which starts at about 600° abs. attains equipartition val. at about 3500° abs., whilst the rotational component which enters at 16° abs. attains equipartition val. at room temp. At 5000° abs. the rotational stretching and the anharmonic character of the oscillations contribute 0·18 and 0·5 g.-cal., respectively, to the mol. heat. Vals. of the entropy and free energy are tabulated. Villars' calculations are criticised (A., 1930, 1121). J. G. A. G.

Calculation of gas radiation at high temperatures. S. UCHIDA (J. Soc. Chem. Ind. Japan, 1933, **36**, 337—338B).—Vals. of the radiation from H_2O vapour at high temp. calc. by Schack's method agree with Schmidt's experimental data. A. G.

Thermal conductivity of water at temperatures up to 270°. E. SCHMIDT and W. SELLSCHOPP (Forsch. Ingenieurwes., 1932, **A**, **3**, 277—286; Chem. Zentr., 1933, i, 742).—The thermal conductivity–temp. curve is practically a symmetrical parabola, and not linear as hitherto assumed, above 75°. The thermal conductivity no. of Cu is 320 kg.-cal. per m. per hr. per degree. L. S. T.

Vapour tension of BaO, SrO, and CaO and their mixtures deduced from measurements of the rates of evaporation. E. PRESTON (J. Soc. Glass Tech., 1933, **17**, 118—121T; cf. this vol., 344).—Vals. of the v.p., obtained from data on the rates of evaporation by means of the Herz–Knudsen equation, are:

BaO (at 1475° abs.) 33×10^{-6}; SrO (1635°) $4{\cdot}0\times10^{-6}$; CaO (1728°) $1{\cdot}8\times10^{-6}$ mm. Hg. It is concluded that volatilisation losses of the oxides in glass-making would be negligible. A. L. R.

Vapour pressure and b.p. of methylacetylene. G. B. HEISIG and C. D. HURD (J. Amer. Chem. Soc., 1933, **55**, 3485—3487).—The v.p. of pure CMe·CH are recorded from −79·5° to −23·5°. Log $p_{mm.}=-1247{\cdot}95/T+7{\cdot}877$. The calc. b.p. is −23·1°. R. S. C.

V.p. of *n*-butyl chloride. C. W. LENTH (J. Amer. Chem. Soc., 1933, **55**, 3283).—The v.p. between 12·5° and 77·5° is given by $2{\cdot}303\log P_{(cm.)}=-8090/1{\cdot}99T+6{\cdot}912$, from which the latent heat of vaporisation is 8090 g.-cal. per mol. J. G. A. G.

Preparation and purification of methyl borate and ethyl borate. S. H. WEBSTER and L. M. DENNIS (J. Amer. Chem. Soc., 1933, **55**, 3233—3235).—Modifications of existing methods are described. The v.p. of Me_3BO_3, m.p. −29·3°, b.p. 68·75°/760 mm., between −27° and 70° is given by $\log P=-1785{\cdot}3/T+8{\cdot}1073$. From the v.-p. equation $\log P=-2298{\cdot}0/T+8{\cdot}8553$, the calc. b.p. of Et_3BO_3, m.p. −84·8°, is 111·8°; decomp. occurs above 65°. J. G. A. G.

Compressibilities and pressure coefficients of resistance of elements, compounds, and alloys, many of them anomalous. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1933, **68**, 27—93).—Vals. at $>$ 12,000 atm. at 30° and 75° were determined for Nb, Rh, Ru, Cr, As, Be, $MnCl_2$, $ZnCl_2$, Al_2O_3, Cu_5Cd_8, Ag–Au, Co–Fe–W, gulonolactone, rhamnose, and sucrose. CH. ABS.

Pressure-volume-temperature relations of fifteen liquids. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1933, **68**, 1—25).—$N(OEt)_3$, PrCl, PrBr, PrI, BuCl, BuBr, BuI, $C_5H_{11}Cl$, $C_5H_{11}Br$, $C_5H_{11}I$, octan-γ-ol, β-methylheptan-γ- and -ε-ol, γ-methylheptan-α- and -δ-ol were examined. $C_5H_{11}Cl$(Br,I) are about 0·8 as compressible as C_5H_{12}. The effect of a halogen in decreasing compressibility is about the same as that of an OH group. A CH_2 group increases the molal vol. 15·36—17·09 at 1 atm. and 11·18—13·69 at 12,000 atm. The difference in vol. between Br and Cl is $<$ that between I and Br. The difference between the vols. of the halides is much $>$ that calc. from the space lattices of the solid elements. No significant differences in vols. or compressibilities of the five isomerides were observed. CH. ABS.

Hydrogen sulphide. T. BATUECAS (J. Chim. phys., 1933, **30**, 482—486).—A criticism of recent work on the *d* of H_2S and at. wt. of S (cf. this vol., 16). E. S. H.

Thermodynamical theory of liquids. N. DE KOLOSSOWSKI (Compt. rend., 1933, **197**, 517—519).—From the thermodynamic potential are deduced an equation of state for the liquid, Mendeleev's law of dilatation for a liquid, Tait's expression for compressibility, the entropy, Schiff's rule regarding the mol. heat of a liquid (cf. A., 1887, 6), and an expression for the mol. latent heat, which applied to C_6H_6 gives vals. agreeing closely with experiment. C. A. S.

Molecular specific heats of some liquids. N. DE KOLOSSOWSKI (Compt. rend., 1933, **197**, 519—520).—To test the relation between mol. heat, thermodynamic potential, and entropy (see preceding abstract) the following sp. heats have been determined at the abs. temp. noted: limonene 0·4380, 293·4°; sabinene 0·4431, 297·04°; linalool 0·5777, 293·15°; pulegone 0·4320, 293·38°; $CH_2Ph\cdot OAc$ 0·3983, 292·71°; Me salicylate 0·3910, 295·20°; and those of 12 other org. liquids were redetermined. C. A. S.

Viscosity of fused salts and Andrade–Sheppard formula for the viscosity of liquids. B. PRASAD (Phil. Mag., 1933, [vii], **16**, 263—268).—The viscosities of fused $NaNO_3$, KNO_3, and $PbBr_2$ follow the simple formula $\log\eta=\alpha+\beta/T$, where η = viscosity, α and β are consts., and T = abs. temp. For $PbCl_2$ the formula is $\log\eta=\alpha+\beta/(T+0)$ (0 = const.), this being attributed to the gradual increase in the dissociation of $PbCl_2$ with temp. Neither formula holds for the viscosity of fused $K_2Cr_2O_7$ at low temp., probably owing to decomp. into K_2CrO_4 and CrO_3. J. W. S.

Densities of hydrocarbon mixtures. E. W. THIELE and W. B. KAY (Ind. Eng. Chem., 1933, **25**, 894—898).—Curves are given for obtaining the density of hydrocarbon oils in the liquid state at various temp. and pressures when $d^{15\cdot5}$ and the viscosity at 37·7° are known. D. K. M.

Viscosity of solutions of camphor. A. CASTIGLIONI (Gazzetta, 1933, **63**, 395—399).—The viscosity of solutions in C_6H_6, $CHCl_3$, EtOH, and Et_2O increases with the concn. With solutions in vaseline, olive and sesame oils, and in oleic acid η decreases up to the saturation concn. O. J. W.

Diffusion in the solid state in the metal pairs gold–nickel, gold–palladium, and gold–platinum. A. JEDELE (Z. Elektrochem., 1933, **39**, 691—695).—The diffusion velocity increases as the difference between the temp. of diffusion and the m.p. of the alloy diminishes. The diffusion velocity of Au in Pt is $<$ that of Pt in Au; at 900° the diffusion coeff. D is $0{\cdot}1\times10^{-5}$ sq. cm. per day for the Pt-rich solid solution and $0{\cdot}5\times10^{-5}$ sq. cm. per day for the Au-rich solid solution. In the Au–Pd system the vals. of D are $0{\cdot}2\times10^{-5}$ and $2{\cdot}0\times10^{-5}$ sq. cm. per day, respectively, for the Pd-rich and Au-rich solid solutions. In the Au–Ni system $D=0{\cdot}3\times10^{-5}$ and 5×10^{-5} sq. cm. per day for the Ni-rich and Au-rich solid solutions, respectively. E. S. H.

Relation between diffusion coefficients and concentrations of solid metals. Nickel–copper system. C. MATANO (Japan. J. Physics, 1933, **8**, 109—113; cf. A., 1932, 1195).—Analysis of Grube and Jedele's results at 1025° shows that the coeff. of diffusion decreases from about 8×10^{-5} sq. cm. per day for 0% Ni to 1×10^{-5} for 30% Ni, thereafter remaining const. up to 100% Ni. J. W. S.

***X*-Ray analysis of alloys of mercury with silver, gold, and tin.** S. STENBECK (Z. anorg. Chem., 1933, **214**, 16—26).—The results of Murphy and Preston (A., 1931, 1244) for Ag–Hg amalgams are confirmed. The lattice dimensions increase with the Hg concn. For Au–Hg amalgams, up to 80% Hg, five solid phases have been observed. In the

hexagonal β-phase the axial ratio is const. between 19·3 and 33·0% Hg (cf. Pabst, A., 1929, 987). The system Sn–Hg forms a hexagonal lattice (8% Hg; b 3·198, c 2·980 Å.), and a rhombic lattice (>14% Hg; a 5·548, b 3·196, c 2·981 Å.) (cf. Simson, A., 1924, ii, 449). H. J. E.

X-Ray investigations of the constitution of alloys. A. Westgren (Assoc. Int. Essai Mat., 1932, **1**, 484—499; Chem. Zentr., 1933, i, 844).—The X-ray method appears to be more trustworthy than thermal analysis or microscopical investigation for the identification of solid phases. Homogeneous fields also can generally be determined. The difference between intermetallic compounds and solid solutions is discussed. The best classification is not on chemical grounds, but on the basis of crystal structure. L. S. T.

X-Ray study of iron–silicon alloys containing 0—15% Si. E. R. Jette and E. S. Greiner (Amer. Inst. Min. Met. Eng., 1933, No. 8, 15 pp.).—The graph of lattice const. as a function of at.-% Si consists of two straight lines intersecting at 4·7% (8·95 at.-%) Si. Two hypotheses of structure are discussed. Ch. Abs.

System beryllium–copper. H. Tanimura and G. Wassermann (Z. Metallk., 1933, **25**, 179—181).—X-Ray analysis of well-annealed Be–Cu alloys shows that the solubility of Be in Cu decreases from 2·1% at the peritectic temp. (864°) to 1·8% at 700°, 0·4% at 400°, and 0·16% at 250°. Pptn. of a constituent from supersaturated solid solutions annealed at 150° can be detected. A. R. P.

Electrical conductivity measurements of zinc–cadmium and lead–antimony systems, with reference to the establishment of stable equilibrium. M. le Blanc and H. Schopel (Z. Elektrochem., 1933, **39**, 695—701).—In the system Zn–Cd the establishment of stable equilibrium is slow when the alloy contains < 10% of either constituent; in the system Pb–Sb a retardation is observed over the whole range. Temp.–resistance curves show that at 263° the solubility limits of the system Zn–Cd lie at 6 and 97·5 at.-% Zn, whilst in the system Pb–Sb the limits are 1·5 and 94·2 at.-% Pb at 249°. The results are confirmed by micrographic examination. E. S. H.

Solubility of the compound $MgZn_2$ in aluminium in the solid state at different temperatures. P. Saldau and M. Zamotorin (Z. anorg. Chem., 1933, **213**, 377—382).—Between 15° and 300° the solubility increases from 1·58% to 3·57% $MgZn_2$. The val. then increases rapidly to 30·0% $MgZn_2$ at the eutectic temp. (475°). H. J. E.

Solubility curves of copper in solid aluminium. P. J. Saldau and N. G. Anisimov (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 69—79).—The solubility of Cu in solid Al is 2·7% from 15° to 300°, 3·12% at 400°, 5·55% at 500°, and 6·5% at the eutectic temp. (543°). The hardness of chilled alloys becomes > that of slowly cooled alloys when the Cu content exceeds 2·7%, and shows a max. at 6% Cu. R. T.

Solubility of silicon in solid aluminium at various temperatures. P. J. Saldau and M. V. Danilovitsch (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 81—89).—The solubility of Si in solid Al is 0·09% from 15° to 300°, 0·3% at 400°, 0·65% at 560°, and 1·32% at the eutectic temp. (570°). R. T.

Densities of iron–nitrogen alloys. A. Sieverts and H. Hagen (Z. Elektrochem., 1933, **39**, 735—736).—The val. d 6·88 found for Fe_2N agrees with that derived from X-ray measurements, but is 6% > Sieverts and Krüll's val. (A., 1930, 878). H. J. E.

Crystal structure of phase A of the system Ag–Li. H. Perlitz (Z. Krist., 1933, **86**, 155—158; cf. A., 1930, 1359).—Phase A, with 76·3—80·2 at.-% Li, has a cubic unit cell containing 52 atoms with a 9·94 Å. C. A. S.

Mode of combination of silicon in aluminium or aluminium–silicon alloys. P. Urech (Z. anorg. Chem., 1933, **214**, 111—112).—The amount of Si hydrides evolved on dissolution in H_2SO_4 (d 1·6) is independent of the Si content of the alloy between 0·2 and 12% Si. This is consistent with the absence of compound formation. H. J. E.

Hardening transformation in manganese steels. H. Scott and J. G. Hoop (Trans. Amer. Soc. Steel Treat., 1933, **21**, 233—248).—The hardening transformation (Ar″) temp. has been determined in steels containing Mn 4·5—12·0, C 0·12—1·0%, all the C being retained in solid solution. Within certain composition limits, C in solid solution has 12 times the effect of Mn. Extrapolated vals. for Ar″ temp. in Fe–C alloys are recorded. Ch. Abs.

Equilibrium A3 and A cm points in pure carbon steels. Chu-Phay Yap (Trans. Amer. Soc. Steel Treat., 1933, **21**, 260—268).—New vals. are: A3 (ordinary pure Fe) 900°; A1 720°; A cm line, straight line from 0·795 at 720° to 1·685% C at 1130°. Ch. Abs.

Influence of heavy metals on aluminium alloys. I. Solid solution formation in aluminium alloys. P. Röntgen and W. Koch (Z. Metallk., 1933, **25**, 182—185).—Micrographic examination of alloys of Ni, Cr, and Mo with Al (0·048% impurity) shows that the solubility of these metals in Al at 560° is ≯ 0·02% and that addition of 2% Cu does not increase this solubility. A. R. P.

System iron–cobalt–manganese. W. Köster and W. Schmidt (Arch. Eisenhüttenw., 1933—1934, **7**, 121—126).—The temp. of the γ–ε and magnetic transformations of Co are reduced by addition of Mn, reaching 0° at about 30 and 38% Mn, respectively. The m.p. and the polymorphic and magnetic transformation points in Fe–Co–Mn alloys with ≯ 50% Mn have been determined. At about 1400° all the alloys consist solely of γ-solid solution, but alloys with ≯ 18% Mn and ≯ 80% Co undergo an irreversible transformation into α, the hysteresis of which increases with increasing Mn content. Alloys with 18—30% Mn are partly converted into ε similar to the ε-Co phase. The lattice parameter of the ternary α-, γ-, and ε-solid solutions with const. Mn content decreases linearly at first, then at an increasing rate with increasing Co. With const. Fe or Co content the at. distance increases linearly with the Mn content

and is greater in the ferromagnetic than in the paramagnetic state. A. R. P.

Alloys of iron. XI. Constitution of iron-manganese alloys. (Miss) M. L. V. Gayler (Iron and Steel Inst., 1933, Sept., Advance copy, 48 pp.).—The Fe–Mn system has been investigated by thermal, micrographic, and *X*-ray methods using alloys made from distilled Mn and electrolytic Fe purified by melting in H_2. The liquidus has three branches: (*a*) from 0 to 7% Mn it is concave to the composition axis and falls from 1527° to 1504°; δ-Fe separates as primary crystals; (*b*) from 7 to 75% it falls linearly to 1265° and corresponds with the crystallisation of γ-Fe, and (*c*) with >75% Mn primary crystals of γ-Mn separate at gradually falling temp. to 1242°. A peritectic reaction δ+liquid⇌γ occurs at 1504° with 1—8% Mn and a second peritectic reaction γ-Fe+liquid⇌γ-Mn at 1270° with 65—74% Mn. The solidus runs almost parallel with the liquidus between 6 and 68% Mn (1504—1270°), and there is a freezing range of only about 10° in alloys containing >68% Mn. The γ–δ transformation of Fe is raised linearly from 1400° to 1504° with addition of Mn up to 6%. Typical martensitic structures are obtained by quenching alloys with 1·7—9·3% Mn from above 780°, but with >10% Mn this treatment produces a finely-twinned structure which is unaffected by heat-treatment and cold work; the nature of this phase and of the complex changes which occur in alloys with <60% Mn have not been elucidated. At the Mn end of the system the γ β-Mn transformation, which occurs in pure Mn at 1188° on heating and at 1195° on cooling, is gradually depressed by addition of Fe to 1036° on heating and 1021° on cooling with 29% Fe, after which it cannot be detected. The transformation which occurs in pure Mn at 1043° on heating and 1005° on cooling is raised to 1128° and 1129°, respectively, by 14% Fe and then depressed to 1088° and 1092°, respectively, with 21·1% Fe, after which it merges into the other transformation. The γ-Mn–Fe phase in alloys with 64—72% Mn decomposes at 1028° into a mixture of γ-Fe+β-Mn and the β-Mn–Fe solid solution with 59—63% Mn decomposes at 600° into γ-Fe+β-Mn. The solubility of β-Mn in γ-Fe falls from 63·5% Mn at 1028° to 60% at 600°, and that of γ-Fe in β-Mn increases from 28% Fe at 1028° to 38% at 600°. The transformation in pure Mn occurs at 742° and a second energy change at 682°; in the alloy with 94·2% Mn these transformations occur at 729° and 682°, respectively, and with more Fe the temp. gradually falls to 600°. A. R. P.

Ternary alloys of thallium with lead, cadmium, and tin. N. S. Kurnakov and I. I. Korenev (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 47—68).—The fusion diagrams of the systems Tl–Pb–Cd and Tl–Pb–Sn afford no evidence of compound formation. The f.-p. curves deviate considerably from linearity as compared with those of the constituent binary systems. The dystectic point of the system Pb–Tl is displaced by addition of Cd or Sn. R. T.

Heats of mixing of liquid Fe–Ni–C alloys. F. Sauerwald and F. Fleischer (Z. Elektrochem., 1933, **39**, 686—687).—The heat of mixture of an alloy containing Ni 46, Fe 49, and C 5 at.-% is 500 g.-cal. per g.-atom. Probably Fe–Ni compounds are formed in considerable amount. E. S. H.

Rare gases. II. Diffusion of helium through crystalline substances and the molecular flow through rock masses. W. D. Urry (J. Amer. Chem. Soc., 1933, **55**, 3242—3249; cf. this vol., 20).—He at 23—200 mm. does not pass through Bi, Fe, or a single crystal of SiO_2 at temp. <700°, but excited He diffuses through Bi. The adsorption of He on steel is zero. The fractional rate of loss of He from ordinary rocks is extremely small compared with that from radioactive minerals, and thus an objection to the He method for determining ages of rocks is ill-founded. From the rate of flow of He through rock materials, structure consts. have been calc. J. G. A. G.

Solubilities of hydrogen chloride, carbon dioxide, and hydrogen in liquid chlorine. Anon. (Trans. State Inst. Appl. Chem., Leningrad, 1932, No. 15, 3—7).—Vals. are low. Corrosion of metal cylinders by HCl is due to ionisation in presence of H_2O or org. compounds. Ch. Abs.

System aniline–acetone–water. A. N. Campbell and E. M. Brown (Trans. Faraday Soc., 1933, **29**, 835—837).—Composition of conjugate phases at 30° and temps. of homogeneity for mixtures of various compositions are given. F. L. U.

Solubilities of sparingly soluble salts using large volumes of solvents. I. Solubility of lead sulphate. R. B. Purdum and H. A. Rutherford, jun. (J. Amer. Chem. Soc., 1933, **55**, 3221—3223).—The solubility at 20° in H_2O (43·5 mg. $PbSO_4$ per litre) and in 0·001—0·05*N*-H_2SO_4 has been determined. J. G. A. G.

Solubility of monopotassium phosphate in presence of phosphoric acid, potassium hydroxide, and potassium chloride. A. I. Krasilschtschikov (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 159—168).—The solubility of KH_2PO_4 (I) at 0° is greatly depressed in saturated aq. KCl, the solubility of which is only slightly reduced by (I). In the system P_2O_5–K_2O–KCl–H_2O addition of K_2O or P_2O_5 depresses the solubility of KCl and increases that of K phosphate. R. T.

Solubility of thallous iodate in solutions of sodium mellitate [at 25°]. C. F. Failey (J. Amer. Chem. Soc., 1933, **55**, 3112—3116).—The unexpectedly large increase in the solubility, *S*, of $TlIO_3$ in 0·0001—0·01*M*-Na mellitate is not related to the slight alkalinity of the solutions. The addition of a third salt to a solution with a const. concn. of Na mellitate depresses *S* to a min. which is much lower for Mg than for Na salts. The phenomenon of an activity coeff. first increasing and then decreasing on the addition of an electrolyte to a moderately dil. solution is contrary to the predictions of the principle of ionic strength and the theory of Debye. Mellitic acid buffers uniformly from p_H 3 to p_H 7, and the shape of the electrometric titration curve with NaOH is similar to that of a protein. J. G. A. G.

Rare earths. XXXIII. [Relative] basicity. G. R. Sherwood and B. S. Hopkins. **XXXIIIa.**

Basicity of illinium and yttrium. XXXIX. Transference numbers of the chlorides of neodymium, samarium, and gadolinium. I. Purification of materials. G. HUGHES and B. S. HOPKINS. **II. Measurement of transference numbers** [at 25°]. D. HAAS and W. H. RODEBUSH. **XL. Magnetic susceptibilities of europium, [gadolinium], and ytterbium salts.** G. HUGHES and D. W. PEARCE (J. Amer. Chem. Soc., 1933, **55**, 3117—3121, 3121—3123, 3236—3237, 3238—3242, 3277—3279).—XXXIII. The pptn. of rare earths by $NaNO_2$ has been modified to increase the efficiency of fractionation and emphasise the differences in basicity. Omitting Sc, Y, Ce, and Il, the order of decreasing basicity is identical with the order of increasing at. no. The differences of basicity in the series Sm > Eu > Gd are extremely slight.

XXXIIIa. The basicities are in the order Nd > Il > Y > Sm.

XXXIX (I). Nd, Sm, and Gd each containing < 0·1% of other rare earths have been obtained by fractional crystallisation.

XXXIX (II). The moving boundary method affords the transference nos. 0·442, 0·442, and 0·433, respectively, for Nd, Sm, and Gd in 0·1*N* solutions of the chlorides. However, it does not follow that the mobility of the Gd ion is < that of Nd or Sm.

XL. The susceptibility, 7510×10^{-6} per g.-atom, of Yb in $Yb_2(SO_4)_3,8H_2O$ is much < previously recorded vals. Data for other salts are confirmed. The susceptibility of an earth in the bivalent state approaches that of the earth of the next higher at. no. in the tervalent state. J. G. A. G.

Regularities in isomorphous separation of small amounts of substances with crystallising salts. A. RATNER, P. TOLMATSCHEV, and A. POLESSITSKI (Z. physikal. Chem., 1933, **165**, 472—476).—The views of Kading, Mumbrauer, and Riehl (A., 1932, 1198) are criticised. A single explanation covering all the experimental data so far obtained is outlined (cf. *ibid.*, 14). R. C.

Regularities in isomorphous separation of small amounts of substances with crystallising salts. R. MUMBRAUER (Z. physikal. Chem., 1933, **165**, 477).—A reply to criticism (cf. preceding abstract). R. C.

Discontinuity and thermodynamics of crystal growth. E. SOMMERFELDT (Zentr. Min., 1932, 321—329; Chem. Zentr., 1932, ii, 3829). L. S. T.

Limits of fractionation of cellulose nitrates. J. DUCLAUX and J. BARBIERE (Bull. Soc. chim., 1933, [iv], **53**, 564—565).—The viscosities of cellulose nitrate solutions in $COMe_2$, fractionally pptd. by H_2O, have been compared. A. S. C. L.

Hantzsch–Landau rule. G. HERRERO (Anal. Fís. Quím., 1933, **31**, 416—421).—The influence of concn. on the distribution of I between H_2O and C_2HCl_3 and between H_2O and C_6H_6 has been examined in reference to the above rule. The solubility of I in C_2HCl_3 at 20° is 34·78 g. per litre. H. F. G.

Distribution coefficients of monocarboxylic acids and esters between immiscible solvents. H. J. HENRIQUES (J. Amer. Chem. Soc., 1933, **55**, 3284—3288).—Data are recorded for HCO_2H, AcOH, Pr^nCO_2H, heptoic (I), lauric (II), myristic, palmitic (III), and oleic (IV) acids between $CMe_3{\cdot}CH_2{\cdot}CHMe_2$ (V) and $OMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (VI); for the Me esters of (I), (II), (III), (IV), and linoleic acid between (V) and MeOH, and also for the esters from (VI) and (I), (II), (III), and (IV) between (V) and (VI), at 0° and −19·5°. R. S. C.

Surface evaporation of boiling liquids. M. STRUBIN (Chem. Apparat., 1932, **19**, 145—147, 157—161; Chem. Zentr., 1933, i, 744).—Theoretical. A. A. E.

Adsorption layers at the surface of solutions. D. G. DERVICHIAN (J. Chim. phys., 1933, **30**, 468—481).—Determination of surface tension by establishing equilibrium with the pressure of an air jet impinging on the surface has been applied to the study of dil. aq. solutions of fatty acids containing 4—11 C atoms. The results show that the surface film is comparable with that obtained by spreading insol. acids on the surface of the H_2O, for a marked change in properties occurs when a certain crit. mol. surface is exceeded. E. S. H.

Adsorption of sulphurous acid by platinum, ferric oxide, and chromic oxide. II. B. NEUMANN and E. GOEBEL (Z. Elektrochem., 1933, **39**, 672—682; cf. this vol., 773).—Reversible adsorption occurs up to 200°, but at higher temp., corresponding with the temp. attained in catalytic reactions, chemical change also occurs with formation of PtS or $FeSO_4$. At 600° chemical reactions are considered to play a greater part than adsorption in catalysis. The heats of adsorption of SO_2 by Fe_2O_3 or Cr_2O_3 are approx. equal; for small amounts of adsorbed SO_2 the val. is about 40,000 g.-cal. per mol., but the val. falls as the amount of adsorption increases and as the temp. rises. E. S. H.

Absorbent power of zinc oxalate partly decomposed by heat with respect to methyl alcohol. G. HÜTTIG and A. MELLER (Chim. et Ind., 1933, Spec. no., 788—791).—A series of products represented by ZnO,nC_2O_3 (n=1—0) has been prepared by heating ZnC_2O_4. The behaviour of these towards MeOH vapour at 20° has been examined. C. I.

Degassing of tantalum. U. S. IVANOV (J. Exp. Theor. Phys., Russia, 1932, **2**, 162—170).—Desorption of H on Ta at 105—1760° follows Grünberg's law. The desorbed atoms are adsorbed by the glass walls to $\nearrow 3{\cdot}6 \times 10^{15}$ atoms per sq. cm. CH. ABS.

Adsorption of hydrogen by silica gel at elevated temperatures. L. H. REYERSON (J. Amer. Chem. Soc., 1933, **55**, 3105—3108).—If appreciable quantities of H_2 are adsorbed by SiO_2 gel at 400—600°, the process must occur immediately and exclusively on admission of the gas, since no change of pressure occurs subsequently (cf. this vol., 572). J. G. A. G.

Nature of spontaneous separation of polonium on silver in various acids. O. ERBACHER (Z. physikal. Chem., 1933, **165**, 421—426).—The separation depends on the exchange of Ag atoms for Po ions and the formation of a solid solution of Po in the Ag_2O_2 formed. R. C.

Theory of film formation. B. F. H. SCHEIFELE (Fettchem. Umschau, 1933, **40**, 141—144).—From a consideration of the cohesive and adhesive forces acting in a film, and the consequent orientation and deformative strains of the constituent (macro-)mols., it is suggested that the "ideal" mol. structure to impart film-forming properties should consist of a central nucleus bearing three radiating, thread-like groups. This structure is realised to some extent by mols. such as linolenodilinolein (I) or the cellulose esters. Since trielæostearin possesses three like fatty acid chains, it should be less stable than (I) under the deformative strain resulting from the unequal forces of cohesion in the film and adhesion to the base, and this may account for the defective adhesion of tung-oil films, and their tendency to wrinkle. E. L.

Surface films of cellulose derivatives on water and dyestuff solutions. II. J. B. HARDING and N. K. ADAM (Trans. Faraday Soc., 1933, **29**, 837—844; cf. this vol., 222).—Measurements of the change in contact potential between solution and air caused by the presence of surface films of methyl-, acetyl-, and benzyl-cellulose confirm the conclusions reached from surface pressure measurements, viz., that the hexose rings lie flat in the surface at low compressions, but are tilted slightly on compression. With methyl-cellulose there is evidence of small gaps in the film at areas $>$ 140 Å.^{2} per hexose group. F. L. U.

Physico-chemical analysis and molecular surface energy. Heat of wetting and inversion of the composition-property diagram. B. V. ILJIN, V. A. OSCHMAN, N. L. REBENKO, and N. K. ARCHANGELSKAJA (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 91—96).—The heat of wetting–composition curve of the system H_2O–Ac_2O is nearly horizontal for hydrophobic colloids (charcoal) with a flat max. at 50 mol.-%; for hydrophilic colloids (SiO_2 gel) a well-defined min. exists at this point. R. T.

Decrease in surface energy of solid bodies and the work of dispersion in the formation of an adsorption layer. P. A. REBINDER and N. A. KALINOVSKAYA (J. Tech. Phys., Russia, 1932, **2**, 726—755).—The following systems have been studied: graphite–H_2O–aliphatic acid; graphite–kerosene–aliphatic acid; graphite–H_2O–tannin, gallic acid, or alizarin-red; witherite–paraffin oil–acid; fluorite–paraffin oil–oleic acid; garnet–H_2O or kerosene–aliphatic acid; glass–paraffin oil–oleic or butyric acid; Cu or galena–kerosene–stearic acid; calcite–H_2O–aromatic base or aliphatic acid; calcite–air; calcite–PhMe–camphor. CH. ABS.

Effect of curvature of surface on surface energy. Rate of evaporation of liquid droplets. Thickness of saturated vapour films. D. J. WOODLAND and E. MACK, jun. (J. Amer. Chem. Soc., 1933, **55**, 3149—3161).—On the assumption that the rate of evaporation of droplets of Bu^a tartrate and phthalate (I) is directly proportional to droplet radius, the relative v.p. of droplets of 2·0—0·7 μ radius have been evaluated from observations with a Millikan oil-drop apparatus. Using the Kelvin equation, the calc. surface energies, σ, are 50—100-fold those for the flat surface. The anomaly is removed by correcting for the thickness (0·6 μ approx.) of the saturated vapour film around the droplet. The data from which Shereshefsky concluded that σ increases at a concave surface (A., 1929, 128) admit an alternative explanation on kinetic grounds. The latter is supported by the constancy of σ (capillary rise) of H_2O in capillaries of radius $>$ 6·7 The v.p. of (I) at 25° is $3\,1\times10^{-6}$ mm. by the Knudsen method. J. G. A. G.

Interaction between soot films and oil. D. M. CARDING (Nature, 1933, **132**, 317—318).—Two effects, the Blacktin effect (cf. A., 1932, 464) and the formation of gas bubbles (cf. this vol., 672), are distinguished and further observations recorded. L. S. T.

Velocity of permeation of electrolytes through a membrane. S. MATUURA (Sci. Rep. Hirosima Higher Tech. School, 1933, **2**, 67—187).—The following relations hold for the permeation of a single electrolyte through a membrane: (1) $(1/t)\log(C_0-C_\infty)/(C-C_\infty)=\lambda A(V-v)/2{\cdot}3Vv=k$; (2) $(1/t)\log(c_\infty-c_0)/(c_\infty-c)-\lambda A(V+v)/2{\cdot}3Vv=k$; (3) $C_\infty-c_\infty=(C_0V+c_0v)/(V+v)$, where C_0 is the initial concn. of the inside solution (I), c_0 is that of the outside solution (II), C the concn. of (I) at time t, c that of (II) at time t, C_∞ and c_∞ are the concns. of (I) and (II) at time ∞, V and v the initial vols. of (I) and (II), A is the surface area of the membrane, and k a const. when V, v, and A are const. The permeation velocities of various electrolytes are in the following order: KCl$>$$NH_4Cl$$>$NaCl$>$LiCl; $BaCl_2>CaCl_2>MgCl_2$; KI$\geq$KBr$>$KCl$>KNO_3>K_2SO_4$; $HCl>H_2SO_4>$AcOH$>H_2C_2O_4>H_3PO_4$; $HCO_2H>$AcOH$>H_3BO_3>CH_2Cl{\cdot}CO_2H>PrCO_2H>$succinic acid$>$malic acid$>$tartaric acid. The velocity of permeation varies linearly with temp.; the temp. coeff. is higher, the lower is the velocity of permeation. The experiments are extended to the case of two electrolytes having a common ion, (*a*) when both electrolytes are initially on the same side of the membrane, (*b*) when they are initially on opposite sides, (*c*) when one electrolyte is initially on one side and the other at equal concn. on both sides. The influence of non-electrolytes (EtOH, glycerol, glucose) is to decrease the velocity of permeation. E. S. H.

Galvanotropism of Traube's copper ferrocyanide cells. FE. SCHEMINZKY and FR. SCHEMINZKY (Z. Biol., 1933, **94**, 78—85).—The growths formed by placing crystals of $K_4Fe(CN)_6$ in aq. $CuSO_4$ incline towards the cathode when an electric current is applied horizontally. Galvanotropism is not shown by silicate growths, which do not suffer rupture of the membrane and thickening with age. The phenomenon is traced to more rapid rupture and re-formation of the ferrocyanide membrane on the anode side. E. S. H.

Behaviour of Traube's cells under the influence of the electric current. R. WAGNER (Z. Biol., 1933, **94**, 86—89).—The direction of growth of the $Cu_2Fe(CN)_6$ membrane cells is towards the cathode when $CuSO_4$ is in excess (cf preceding abstract) and towards the anode when crystals of $CuSO_4$ are placed in $K_4Fe(CN)_6$ solution. Electro-osmotic effects are

excluded, and the phenomenon is traced to the changes of ion concn. under the influence of the current. E. S. H.

Behaviour of Traube's cells under the influence of the electric current. Fe. Scheminzky and Fr. Scheminzky (Z. Biol., 1933, **94**, 90—91).—The results obtained by Wagner (cf. preceding abstract) are explicable only on the assumption that the walls of the membrane are rendered porous by structural alterations. E. S. H.

Distribution of molecules in liquids. E. Amaldi (Nuovo Cim., 1932, **9**, 141—151; Chem. Zentr., 1932, ii, 3833).—Theoretical. A. A. E.

Electrostriction produced by salts in aliphatic alcohols. W. C. Vosburgh, (Miss) L. C. Connell, and J. A. V. Butler (J.C.S., 1933, 933—942).—The apparent mol. vols. of NaCl, KCl, NaI, and KI in MeOH, and of LiCl in MeOH, EtOH, Pr$^{\alpha}$OH, Bu$^{\alpha}$OH, and Bu$^{\beta}$OH have been determined. Except for conc. solutions of LiCl in the higher alcohols, $\phi=\phi_0+a\sqrt{c}$ in all cases. The val. of a for the different salts in MeOH varies slightly, but approximates to the limiting val. for uni-univalent salts as calc. by Redlich and Rosenfeld's equation (A., 1931, 905, 1122), being six times the val. in H_2O. The electrostriction in the alcoholic solutions is much $>$ in H_2O. The apparent mol. vols. at infinite dilution agree approx. with Webb's theory (A., 1926, 1208). D. R. D.

Hydrotropy amongst inorganic salts. J. V. Tamchyna (Biochem. Z., 1933, **264**, 24—27).—Conc. aq. solutions of readily sol. inorg. salts exhibit hydrotropic properties (I) much less frequently than salts with org. anions. As regards (I) Li halides form the series I$>$Br$>$Cl. Saturated aq. LiI dissolves uric acid (II) very readily and also insol. inorg. salts, *e.g.*, $MgCO_3$. Triethanolamine borate has very pronounced (I), especially towards (II). W. McC.

Action of electrolytes on kaolin suspensions. Pichot (Compt. rend., 1933, **197**, 451—453).—Observations on the opacity in relation to the depth below the surface and the period of settling are described. C. A. S.

Preparation and properties of zirconium sulphosalicylic acid jellies. S. Prakash (J. Indian Chem. Soc., 1933, **10**, 281—285).—Sols are produced by mixing aq. solutions of $ZrOCl_2$ and sulphosalicylic acid. These set to hard, transparent jellies, but jellies cannot be obtained in neutral or alkaline systems. The particles are positively charged. E. S. H.

Diamagnetism of bismuth and antimony in the colloidal state. M. R. Verma and R. N. Mathur (J. Indian Chem. Soc., 1933, **10**, 321—328).—The diamagnetic susceptibility is practically independent of particle size of the metal. Contrary results are ascribed to the presence of oxide films. E. S. H.

Ionic interchange in sulphur sols. II. Influence of acids. T. R. Bolam and J. J. Muir (J.C.S., 1933, 1022—1028; cf. this vol., 24).—The replacement of H$^{\cdot}$ by metallic cations has been studied with undialysed S sols containing a higher concn. of acid. Total coagulation occurs before all the H$^{\cdot}$ has been replaced. The degree of displacement at the coagulation point is the same for all the cations examined (Na, K, Rb, Ca, Ba, Al) for the same concn. of HCl in the sol, but decreases with increasing acidity. The more acid is the sol, the greater is the concn. of salt necessary to secure this amount of replacement. D. R. D.

Effect of genotypism on properties of colloidal dispersions of fatty acid salts. P. A. Thiessen and E. Ehrlich (Z. physikal. Chem., 1933, **165**, 464—471; cf. this vol., 116).—The vol.–temp. curve of a hydrogel of Na palmitate and the viscosity–temp. curve of a hydrosol each undergo an abrupt change in slope at a temp. near the m.p. of the acid. Hydrosols of Na soaps on cooling become turbid at a temp. near the m.p. of the acid, T, and opaque gels with a framework of cryst. fatty acid salts melt, whether they have been formed from fibrils or granules, at a temp. near T. R. C.

Phase-rule equilibria of acid soaps. II. Anhydrous acid sodium palmitates. J. W. McBain and M. C. Field. **III. Anhydrous acid potassium oleate.** J. W. McBain and A. Stewart (J.C.S., 1933, 920—924, 924—928).—II. NaPl,HPl and 2NaPl,HPl exist as solid phases which decompose at 74·2° and 91·1°, respectively. No solid solutions are formed, but there is an extensive liquid crystal area.

III. The system KOl–HOl is similar, but there is only one acid soap, KOl,HOl, which decomposes at 47°. A preliminary investigation indicates the probable existence of NaStr,2HStr and 2NaStr,HStr. D. R. D.

Conductivity in the three-component system oleic acid–potassium oleate–water. J. W. McBain and A. Stewart (J.C.S., 1933, 928—932).—At 25°, aq. K oleate (I) dissolves oleic acid (II) until a composition 2KOl,HOl is reached. With conc. solutions a liquid crystal phase is formed with the same ratio of (I) to (II) but with a smaller proportion of H_2O. With more dil. solutions the second phase is isotropic and consists mainly of (II), with dissolved (I) and H_2O. Conductivity, cryoscopic, and p_H data indicate that the acid soap is mostly in a colloidal undissociated state. D. R. D.

Kinetics of coagulation of colloids. V. Variation of viscosity during coagulation. S. S. Joshi and K. S. Viswanath (J. Indian Chem. Soc., 1933, **10**, 329—340).—The change of viscosity has been followed during coagulation of As_2S_3 sols (4·5 g. per litre) at 35°. Viscosity cannot be used as a quant. indicator of coagulation. A. S. C. L.

Protective action of colloids. III. Influence of sucrose and sodium oleate on stability of colloid manganese dioxide. S. S. Joshi and A. N. Lal (J. Indian Chem. Soc., 1933, **10**, 367—371).—Coagulation of MnO_2 sols (0·75 g. per litre) has been observed when solutions of sucrose and Na oleate are added as protectors. A. S. C. L.

Influence of lyophile colloids on precipitation from solution. Gelatin and silver chromate. III. T. R. Bolam and W. J. Donaldson (Trans. Faraday Soc., 1933, **29**, 864—877; cf. A., 1930, 414).—Measurements of potential in aq. mixtures

of $AgNO_3$ and K_2CrO_4 in which pptn. of Ag_2CrO_4 is hindered by the presence of gelatin show that (1) part of the Ag_2CrO_4 is in the form of a highly supersaturated solution, (2) the remainder is accounted for by $Ag^{\cdot}$ and CrO_4'' combined with gelatin. The inhibitive action of gelatin is greatest at about p_H 5. The degree of supersaturation at a given p_H is independent of the concn. of gelatin, above some undetermined low val. F. L. U.

Lyotropic series in swelling and its extension to organic and non-ionising substances. X. Influence of benzene derivatives with two or more hydrophile groups on the swelling of potato starch. J. R. KATZ, A. WEIDINGER, and F. J. F. MUSCHTER, jun. **XI. Influence of substances with two or more hydrophile groups on the swelling of collagen.** J. R. KATZ and A. WEIDINGER (Biochem. Z., 1933, **263**, 323—331, 421—427).—X. With one hydrophile group, the increased swelling is in the order $PhOH > NH_2Ph > PhOBz > PhSO_3Na$. A second group impairs this activity in the same order, the impairment being slight with two phenolic groups. Similar results are given for substances with one phenolic and one non-phenolic hydrophile group (CO_2Na, SO_3Na, NH_2) and with two non-phenolic hydrophile groups.

XI. Curves show the effect of a variety of aliphatic substances having $\leqslant 2$ CO_2H and OH groups and aromatic substances with $\leqslant 2$ CO_2H, SO_3H, and OH groups. In all cases, introduction of a second hydrophile group impairs the effect of the first. P. W. C.

Determination of the swelling of casein. W. MOHR and J. MOOS (Milch. Forsch., 1933, **15**, 384—389).—The swelling has been examined microscopically at p_H 1—4·5 in different acids. At p_H 4·5 there is slight contraction. E. B. H.

Graphic representation of chemical equilibria. P. JOLIBOIS (Compt. rend., 1933, **197**, 451; cf. this vol., 904).—A claim to priority regarding the method described (cf. this vol., 464). C. A. S.

Multiple equilibria. F. SCHUSTER (Brennstoff-Chem., 1933, **14**, 310—311).—The general problem of multiple equilibria is briefly discussed and various types are classified. A. B. M.

Nomenclature of dissociating compounds. (Acid–base problem.) F. KLAGES (Z. Elektrochem., 1933, **39**, 663—668). E. S. H.

Equilibrium in the system *cyclo*hexane–benzene–hydrogen. R. B. PURDUM and R. N. PEASE (J. Amer. Chem. Soc., 1933, **55**, 3109—3111).—The equilibrium const. of the reaction $C_6H_6(g)+3H$ $C_6H_{12}(g)$ has been determined dynamically between 250° and 275° using a Cu catalyst. The free energy of the reaction in this range is given by $\Delta F = -43{,}800 + 18{\cdot}2T \log T - 0{\cdot}008T^2 - 31{\cdot}0T$. J. G. A. G.

Dissociation constant of hypochlorous acid. J. M. GALLART (Anal. Fis. Quím., 1933, **31**, 422—426).—The decomp. of NaOCl in dil. solution (approx. 0·02*N*) at 25° is termol. With increase of p_H of the solution the velocity coeff. rises from 7 at p_H 5·75 to a max. (32·8) at p_H 6·7, and falls to 7·2 at p_H 7·87. The ionisation const. of HOCl at 25° is $1{\cdot}05 \times 10^{-7}$. H. F. G.

Dissociation constants of bile acids. B. A. JOSEPHSON (Biochem. Z., 1933, **263**, 428—443).—Vals. for cholic, deoxy-, glyco-, glycodeoxy-, tauro-, and taurodeoxy-cholic acids are given. The results agree fairly closely with those of Hammarsten (A., 1924, i, 1139) but are very different from those of Henriques (A., 1931, 1369). P. W. C.

Peptides of tervalent amino-acids. III. Apparent dissociation constants, free energy changes, and heats of ionisation of peptides involving arginine, histidine, lysine, tyrosine, and aspartic and glutamic acids, and the behaviour of lysine peptides towards nitrous acid. J. P. GREENSTEIN (J. Biol. Chem., 1933, **101**, 603—621).—The heats of ionisation of the free groups of peptides are independent of the constitution of the mol. and afford a means of identification of the ionising group. The change in free energy due to the ionisation of CO_2H in peptides (I) is $>$ in NH_2-acids (II) and has an appreciable temp. coeff.; on the other hand, the energy change in (I) is $<$ in (II) for NH_2 and is independent of temp. In the transition of (II) to (I) NH_2 and CO_2H are considerably weakened and may be modified by the presence of other groups. Whereas lysine requires 15 min. for complete deamination, lysyl-peptides require about half this time. H. G. R.

[Electrolytic] dissociation of zinc sulphate. C. W. DAVIES (Trans. Faraday Soc., 1933, **29**, 834—835).—Attention is directed to errors in a paper by Cowperthwaite (this vol., 569). F. L. U.

Study of saline solutions. V. P. SCHISCHOKIN (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 21—24).—Theoretical. R. T.

Relations between kinetics and chemical equilibria. III. Synthesis and decomposition of potassium pyrogallol carbonate. A. BERTHOUD and D. PORRET (J. Chim. phys., 1933, **30**, 453—466; cf. this vol., 903).—The synthesis of K pyrogallol carbonate from $KHCO_3$ and pyrogallol, and its decomp. in aq. solution, takes place through the formation of an intermediate compound, probably $C_6H_3(OH)_2{\cdot}O{\cdot}CO_2K$. The equilibrium const. increases with the temp. The results differ from those obtained by Widmer (A., 1929, 517). E. S. H.

Vapour pressure of the systems sodium sulphate–water and sodium carbonate–water. E. J. RODE (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 97—134).—V.p.–temp. and v.p.–composition curves are recorded. R. T.

F.-p. curves of binary mixtures: $TiCl_4$–$SiCl_4$, $TiCl_4$–CCl_4, $TiCl_4$–$SnCl_4$, and $TiCl_4$–$SbCl_5$. N. NASU (Bull. Chem. Soc. Japan, 1933, **8**, 195—207).—$TiCl_4$ and $SnCl_4$ form a continuous series of mixed crystals. The remaining systems give simple eutectics. F. L. U.

System chlorine–phosphoryl chloride. A. P. ROLLET and W. GRAFF (Compt. rend., 1933, **197**, 555—557).—The thermal diagram shows the existence of $2POCl_3,Cl_2$. This has been isolated as yellow prisms, dissociating above −55°. $POCl_3$ has m.p. $1{\cdot}15 \pm 0{\cdot}05°$. C. A. S.

Ceramic refractory materials. VI. System ZrO_2–MgO. VII. Binary systems MgO–CaO, MgO–BeO, CaO–BeO. O. Ruff, F. Ebert, and U. Krawczynski (Z. anorg. Chem., 1933, **213**, 321—332, 333—335; cf. B., 1929, 474).—VI. The system is characterised by a eutectic at 2150° (50% MgO) and by a series of mixed crystals. The compound $MgZrO_3$ reported by Wartenburg was not observed (cf. A., 1930, 847). *X*-Ray photographs were used in elucidating the nature of the solid phases.

VII. The authors' vals. for the eutectic temp. in the systems CaO–MgO and MgO–BeO are respectively 80° and 280° > those previously recorded (this vol., 27). The discrepancy is discussed. H. J. E.

Sodium hydroxide–sodium cyanide melts. R. Holtje (Z. anorg. Chem., 1933, **214**, 65—72; cf. A., 1932, 587).—Fused NaOH and NaCN react above 500° in absence of H_2O and O_2, forming Na_2CO_3, Na_2CN_2, Na_2O, and H_2. In presence of H_2O reaction starts at 300°, forming NH_3 and HCO_2Na, which reacts with NaOH to form Na_2CO_3 and H_2. In presence of O_2, excess of NaCN is partly oxidised to N_2, and partly forms NH_3, H_2, and Na_2CO_3 due to the resulting H_2O. Excess of O_2 forms Na_2CO_3, N_2, $NaNO_3$, and H_2O. The ready reaction of NaOH–NaCN melts with SnO_2 probably depends on the removal of H_2O, produced when stannate is formed, by reaction with NaCN. Addition of Na also removes H_2O, facilitating the attack of SnO_2 by NaOH. NaCN is better than Na because it does not attack the Ni crucible. H. J. E.

Thermal analysis of the system lithium fluoride–lithium metaborate. I. I. Kitaigorodski, T. A. Popova, and O. K. Botvinkin (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 135—139).—LiF undergoes a change of form at 812°, and $LiBO_2$ at 785°. The fusion diagram of the system indicates formation of the compound, $2LiF,3LiBO_2$, m.p. 755°, which shows transition points at 545° and 585°. R. T.

Acid salts of monobasic organic acids. I. [r-Mandelic acid.] J. D. M. Ross and T. J. Morrison (J.C.S., 1933, 1016—1022).—Isotherms at 25° indicate the existence of KM,HM, KM,2HM, NaM,HM, NaM,2HM, BaM_2,2HM,H_2O; and the *salts* KM,3HM; NaM,3HM; LiM,HM; SrM_2,2HM, and CaM_2,2HM (M=OH·CHPh·CO_2). The structural formulæ and relative stabilities of these compounds are discussed. D. R. D.

Phase-rule study of mixed derivatives of alcohols. W. S. Caldwell and K. R. Maclean (J. Amer. Chem. Soc., 1933, **55**, 3458—3460).—Mixed crystals are formed by Me and Et *p*-nitrobenzoates (min. m.p. 52° with 20% of Me ester) and 3 : 5-dinitrobenzoates (min. m.p. 73° with equimol. mixtures), but not by Et and Bu 3 : 5-dinitrobenzoates (eutectic m.p. 51°, with 64% of Bu ester). R. S. C.

Fusion curves of solid solutions with compound formation. A. B. Mlodziejowski (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 13—20).—Mathematical. R. T.

Singular points of fusion curves. A. B. Mlodziejowski (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 5—12; cf. A., 1931, 1127).—Mathematical. R. T.

Systems of sulphur dioxide and hydrogen derivatives of benzene. W. F. Seyer and E. G. King (J. Amer. Chem. Soc., 1933, **55**, 3140—3149).—SO_2, in the presence of O_2, forms the white *substance* $(C_6H_{10},SO_2)_x$ with C_6H_{10}, whilst even in the absence of O_2, C_6H_8 yields the white *polymeride* $(C_6H_8,SO_2)_x$. No compound is formed in the O_2-free system C_6H_{10}–SO_2, but the f.-p. curve has a eutectic at −110° with 89·5 mol.-% of C_6H_{10}. Physical properties do not provide a basis for predicting the behaviour of SO_2 with C_6H_6 and its hydrogenation products (cf. A., 1930, 405). A ring structure for SO_2 is proposed. J. G. A. G.

***X*-Ray study of the system nickel–oxygen–water.** M. le Blanc and E. Mobius (Z. Elektrochem., 1933, **39**, 753—754).—The existence of new lines reported by Cairns and Ott (this vol., 352) is confirmed. Dissociation pressure measurements do not confirm the existence of Ni_2O_3,H_2O, $Ni_2O_3,2H_2O$, and hydrates of Ni_3O_4 and Ni_6O_7. H. J. E

Ternary system ammonia–nitric anhydride–water. N. S. Kurnakov and M. N. Ravitsch (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 169—184).—The equilibrium relations have been studied at −10°, 0°, 25°, 35°, 55°, 80°, 86°, 100°, and 130°. At −10° and 0° the solid phases consist of NH_4NO_3 and $NH_4NO_3,2HNO_3$ (alone or together), whilst at higher temp. NH_4NO_3 is the only solid phase. The transition point of α- into β-NH_4NO_3 is at 32°. R. T.

Separation in the system KOH–NH_3–H_2O and ternary systems of the type ether–water–X. E. Janecke (Z. Elektrochem., 1933, **39**, 682—686).—Equilibrium data are given for the portion of the KOH–NH_3–H_2O system in which the formation of two liquid phases is possible. The results are discussed in relation to other ternary systems. E. S. H.

System strontium nitrate–nitric acid–water. A. Sieverts and W. Petzold (Z. anorg. Chem., 1933, **214**, 27—32; cf. this vol., 782).—Solubilities have been measured between −25° and 50°. In 60% HNO_3, $Sr(NO_3)_2$ is almost insol. Only the tetrahydrate was observed. H. J. E.

Equilibria in the systems $(NH_4)_2SO_4$–$NiSO_4$–H_2O, $(NH_4)_2SO_4$–$CoSO_4$–H_2O, $(NH_4)_2SO_4$–$ZnSO_4$–H_2O, Na_2SO_4–$NiSO_4$–H_2O, and Na_2SO_4–$CoSO_4$–H_2O, at 25°. R. M. Caven and W. K. Gardner (J.C.S., 1933, 943—946).—Isotherms at 25° afford evidence of two series of double salts corresponding with $(NH_4)_2SO_4,MSO_4,6H_2O$, and $Na_2SO_4,MSO_4,4H_2O$. D. R. D.

System ferrous sulphate–manganous sulphate–water at 0° and 25°. A. McL. White (J. Amer. Chem. Soc., 1933, **55**, 3182—3185).—The data refer to the entire concn. range. At 0° a heptahydrate solid solution is produced, whilst at 25° two series of solid solutions, hepta- and penta-hydrate, are formed. J. G. A. G.

Equilibrium in the oxidation of liquid iron by steam and the free energy of ferrous oxide

in liquid steel. J. CHIPMAN (J. Amer. Chem. Soc., 1933, **55**, 3131—3139).—From determinations of the O content of cold Fe previously molten and in equilibrium with a stream of H_2–steam mixture, the O concn. in molten Fe is found to be almost directly proportional to the mol. ratio of steam to H_2; from this it is inferred that the solute is an oxide of Fe containing 1 atom of O per mol. The activity of the FeO has been evaluated and the data for the range 1550—1770° are expressed by $\log K = -6200/T - 3{\cdot}28$ and $\Delta F° = -28{,}400 + 15{\cdot}0T$, where $K = p_{H_2O}/(p_{H_2} \times a_{FeO})$. The free energy of formation of FeO from its elements in molten Fe is $\Delta F° = -31{,}200 - 1{\cdot}0T$, which does not accord with previous results (this vol., 466).

J. G. A. G.

Causticisation of sodium carbonate by ferric oxide. XVI. Dissociation of sodium carbonate in presence of ferric oxide. III. M. MATSUI, K. BITO, and M. KADONO (J. Soc. Chem. Ind., Japan, 1933, **36**, 468—471B).—The pressure–temp. curve for $Na_2CO_3 + Fe_2O_3$ is given from 310° to 850°. A. G.

Action of strong acids on the equilibrium $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$. W. LANGE (Z. anorg. Chem., 1933, **214**, 44—54; cf. A., 1932, 132).—The abnormal effect of H_2O on the equilibrium does not depend on ionisation of H_3PO_4. HNO_3, H_2SO_4, and $PhSO_3H$ lessen the abnormal effect, and $HClO_4$ causes increased formation of H_2PO_3F. The action of these acids is attributed to removal of H_2O from the equilibrium mixture, due to hydrate formation.

H. J. E.

Activity coefficient of potassium chloride in aqueous solutions at 0° from e.m.f. and f.-p. data. R. P. SMITH (J. Amer. Chem. Soc., 1933, **55**, 3279—3282).—Vals. derived from the e.m.f. of the cell $Ag|AgCl|KCl(c)|K_xHg|0{\cdot}1M\text{-}KCl|AgCl|Ag$ for $c = 0{\cdot}1$—$3{\cdot}5$ agree with those from f.-p. data (this vol., 126). The concordance confirms the trustworthiness of the flowing amalgam electrode.

J. G. A. G.

V.p., [density], and activity coefficients of aqueous solutions of perchloric acid at 25°. J. N. PEARCE and A. F. NELSON (J. Amer. Chem. Soc., 1933, **55**, 3075—3081).—The data refer to 0·1—11·9M-$HClO_4$. The activity of H_2O in corresponding solutions of HCl and $HClO_4$ is identical up to $2M$, but at higher concns. decreases more rapidly in $HClO_4$. The ion activity coeffs., γ, of these acids have min. in 0·4M solutions, but γ for $HClO_4$ rises more rapidly to very high vals. at high concn., as anticipated from the relative hydrating powers of the ions. Free energies of transfer and partial mol. vols. have been calc. J. G. A. G.

Activity coefficients of salts in anhydrous acetic acid solutions from solubility measurements [at 25°]. A. W. SCHOLL, A. W. HUTCHISON, and G. C. CHANDLEE (J. Amer Chem. Soc., 1933, **55**, 3081—3088).—The solubility of $KClO_4$ in anhyd. AcOH containing LiCl, NaBr, and $MgCl_2$, and that of $BaCl_2$ in the presence of NaBr, have been determined. The data accord with the predictions of the interionic attraction theory as extended by Gronwall, La Mer, and others. J. G. A. G.

Thermal effects produced by the exposure of massive gold to saturated water vapour. F. BARRY and E. P. BARRETT (J. Amer. Chem. Soc., 1933, **55**, 3088—3098; cf. A., 1922, ii, 473).—The rate of deposition of H_2O, from its saturated vapour, on massive Au at 22—23° decreases exponentially with time. The heat, H (millical. per sq. cm.), evolved in time t is given by $\log_{10} H = 1{\cdot}5990 - 0{\cdot}3486/t^{0{\cdot}409}$, leading to the total heat 0·0397 g.-cal. per sq. cm. when $t = \infty$. Initially, 7570 g.-cal. are evolved per g. of H_2O deposited, and the val. falls to 560, affording a total heat of 1601. Capillary inhibition may account for the phenomena. J. G. A. G.

Affinity of metals for sulphur. III. Heats of combustion and formation of the arsenic sulphides, As_2O_3,As_2O_5, and of As_2O_3,SO_3. E. V. BRITZKE, A. F. KAPUSTINSKI, and L. G. TSCHENZOVA (Z. anorg. Chem., 1933, **213**, 58—64; cf. A., 1932, 573).—Heats of combustion of As_2S_2 and As_2S_3, and heats of dissolution of As_2O_3, As_2O_3,As_2O_5, and As_2O_3,SO_3 were measured directly. The heats of formation of As_2S_2 and As_2S_3 from solid As and rhombic S are 28·93 and 34·75 kg.-cal., respectively.

H. J. E.

Thermal data on organic compounds. XII. Heats of combustion of nine hydrocarbons. H. BANSE and G. S. PARKS (J. Amer. Chem. Soc., 1933, **55**, 3223—3226).—The standardised heats of combustion per g. in vac. at 19° are: di*iso*butylene (*l*) 11,273, *n*-C_8H_{18} (*l*) 11,434, durene (*s*) 10,337, *iso*-durene (*l*) 10,348, prehnitene (*l*) 10,370, C_6HMe_5 (*s*) 10,432, C_6Me_6 (*s*) 10,500, *n*-$C_{12}H_{26}$ (*l*) 11,335, and dibenzyl (*s*) 9,914 g.-cal. The increment per CH_2 is 156,350 g.-cal. J. G. A. G.

Entropy and free energy relations among hydrocarbons. G. S. PARKS (Ind. Eng. Chem., 1933, **25**, 887—891).—The molal entropy at 25° (S) for paraffins $= 25{\cdot}0 + 7{\cdot}7n - 4{\cdot}5r$, where n=no. of C atoms and r=no. of side branches in the main chain. An olefinic linking generally decreases the entropy by 2·7, but the effect is influenced by the neighbouring groups. For benzenoid hydrocarbons $S = 25{\cdot}0 + 7{\cdot}7N - 4{\cdot}5R + 19{\cdot}5p_1$, where N=no. of C atoms outside the C_6H_6 ring, R=no. of hydrocarbon groups in excess of two attached to any C atom in the aliphatic chain, and p_1=no. of Ph groups. For 5- or 6-membered polymethylene ring compounds $26{\cdot}5p_2$ is substituted for $19{\cdot}5p_1$. The free energy of formation at 25° (F) for paraffins $= -11{,}700 + 1080n + 800r$ g.-cal.; for olefines it is 23,000—17,000 g.-cal. > that of the corresponding paraffin. Passing from C_6H_6 through the Me derivatives F decreases from 29,000 to a min. 20,000 for $C_6H_2Me_4$ and then increases to 27,000 for C_6Me_6. In the series CH_4 to CPh_4 F increases by 36,000 g.-cal. for each additional Ph group. The free energy of a no. of typical hydrocarbons is a linear function of the temp. The application of free energy data to (1) the conversion of *cyclo*hexane into methyl*cyclo*pentane, (2) the polymerisation of *n*-hexene, and (3) the production of higher alcohols is considered. D. K. M.

Simultaneous conduction by electrolytes during the measurement of resistance of palladium wires containing hydrogen. D. P. SMITH (Z.

Elektrochem., 1933, **39**, 743—744; cf. Knorr and Schwartz, this vol., 676).—The effect due to simultaneous conduction by the electrolyte is shown theoretically to lie almost within the error of measurement. The lowering of resistance of the wire is attributed to ionised H in the Pd (cf. A., 1921, ii, 423). H. J. E.

Mobility of ions in H^2H^2O. G. N. Lewis and T. C. Doody (J. Amer. Chem. Soc., 1933, **55**, 3504—3506).—Conductivities of HCl and KCl in 97% H^2H^2O between 5° and 35° have been determined. The mobilities at 18° of H^{2+}, K^+, and Cl^- in pure H^2H^2O are 213·7, 54·5, and 55·3, respectively. J. G. A. G.

Conductivity [and density] of sodium iodide solutions at 25° and the limiting conductance of the iodide ion. P. A. Lasselle and J. G. Aston (J. Amer. Chem. Soc., 1933, **55**, 3067—3071).—The data refer to 0·0007—0·17*M* solutions. The limiting equiv. conductivity of NaI is 126·85 reciprocal ohms and that of I′ is 76·75. Shedlovsky's modification of the Onsager equation is obeyed at concn. $< 0{\cdot}04N$. J. G. A. G.

Conductivity of some weak electrolytes and glycerol solutions with 75-cm. waves. B. G. Whitmore (Physikal. Z., 1933, **34**, 649—659).—The following solutions were used: LiBr, $Co(NO_3)_2$, CdI_2, $CdBr_2$, $ZnCl_2$, ZnI_2, in $COMe_2$; $HgCl_2$ in $COMe_2$–H_2O; tartaric and propionic acids in H_2O. The increase of conductivity at high frequency observed in most cases agrees with the Debye–Falkenhagen theory, if only the ions present are considered. $HgCl_2$ showed smaller effects than the theoretical, whilst $ZnCl_2$ and ZnI_2 in $COMe_2$ gave unexpectedly large effects, although in H_2O these behave quite normally. The solutions of $ZnCl_2$ and ZnI_2 in $COMe_2$ must contain large complex ions, or the absorption may be an "anomalous dipole absorption" of the undissociated mol. The anomalous absorption of glycerol was lowered by addition of $Ca_2Fe(CN)_6$; the extent of lowering is dependent on the valency of the added salt. The explanation of this effect as a consequence of "ionic saturation" is discussed. A. J. M.

Electrical conductivities of liquid mixtures of phenol–aniline, phenol–*p*-toluidine, and phenol–*m*-cresol. O. R. Howell and H. G. B. Robinson (J.C.S., 1933, 1032—1037).—The conductivity–composition curves (at 50°) afford no evidence of the compounds which separate out on freezing. D. R. D.

Conductivity and dielectric constant of liquids in high-frequency fields. M. Wien (Physikal. Z., 1933, **34**, 625—627).—According to the Debye–Falkenhagen theory the dielectric const. and equiv. conductivity should be related to the square root of concn. This is complicated by (1) potential effect, (2) potential dissociation effect with weak electrolytes, (3) time effect, (4) dipole effect. A. J. M.

Dependence of dispersion of conductivity on temperature. H. Geest (Physikal. Z., 1933, **34**, 660—671).—The dependence of dispersion of conductivity on temp. has been studied with waves of 8 m. length, using a resonance method. Solutions of $MgSO_4$, $La_2(SO_4)_3$, and $Ca_2Fe(CN)_6$, were examined at 0—50°. The results for the last substance do not agree with the Debye–Falkenhagen theory. A. J. M.

Calculation of the e.m.f. of an element from osmotic data. A. Valentini (Boll. Chim. farm., 1933, **72**, 565—566).—A method of calculation is given. H. F. G.

Junction potentials between glass and salts in fusion. H. B. Elkins and G. S. Forbes (J. Amer. Chem. Soc., 1933, **55**, 3250—3260).—From the e.m.f. at 490° of the cell Ag|0·952 mol.-% AgCl+NaCl|glass|KNO_3+$NaNO_3$|glass|AgCl+XCl(*c*)|Ag, where X is an alkali metal, the "transference consts.," depending on the case with which X enters the glass, are $K_{Li} > K_{Na} \gg K_K > K_{Pb} \gg K_{Cs} > K_{Ag}$. High mobility is attributed to smallness of ion and the low val. of K_{Ag} to the great stability of AgCl. An equation derived on the assumption of a concn. cell with transference by cation alone accounts for the e.m.f. of cells of the type Ag|AgCl+LiCl(+KCl . . .)|glass|KNO_3+$NaNO_3$|glass|AgCl+LiCl(+KCl . . .)|Ag at 490°. Reproducible results are also obtained with bromides in place of chlorides, except in the case of KBr. Vals. of the activity coeff. agree with data (A., 1931, 309, 800) for AgBr in LiBr and NaBr. AgCl in LiCl and KCl yields less ideal solutions than the bromides. The results of Günther-Schulze (A., 1913, ii, 192) and new data are consistent with the view that the rate of diffusion of Ag into glass from fused AgCl is controlled by the rate of exit of Na^+ rather than by weak dissociation of AgCl. J. G. A. G.

Acetic acid–acetate buffers in potassium chloride and sodium chloride solutions using the quinhydrone electrode. E. F. Chase (J. Amer. Chem. Soc., 1933, **55**, 3072—3075).—The classical dissociation const. of AcOH in 0·1*M*-NaOAc and either 0·9*M*-KCl or -NaCl increases almost linearly with concn. of mol. AcOH from 0·001 to 5*M*. J. G. A. G.

Acid–base titrations in alcohol–water mixtures. I. Relative p_H values for some buffer solutions in alcohol–water mixtures. H. Baggesgaard-Rasmussen and F. Reimers (Dansk Tidsskr. Farm., 1933, **7**, 164—178).—Buffers of $CH_2Cl{\cdot}CO_2H$, HCO_2H, and AcOH with their Na salts have been studied electrometrically in 20—85% EtOH. Relative dissociation consts. of the acids are calc. and found to increase with increasing salt concn. R. P. B.

Electrometric titration of *dl*-2-thiolhistidine. G. M. Richardson (Biochem. J., 1933, **27**, 1036—1039).—The titration curve of 0·03*M*-*dl*-2-thiolhistidine (I) against 0·10*N*-NaOH and -HCl leads to p_{K_1} 1·84, p_{K_2} 8·47, and p_{K_3} 11·4 for the CO_2H, NH_2, and SH groups, respectively. Basic dissociation of a cyclic N atom is not evident. (I) does not readily form a reversible oxidation–reduction system. F. O. H.

Potentials of ascorbic acid. D. E. Green (Biochem. J., 1933, **27**, 1044—1048).—The potentials of ascorbic acid (I), which are of a drifting and readily polarisable nature, are for given p_H vals. a function only of the reductant and not of the oxidant. The

mol. strength of the reductant is also not a determining factor. Potential measurements confirm the presence of (I) in lemon juice. The presence of the reduced form of (I) in natural sources is discussed. F. O. H.

Chemical behaviour of polonium. O. ERBACHER and H. KADING (Z. physikal. Chem., 1933, **165**, 427—432).—The bivalent cation present in solutions of Po in mineral acids is not $PoO^{\cdot\cdot}$; it is probably $Po^{\cdot\cdot}$. Assuming it to be $Po^{\cdot\cdot}$, the normal electrode potential of Po calc. from the discharge voltage is more positive than the potential of Ag, which is consistent with the electrochemical separation of Po on Ag. R. C.

Size of electrolytically generated gas bubbles. B. KABANOV and A. FRUMKIN (Z. physikal. Chem., 1933, **165**, 433—452).—Coehn and Neumann's theory of the dependence of bubble diameter, d, on the conditions of electrolysis (Z. Physik, 1923, **20**, 54) is untenable. For Hg, Ag, and Pt electrodes in 0·001—1N solutions of Na_2SO_4, NaOH, and H_2SO_4 the variation of d with the angle of contact θ is represented by the same curve. Since θ depends on the electrode potential, E, the latter determines d. For a Hg electrode the d–E curve is similar in form to the electrocapillary curve and the max. have approx. the same position. The above theory agrees with Coehn's experimental data. The equilibrium state of the bubble prior to detachment is determined solely by the surface tension, the hydrostatic pressure, and the gas pressure. R. C.

Hydrogen overvoltage of lead and lead–antimony alloys. I, II. Y. KATO (J. Electrochem. Soc., Japan, 1932, 120—124, 161—167).—I. The H overvoltage of a Pb-Sb (1—10%) alloy varies from the beginning of the passage of the current; it is unaffected by the rate of cooling of the alloy. Antimonised Sb gives very low vals.

II. The H overvoltage at the same c.d. varies at first with the time, and then approaches a definite val. The H overvoltage on Pb is high for a smooth, and low for a rough, surface. Single-crystal Pb gives high vals., even when the surface is etched. CH. ABS.

Anodic behaviour of iron. K. GEORGI (Z. Elektrochem., 1933, **39**, 745—749; cf. this vol., 468).—C.d.-potential curves for the dissolution of Fe anodes in N-H_3PO_4, -H_2SO_4, -HCl, -$HClO_4$, -$CCl_3{\cdot}CO_2H$, -NaBr, -NaCl, -$NaClO_4$, -Na_2SO_4, -$CCl_3{\cdot}CO_2Na$, and in 0·5M-Na phosphate show that $Fe^{\cdot\cdot}$ is formed without appreciable polarisation in solutions of the free acids, NaCl, and NaBr. For $NaClO_4$ the c.d. rises rapidly at +1·4 volts, hydroxide being formed and no O_2 evolved. For the other salts the rise occurs at >1·7 volts, with evolution of O_2. The change of potential with time at different p_H has been investigated. The mechanism of dissolution suggested is $Fe+2H^{\cdot} \longrightarrow FeH_2^{\cdot\cdot}$, $FeH_2^{\cdot} - 2\ominus \longrightarrow Fe^{\cdot\cdot}+2H^{\cdot}$. The abnormal behaviour of ClO_4' is due to its small tendency to form complex ions. The behaviour of Fe in general resembles that of Co and Ni. H. J. E.

Passivity of tantalum in non-aqueous solvents. B. Formamide, acetone, methyl ethyl ketone, pyridine, acetic acid, and sulphuric acid. P. O. SCHUPP (Z. Elektrochem., 1933, **39**, 731—735; cf. A., 1932, 1209).—The thickness of the oxide layer on a Ta anode, rendered passive by electrolysis of $Ca(NO_3)_2$ in the above solvents, is proportional to the voltage and independent of the solvent. At a given voltage the val. is the same as in H_2O, when aq. $CaCl_2$ is used to measure the capacity and thickness of the oxide layer. Using 10% H_2SO_4 for the capacity measurements the layer thickness in non-aq. solvents is approx. 10% < for Ta rendered passive in H_2O. H. J. E.

Reaction kinetics of coupled oscillators. H. PELZER (Z. Elektrochem., 1933, **39**, 608—611).—Theoretical. The rate of the homogeneous unimol. decomp. of a chain-like mol. is independent of the chain length. The rate of breaking of a particular linking is determined only by the strength of binding and the neighbouring mols. H. J. E.

Influences of electrical and magnetic fields on "spin" in gaseous detonations. W. A. BONE (Nature, 1933, **132**, 348).—A preliminary announcement of results. L. S. T.

Method of investigating gas reactions in absence of wall effects. A. REIS and E. GLUCKAUF (Z. Elektrochem., 1933, **39**, 607—608).—A stream of the reacting gas is mixed with a heated inert gas, and the mixture passed through a heated porous tube. The latter is surrounded by inert gas under pressure, inward penetration of which prevents contact of the reacting gas with the tube wall. The decomp. of HCO_2H, using H_2 as the inert gas, is described. H. J. E.

Kinetics of the hydrogen–oxygen low-pressure explosion. A. A. FROST and H. N. ALYEA (J. Amer. Chem. Soc., 1933, **55**, 3227—3233).—Upper and lower limits of the thermal explosion of H_2 (0·04—0·9 mol. fraction)–O_2 mixtures were determined at 480—540° in a KCl-coated Pyrex vessel and the effect of N_2 was investigated. The results for both limits are expressed by a kinetic equation including terms for (*a*) branching of reaction chains by collisions between a carrier and O_2, E=24,200, (*b*) breaking of chains at the wall governed by diffusion, apparent E=13,500, and (*c*) breaking of chains in gas phase by triple collisions, E < 4000 g.-cal. J. G. A. G.

Influence of pressure on the spontaneous ignition of inflammable gas–air mixtures. I. Butane–air mixtures. D. T. A. TOWNEND and M. R. MANDLEBAR (Proc. Roy. Soc., 1933, **A**, **141**, 484—493).—The influence of pressure on the spontaneous ignition of various C_4H_{10}–air mixtures at pressures up to 15 atm. has been studied. At 1 atm. the ignition points fell from > 600° to about 550° with increase in the C_4H_{10} content of the mixtures, and at 1·5 atm. from 560° to 480°; at 1·75 atm., however, a fall of 130—140° took place for mixtures of C_4H_{10} content > 3·5%. A similar sharp fall was observed with all other mixtures, the crit. transition pressure depending on the composition of the mixture. The ignition points lie in two groups, the one, for determinations below 3 atm., at > 450°, and the other, for determinations above 3 atm., at < 370°. The effect of

$PbEt_4$ in raising ignition temp is much greater at the crit. transition pressure than at atm. pressure. L. L. B.

Kinetics of dissociation of typical hydrocarbon vapours. R. N. Pease and J. M. Morton (J. Amer. Chem. Soc., 1933, **55**, 3190—3200).—At 550—630°, the order of stability is o-$C_6H_4Me_2$ > PhMe > C_6H_6 > m-$C_6H_4Me_2$ > PhEt > *cyclo*hexane > Δ^β-pentene > ethyl*cyclo*hexane > n-C_7H_{16}. The dissociations at 525—605° of n-C_7H_{16}, PhEt, Δ^β-pentene, and *cyclo*hexane are pseudo-unimol. homogeneous gas reactions, the first step in the last being the formation of methyl-*cyclo*pentane, whilst PhEt affords H_2 and styrene. Velocity coeffs. and energies of activation are calc., and the stability of the C_6H_6 ring as compared with the *cyclo*paraffins is emphasised. J. G. A. G.

Thermal decomposition of methyl azide. A homogeneous unimolecular reaction. J. A. Leermakers (J. Amer. Chem. Soc., 1933, **55**, 3098—3105; cf. A., 1929, 1018).—MeN_3, at 200—240° and pressures between 0·07 and 46·6 cm., decomposes into N_2, HN_3, C_2H_6, C_2H_4, NH_3, and $(CH_2)_6N_4$ in a homogeneous unimol. reaction. With initial pressures < 10 cm., the velocity coeff. falls below $k=3{\cdot}02\times10^{15}e^{43,500/RT}$. The theoretical expression relating k and pressure accords with the data when a mol. diameter 5×10^{-8} cm. and 13 classical oscillators are assumed. J. G. A. G.

Thermal decomposition of 2 : 4 : 6-trinitro-1 : 3 : 5-triazobenzene. S. Z. Roginski and C. C. Andreev (J. Chim. phys., 1933, **30**, 487—492).—Analysis of the kinetics of decomp. of 2 : 4 : 6-trinitro-1 : 3 : 5-triazobenzene at low temp. (35—50°) shows that the velocity of reaction is proportional to the 2/3 power of the mass of the substance. The calc. heat of activation is 32,300 g.-cal., which is the lowest val. recorded for an explosive. E. S. H.

Kinetic study of action of chlorine water on silver nitrate. (Mlle.) M. L. Josien (Compt. rend., 1933, **197**, 449—450).—The interaction of $AgNO_3$ and aq. Cl_2 proceeds in two stages: (1), instantaneous, $Cl_2+H_2O \rightleftharpoons HCl+HOCl$, with pptn. of AgCl, and (2), more slowly, $3HOCl=HClO_3+2HCl$, also with pptn. of AgCl. In absence of excess of $AgNO_3$, HOCl is relatively stable. Dilution retards, whilst a higher temp. accelerates, disappearance of HOCl (cf. A., 1899, ii, 736). C. A. S.

Autoxidation. IX. Kinetics of sulphite autoxidation according to theory of radical chains. P. Goldfinger and H. D. Graf von Schweinitz (Z. physikal. Chem., 1933, **B**, **22**, 241—256; cf. this vol., 911).—The kinetics of the autoxidation of sulphite by $Cu^{\cdot\cdot}$ worked out by the radical chain theory, utilising the radicals OH and HSO_3, and according to the method of stationary concns., agree with the observed velocity and heat effect data. A chain-breaking reaction, of the first order in respect of one radical, is postulated, and the reconversion of Cu^{I} into Cu^{II} is assumed to depend on the action of O_2 on $CuSO_3'$. These assumptions lead to a linear relation between the rate of disappearance of O_2 and (SO_3''), (O_2), and the total Cu concn. The absence of proportionality to (O_2) when an inhibitor is present is also explained. R. C.

Neutral salt action in the reaction between formic acid and iodine. A. von Kiss and A. Urmanczy (Z. anorg. Chem., 1933, **213**, 353—364).—The reaction velocity was measured at 25° in the dark in presence of various neutral salts. The primary and secondary salt action and the action of the medium were separated (cf. Bronsted, A., 1925, ii, 681). For the effect of the medium the log of the velocity coeff. was proportional to the salt concn. H. J. E.

Oxidation of cystine in non-aqueous media. II. Hydration of acetonitrile and acetic anhydride by a non-aqueous titration method. T. F. Lavine and G. Toennies (J. Biol. Chem., 1933, **101**, 727—734; cf. this vol., 598).—The two colour changes of thymol-blue distinguish between strong and weak acids in non-aq. titrations with NaOMe as base and $CHCl_3$ as solvent. The titration is used to study the hydrolysis of MeCN and the rate of dehydration by Ac_2O as applied to the prep. of cystine perchlorate in MeCN. A. L.

Combustion of graphite in Osram filaments in a stream of gas. V. Sihvonen (Ann. Acad. Sci. Fennicæ, 1933, **A**, **38**, No. 2, 3—34).—The action of streaming H_2O vapour, CO_2, and O_2 at low pressures (10^{-4} to 10^{-1} mm.) on C filaments at various temp. has been studied. In H_2O vapour CO is formed; part of this is then oxidised by the H_2O. Diminished production of CO as the temp. is raised is due to desorption of H_2O. In CO_2, CO is formed only above 1400°. At 800—1400° O_2 forms CO_2+2CO at an unpoisoned surface, whereas if the filament is poisoned by CO, this gas is the sole product above 900°. Velocities and thermal effects of certain of the processes have been determined. F. L. U.

Atmospheric corrosion of magnesium. L. Whitby (Trans. Faraday Soc., 1933, **29**, 844—853).—Wt.-increment–time curves are given for Mg exposed to outdoor and indoor atm. during 200 and 400 days, respectively. The rate of corrosion increases with R.H. Outdoors a loss of wt. always follows rain, owing to removal of $MgSO_4$, which is formed to a considerable extent. Both indoors and outdoors $MgCO_3$ predominates in the corrosion product. No indication of protective film formation was observed. F. L. U.

Dissolution of magnesium in aqueous salt solutions. II. L. Whitby (Trans. Faraday Soc., 1933, **29**, 853—861; cf. this vol., 233).—Dissolution–time curves for different specimens of Mg in aq. NaCl and Na_2SO_4 are given. There is no evidence that inclusions of Mg_3N_2 or MgO act either as cathodes or as nuclei for anodic attack in NaCl solution. The influence of variations in metallic impurities on the rate of dissolution is marked in 0·1*N*-NaCl, but small in 0·002*N*-NaCl or in 0·1*N*-Na_2SO_4. The mechanism of attack is discussed. F. L. U.

Rusting of iron with excess of oxygen. G. Schikorr.—See B., 1933, 750.

Kinetics of the transformation of austenite. H. Lange and F. Wever.—See B., 1933, 708.

Corrosion passivity. III. Changes in the natural oxide film on iron during corrosion. W. Machu.—See B., 1933, 709.

Kinetics of the reaction of the hydrogen peroxide decomposing property of soil. K. SCHARRER (Z. Pflanz. Düng., 1933, **31**, A, 27—36).—Decomp. of H_2O_2 by soils of varied origin and composition in no case corresponded with a unimol. reaction throughout its course, although certain sections of the reaction curves approximated closely with that of a reaction of this type. Deviations from the course of a unimol. reaction were greater in acid than in alkaline soils, and may be ascribed in part to the presence or absence of catalysts and to differences in the effective reactive surfaces in soils of different structure. A. G. P.

Catalysis of Eder's reaction by cobalt compounds. G. H. CARTLEDGE and T. G. DJANG (J. Amer. Chem. Soc., 1933, **55**, 3214—3221).—At room temp., the reduction of $HgCl_2$ to Hg_2Cl_2 by oxalates is strongly catalysed in the light and in the dark by $Co(C_2O_4)_3'''$; $CoSO_4$ at concn. > 0·0002*M* accelerates the dark catalysis, whilst O_2 retards all of these reactions. However, $CoSO_4$ alone, in presence of O_2, produces only traces of Hg_2Cl_2, whilst oxidation by H_2O_2 of Fe'' instead of Co'' is much more effective in inducing Eder's reaction. At 100° in $H_2C_2O_4$ solution, the yield of Hg_2Cl_2 is parallel with the stability of the catalyst: $Co(C_2O_4)_3''' > MnO_4' > Mn(C_2O_4)_3'''$, and the life of the catalyst is decreased by rise of temp. and increase of acidity. $Fe(C_2O_4)_3'''$ and $Co(C_2O_4)_3'''$ accelerate the oxidation of $H_2C_2O_4$ by dil. $KMnO_4$. $Co(C_2O_4)_3'''$ and $Mn(C_2O_4)_3'''$ are therefore significant in the enhanced oxidising activity of $HgCl_2$. J. G. A. G.

Effect of hydrogen-ion concentration on the rate of oxidation of solutions of ferrous citrate. J. M. BRYAN (Trans. Faraday Soc., 1933, **29**, 830—833; cf. A., 1931, 1133).—Oxidation (by air) is rapid at p_H 5·35 and 5·71 and relatively slow at p_H 3·31. Secondary oxidation of the citric acid is a factor of considerable importance at the less acid end of the p_H range. The experiments were performed at 25°. F. L. U.

Oxidation of thiol compounds by hydrogen peroxide. II. Catalysis of oxidation of cysteine by thiocarbamides and thiolglyoxalines. N. W. PIRIE (Biochem. J., 1933, **27**, 1181—1188).—$CS(NH_2)_2$ (I) catalyses the oxidation of cysteine (II) to cystine (III) by H_2O_2 in acid solution; the kinetics of the reaction resemble those using Cu as catalyst (A., 1932, 27). Dithioformamidine has no action on (III), but oxidises (II) (under suitable conditions) to (probably) $OH{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, which is then reduced by (II) to (III). *N*-Allyl- and -phenylthiocarbamides, ergothioneine (IV), *dl*-2-thiolhistidine, and 2-thiolglyoxaline are almost as active as (I); the effects of other thiocarbamides are investigated. The catalytic effect of a mixture of Cu and (I) is the sum of their independent effects for slow rates of oxidation only; with larger amounts of the catalysts, one does not increase the rate due to the other. Similar results are found for Fe+(I) and metal+(IV). A reaction mechanism is given. Glutathione behaves similarly to (II). (I) appears to have no effect on the aerobic oxidation of (II) or methylene-blue at p_H 7·6. H. B.

Theory of heterogeneous catalysis. L. V. PISARSHEVSKI (Bull. Acad. Sci. U.R.S.S., 1933, **7**, 571—588).—The action of metallic catalysts is ascribed to the facility with which their free electrons react with those of the substrate; thus, Pt is assumed to catalyse hydrogenation by causing dissociation of H into proton and electron. R. T.

Catalyst activity. E. ROSENKRANZ (Chim. et Ind., 1933, Spec. no., 755—756).—A catalyst prepared by a reaction of the type solid I⟶ solid II + gas at a temp. > that at which it is to be used is to be considered as having undergone both decomp. and stabilisation (from the nascent state). It is deduced that for every catalyst there is a time of treatment necessary for max. activity, stabilisation being detrimental. Examples are ZnO prepared by the ignition of ZnC_2O_4 for the decomp. of MeOH and Fe_2O_3 prepared by the heating of $Fe(OH)_3$ for the decomp. of H_2O_2. C. I.

Conversion of ortho- into para-hydrogen over promoted iron synthetic ammonia catalysts at −190°. R. W. HARKNESS and P. H. EMMETT (J. Amer. Chem. Soc., 1933, **55**, 3496—3497).—The efficiency of the catalyst, outgassed at 450°, is greatly diminished by cooling in H_2 instead of He, and it appears that the activated adsorption of H_2 at 100—450° is primarily surface adsorption and not dissolution in the Fe. Exposure of the catalyst to O_2 between room temp. and 450° eliminates the high-temp. activity towards ortho–para conversion, but only slightly impairs the activity at −190°. J. G. A. G.

Present position of the theory of ammonia catalysis. C. KRÖGER (Z. Elektrochem., 1933, **39**, 670—671).—A criticism (cf. this vol., 681). E. S. H.

Thermodynamic measure of activity of catalysts. P. DOLCH (Z. Elektrochem., 1933, **39**, 602—607).—The application of the reaction isochore in representing experimental data for the reactions $CO+H_2O \rightleftharpoons CO_2+H_2$ and $2SO_2+O_2 \rightleftharpoons 2SO_3$ is discussed. H. J. E.

Catalytic reduction of carbon dioxide by hydrogen. H. KOCH and H. KÜSTER.—See B., 1933, 737.

Chemical inertia and heterogeneous catalysis. M. LEMARCHANDS (Chim. et Ind., 1933, Spec. no., 747—754).—Many metals are attacked only very slowly by Cl_2 or Br at low temp. Pure CaO at low temp. is only very slowly acted on by H_2O vapour or Cl, and Na, Mg, and Zn by SO_2 or CO_2. These phenomena, which are unexpected from the thermal balances, are described as instances of chemical inertia. The effect is due to adsorption which, in consequence of the surface reaction, produces a temp. at which further adsorption is impossible if the film is impermeable. In the case of Cl_2 reactions the elements capable of giving volatile chlorides, Hg, Al, Sn, S, P, As, Sb, are attacked at low temp. Those with less volatile chlorides are not. (It is assumed that the solids tested have been deprived of the normally present film of adsorbed air.) Deductions from this theory enable the properties necessary for a catalyst of a gaseous reaction to be predicted. It must be capable of effective adsorption,

and it should not itself have an exothermic reaction with one of the gaseous components. Thus catalysts for NH_3 syntheses are metals which do not readily form nitrides. In the Deacon Cl_2 process the val. of $CuCl_2$ lies in the fact that it has no action on HCl. The oxychloride is ineffective. "Chemical" explanations of this catalysis are unsound. C. I.

Formation of hydrogen peroxide in catalytic dehydrogenation. T. F. MACRAE (Biochem. J., 1933, **27**, 1248—1252).—With Pd-black as catalyst, the combination of H_2 and O_2 and the aerobic dehydrogenation of MeOH and EtOH yield, as an intermediate product, H_2O_2, which is detectable by $Ce(OH)_3$ (A., 1931, 390). Support is thus afforded to Wieland's theory of dehydrogenation. F. O. H.

Topochemical replacements. VII. Compact disperse materials. H. W. KOHLSCHUTTER and H. SIECKE (Z. Elektrochem., 1933, **39**, 617—623; cf. this vol., 919).—Pseudomorphic Fe_2O_3,xH_2O was prepared from $Fe_2(SO_4)_3$ and aq. NH_3. Its catalytic activity in the decomp. of H_2O_2 decreases with increasing H_2O content, depending also on the prep. and heat- and mechanical treatment of the specimen. The resemblance to $3Cu(OH)_2,Cu(NO_3)_2$ is discussed. H. J. E.

Kjeldahl reaction and carbon disulphide. J. MILBAUER and J. DOSKAŘ (Chim. et Ind., 1933, Spec. no., 782—783).—CS_2 vapour commences to be oxidised by H_2SO_4 at 180° or in presence of finely-divided Pd at 105°. Positive catalysts, in order of decreasing efficacy, are Pd, Se, Pt, $CuSO_4$, $HgSO_4$. C. I.

Catalytic properties and structure of metal films. I. Sputtered platinum. G. I. FINCH, C. A. MURISON, N. STUART, and G. P. THOMSON (Proc. Roy. Soc., 1933, **A**, **141**, 414—434).—The method of prep. of sputtered Pt films and their catalytic properties have been correlated with the structure as determined by electron diffraction. L. L. B.

Distribution of arsenic in contact systems. S. BYCHOVSKI.—See B., 1933, 746.

Influence of admixtures of sodium sulphate to magnesium sulphate carriers on the activity of platinum catalyst in the reaction $2SO_2+O_2 \longrightarrow 2SO_3$. N. S. ARTAMONOV.—See B., 1933, 746.

Determination of the activity of catalysts which accelerate the synthesis of benzine from carbon monoxide and hydrogen at ordinary pressure. S. WATANABE and K. MORIKAWA.—Sec B., 1933, 738.

Catalytic oxidation of organic compounds in the vapour state. I. Toluene, its derivatives and homologues. II. Various compounds. G. CHARLOT (Bull. Soc. chim., 1933, [iv], **53**, 572—577, 577—581).—See this vol., 680. Data relating to PhMe, xylenes, *p*-cymene, cumene, chloro- and nitro-toluenes, CH_2Ph_2, C_6H_6, $C_{10}H_8$, EtOH, BzOH, C_7H_{16}, and benzylic acid are given.

Spongy zinc deposits obtained by electrolysis of aqueous solutions of zinc sulphate. W. S. SEBBORN (Trans. Faraday Soc., 1933, **29**, 825—829).—The relations between concn. of solution, c.d., and character of deposit have been determined. Spongy Zn contains 15—25% of ZnO and $Zn(OH)_2$. Coherent deposits are formed on the lower surface of a horizontal electrode under conditions which would yield a spongy deposit with a vertical electrode. F. L. U.

Electrolysis of zinc sulphate solutions. P. GUARESCHI.—See B., 1933, 751.

Electrolytic refining of copper using complex salt of cuprous chloride. XI. Behaviour of bismuth. N. KAMEYAMA and S. MAKISHIMA.—See B., 1933, 750.

Theory of chromium plating. E. LIEBREICH (Z. Elektrochem., 1933, **39**, 628—629).—The effect of added acids on the current–potential curve for the electrolysis of pure H_2CrO_4 is to cause two new breaks. At very high concn. $HClO_4$ and H_3PO_4 cause reduction; H_3BO_3 does not. The formation of films on the electrodes is discussed. H. J. E.

Electrodeposition of palladium. R. H. ATKINSON and A. R. RAPER.—See B., 1933, 710.

Oxidation of graphite by electric discharges. V. SIHVONEN (Ann. Acad. Sci. Fennicæ, 1933, **A**, **38**, No. 3, 3—22; cf. this vol., 1020).—With a d.c. discharge at high potential between plates of graphite and Pt in CO_2 the reactions $CO_2+Pt_x \rightleftharpoons CO+Pt_xO$ and $CO_2+C_x \rightleftharpoons 2CO+C_{x-1}$ occur. With a.c. discharge in O_2 the cathodic component is alone effective in promoting oxidation of C. Both CO_2 and CO are formed, the proportion of the latter increasing with decreasing pressure of O_2. A very small a.c. at high potential between widely separated electrodes gives rise to more CO_2 and CO than corresponds with the current, in consequence of the intense ionisation of the gas. F. L. U.

Behaviour of dichlorodifluoromethane and of chlorotrifluoromethane in the electric discharge. N. V. THORNTON and A. B. BURG [with H. I. SCHLESINGER] (J. Amer. Chem. Soc., 1933, **55**, 3177—3182).—CCl_2F_2 attacks metals slowly at high temp. and at the same time reacts with the glass or SiO_2 containers giving SiF_4, CO_2, and CO; in the absence of the metal no reaction occurs. In the high-tension electric discharge, CCl_2F_2 decomposes partly into Cl_2, $CClF_3$, and smaller quantities of CF_4, $C_2Cl_2F_4$, C_2F_4, and less volatile substances. $CClF_3$ under similar conditions yields CF_4, Cl_2, CCl_2F_2, and small quantities of solid. The v.p. of CCl_2F_2 is given by $\log_{10} p=7{\cdot}385-1105/T$, from which the b.p. is −27·8°; for $C_2Cl_3F_4$, $\log p=7{\cdot}568-1300/T$ and b.p. 4·1°, and for $CClF_3$, $\log p=7{\cdot}347-857{\cdot}3/T$ and b.p. −81·1°. Latent heats and Trouton's consts. are calc. J. G. A. G.

Formation of silver in the photographic layer under the influence of *X*-rays. P. GUNTHER and H. TITTEL (Z. Elektrochem., 1933, **39**, 646—655).—At wave-lengths 0·245, 0·63, 1·09, and 1·54 A., 920, 363, 210, 148 atoms of Ag were liberated per absorbed quantum, agreeing approx. with Eggert and Noddack's vals. (A., 1927, 1154). The Ag was determined potentiometrically. The secondary electron energy

was calc., and at each wave-length approx. 1000 kg.-cal. was shown to be necessary to form 1 mol. Ag. H. J. E.

Oxidation of graphite by means of *X*-rays. V. SIHVONEN (Ann. Acad. Sci. Fennicæ, 1933, **A**, **38**, No. 4, 3—13).—In CO_2 at low pressure *X*-rays promote the same reactions as does a high-potential d.c. discharge (cf. this vol., 1019), whether the graphite plate is directly exposed to the radiation or not. No O_2 is formed. In O_2 the product is at first CO_2+2CO, the proportion of the latter increasing later to CO_2+CO. At extremely low pressures oxidation occurs only when the C plate is directly irradiated. F. L. U.

Chemical reactions brought about by *X*-rays and their determination. N. WATERMAN and H. LIMBURG (Biochem. Z., 1933, **263**, 400—409).—An electrometric method for quant. observation of the changes in a reaction mixture on irradiation has been used in the reduction of benzoquinone, methylene-blue, and cysteine. P. W. C.

Action of α-rays from polonium, *X*-rays, and ultra-violet rays on nitrogen iodide and other explosives. H. MURAOUR (Bull. Soc. chim., 1933, [iv], **53**, 612—613).—None of the radiations has any effect. A. S. C. L.

Simple type of isotopic reaction. G. N. LEWIS (J. Amer. Chem. Soc., 1933, **55**, 3502—3503).—The isotopic composition of H_2O is determined by means of the rapid reactions $H^1H^2O+NH^1H^1H^1=H^1H^1O+NH^1H^1H^2$ and $H_2O^{18}+SO^{16}O^{16}=H_2O^{16}+SO^{16}O^{18}$ and determination of d after the removal of the more volatile products. J. G. A. G.

Reaction between atomic hydrogen and carbon tetrachloride. H. F. SMYSER and H. M. SMALLWOOD (J. Amer. Chem. Soc., 1933, **55**, 3498—3499).—A greenish-blue luminescence accompanies the interaction of Wood's at. H with CCl_4. The products are a solid containing 55% Cl, HCl, and small quantities of an explosive volatile substance. J. G. A. G.

Formation of metallic hydrides by atomic hydrogen. E. PIETSCH [with F. SEUFERLING, W. ROMAN, and H. LEHL] (Z. Elektrochem., 1933, **39**, 577—586; cf. A., 1931, 1019, 1020, 1379, 1380).—Hydrides of Ag, Cu, Au, Be, Ga, In, and Ta were formed by the action of at. H on the solid element. Products were contaminated with unattacked element. Reaction between In vapour and H gave a blue luminescence. The In line 4511 Å. ($2p_1—2s$) was prominent, particularly on the glass walls, the excitation energy coming from the recombination of H atoms. This vapour reaction also yielded In hydride. H. J. E.

Solubility of silver thiocyanate in potassium thiocyanate. K. SCHERINGA (Chem. Weekblad, 1933, **30**, 598).—AgCNS,3KCNS is obtained by dissolving AgCNS in a saturated solution of KCNS. S. C.

Absorption of silver by glasses. I. WESTERMANN (Z. tech. Physik, 1932, **13**, 617; Chem. Zentr., 1933, i, 1263).—Ca–Na glass in contact with $AgNO_3$ (but not AgBr) at 380° absorbs Ag as Ag_2O arising from decomp. of the $AgNO_3$. A. A. E.

Preparation of colloidal gold solution. T. L. RAMSEY and H. J. EILMANN (J. Lab. Clin. Med., 1932, **18**, 298—300). CH. ABS.

Action of alkali carbonates on lime-water and solutions of calcium salts, and the so-called Loiseau's lime. I. O. SPENGLER and G. DORFMULLER (Z. Ver. deut. Zucker-Ind., 1933, **83**, 562—581).—A microscopical study has been made of successive stages in the pptn. of aq. CaO and $Ca(OAc)_2$ by Na_2CO_3 at various concns. and temp. The primary product is highly hydrated $CaCO_3$ which is usually pptd. in a gelatinous form and is transformed into spherules and crystals of $CaCO_3$ or its hydrates or double compound with Na_2CO_3 (cf. Adler, B., 1897, 767; Hume and Topley, A., 1927, 12, 526; Krauss and Schriever, A., 1930, 718). J. H. L.

Synthesis of calcium silicates. VII. S. NAGAI and K. MURAKAMI (J. Soc. Chem. Ind. Japan, 1933, **36**, 458—460B).—Mixtures of $3CaO,SiO_2$ and $2CaO,SiO_2$ were prepared by heating $CaCO_3$ and SiO_2 together in various proportions, and the compressive strength was tested after mixing with H_2O, storing for 1 day, and immersing in H_2O for several days. Pure $2CaO,SiO_2$ collapsed when immersed in H_2O, and pure $3CaO,SiO_2$ was much weaker than the mixed di- and tri-silicates. A. G.

Chemical constitution of hydrated calcium aluminates. P. ERCULISSE and S. SAPGIR (Chim. et Ind., 1933, Spec. no., 806—819).—The composition of hydrated Ca aluminates is best studied by phase-rule methods, as chemical analysis alone cannot differentiate between compounds and solid solutions or mechanical mixtures. Known quantities of the solid constituents are placed in contact with H_2O; when equilibrium is attained, a portion of the liquid phase is removed for analysis and replaced by pure H_2O, and the process repeated. The systems $CaO–Al_2O_3–H_2O$ and $CaO–Fe_2O_3–H_2O$ were studied in this manner. In the first it appears probable that solid solutions are formed. In the second a solid phase, $Fe_2O_3,CaO,aq.$, is believed to exist during the gradual removal of solid CaO by successive additions of H_2O. The only compounds of which there is evidence in the first system are $CaO,4Al_2O_3,xH_2O$ and $Al_2O_3,3$(or 4)CaO,xH_2O, the first forming solid solutions with Al_2O_3 or with the second. This conclusion is derived from the method of separate tests, not successive as above. The tetra-aluminate is analogous to borax. C. I.

Substitution of O″ by F′ in aluminates and silicates. E. KORDES (Fortschr. Min. Kryst. Petr., 1932, **17**, 432—433; Chem. Zentr., 1933, i, 1264).—Fusion of SiO_2 with NaF and LiF does not lead to compound formation. NaF and Al_2O_3 afford needles of undetermined composition. Substitution of MgO in MgO,Al_2O_3 by LiF affords crystals of the spinel type, m.p. > 1400°, d 3·6. CaF_2 and Al_2O_3 afford at least one cryst. compound. A. A. E.

Thermal decomposition of aluminium and ferric hydroxides. Reactions in the solid. H. SCHWIERSCH (Chem. Erde, 1933, **8**, 252—315).—Isobaric and isothermal dehydration curves were determined for Al_2O_3,H_2O [diaspore (I) and bohmite (II)] and Fe_2O_3,H_2O [goethite (III) and lepidocrocite (IV)]

and also for gibbsite and limonite, and the changes were followed by optical and *X*-ray examinations. There is no intermediate stage with the formation of a hemihydrate. The aggregate of crystals of the resulting oxide has a definite orientation with respect to the original crystal. (I) and (II) give similar results, but (III) and (IV) show marked differences in their behaviour. L. J. S.

Preparation of thallous hydroxide. R. PHILLIPS and W. W. HARTMAN (J. Amer. Chem. Soc., 1933, **55**, 3065—3066).—TlOH is prepared by passing a mixture of steam and air through a tube containing "mossy" Tl. J. G. A. G.

Combustion of graphite. V. SIHVONEN (Acta Chem. Fennica, 1932, B, **5**, No. 6/7, 1—6; cf. A., 1930, 1379).—A summary of work previously published. F. L. U.

Calcium cyanamide. II. Ammonolysis of dicyanodiamide. Y. KATO, K. SUGINO, K. KOIDZUMI, and E. MITSUSHIMA.—See B., 1933, 748.

Combination between zirconyl bromide and alkali bromides. E. CHAUVENET and (MLLE.) J. BOULANGER (Compt. rend., 1933, **197**, 410—411; cf. A., 1920, ii, 757).—By thermochemical analysis of mixed solutions of the constituents the existence of the following is indicated: $NaBr,ZrOBr_2$; $NH_4Br,ZrOBr_2$; $KBr,2ZrOBr_2$; $2RbBr,3ZrOBr_2$; $2CsBr,3ZrOBr_2$, but no compound with LiBr. Of these only $2CsBr,3ZrOBr_2,27H_2O$ was isolated; it passed into $2CsBr,3ZrOBr_2,21H_2O$ in dry air at room temp. C. A. S.

Preparation of acid ammonium fluoride. N. I. SPITZIN, G. V. SOKOLOVA, T. M. POPOVA, and I. I. ZORIN.—See B., 1933, 747.

Behaviour of hydronitrogens and their derivatives in liquid ammonia. VIII. Influence of pressure on yields of hydrazine obtained by pyrolysis of liquid ammonia. D. H. HOWARD, jun., and A. W. BROWNE (J. Amer. Chem. Soc., 1933, **55**, 3211—3214; cf. this vol., 683).—With a W filament at 3000°, the yield of N_2H_4 varies inversely with pressure between 80 and 1870 mm. Inorg. and org. solutes did not increase the yield of N_2H_4. J. G. A. G.

Direct combination of hydrogen with phosphorus. R. DOLIQUE (Bull. Soc. chim., 1933, [iv], **53**, 603—611).—Red P heated at 400° in a stream of H_2 vaporises and condenses in cooler parts of tube as yellow P. No liquid or solid PH_3 is formed; small traces of the gas are formed, but it decomposes at the temp. employed. The rate of change of red to yellow P increases with rise of temp. A. S. C. L.

Reversibility of the transformation of dimetaphosphates into Graham's salts. P. PASCAL and BONNEMAN (Compt. rend., 1933, **197**, 381—384).—If Ag hypophosphate is heated at 145° for 15 days, treated with aq. NaCl at 0°, and the resultant Na salt pptd. by EtOH the dimetaphosphate, $Na_2(PO_3)_2,6H_2O$ (cf. this vol., 475) is obtained: $Ag_4P_2O_6=Ag_2(PO_3)_2+2Ag$. If heated for a shorter time the product is gummy, due to incomplete transformation; if for longer, complex polymetaphosphates (Graham's salts), pptd. as oils, are produced. $Ag_2H_2P_2O_7$ heated at 320° and similarly treated gives an uncrystallisable oily hydrated Na polymetaphosphate; the viscosity of a 1% solution of this is 25 times that of H_2O, but becomes equal to it after 3 weeks, when the mol. wt. and conductivity become those of the dimetaphosphate, the ready change of which to acid pyrophosphate explains the slightly acid character of solutions of Graham's salts. C. A. S.

Decomposition of phosphates. I. Treatment of calcium phosphate with chlorine and carbon. Y. KATO and S. FUJINO.—See B., 1933, 747.

Decomposition of the arsinic acids. B. ENGLUND.—See this vol., 1061.

Constitution of potassium antimonyl tartrate and related antimony compounds. K. BODENDORF (Pharm. Presse, 1933, **38**, Wiss.-prakt. Heft 8—9; Chem. Zentr., 1933, i, 1930).—Reihlen's formula is supported by therapeutic properties and analogies. Formulæ are given for NH_4 Sb dipyrocatecholoxide and K (K Sb bispyrocatecholdisulphonate). A. A. E.

Method of preparation of radium-*E*. M. HAISSINSKY (Nature, 1933, **132**, 317).—Ra-*E* is pptd. from a slightly acid solution of radio-Pb nitrate by pyrogallol in presence of Sb. Under suitable conditions, Ra-*E* and Po are practically completely pptd. with the Sb, which is then eliminated from the ppt. by electrolysis, as nitrate, in presence of tartaric acid and NH_4 tartrate: yield 47—80%. L. S. T.

Production of gaseous oxygen by chemical methods. A. HLOCH.—See B., 1933, 702.

Sulphur monoxide. H. CORDES and P. W. SCHENK (Z. Elektrochem., 1933, **39**, 594—596; cf. this vol., 475).—SO was prepared by the method previously described. Its absorption spectrum was observed even after keeping 2 days at room temp. At 100° the decomp. was rapid. SO is very sensitive to H_2O, and reacts with Hg, Fe, and Cu. It is inert towards dry O_2. Absorption spectrum observations prove that it is formed in the reaction of $SOCl_2$ and Ag at 180—350° and in the combustion of excess S in O_2 at low pressure. H. J. E.

Molybdenum compounds. R. MONTEQUI and M. GALLEGO (Anal. Fís. Quím., 1933, **31**, 434—448).—Principally a reply to Malowan's criticism (A., 1931, 927) of Montequi's paper (A., 1930, 1028). Further experiments confirm that there exists an amphoteric molybdenyl hydroxide $Mo_2O_3(OH)_4$, which in acid solution yields an insol. xanthate and in alkaline solution decomposes into $Mo(OH)_4$ and $Mo(OH)_6$. Titration with $KMnO_4$ shows that Mavrov and Nikolov's formula for the alkali salts derived from Mo_2O_5, viz., $RMo_2O_5,3H_2O$, cannot be correct; these compounds are more probably of the type $RH_3Mo_2O_7,H_2O$. H. F. G.

Atomic chlorine. G. M. SCHWAB and H. FRIESS (Z. Elektrochem., 1933, **39**, 586—594; cf. this vol., 580).—At. Cl was produced by an a.c. discharge through streaming Cl_2. The discharge spectrum is recorded. The life of the Cl atoms, determined by measuring the heating effect accompanying recombin-

ation at different distances from the discharge, was 3×10^{-3} sec. Addition of CH_4 poisons wall recombination. A concn. of 40% at. Cl was attained. The catalytic recombination on various materials was examined. It requires no appreciable activation energy. The reactions with H, CH_4, $CHCl_3$, CO, N_2O, and O_2 were examined and the mechanisms are discussed. H. J. E.

Thermal decomposition of manganous carbonate and its products. J. CHLOUPEK (Chem. Listy, 1933, **27**, 315—319).—$MnCO_3$ when heated at 200—300° in presence of O_2 yields Mn_3O_4, Mn_2O_3, and MnO_2. A product with an oxidising power equal to that of Mn_2O_3 is obtained by heating anhyd. $MnCO_3$ at 220° during 9 hr., with frequent stirring. R. T.

Investigation of corrosion of iron by electron diffraction. J. CATES (Trans. Faraday Soc., 1933, **29**, 817—824).—Rusts formed on different specimens of Fe and steel give electron diffraction patterns identical with that given by γ-FeO_2H. The same pattern was observed with chemically prepared Fe_3O_4. The diffraction pattern of heated rust was that of γ-Fe_2O_3. F. L. U.

Formation of α-Fe_2O_3 from γ-Fe_2O_3,H_2O by friction. O. BAUDISCH and L. A. WELO (Naturwiss., 1933, **21**, 593).—If orange-yellow γ-Fe_2O_3,H_2O is shaken with porcelain balls for 3 weeks, it becomes red, but remains paramagnetic. By removal of H_2O from γ-Fe_2O_3,H_2O at 180—200°, red ferromagnetic γ-Fe_2O_3 is produced, but the red form, produced by grinding, remains non-magnetic on similar treatment. γ-Fe_2O_3,H_2O probably passes directly to α-Fe_2O_3 when heated, without the intermediate formation of α-Fe_2O_3,H_2O. A. J. M.

Iron borates. N. S. KURNAKOV, D. S. BELIANKIN, and F. A. KOTOMIN-BUDARIN (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 141—158).—FeO and B_2O_3 on fusion with subsequent cooling in a reducing atm. yield $2FeO,B_2O_3$, $FeO,2B_2O_3$, and $5FeO,B_2O_3$. These salts absorb O_2 at higher temp. with production of solid solutions of the general formulæ $(Fe^{II}_{2-n}Fe^{III}_{n})O_2,B_2O_3,O_{0\cdot5n}$ and $(Fe^{II}_{5-n}Fe^{III}_{n})O_5,B_2O_3,O_{0\cdot5n}$; at the same time the colour of the salts deepens from green to black. The black enamel of Etruscan pottery is a compound of this type. R. T.

Spectroanalytical determination of traces. W. GERLACH (Angew. Chem., 1933, **46**, 557—562).—A review of the methods of quant. spectral analysis. E. S. H.

Completion of combustion in gas analysis. R. S. JAKOVLEV.—See B., 1933, 690.

Alkaline pyrogallol solution in gas analysis. J. S. HALDANE and R. H. MAKGILL.—See B., 1933, 737.

Modes of expression of results of hydrochemical analyses. B. N. FORSCH (Bull. Acad. Sci. U.R.S.S., 1933, **7**, 589—595).—A discussion. R. T.

Apparatus for detection of elements by the sodium fusion test (copper ignition tube and pellet press). C. L. TSENG (J. Chinese Chem. Soc., 1933, **1**, 37—45).—Cu is a more suitable material for the tube than glass or Fe. The construction and use of such a tube are described. The tube is heated to redness and Na dropped in, followed by pellets of a mixture of $C_{10}H_8$ and EtOH or Et_2O. The product is afterwards washed out with EtOH and then H_2O, and tested by the ordinary procedure. D. R. D.

Electrometric titrations with oxygen electrodes. J. A. V. BUTLER and G. ARMSTRONG (Trans. Faraday Soc., 1933, **29**, 862—863; cf. A., 1932, 1092).—If a bright Pt electrode is polarised anodically for a short time and then given a very short cathodic polarisation, reproducible potentials depending on the p_H of the solution can be obtained. F. L. U.

Use of antimony electrode in the electrometric determination of p_H. T. GYSINCK (Archief Suikerind. Nederl.-Indie, 1932, [iii], Med. 10, 711—749).—Cast Sb rods gave the best results, but if the metal was not sufficiently pure the reproducibility suffered. Electrodes obtained by electrolytically coating a Pt rod with Sb gave gradually declining e.m.f. readings, owing to the oxidation of the layer of Sb. In general, the most const. results were obtained when the liquid was gently stirred, but if the rate of stirring was such that air was entrained in the buffer solution there was a strong drift of the potential towards the acid side. Better reproducibility was attained when the buffer solution under examination was covered with a layer of mineral oil to protect it from the air. J. P. O.

Application of the antimony electrode to the measurement of p_H in acidimetric titration in aqueous and organic solutions. E. VELLINGER (Chim. et Ind., 1933, Spec. no., 218—230).—The technique of using the Sb electrode is described in detail. The errors of the method and their elimination are discussed, and industrial applications suggested. J. W. S.

Colorimetric determination of p_H at higher temperatures. I. Water. W. NEUMANN (Z. anal. Chem., 1933, **94**, 89—96).—H_2O with various indicators showed on heating to its b.p. a colour change corresponding with a p_H change of about 1 unit, as anticipated from the dissociation const., the original val. being regained at room temp. Dissolution of alkali from the glass can produce a permanent p_H change which with Fiolax is < with SiO_2 or Na_2O glass. J. S. A.

Determination of hydrogen peroxide. A. K. BALLS and W. S. HALE (J. Assoc. Off. Agric. Chem., 1933, **16**, 395—397).—The presence of pyrogallol hinders the slow continued liberation of excess I in the iodometric determination of H_2O_2. Addition of 0·5 g. of pyrogallol per titration permits the accurate determination of small amounts of H_2O_2 in presence of reducing substances interfering with the usual procedure. J. S. A.

Electrode potential of chlorine, and its applications in analysis. A. RIUS and V. ARNAL (Anal. Fis. Quím., 1933, **31**, 325—347).—When a solution of Cl_2 is titrated potentiometrically with NaOH, inflexions occur at 0·95—1·15 volts and 0·6—0·7 volt; the variations, and the smaller quantity of NaOCl formed as compared with the quantity of NaOH added, are due to volatilisation, decomp.,

and the action of CO_2. Potentiometric titration with HCl of NaOCl solution containing free NaOH yields three points of inflexion, corresponding with neutralisation of the NaOH, liberation of free HOCl, and decomp. of the HOCl; the method may be used for the determination, to within about 1%, of NaOCl, provided that recently-ignited Pt electrodes are used and that CO_3'', if present, is first removed by means of $BaCl_2$. Low results are obtained if much Cl' is present. H. F. G.

Starch iodide colour reaction and its application to quantitative analysis. P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1933, **A**, **2**, 105—128).—For micro- or colori-metric determinations the intensity of the blue colour is directly proportional to the I (optimum concn. 0·004—0·012 mg. per c.c.) only if the reducing substances in the starch solution are first removed by saturating with I. Inorg. ions, especially KI, affect the colour produced; hence acidity and KI concn. must be kept at a (const.) mn. (1 c.c. each of N-H_2SO_4, 1% KI, and 1% starch with 25 c.c. of I solution giving a colour stable for 4 hr.). For determination of KI oxidation is best effected with 0·01N-$KMnO_4$, excess of which is removed by exact titration with 0·01N-$H_2C_2O_4$, and by this method 0·0167—0·05 mg. I may be determined in the presence of 5 mg. of ovalbumin. The new colorimetric method is successfully applied (details given) to the determination of I in defibrinated blood (proteins removed by Na_2WO_4 method), iodo-ovalbumin and the ppt. produced by the latter on its anti-serum. J. W. B.

Rapid determination of sodium hydrosulphide in sodium sulphide etc. E. Benesch.—See B., 1933, 701.

Determination of sulphur in steel and ferro-alloys. I. Kassler.—See B., 1933, 750.

Micro-determination of phosphorus. N. Proskuriakov and S. Temerin (Biochem. Z., 1933, **263**, 387—394).—Using a modification of Roche's method for the micro-determination of P by pptn. as strychnine phosphomolybdate (A., 1928, 1392), the influence of various factors (concn. of reagents, p_H, influence of salts) on the completeness of pptn. has been investigated. An improved method which permits the determination of 0·05—0·15 mg. P with considerable accuracy is described. P. W. C.

Detection and differentiation of phosphites and hypophosphites. D. Raquet and P. Pinte (J. Pharm. Chim., 1933, [viii], **18**, 89—93).—PO_3''' is detected by the decolorisation of a few drops of 0·1N-I in presence of NaOAc, whilst H_2PO_2' is detected by the decolorisation of the same reagent in presence of H_2SO_4. H. D.

Volumetric determination of arsenic. Potentiometric titrations of reduced arsenic solutions with potassium iodate in sulphuric and hydrochloric acid solutions. I. C. Schoonover and N. H. Furman (J. Amer. Chem. Soc., 1933, **55**, 3123—3130).—The first end-point corresponds with the completion of the reaction $5H_3AsO_3+2KIO_3+2HCl=I_2+5H_3AsO_4+2KCl+H_2O$ (i) in 0·10—2N-HCl. The second end-point is achieved in 4—6N-HCl and corresponds with $2I_2+KIO_3+6HCl\longrightarrow 5ICl+KCl+3H_2O$. The non-appearance of I at the beginning of titration (i) is attributed to the slowness of $IO_3'+5I'+6H^{\cdot}=3I_2+3H_2O$. In the presence of Hg_2SO_4 and 0·5—2·0N-HCl, the first end-point is reached when IO_3' is reduced to I', which forms a complex with the $Hg^{\cdot\cdot}$; the second, ICl, end-point is attained by increasing the HCl to 4—6N. The accurate potentiometric titration $5H_3AsO_3+2KIO_3+H_2SO_4=I_2+5H_3AsO_4+K_2SO_4+H_2O$ proceeds in 0·5—8N-H_2SO_4, but requires 0·0002N-HCl as catalyst with $<N$-H_2SO_4. J. G. A. G.

Sources of error in the Gutzeit method for the determination of arsenic. C. R. Gross (J. Assoc. Off. Agric. Chem., 1933, **16**, 398—403).—(1) C_5H_5N compounds (when present) must be separated completely by pptg. the As as $MgNH_4AsO_4$ together with PO_4'''. (2) Complete reduction of AsO_4''' by KI and $SnCl_2$ requires at least 30 min. at 25°. The use of stick- in place of 30-mesh Zn increases the % recovery of As. J. S. A.

Gravimetric determination of arsenic as $MgNH_4AsO_4,6H_2O$. J. Dick (Z. anal. Chem., 1933, **93**, 429—433).—For the quant. pptn. of $MgNH_4AsO_4.6H_2O$ the ppt. should be filtered and washed after approx. 2 hr. at 0—5°, washed with EtOH and Et_2O, and dried in vac. at room temp. If the solution is not cooled, it must be kept for at least 12 hr. The process is suitable for semi-micro-determinations. D. R. D.

Determination of silica in tissues. E. Kahane and M. Kahane (Bull. Soc. Chim. biol., 1933, **15**, 805—813).—The material is treated with HNO_3 and $HClO_4$ in presence of H_3BO_3. A. L.

Interference with the volumetric determination of carbon dioxide by the silicic acid content of the barium hydroxide solution. J. Lindner (Z. anal. Chem., 1933, **94**, 1—7).—The amount of silicate derived from glass vessels when aq. $Ba(OH)_2$ (0·05—0·1N) is stored therein for a few months renders the reagent useless for determining CO_2. E. S. H.

Mercurimetric determination of cyanide and thiocyanate. A. Ionesco-Matiu and (Mme.) A. Popesco (Chim. et Ind., 1933, Spec. no., 1011—1013; cf. A., 1928, 1230).—The solution of KCN is treated with $Hg_2(NO_3)_2$ [$2KCN+Hg_2(NO_3)_2=2KNO_3+Hg(CN)_2+Hg$] and after 5 min. the mixture is centrifuged. The ppt. is washed and dissolved in H_2SO_4–HNO_3. The solution is diluted, boiled to remove HCN, treated with $KMnO_4$ until a pink colour persists, and subsequently with $Na_2(NO)C_5N_5$. The mixture is titrated with NaCl until the ppt. just disappears. KCNS (NH_4CNS) is determined similarly: $3KCNS+Hg_2(NO_3)_2=2KNO_3+KHg(CNS)_3+Hg$ and $KHg(CNS)_3+Hg_2(NO_3)_2\longrightarrow KNO_3+Hg(NO_3)_2+Hg(CNS)_2$. The practical factors are 1 c.c. 0·1N-NaCl=0·00657 g. KCN, 0·00778 g. KCNS, or 0·00655 g. NH_4CNS. In mixtures of KCN and KCNS, $CN'+CNS'$ is determined as above and CNS' as $BaSO_4$ after oxidation with fuming HNO_3. H. W.

Sodium cobaltinitrite as a reagent for potassium. K. Scheringa (Chem. Weekblad, 1933, **30**,

598).—This method of detecting K is much more sensitive if solid reagent is added to the solution. S. C.

Sodium hydrogen tartrate as a reagent for potassium. K. SCHERINGA (Chem. Weekblad, 1933, **30**, 598).—Solid $NaC_4H_5O_6$ reacts much more readily with K salt solutions than either tartaric acid or the latter buffered with NaOAc. S. C.

Potassium perchlorate. E. KAHANE (Bull. Soc. chim., 1933, [iv], **53**, 547—555).—The solubility of $KClO_4$ in H_2O is 1·67% at 20°, but addition of $HClO_4$ reduces it until in 66% solution it is 0·07% of K. The reagent recommended for the determination of K as $KClO_4$ is $HClO_4$ 75, $KClO_4$ 1, and NH_4ClO_4 67·5 g. in 1 litre of H_2O. Cs and Rb are pptd. with K, and NH_3 must be removed. A. S. C. L.

Uranyl magnesium sodium acetate. E. KAHANE (Bull. Soc. chim., 1933, [iv], **53**, 555—563).—From EtOH solution the triple salt separates at Na $\not<$ 10^{-6} g. per litre. For general use, the reagent suggested is: $UO_2(OAc)_2$ 25 g., $Mg(OAc)_2,4H_2O$ 150 g., AcOH 780 g., diluted to 1 litre with H_2O. Na, but not K or Li, is pptd. A list is given of metals pptd. and of anions which must be absent. A. S. C. L.

Colorimetric determination of sodium. F. ALTEN and H. WEILAND (Z. Pflanz. Düng., 1933, **31**, A, 252—255).—Na is pptd. as the complex Na Mg U acetate and the ppt. treated with AcOH and $K_4Fe(CN)_6$. The colour intensity is determined after 3 hr. Test solutions should contain 0·1—1·0 mg. Na per 100 c.c. A. G. P.

Determination of sodium fluoride by Penfield's method. C. G. SCHWALBE and G. JUST (Z. anal. Chem., 1933, **94**, 86—89).—Aeration of the SiO_2–H_2SO_4–fluoride mixture on a glass filter-plate avoids risk of clogging and improves the accuracy of the method. J. S. A.

Rapid determination of soda in glasses. S. R. SCHOLES.—See B., 1933, 704.

Application of the polarographic method to the rapid determination of small quantities of alkalis, especially in silicates with high aluminium content. V. MAJER (Chim. et Ind., 1933, Spec. no., 211—214).—5—20 mg. of the substance are dissolved in 0·3 c.c. of H_2SO_4 and 0·5 c.c. of HF (40%). After evaporating to dryness, a drop of H_2SO_4 is added, and the solution made alkaline with NMe_4OH. It is then analysed polarographically. The method has been applied particularly to refractory clays. The determination requires only about 40 min. and for 2% alkali content the accuracy is about 0·1%. J. W. S.

Influence of foreign metals on the potentiometric silver titration. H. MOSER, E. RAUB, and W. STEIN (Z. Elektrochem., 1933, **39**, 623—628).—Fe, Pt, and Pd in solution interfere with the potentiometric determination of Ag with Cl′, Br′, or CNS′, using a pure Ag electrode. Cu interferes only when CNS′ is used. A Au electrode behaves similarly to Ag. H. J. E.

Must ammonium chloride be added in calcium determinations? K. SCHERINGA (Chem. Weekblad, 1933, **30**, 598).—NH_4Cl is unnecessary in presence of Al; the latter can be separated by neutralising the solution to phenolphthalein and filtering with a filter aid. In presence of Mg it delays pptn. of MgC_2O_4 (I), but this can be achieved by using excess of C_2O_4''. The solubility of (I) is 1 in 1800 in H_2O, 1 in 700 in saturated NH_4Cl, and 1 in 500 in saturated $(NH_4)_2C_2O_4$. When Mg is to be determined with soap, all NH_4 salts must be avoided and $K_2C_2O_4$ employed. S. C.

Gravimetric determination of calcium and its separation from magnesium. O. BRUNCK (Z. anal. Chem., 1933, **94**, 81—86).—Ca, pptd. as CaC_2O_4, is best weighed as CaC_2O_4,H_2O. The ppt. should be dried first at 60—70° or by EtOH and Et_2O, and then at 110°. Separation from Mg is quant. even with ten-fold amount of Mg provided [Mg] is $\not>$0·08 g. per 100 c.c. J. S. A.

Characteristic reaction of magnesium and iodine. S. AUGUSTI (Annali Chim. Appl., 1933, **23**, 348—350).—With I or NaOI, Mg salts give a cryst. brownish-red ppt. the composition of which varies with the conditions and with washing. The filtrate from the group V ppt. is evaporated and calcined to expel NH_4 salts, the residue being taken up in H_2O and the solution treated with I in KI and then dropwise with NaOH. Free I in a solution is detected by adding NaOH to almost complete decolorisation and then $MgSO_4$ or $MgCl_2$ solution. The reaction is not disturbed by Cl′ or Br′. T. H. P.

Precipitation and titration of magnesium "oxyquinolate" in presence of calcium oxalate, and its application in the analysis of Portland cement and similar silicates. J. C. REDMOND.—See B., 1933, 749.

Volumetric determination of magnesium in salt-lake saline, using 2-hydroxyquinoline. N. V. KOMAR and R. E. KIRILLOVA.—See B., 1933, 747.

Detection of the elements belonging to the analytical group IV. A. FOSCHINI (Annali Chim. Appl., 1933, **23**, 294—296).—The ppt. of Zn, Mn, Co, and Ni sulphides is converted into a conc. solution of the chlorides. To this NaOH is added dropwise until the solution is slightly alkaline. Co, Ni, and Mn hydroxides are filtered off, and Zn is detected in the filtrate with H_2S. The pptd. hydroxides are dissolved in HCl, and Mn is separated by adding a large excess of $(NH_4)_2CO_3$. Ni and Co are detected separately in the filtrate. O. J. W.

Electrolytic zinc: determination of small amounts of germanium. H. LUNDIN.—See B., 1933, 751.

Utility of the mercury cathode. W. BOTTGER, N. BLOCK, and M. MICHOFF (Z. anal. Chem., 1933, **93**, 401—422).—Paweck's Hg cathode (A., 1924, ii, 562) is suitable for the determination of Zn in acid solution, H_2SO_4 being the best acid to use. It is less suitable for Cd, but gives good results with Bi and with Pb in alkaline solution, certain modifications being introduced into Paweck's procedure in this case. The liquid Hg cathode is more suitable for the determination of Fe and Ni. D. R. D.

Separation of metals of the ammonium sulphide and alkaline-earth groups. A. KRÜGER (Z. anal. Chem., 1933, **93**, 422—429).—The pptn. of ZnS by H_2S in slightly acid solution at 70° is rendered quant. by addition of $Na_2S_2O_3$. $Fe^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, and $Mn^{\cdot\cdot}$ do not interfere, but HNO_3 must be absent and $NH_4^{\cdot}$ and alkali metals must not be present in high concn. S is pptd. with the ZnS, but is removed on roasting to convert into ZnO. If NH_4Cl and excess of $Na_2S_2O_3$ are added to the filtrate and H_2S is passed under pressure, FeS, NiS, CoS, and MnS are pptd. quantitatively. Under similar conditions, Al and Cr are pptd. quantitatively as hydroxides. All these ppts. are granular. There is no danger of co-pptn. of Ca, Sr, Ba, or Mg. D. R. D.

1 : 2-Diaminoanthraquinone-3-sulphonic acid as a reagent for the detection of copper, cobalt, and nickel. J. V. DUBSKÝ and V. BENCKO (Z. anal. Chem., 1933, **94**, 19—20).—The colorations produced are due to adsorption compounds. No stoicheiometric compounds are formed. E. S. H.

Rapid determination of the copper content of sea-water. W. R. G. ATKINS (J. Marine Biol. Assoc., 1933, **19**, 63—76).—Cu can be determined colorimetrically by means of Na diethyldithiocarbamate, extracting with $CHCl_3$. C. W. G.

Ceric sulphate as a volumetric oxidising agent. XIV. Indicator methods for the standardisation and use of ceric sulphate. H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1933, **55**, 3260—3269; cf. this vol., 924).—The *o*-phenanthroline ferrous complex (I) indicates accurately the end-points of the oxalate–0·01—0·1*N*-$Ce(SO_4)_2$ and arsenite-$Ce(SO_4)_2$ titrations at 50° in presence of appropriate concn. of HCl or H_2SO_4 with ICl as catalyst. Consistent with previous results, the potentiometric arsenite-$Ce(SO_4)_2$ titration in the presence of ICl is stoicheiometric in HCl at concn. $< 3N$. The titration with $Ce(SO_4)_2$ in presence of (I), of $Fe(CN)_6^{\cdot\cdot\cdot\cdot}$, $Tl^{\cdot}$, and H_2O_2 is rapid at room temp., and of $U^{\cdot\cdot\cdot\cdot}$ at 50°, whilst the end-point for $Sb^{\cdot\cdot\cdot}$ is obscured by high acidity. (I) is added just before the end-point in the titration of $Ce(SO_4)_2$ with H_2O_2 and $NaNO_2$. J. G. A. G.

Analytical chemistry of rhenium. IX. Determination of hydrochlororhenic acid in presence of perrhenic acid. W. GEILMANN and L. C. HURD (Z. anorg. Chem., 1933, **213**, 336—342).—H_2ReCl_6 is pptd. from slightly acid solution at 40—50° by a HCl or H_2SO_4 solution of NN′-tetramethyl-*o*-tolidine. The cryst. ppt. is $(C_6H_3)_2Me_6N_2,H_2ReCl_6$. It is dried at 110—130° and weighed. $HReO_4$ is determined in the filtrate with nitron, or, better, by first treating with H_2S, and converting the sulphide into nitron perrhenate (cf. Geilmann and Weibke, A., 1931, 328). H. J. E.

Colorimetric determination of iron. L. SZEGÖ and B. CASSONI (Giorn. Chim. Ind. Appl., 1933, **15**, 281—283).—Fe can be determined colorimetrically as $Fe(CNS)_3$ if the Fe is kept in the ferric state by means of an oxidising agent (*e.g.*, HNO_3) and if the concn. of KCNS is kept const. and $\not< 8$ g. per 100 c.c. O. J. W.

Interference by ferric ion in the colorimetric determination of copper and lead in potable water. P. KARSTEN.—See B., 1933, 734.

Detection and determination of cobalt by 1-nitro-β-naphthol. A. HERFELD and O. GERNGROSS (Z. anal. Chem., 1933, **94**, 7—12).—A solution of 1-nitro-β-naphthol (I) in 50% AcOH is added to the hot $CoCl_2$ solution containing dil. H_2SO_4. $[C_{10}H_6(NO_3)\cdot O]_2Co$ is pptd., but salts of Ni or Fe are not pptd. Co is determined as $CoSO_4$. The red coloration produced enables $Co^{\cdot\cdot}$ to be detected at a dilution of 1 in 400,000 in warm solutions, but the sensitivity is increased to 1 in 2×10^7 by using the Na salt of (I). E. S. H.

Macro-electroanalysis of cobalt, zinc, cadmium, silver, and mercury. J. GUZMAN and A. RANCANO (Anal. Fís. Quím., 1933, **31**, 348—355; cf. A., 1932, 923).—A passive Fe anode is used for all the metals except Hg, for which a Pt anode is necessary. For Ag and Hg the Cu cathode should be silvered, and for Cd Cd-plated. For Co, Cd, and Ag an ammoniacal solution is used, for Zn an ammoniacal cyanide solution, and for Hg a HNO_3 solution. Full details are given for the procedure in each case. The determinations take < 1 hr. H. F. G.

Volumetric determination of chromium in chromates. L. IRRERA (Annali Chim. Appl., 1933, **23**, 346—348).—The disadvantages attending the use of $SnCl_2$ for this determination are removed by using $K_2SnCl_4,2H_2O$ (cf. A., 1932, 712), which is stable in air. The excess of the salt is titrated with $KMnO_4$. T. H. P.

Acidimetry of orthotungstates, using methyl-red. A. DEL CAMPO and F. SIERRA (Anal. Fís. Quím., 1933, **31**, 356—360).—A nearly saturated solution of benzidine acetate is added to the neutral alkali orthotungstate solution (0·5—1·0% WO_3) containing Me-red. The colour change occurs sharply at the end-point, owing to hydrolysis of the excess of reagent adsorbed on the ppt. In absence of the ppt. a considerable quantity of reagent is needed to produce the colour change. Satisfactory results are not obtained with other indicators. The reagent is standardised against Na_2WO_4. H. F. G.

Volumetric determination of bismuth. C. MAHR (Z. anal. Chem., 1933, **93**, 433—437).—To an acid solution of the Bi salt in aq. KBr, aq. NaOH is added so long as the ppt. formed redissolves. Saturated aq. $[Cr(NH_3)_6](NO_3)_3$ is then added. The *compound* $[Cr(NH_3)_6][BiBr_6]$ is pptd. and is decomposed by distillation with aq. NaOH, giving NH_3, which is titrated. Alkali and alkaline-earth metals, Fe, Mn, Cr, Co, Ni, Al, Cu, and small quantities of Zn do not interfere. In presence of Hg, Cd, or much Zn, the ppt. must be decomposed to BiOBr by boiling with H_2O, redissolved in aq. KBr, and re-pptd. as before. Addition of tartaric acid prevents pptn. of Sn with the Bi. D. R. D.

Electrolytic analysis of bismuth, tin, lead, and antimony without mechanical agitation of the electrolyte. T. GROSSET.—See B., 1933, 751.

Electric furnaces with interchangeable elements. M. BILLY and F. TROMBE (Bull. Soc.

chim., 1933, [iv], **53**, 536—541).—Details of the construction of open-tube and muffle electric furnaces with standard interchangeable heating elements, and of regulating resistances, are given. Curves are given for relation between current input and temp. attained, and for temp. distribution along the tube. A. S. C. L.

Molybdenum resistance furnace. G. BURROWS and F. L. CLARK (J. Sci. Instr., 1933, **10**, 248—250).—A durable furnace for continuous use up to 1850°, having Mo resistance strips instead of wires, is described. N. M. B.

Freezing gases at low temperatures. P. SAKMIN (Khimstroi, 1933, **5**, No. 1, 1985—1990).—Technique applicable to small quantities of gas is described. CH. ABS.

Automatic refrigeration chamber. J. WIRFEL (Chim. et Ind., 1933, Spec. no., 264—265).—The laboratory plant described permits the automatic maintenance of any desired low temp. down to −60°. Adequate space is provided and reactions carried out in the refrigerator can be followed, regulated, and modified from without through a window in the wall. Refrigeration is produced by expansion of liquid CO_2. J. W. S.

Extremely low temperatures. W. J. DE HAAS (Nature, 1933, **132**, 373).—The magnetic method by which extremely low temp. have been reached is described. With CeF_3, Dy Et sulphate, and Ce Et sulphate the upper temp. limits reached are 0·27°, 0·17°, and 0·085° abs., respectively. L. S. T.

Determination of absolute thermal coefficients of expansion of liquids. J. ZAHRADNICEK (Physikal. Z., 1933, **34**, 624).—Apparatus similar to that described by the author (this vol., 689) has already been used by Hiedemann (A., 1931, 592). A. J. M.

Temperature regulation by means of contact thermometers. H. BRUCKNER (Chem. Fabr., 1933, **6**, 342—343).—The apparatus described enables an oven to be kept at 300±1° for a period of months. E. S. H.

[Duboscq colorimeter.] A. VAN RAALTE [with J. KOSTER] (Chem. Weekblad, 1933, **30**, 555).—The use of cylindrical ebonite jackets around the glass vessels is recommended; difficulties arising from the varying thickness of the walls of the vessel are thus obviated. H. F. G.

Colorimeter. H. SCHNEIDER (Boll. Chim. farm., 1933, **72**, 529—530).—The apparatus (of Rojahn and Heinrici), which is of the comparator type with matching discs of white, black, and colours, is described and its application to normal and fluorescence colours discussed. F. O. H.

High-vacuum spectrograph for chemical analysis with *X*-rays. E. ALEXANDER (Z. Physik, 1933, **83**, 512—516). A. B. D. C.

***X*-Ray spectrometer for high vacuum with Johann concave crystal.** A. SANDSTROM (Z. Physik, 1933, **84**, 541—556). A. B. D. C.

Integrating photometer for *X*-ray crystal analysis. B. W. ROBINSON (J. Sci. Instr., 1933, **10**, 233—242).—A simple photo-electric photometer for measuring integrated *X*-ray intensities in crystal-analysis photographs, but adaptable to almost any form of *X*-ray photometry, is described. N. M. B.

Plane-polarised light in the microscopal investigation of ores and metals. F. F. OSBORNE (Trans. Canad. Inst. Min. Met., 1933, **35**, 1—13).—A review of recent work on, and a description of modern optical apparatus for, detecting anisotropism in ores and metals. Vertical illuminators are less satisfactory than the film type, since they produce depolarising effects. A. R. P.

High-temperature *X*-ray camera. A. H. JAY (Z. Krist., 1933, **86**, 106—111; cf. A., 1932, 1078).—The camera is a modification of the powder camera, and enables the substance to be examined at a uniform temp. > 800°, accurate to within 5°. C. A. S.

***X*-Ray microscope.** W. BRAGG (Anal. Fís. Quím., 1933, **31**, 399—400). H. F. G.

Simple arrangement for photo-electric absorption measurement. R. SEIFERT (Pharm. Zentr., 1933, **74**, 501—503).—A modification of the method (this vol., 366), in which the photo-cell is used merely as a comparator and whereby the disturbances caused by the apparatus are avoided, and its satisfactory and simple application for colorimetric analysis are described. E. H. S.

Capillary mercury-vapour lamp. A. HOLLAENDER and J. F. STAUFFER (Science, 1933, **78**, 62).—Improvements in the Daniels–Heidt lamp (A., 1932, 827) are described. L. S. T.

Use of cuprous oxide and other rectifier photo-cells in submarine photometry. W. R. G. ATKINS and H. H. POOLE (J. Marine Biol. Assoc., 1933, **19**, 67—72).—The current–illumination ratio is not linear. C. W. G.

Determination of colour-sensitivity of photographic layers. J. O. BRAND (Physikal. Z., 1933, **34**, 677—682).—An arrangement for producing a spectrum of equal energy distribution is described. The spectral sensitivity curves of some modern photographic emulsions are obtained. A. J. M.

Application of immersion method. T. CARPANESE (Z. Krist., 1933, **86**, 145—152).—The observations obtainable with any possible position of the crystal fragment are tabulated, and methods described for determining n_α, n_β, and n_γ for biaxial fragments without knowledge of their optical or crystallographic orientation. C. A. S.

Direct-current grid as a source of alternating current for measuring purposes. A. BUCHNER and A. ETZRODT (Z. Elektrochem., 1933, **39**, 668—670).—The circuit is described. E. S. H.

Insulation for the introduction of electrical connexions into high-pressure vessels. H. J. WELBERGEN (J. Sci. Instr., 1933, **10**, 247—248).—Pyrex glass insulation embedded in a plug of high-Cr steel gives a seal suitable for work at 3000 atm. up to 200° with liquids, and 800 atm. with gases. N. M. B.

Electric sieve. A. SCHLOEMER (Chem.-Ztg., 1933, **57**, 682—683).—An apparatus constructed on the electrofiltration principle, suitable for separating powdered material into fractions of different particle size, is described. E. S. H.

Technique of glass-electrode measurements. B. S. PLATT and S. DICKINSON (Biochem. J., 1933, **27**, 1069—1076).—The design, construction, and manipulation of a glass-electrode system, employing a thermionic valve for the potential measurement, are described, emphasis being laid on the need for careful temp. regulation. W. O. K.

Electrode pair for rapid potentiometric analysis. W. HILTNER (Chem.-Ztg., 1933, **57**, 704).—The electrodes are Pt and Pt covered with fused AgI. The potential of the latter depends on the concn. of $Ag^{\cdot}$ and of all ions forming therewith insol. salts or complexes difficult of dissociation. In acidimetry Pt may be replaced by Sb. AgI serves as an indicator electrode for Cl′, Br′, I′, CNS′, CrO_4'', SO_3'', S″, etc., but not for S_2O_3'' and CN′, which attack it. It is also suitable for many pptn. reactions. For S_2O_3'' a Ag_2S electrode is better and serves, *e.g.*, for the determination of Cu with S_2O_3''. A salt to be used as electrode in this way must be both insol. and conductive to cations. C. I.

Simple, portable Wilson chamber. K. PHILIPP and F. DORFFEL (Physikal. Z., 1933, **34**, 491—492).—An apparatus which is portable and can be used in any position is described. A. J. M.

Gas-analysis apparatus. R. MARGARIA (J. Sci. Instr., 1933, **10**, 242—246).—An improved Haldane apparatus, giving more rapid absorption by forcing the gas to circulate in the pipette and to bubble in the absorbing solution, is described. Hydroxyquinol solution is used for O_2 absorption, giving increased stability and speed. N. M. B.

Simple and serviceable membrane-manometer of glass or quartz. J. FISCHER (Chem. Fabr., 1933, **6**, 377—378).—A manometer with a flexible diaphragm of the "oil-can" type and with simple devices for increasing the accuracy of the readings is described. D. F. T.

Procedure with hydrogen sulphide in qualitative analysis. J. V. DUBSKÝ and V. DOSTAL (Z. anal. Chem., 1933, **94**, 21—22).—A modified Kipp apparatus is described. E. S. H.

Collodion thimbles for ultra-filtration. B. K. MAREJKOWSKY and C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1933, **15**, 849—854).—Details of manufacture are given. A. L.

Stainless steel high-pressure ultra-filter. S. J. FOLLEY and A. T. R. MATTICK (Biochem. J., 1933, **27**, 1113—1115).—A stainless steel apparatus suitable for high-pressure ultra-filtration is described. The apparatus has proved useful for clarification of biological solutions, sterilisation of bacteriological media without heat, and fractionation of colloidal solutions by ultra-filtration. A. W.

Apparatus for continuous extraction in a vacuum. M. A. MACHEBŒUF and N. FETHKE (Bull. Soc. Chim. biol., 1933, **15**, 796—800).—The apparatus consists of a cylindrical glass extraction vessel fitted with a siphon, the whole being suspended inside two overlapping glass tubes, the overlap being sealed with Hg. A. L.

Apparatus for continuous extraction of an aqueous solution by ether. A. LEMAN (Bull. Soc. chim., 1933, [iv], **53**, 635—636). A. S. C. L.

Apparatus for the removal of supernatant liquids in centrifuge tubes. J. CHEYMOL (Bull. Soc. Chim. biol., 1933, **15**, 847—848). A. L.

Apparatus for sublimation of iodine. R. JACQUEMAIN (Bull. Soc. chim., 1933, [iv], **53**, 633—635). A. S. C. L.

Evaporation of metals in vacuum. H. W. EDWARDS (Rev. Sci. Instr., 1933, [ii], **4**, 449).—Small pieces of the metal may be hung along a heated W wire. C. W. G.

Electrically heated sand-bath. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1933, **16**, 418—420). J. S. A.

Production of strong cellulose acetate films. L. HARRIS and E. A. JOHNSON (Rev. Sci. Instr., 1933, [ii], **4**, 454—455).—Films 10^{-3} cm. thick are best prepared by spreading the solution on glass plates previously coated with a 5% solution of paraffin in CCl_4. C. W. G.

Simple arrangement to demonstrate liquid crystals. G. VAN ITERSON, jun. (Trans. Faraday Soc., 1933, **29**, 915—919).—Apparatus suitable for the observation of liquid crystals by laboratory classes is described. E. S. H.

γ-Ray radiographic testing. G. E. DOAN (J. Franklin Inst., 1933, **216**, 183—216, 351—385).—A lecture.

Microscopical and microchemical examination of Egyptian pigments. M. WAGENAAR (Pharm. Weekblad, 1933, **70**, 894—902).—An examination of ancient Egyptian pigments (*circa* B.C. 1000) showed them to consist of powdered shells (white and rose), Cu silicate (green), lapis lazuli (blue), ochres (reds and yellows), blood (?) C (black), and malachite (green). S. C.

Combining power of krypton and of xenon. G. ODDO (Gazzetta, 1933, **63**, 380—395).—Two letters dated 1902 from Sir W. Ramsay are published. O. J. W.

Geochemistry.

Vertical distribution of ozone in the atmosphere. F. W. P. GOTZ, G. M. B. DOBSON, and A. R. MEETHAM (Nature, 1933, **132**, 281).—A new method gives a revised val. of 20 km. for the average height of O_3 at Arosa. There is an appreciable amount of O_3 in lower layers of the atm., but the main amount appears between 15 and 50 km. L. S. T.

Composition of rain-water of Sylhet. A. K. DAS, G. C. SEN, and C. K. PAL (Indian J. Agric. Sci.,

1932, **3**, 353—359).—The ratio $NH_3:NO_3$ is 1 : 0·82, a higher val. for NO_3 than is obtained in non-tropical countries (cf. Rothamsted, 1 : 0·43). Biochemical decomp. in the swamps is the main factor concerned in the high NH_3 content; it is lowest during the monsoon when the ground is under H_2O. P. G. M.

Lake Elton. N. S. KURNAKOV and B. L. RONKIN (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 185—203).—Lake Elton (lower Volga district) H_2O has a max. *d* 1·3642 during summer, and contains NaCl 1·57, $MgCl_2$ 26·97, $MgSO_4$ 6·45, $MgBr_2$ 0·343, $Mg(HCO_3)_2$ 0·36, and KCl 0·68%. During spring and autumn the $MgSO_4$ and NaCl contents rise at the expense of $MgCl_2$. The lake is estimated to contain 10^7 tons of $MgCl_2$. R. T.

Composition of water of certain salt lakes of the Omsk district. A. P. USPENSKI (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 205—213).—The H_2O of Lake Ebeity consists during summer of a saturated solution of $Na_2SO_4,10H_2O$. 80% of the substances in solution in lakes Kızil-Kak, Selety-Dengiz, and Teke are NaCl and 12% $MgSO_4$. R. T.

Lake Medveshje. D. V. RISHIKOV (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 215—227).—Analytical data are given for the mud and H_2O of Lake Medveshje (Ural). The chief solutes are NaCl (68·37%), $MgCl_2$ (13·56%), and $MgSO_4$ (12·72%). R. T.

Composition of ice from the Gulf of Finland in connexion with its mechanical strength. V. I. ARNOLD-ALJABJEV (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 229—233).—The ice contains 0·23—0·75% of salts, the relative SO_4'' content of which is $<$ in the case of Baltic sea-salt. No connexion exists between salt content and mechanical strength of ice. R. T.

Batalpaschinsk lakes. M. A. KLOTSCHKO (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 235—247).—Analytical data are given for two salt lakes, the larger of which is estimated to contain Na_2SO_4 200,000, NaCl 195,000, and $MgSO_4$ 91,000 tons. R. T.

Soda lakes of Egypt. B. L. RONKIN (Ann. Inst. Anal. Phys. Chem., 1933, **6**, 311—322).—A theory of formation of Na_2CO_3 in the lakes is given. R. T.

Formation of ore-deposits in lakes. F. W. FREISE (Chem. Erde, 1933, **8**, 1—24).—Analyses are given of the H_2O and sediments from several lakes in Brazil. The black muds show appreciable amounts of Fe and Mn. L. J. S.

Physico-chemical studies of the mine waters of Pribram. SPLICHAL, ŠANA, and JIRKOVSKÝ (Chim. et Ind., 1933, Spec. no., 284—292).—Radioactivity and conductivity have been studied. Analyses are given. C. W. G.

Vertical distribution of hydrogen-ion concentration in eutrophic lakes during the stagnation period. D. MIYAJI (Chikyu, 1929, 404—412).—Many Japanese eutrophic lakes show neutral reaction in the bottom layers. Weathering is retarded by lack of acid. CH. ABS.

Spectroscopic researches on the Portuguese mineral waters. Germanium as indicator of deep waters. A. P. FORJAZ (Chim. et Ind., 1933, Spec. no., 260—261).—Spectroscopic examination of the saline constituents of some Portuguese mineral waters shows that secondary mineralisation is always accompanied by the presence of Ge, this confirming the view that this element is a sure indicator of a deep H_2O. J. W. S.

p_H values in some sulphurous waters from the [Italian] Marche. A. HEMMELER and N. SETTE (Annali Chim. Appl., 1933, **23**, 297—306).—Composition and p_H data for various sulphurous waters are given. The influence of bacteriological factors on the p_H is emphasised. O. J. W.

Composition and classification of Italian mineral waters. II. D. MAROTTA and C. SICA (Annali Chim. Appl., 1933, **23**, 245—290; cf. A., 1930, 448).—Tabulated analyses and schemes of classification of potable and spa-waters are given. O. J. W.

Action of iodine on sea-water. G. DENIGES (Bull. Trav. Soc. Pharm. Bordeaux, 1932, **70**, 241—255; Chem. Zentr., 1933, i, 1923—1924).—I in I-rich sea-H_2O is not present in org. combination; the reaction $I'+Ag^{\cdot}\longrightarrow AgI$ in aq. NH_3 is masked by pptn. of $CaCO_3$ and $MgCO_3$, which should be removed before $Ag^{\cdot}$ is added. The H_2O also contains IO_3': $6I^{\cdot}_2+6Ca(HCO_3)_2=Ca(IO_3)_2+5CaI_2+6H_2O+12CO_2$. A. A. E.

Chemical constituents of biological importance in the English Channel. III. June–December, 1932. Phosphate, silicate, nitrite, hydrogen-ion concentration, with a comparison of wind records. L. H. N. COOPER (J. Marine Biol. Assoc., 1933, **19**, 55—62).—An unusual distribution occurred in Aug., 1932. C. W. G.

Interrelationships of sunlight, aquatic plant life, and fishes. T. A. OLSON (Trans. Amer. Fish Soc., 1932, **62**, 278—289).—>24 p.p.m. of dissolved O_2 is present in H_2O of Minnesota lakes during periods of active photosynthesis. Shallow lakes may show severe O_2 depletion in the winter. CH. ABS.

Meteorite (diogenite) of Tataouine, Tunis (June 27, 1931). A. LACROIX (Bull. Soc. franç. Min., 1932, **55**, 101—122; Chem. Zentr., 1933, i, 1425).—The meteorite contained SiO_2 54·94, TiO_2 0·19, Al_2O_3 0·62, Cr_2O_3 0·35, FeO 15·30, MnO 10·26, MgO 27·42, CaO 0·76, S 0·13, Fe 0·22, H_2O+ 0·06, H_2O- 0·08%; Fe_2O_3, NiO, and P_2O_5 were absent. A. A. E.

Stony meteorite which fell in Morocco, on August 22, 1932. A. LACROIX (Compt. rend., 1933, **197**, 368—370).—Stones which fell at Dwar Maghila had a greyish and brecciated fracture, showing a few chondrules. The constituents are olivine and hypersthene with about 8% of Ni–Fe, some maskelynite, and a little pyrrhotite and plagioclase. C. A. S.

Young's modulus and Poisson's ratio with reference to geophysical applications. W. A. ZISMAN (Proc. Nat. Acad. Sci., 1933, **19**, 653—665).—Vals. have been obtained for a large no. of rocks. C. W. G.

Compressibility and anisotropy of rocks at and near the earth's surface. W. A. ZISMAN

(Proc. Nat. Acad. Sci., 1933, **19**, 666—679).—Measurements on a no. of rocks at 30° up to 840 kg. per sq. cm. show a rapid decrease in compressibility as pressure increases. C. W. G.

Comparison of the statically and seismologically determined elastic constants of rocks. W. A. ZISMAN (Proc. Nat. Acad. Sci., 1933, **19**, 680—686).—Lack of agreement is due to the presence of cracks and cavities. C. W. G.

Geochemical considerations. V. M. GOLDSCHMIDT (Fortschr. Min. Krist. Petr., 1932, **17**, 415—417; Chem. Zentr., 1933, i, 1267).—The average amount of weathering of eruptive rocks has been calc. In the formation of sedimentary rocks partial oxidation simultaneously took place; the amount of O_2 required has been calc. Calculations have also been made of the amounts of various heavy metals liberated by weathering of eruptive rocks. A. A. E.

Composition of leucoxene in the Permian of Oklahoma. F. COIL (Amer. Min., 1933, **18**, 62—65).—Leucoxene, TiO_2,nH_2O, contained TiO_2 72·12, SiO_2 24·49, Fe_2O_3 0·50, FeO 1·35, H_2O 1·66, total 100·12%; quartz, hæmatite, and ilmenite were present. CH. ABS.

Triplite from La Rioja Province, Argentina. E. P. HENDERSON (Amer. Min., 1933, **18**, 104—105).—The mineral, n_α 1·675, n_β 1·683, n_γ 1·692, contained MnO 34·84, FeO 23·54, CaO 3·48, Na_2O 0·27, K_2O 0·33, P_2O_5 31·50, F 6·41, H_2O 1·58, Cl trace, insol. 0·28, total (corr.) 99·54%. CH. ABS.

Origin and classification of pegmatites. K. K. LANDES (Amer. Min., 1933, **18**, 33—56, 95—103).—A discussion. Pegmatites are classified as (simple or complex) (*a*) acid, (*b*) intermediate, (*c*) basic. CH. ABS.

Basalt of the Kammerbuhl near Eger. H. JUNG (Chem. Erde, 1933, **8**, 48—57).—A petrographical description of the rock and a chemical analysis of the fragmentary material are given. L. J. S.

Rocks from the volcano "Pacaya," Guatemala. E. DEGER (Chem. Erde, 1933, **8**, 45—47).—Two analyses are given of basalts. The high summation is attributed to the presence of silicide. L. J. S.

Hydrothermal alteration of Greenland basalts. K. HOLLER (Chem. Erde, 1933, **8**, 25—44).—In certain layers adjacent to layers of brecciated basalt cemented with zeolites the rock shows a gradual transition to a red laterite-like material containing free Al hydroxide. L. J. S.

Radioactivity measurements. I. Radium content of the Keweenawan basalts and some accessory minerals. II. Occurrence of radium, uranium, and potassium in the earth. W. D. URRY (Proc. Amer. Acad. Arts Sci., 1933, **68**, 125—136, 137—144).—I. A felsitic pebble had the highest Ra content ($7·00\times10^{-13}$ g. Ra per g.) and an algodonite the lowest ($0·08\times10^{-13}$). The average Ra content of the plateau basalts, not including felsitic rocks, was $1·29\times10^{-13}$ g. Ra per g. Evidence was obtained of correlation between Ra content and both depth and stratigraphical arrangement, and of a regular order in the Ra content of the accessory minerals in the Cu lodes according to the method of pptn. from the mineralising solutions.

II. Average vals. are calc. The results show a considerably lower mean U content than has usually been adopted for the three outer shells and excludes the possibility of a complete concn. into the upper two shells. CH. ABS.

Borsov deposit of corundum. V. KOPTEV-DVORNIKOV and E. KUZNETZOV (Trans. Inst. Econ. Min., Moscow, 1931, No. 47, 1—304).—Dunite, peridotite, pyroxenite, and gabbro were during one stage recryst. into olivine and pyroxene schists and amphibolites. In another the sedimentary rocks were transformed into cordierite, micaceous garnet gneiss, micaceous quartzite, and marble. In another, diopside and hornblende rocks were formed by a pneumatolytic process. Pyroxene alters to amphibole at about 550°. Olivine-bronzite rocks south of Borsov are also described. CH. ABS.

Structural and morphological relations between ores of the formula type ABC. W. HOFMANN (Fortschr. Min. Krist. Petr., 1932, **17**, 422—425; Chem. Zentr., 1933, i, 1268—1269).—Wolfsbergite, $CuSbS_2$, has a $6·00_8\pm0·01$, b $3·78_4\pm0·01$, c $14·45_6\pm0·03$ Å., with 4 mols. in the unit cell; space-group V_h^{16}. Emplectite, $CuBiS_2$, has a $6·12_3\pm0·01$, b $3·89_0\pm0·01$, c $14·51_2\pm0·03$ Å. Miargyrite, $AgSbS_2$, has a $13·16_8$, b $4·39_1$, c 12·82 Å.; β 98° 37½′. The unit cell is (100)-centred and contains 8 mols.; space-group C_{2h}^6. Lorandite, $TlAsS_2$, has a $15·02_3$, b $11·31_5$, c $6·10_2$ Å.; β 127° 45′; the unit cell contains 8 mols.; space-group or C_{2h}^5. A. A. E.

Crystal structure of boracite. M. MEHMEL (Fortschr. Min. Krist. Petr., 1932, **17**, 436—437; Chem. Zentr., 1933, i, 1268).—The rhombic modification has a 12·07, b 17·07, c 17·07 Å., with 8 mols. in the unit cell. The cubic modification stable at > 265° has a 12·1 Å., with 4 mols. in the unit cell; space-group T_d^5. The structure is best expressed by the formula $[B_7O_{13}]Mg_3Cl$. A. A. E.

Carbonate-weathering of the gabbro of Neurode, Silesia. E. KIJAK (Chem. Erde, 1933, **8**, 58—166).—Petrographical descriptions and chemical analyses of the fresh and altered rock in which clay and carbonate minerals are developed are given. L. J. S.

Varieties of microlite from Donkerhuk, South-West Africa. E. REUNING (Chem. Erde, 1933, **8**, 186—217).—Microlite occurs in pegmatite veins with tantalite and large crystals of beryl, apatite, and tourmaline. The yellow octahedra are often surrounded by a fibrous zone, and this appears to grade into brown pitchy metamict material. Analyses (in which some of the constituents were determined by the *X*-ray method) show Ta_2O_5 74·78—74·2, Nb_2O_5 2·85—6·2, UO_2 0·3—11·2, CaO 13·96—1·9, PbO 0·4—3·0, H_2O 1·31—9·7%, etc., d 6·0—4·14, H 5½—4. No definite formula can be deduced, and the mineral perhaps consists of a mixture of meta- and pyrotantalates. *X*-Ray photographs (of the metamict variety after heating at 800°) give a unit cell of edge 10·381 Å. (mean); the patterns are compared with

those given by loparite and betafite. *X*-Ray quant. analyses are given of the tantalite, *d* 6·17. L. J. S.

Geochemistry of strontium. W. NOLL (Fortschr. Min. Krist. Petr., 1932, **17**, 440—442; Chem. Zentr., 1933, i, 1267—1268).—For the determination of small quantities of Sr the usual EtOH–Et_2O method is inaccurate; an *X*-ray spectroscopic method was employed. The distribution of Sr and the substitution of Ca by Sr are discussed. A. A. E.

Optically uniaxial titanaugite. B. E. DIXON and W. Q. KENNEDY (Z. Krist., 1933, **86**, 112—120).—The titanaugite occurs in a plagioclase–diopside–hornfels xenolith in norite near Schivas (Aberdeenshire) as small plum-coloured crystals, d^{18} 3·43. It is monoclinic, pleochroic (plum-coloured and light yellow), $n_\alpha=n_\beta=1{\cdot}741$, $n_\gamma-n_\alpha=0{\cdot}021$ (Na light); analysis: SiO_2 37·52, Al_2O_3 14·29, Fe_2O_3 4·43, Cr_2O_3 0·11, TiO_2 5·72, FeO 7·12, MgO 6·72, MnO 0·14, CaO 24·06, Na_2O 0·09, K_2O trace, total 100·20%. The role of Ti in this and other pyroxenes is discussed and Machatschki's formula (cf. A., 1930, 732; 1932, 12) deemed most applicable, but with the probability of some direct replacement of Si by Ti. C. A. S.

Deposits of giobertite in Czecho-Slovakia and the present state of their exploitation. F. ULRICH (Chim. et Ind., 1933, Spec. no., 298—304).—Geological, mineralogical, and chemical particulars are given. C. W. G.

Thermo-optic studies of lepidomelane from Ishikawa. B. YOSHIKI (Proc. Imp. Acad. Tokyo, 1933, **9**, 324—326).—The change of n on heating has been measured. C. W. G.

Thermal and chemical studies of lepidomelane from Ishikawa. S. TSURUMI (Proc. Imp. Acad. Tokyo, 1933, **9**, 320—323).—An analysis and the change in wt. on heating are recorded. C. W. G.

Thermal expansion of diopside. S. KOZU and J. UEDA (Proc. Imp. Acad. Tokyo, 1933, **9**, 317—319).—Between 20° and 1000° expansion along the *b*-axis is about three times that along the other two, and is not much affected by changes in chemical composition. C. W. G.

Effusive rocks from South-West Sardinia. A. DEBENEDETTI (Atti R. Accad. Lincei, 1933, [vi], **17**, 659—664).—Chemical and mineralogical data are given for some rocks of the andesite type. O. J. W.

Microscopical and chemical examination of two clays. F. K. SCHLUNZ (Chem. Erde, 1933, **8**, 167—185).—Mechanical and chemical analyses of a glacial clay and one of Tertiary age from north Germany are given. L. J. S.

Physico-chemical properties of Japanese acid clay. VII. Solubility in alkaline solutions and the essential constituents of acid clay. II. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1933, **36**, 460—466B).—When acid clays containing various mol. ratios SiO_2 : Al_2O_3 are shaken with 5% aq. NaOH at 90° more SiO_2 is dissolved from clays with higher ratios and the ratio in the residue is usually 4—5. It is concluded that the clays are mixtures of SiO_2 and silicate. When the concn. of NaOH is increased, a rapid increase in the SiO_2 and Al_2O_3 dissolved at 70° occurs at 6—7*N*, corresponding with dissolution of the cryst. silicate, and this effect is not shown by ordinary kaolinic clays. A. G.

Manganese mineral deposits in the Carpathians in the north-west of Czecho-Slovakia and their genesis. F. ULRICH and R. MUNK (Chim. et Ind., 1933, Spec. no., 305—313).—Analyses and geological details are given. C. W. G.

New map of mineral deposits and useful minerals in Czecho-Slovakia. SLAVÍK (Chim. et Ind., 1933, Spec. no., 314).—Nine categories of metalliferous, 6 of combustible, and 17 of non-metallic minerals are shown. C. W. G.

Accumulation of copper in sedimentary rocks. A. D. ARKHANGELSKI and E. V. ROZHKOVA (Bull. Soc. Nat. Moscow, 1932, [ii], **40**, Geol. 10, No. 2, 295—307).—In 26 samples Cu was found combined with org. matter; none of the other samples contained Cu. The ratio Cu : C was: Recent, 0·0016—0·0022; Tertiary 0·0017—0·0041; Cretaceous, 0·0005; Jurassic, 0·0012—0·0036; Permian, 0·020—0·090; Devonian, 0·0012—0·0018; Cambrian, 0·0019. CH. ABS.

Mednorudyansk and Mount Vuisokaya (Ural) copper mines. V. P. YARKOV (Tzvet. Met., 1932, 238—246).—The deposits of cupriferous magnetites (Fe 40—65, Cu 1—3%) are described and their utilisation is discussed. CH. ABS.

Copper deposit at Devdorak. V. BOULYGO (Trans. Geol. Prospect. Serv. U.S.S.R., 1930, No. 15, 1—31).—The Cu content is 1·49—16%. CH. ABS.

Copper deposits of Laiskaja Datscha, Ural. V. DOMAREV (Bull. Geol. Prospect. Serv. U.S.S.R., 1930, No. 49, 645—667).—The ore contains 1—2% Cu. CH. ABS.

Magnetite-bearing quartzites of Man and neighbourhood (Ivory Coast). M. BOLGARSKY (Compt. rend., 1933, **197**, 559—561).—The magnetite-bearing quartzites of the Nimba Mts. consist almost wholly of quartz and magnetite, with a little pyroxene or amphibole, and small quantities of Mn, Al, Ti, and Ni. They are probably of eruptive origin, apparently passing into basic eruptive rocks. Similar quartzites containing hæmatite in place of magnetite also occur. C. A. S.

Magnetic susceptibility of magnetites from basic eruptive rocks. G. JOURAVSKY, P. CHARCZENKO, and G. CHOUBERT (Compt. rend., 1933, **197**, 522—525).—Magnetite is distinguishable from ilmenite by its being more readily attacked by conc. HCl or HI (*e.g.*, in 0·5—10 min.). The polished and attacked surface is examined in a metallurgical microscope provided with a Shand stage. Thus determined the amount of magnetite in a gabbro agrees closely with that deduced from the magnetic susceptibility. The results with this and titanomagnetite, dolerite, and basalts show that the susceptibility of the rock is almost entirely due to magnetite, the susceptibility of which, however, is much smaller (48·7—86·1%) when so present than in the pure state. C. A. S.

Iron ores at Itabira, Brazil. B. H. SANDERS (Bull. Inst. Min. Met., July, 1933, No. 346, 23 pp.).—An account is given of the geology of the Fe ore deposits with a description and analysis of the various types of Fe minerals. Au exists in certain parts of the deposits as scales and grains of an alloy with 8—10% Pd and < 3% Ag (cf. A., 1932, 402).

A. R. P.

Genetic peculiarities of the Briey basin and their relation to the distribution, constitution, and metallurgical properties of the oolitic [iron] minerals. J. P. AREND (Rev. Met., 1933, **30**, 43—53, 142—151, 188—199, 227—237).—The genesis of the Fe ore deposits in the Briey basin has been investigated by experiments with the H_2O which now circulates through the fissures in the faults; these indicate that the deposits constitute a perfect equilibrium between two gels, α formed by (*a*) the colloidal compounds of the ter- and multi-valent elements and (*b*) the polymerisable compounds of the intermicellar liquid, and β the colloidal ppt. of alkaline earths enclosing (*b*). Both gels hold in physical suspension the marls which occur on the borders of the Toarcian lake. According to the conditions of oxidation or reduction in the solid system α gives rise to oolites or to definite chemical compounds according to the scheme: oolite——$[(Fe_2O_3)_n,xFe(OH)_3]$←—$[(Fe_2O_3)_n,x$ (groups of protective colloids consisting of hydroxides, hydrogen sulphides, carbonates, or org. compounds)] $\overset{\pm O}{\rightleftharpoons}$ $[FeCO_3, FeS_2$, etc.]←—$[(FeO{\cdot}OH)_n,xFe(HCO_3)_2]$. The course, alternation, and composition of the carbonates, the intermediate products, and the various more or less pure minerals are determined by the changing effects of the marl and by variation in the oxidising or reducing powers of the lake waters caused by changes in the fauna and flora through the geologic ages. The speed of reduction of minerals is influenced by the degree of polymerisation of the α granules. The formation of oolites occurs in an absolutely homogeneous solid system which allows the establishment of centres of osmotic depression which can produce their effect in an identical manner in all directions and cause the larger ions to be displaced symmetrically to produce oolites the curvature of which varies with the degree of attraction between the colloidal matter being pectised on the surface and the sol from which it is derived. A. R. P.

Iron ore for the central [Russian] metallurgical industry. N. N. CHINKIN (Gorno-Obogat. Delo, 1932, No. 9, 27—37).—The ore is chiefly of the brown type, containing Fe 23·25—40·79, SiO_2 10·74—53·62, Al_2O_3 0·32—6·17, MnO 0·10—0·74, CaO 0—1·44, MgO trace—0·51, P_2O_5 0·39—1·38, and S 0·05—0·25%. Methods of concn. were studied.

CH. ABS.

Iron deposits of the Nikolaevski works, Irkutsk. S. DOKTOROVICH-GREBNITSKI (Trans. Geol. Prospect. Serv. U.S.S.R., 1931. No. 33, 1—14).—The FeO is 12·44—16·20%, and Fe_2O_3 57·90—68·23%.

CH. ABS.

Alapaevsk iron ore deposits. B. KROTOV (Trans. Geol. Prospect. Serv. U.S.S.R., 1931, No. 70, 1—52).

CH. ABS.

Non-ferrous metals in Central Asia. Deposits of Kara-Mazara. V. A. GLAZKOVSKI and I. SHCHUKIN (Gorno-Obogat. Delo, 1932, No. 1, 1—10).—The deposits (near Khodjent) contain 1·2—8·27% Cu. Other elements present are Pb 5—18, Zn 5—21, and As 1·5—3·5%, together with U, V, W, Sn, Mo, and Bi. CH. ABS.

Nickel sulphide at Grebni, Urals. A. TALVINSKI (Bull. Geol. Prospect. Serv. U.S.S.R., 1930, No. 49, 120—123).—The Ni content is 0·92—1·60%.

CH. ABS.

Alteration of black uranium mineral from Portugal [by weathering]. A. P. LEITE (Chim. et Ind. 1933, Spec. no., 805).—H_2O in contact with this mineral becomes yellow and the mineral crumbles and becomes covered with a white deposit. The solution is found to contain U in proportion to the SO_4 present. P_2O_5 is present when the SO_4 content of the solution exceeds a certain val. Dissolution of U in ordinary H_2O is > in distilled H_2O, but dissolved CO_2 is without influence. C. I.

Gem stones. W. T. GORDON (Nature, 1933, **132**, 267—269).—A lecture. L. S. T.

"Peat-dolomites" ["coal-balls"]. G. LINCK and E. KOHLER (Chem. Erde, 1933, **8**, 213—223).—The calcareous nodules containing plant remains found in coal seams are analysed and their origin is discussed. L. J. S.

Soil processes in volcanic ash beds. Beds of the northern King-country and their secondary alumina minerals. II. N. H. TAYLOR (New Zealand J. Sci. Tech., 1933, **14**, 338—352).—The nature and composition of the mineral matter in these soils have been examined and the probable process of their formation is discussed. A. G. P.

Processes of salinisation and desalinisation and the salt-profile of soils. B. B. POLYNOV (Trans. Irrigation Commission, Acad. Sci., U.S.S.R., 1933, **1**, 107—131).—A study of the formation and evolution of saline soils based on an examination of the salt-profile. A. M.

Rendzina soils of Polessie. S. NIDA (Abh. Inst. Bodenk. Pulawy, 1932, **2**, 124—156).—The parent material of these soils is cretaceous marl with more or less morainic material and varies widely in $CaCO_3$ content. No traces of podsolisation were found in pure rendzinas, but on mixed rendzinas (with loess) distinct podsolisation was observed. A. M.

Dissolution phenomena in the granite soils of Brittany. M. VINCENT (Ann. Agron., 1933, **3**, 323—332).—The decomp. of ground granitic rock by treatment with salt solutions, with consequent leaching of Na, K, and Mg, is examined and discussed in relation to the nutrient condition of granitic soils and the composition of the drainage H_2O.

A. G. P.

Chemical equivalents of clay acid and humic acids. S. OHSUGI and S. MORITA (J. Agric. Chem. Soc. Japan, 1933, **9**, 274—284).—The equivs., determined by Hissink's method, are 890—2513 and 149—181, respectively. When the acids were neutralised with $Ba(OH)_2$ the p_H was approx. 10—11.

CH. ABS.

Iodine content of Dutch soils in relation to geological and agricultural problems. J. F. REITH (Z. Pflanz. Düng., 1933, **31**, **A**, 215—224).—Summarised data from soils of different areas are given. The high I content of marine soils is attributed to deposition of I-rich plankton. Losses of free I by volatilisation from soils are unrelated to their Fe or Mn contents. Use of artificial instead of natural manures does not result in I impoverishment in soils. A. G. P.

Micropedological examination of crystal formation in the pore spaces of soil. W. KUBIENA (Z. Pflanz. Düng., 1933, **31**, **A**, 255—278).—The formation of crystals of $CaCO_3$ and $CaSO_4$ in natural soils has been examined by a special microscopical technique. Crystal forms produced in air-filled pore spaces differ from those appearing in spaces filled with soil solution. Conditions of crystallisation are examined and the effects of the presence of org. and inorg. colloids described. A. G. P.

Classification of soils on the basis of the composition of their colloidal fractions. A. REIFENBERG (Z. Pflanz. Düng., 1933, **31**, **A**, 287—303).—Characteristic vals. of silica : sesquioxide ratios for soils of various types are recorded. A. G. P.

Systematic examination of soils and soil mapping in Bavaria. R. PÜRCKHAUER (Z. Pflanz. Düng., 1933, **31**, **A**, 340—346).—The val. and uses of soil maps are discussed. A. G. P.

Principles of soil mapping. W. WOLFF (Z. Pflanz. Düng., 1933, **31**, **A**, 1—13).—The val. of systematic classification of soils is discussed. A. G. P.

Soil profiles from Cyprus. II. Profiles over diabase, gabbro-norite, and pillow lava. A. REIFENBERG and E. K. EWBANK (Empire J. Exp. Agric., 1933, **1**, 156—164; cf. this vol., 803).—Chemical changes involved in the weathering of, and soil formation from, these rocks are examined. A. G. P.

Mineralogical composition and oil yield from sands. V. P. BATURIN (Azerbaid. Neft. Choz., 1933, No. 1, 73—75).—Oil present in heavy-spar formations is retained more tenaciously by the mineral than that present in quartz sands. The nature of sand present in various Russian oilfields is discussed. CH. ABS.

Organic Chemistry.

Possible mechanism of racemisation and of the Walden inversion. G. B. BONINO (Gazzetta, 1933, **63**, 448—452).—Theoretical. The groups X, X′, X″ of a compound CHXX′X″ are considered as forming a barrier of potential opposing oscillation of the H atom from one equilibrium position to another (representing the optical antipodes); in racemisation the CXX′X″ pyramid is turned inside out, with ease depending on the weakness of the potential barrier, the oscillation level of the C and H atoms, and on steric factors. The Walden inversion may be similarly regarded, taking into account the oscillation of the N atom. E. W. W.

Effect of the decisive factors on the oxidation of paraffin to fatty acids under atmospheric pressure and the reaction mechanism of this oxidation. H. PFLUGK (Braunkohlenarch., 1932, No. 37, 1—36; Chem. Zentr., 1932, ii, 3959—3960).—The optimum temp. for the oxidation of paraffin (I) to fatty acids (II) with air is 160°. An increase in the velocity of the air increases the yield of (II) to a defined limit. A low moisture content (1·2%) favours the yield. H_2O_2, peracids, and peroxides were detected in the reaction product. Two H of the paraffin are oxidised forming H_2O_2 and unsaturated hydrocarbons which are further oxidised to (II) by fission of the chain. Acid anhydrides result from removal of H_2O, whilst oxidation by H_2O_2 gives the peracids from the acid anhydride peroxide. Oxidation of the terminal Me groups gives alcohols which then form esters. Cracking of (I) does not occur at this temp. L. S. T.

Syntheses in the olefine series. IV. Heptenes. F. J. SODAY and C. E. BOORD (J. Amer. Chem. Soc., 1933, **55**, 3293—3302; cf. A., 1932, 361).—The following are prepared by extensions of the β-Br-ether synthesis: *α-bromo-β-ethoxy-heptane*, b.p. 89·9—90°/8 mm., -ε-, b.p. 164·6°/250 mm., -δ-, b.p. 88·5—89·5°/10 mm., -β-, b.p. 103—104°/22 mm., and *-γ-methylhexane*, b.p. 75—76°/1·5 mm., *-βγ-*, b.p. 75·5—76·5°/4 mm., *-γδ-dimethyl-*, b.p. 72—73°/3 mm., and *-β-ethyl-pentane*, b.p. 73—75°/6 mm., and *-γ-methyl-β-ethyl-butane*, b.p. 66—68°/? mm.; *β-bromo-γ-ethoxy-heptane*, b.p. 90—91°/3 mm., -ε-, b.p. 91—92°/19 mm., -δ-, b.p. 89—90°/10 mm., and *-γ-methylhexane*, b.p. 69—70°/3 mm., *-γδ-dimethyl-*, b.p. 71—72°/3 mm., and *-γ-ethyl-pentane*, b.p. 69—70°/3 mm.; *γ-bromo-δ-ethoxy-heptane*, b.p. 88—89°/13·5 mm., and *-ε-methyl-hexane*, b.p. 88—90°/15 mm.: *αβ-dibromo-heptane*, b.p. 106·2°/13 mm., -ε-, b.p. 142·6—143·6°/101 mm., -δ-, b.p. 94·7—95·7°/11 mm., *-γ-*, b.p. 84·0—84·2°/6 mm., and *-β-methylhexane*, b.p. 100·5—101·5°/23 mm., *-βγ-*, b.p. 72·5—73°/3 mm., and *-γδ-dimethyl-*, b.p. 65·5—66°/4 mm., and *-β-ethyl-pentane*, b.p. 77—78°/4 mm., and *-β-ethyl-γ-methylbutane*, b.p. 72·5—73·5°/3 mm.; *βγ-dibromo-heptane*, b.p. 96·2°/12 mm., b.p. 89—90°/11 mm., -δ-, b.p. 91—92°/11 mm., -β-, b.p. 73·0—73·1°/8 mm., and *-γ-methyl-hexane*, b.p. 65·0—65·1°/2 mm., and *-γδ-dimethyl-*, b.p. 65·5—66°/3 mm., and *-γ-ethyl-pentane*, b.p. 76·0—76·4°/3 mm.; *γδ-dibromo-heptane*, b.p. 105·5—106·5°/23 mm., and *-β-methylhexane*, b.p. 96°/19 mm.; Δ^{α}-, b.p. 94·9°, Δ^{β}-, b.p. 98·1—98·4°, and Δ^{γ}-*heptene*, b.p. 95·8—96·1°; *β-methyl-*Δ^{α}-, b.p. 91·1—91·5°, -Δ^{β}-, b.p. 94·4—94·6°, and *-*Δ^{γ}*-hexene*, b.p. 86·4—86·9°; *γ-methyl-*Δ^{α}-, b.p. 83·4—84°, and -Δ^{β}-*hexene*, b.p. 93·1—93·3°; *δ-methyl-*Δ^{α}-, b.p. 87·2—87·5°, and -Δ^{β}-*hexene*, two forms, b.p. 87·1—87·6° and 85·1—85·6°, respectively; *ε-methyl-*Δ^{α}-, b.p. 84·7°, and -Δ^{β}-*hexene*, two forms, b.p. 91·1—91·6° and 85·6—86·1°, respectively; *βγ-*, b.p. 84·1—84·3°, and *βδ-dimethyl-*,

b.p. 80·9—81·3°, and β-*ethyl*-Δ^{α}-*pentene*, b.p. 93·9—94·3°; *γδ-dimethyl*-, b.p. 86·2—86·4°, and *γ-ethyl*-Δ^{β}-*pentene*, b.p. 94·8—94·9°; and β-*ethyl*-*γ-methyl*-Δ^{α}-*butene*, b.p. 88·7—89·1°. Physical consts. are recorded for these compounds. R. S. C.

Reaction of α-iodoacetylenes; mercury acetylides. T. H. VAUGHN (J. Amer. Chem. Soc., 1933, **55**, 3453—3458).—Diamylacetylene and $NaNH_2$ in mineral oil at 210° give a 28% yield of Δ^{α}-dodecinene, b.p. 95—98°/12 mm.; Δ^{α}-decinene (I) was obtained similarly from CBu·CBu. C_2H_2 derivatives and $Hg(CN)_2$–KOH in EtOH give Hg diacetylides, also obtained similarly from substituted α-iodoacetylenes, which may be identified in this way. The following new *Hg diacetylides*, $Hg(C{:}CR)_2$, are described, the radical named being R: *Pr*, m.p. 118·4—118·8°; *Bu*$^{\alpha}$ (II), m.p. 96·2—96·4°; *hexyl*, m.p. 80·4—80·7°; *heptyl*, m.p. 67·8—68·5°; octyl, m.p. 79·5—80° (lit. 83—84°); *nonyl*, m.p. 79—79·3°; *decyl*, m.p. 84·3—85·1°; *vinyl*, unstable, m.p. 142—142·5°; m-*xylyl*, m.p. 140·3—140·5°; *mesityl*, m.p. 238—239°. (I), MgEtBr, and I in Et_2O give α-*iodo*-Δ^{α}-*decinene* (70%), b.p. 84°/0·7 mm.; α-*iodo*-Δ^{α}-*octinene* (88%), b.p. 95—97°/7·5 mm., and -*dodecinene* (94·5%), b.p. 99—102°/0·3 mm., were similarly prepared. (II), KI, and I at room temp. give α-*iodo*-Δ^{α}-*hexinene* (III) (22%), b.p. 58—59°/8 mm., and (probably) ααβ-*tri-iodo*-Δ^{α}-*hexene*, decomp. when distilled. (II) and I in liquid NH_3 give a 54% yield of pure (III). H_2S ppts. HgS from the Hg compounds. R. S. C.

Preparation of *iso*butyl bromide. V. LONGINOV and K. LERMAN (Khim. Farm. Prom., 1933, 14—18).—Purified HBr is passed through $Bu^{\beta}OH$ at 88° rising to 135°. The product is washed with conc. H_2SO_4, 5% $NaHCO_3$, 2% $KMnO_4$, and H_2O. CH. ABS.

1-Nitroanthraquinone-2-carboxylic acid as a reagent for alcohols. P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1933, **1**, 51—58).—The following esters of 1-nitroanthraquinone-2-carboxylic acid are prepared by interaction of the chloride with the appropriate alcohol at 120—140° during 15 min.: *Me*, m.p. 249—251°; *Pr*$^{\alpha}$, m.p. 182—183°; *Pr*$^{\beta}$, m.p. 204—206°; *Bu*$^{\alpha}$, m.p. 174—175°; *Bu*$^{\beta}$, m.p. 159—160°; sec.-*Bu*, m.p. 155—156°; tert.-*Bu*, m.p. 220—221°; n-*amyl*, m.p. 166—168°; iso*amyl*, m.p. 165—167°; sec.-*amyl*, m.p. 136—137°; tert.-*amyl*, m.p. 221—223°; n-*hexyl*, m.p. 153—154°; n-*heptyl*, m.p. 140—141°; n-*octyl*, m.p. 131—132°; sec.-*octyl*, m.p. 114—115°; n-*nonyl*, m.p. 125—126°; n-*decyl*, m.p. 123—124°; *cetyl*, m.p. 105—106°; *allyl*, m.p. 184—185°; *benzyl*, m.p. 211—212°; β-*chloroethyl*, m.p. 192—193°; *menthyl*, m.p. 189—190°. J. L. D.

Tautomeric forms of substituted allyl alcohols. H. W. J. HILLS, J. KENYON, and H. PHILLIPS (Chem. and Ind., 1933, 660—661).—Hydrolysis of (+)αγ-dimethylallyl H phthalate (I) with dil. H_2SO_4 yields the *dl*-alcohol, but with dil. alkalis the (+)alcohol (II) is formed, which has a marked temp.–rotation coeff., is lævorotatory in Et_2O, and exhibits anomalous rotatory dispersion and sometimes mutarotation. The parachors of α- and some γ-substituted allyl alcohols are not in accordance with the usually accepted formulæ; the vals. for αγ-dimethyl- and α-ethyl-allyl and cinnamyl alcohols suggest that (< 60° in the first two cases) these exist mainly in cyclic forms, and the properties of (II) may therefore be due to the additional position of asymmetry. The H phthalate group of (I) is mobile and by replacement a (−)Bu^{α} ether is formed opposite in rotational sign to that from (II) and $Bu^{\alpha}Br$, indicating the occurrence of a Walden inversion during replacement. H. A. P.

Dehydration of capryl alcohol [octan-β-ol]. F. C. WHITMORE and J. M. HERNDON (J. Amer. Chem. Soc., 1933, **55**, 3428—3430).—Dehydration of octan-β-ol by H_3PO_4 gives a mixture of Δ^{α}- and Δ^{β}-octene (cf. A., 1932, 830) in the ratio 2 : 1. R. S. C.

Grignard reagents from dialkyl sulphates. C. M. SUTER and H. L. GERHART (J. Amer. Chem. Soc., 1933, **55**, 3496).—$Bu^{\alpha}{}_2SO_4$ and $MgBu^{\alpha}Br$ give $Bu^{\alpha}Br$ and the *compound*, $Bu^{\alpha}(MgBu^{\alpha})SO_4$. Et_2SO_4 and Mg in dry Et_2O give the slightly sol. Grignard reagent, $Et(MgEt)SO_4$, which with PhCHO gives a good yield of CHPhEt·OH. $Bu^{\alpha}{}_2SO_4$ gives a similar reagent, readily hydrolysed to *n*-C_4H_{10}. R. S. C.

Preparation of pure sulphuric acid esters of hydroxystearic acid and octadecanediol. W. SECK and F. DITTMAR (Fettchem. Umschau, 1933, **40**, 146—149; cf. this vol., 47).—Pure preps. of Na_2 ι-sulphostearate from ι-hydroxystearic acid, and of *Na_2 octadecyl disulphate* (I) from octadecane-αχ-diol, have been obtained. Sulphation of oleyl alcohol affords only a very small yield of (I) (impure). E. L.

Preparation of esters of chlorosulphonic and sulphurous acids. R. LEVAILLANT (Compt. rend., 1933, **197**, 335—337).—The following *chlorosulphonates*, lachrymatory, are prepared from SO_2Cl_2: *Bu*$^{\alpha}$, b.p. 76—77°/13 mm., n-*amyl*, b.p. 75—76°/4 mm., -*chloropropyl*, b.p. 85°/4 mm., and βγ-*dichloropropyl*, .p. 122—123°/15 mm. The stability of this series is a min. with the Pr$^{\alpha}$ compound, but is increased by substitution by Cl. *n*-Amyl alcohol, prepared from MgBuBr and $(CH_2O)_3$, is accompanied by *di*-(n-*amyloxy*)*methane*, b.p. 99—101°/14 mm. $SOCl_2$ gives the following s-*sulphites*, SO_2R_2: *di*-n-*amyl*, b.p. 124°/13 mm., *di*-n-*heptyl*, b.p. 181°/13 mm., *di*-β-*bromoethyl*, b.p. 158—159°/13—14 mm., *di*-γ-*chloropropyl*, b.p. 161—162°/13 mm., and *di*-βγ-*dichloropropyl*, b.p. 175°/4 mm. Physical consts. are recorded. R. S. C.

New method of fluorination of organic compounds. P. C. RAY (Nature, 1933, **132**, 173).—*Me*, b.p. 40°, and *Et*, b.p. 57°, *fluoroformate* are prepared by the action of TlF on the corresponding cold chloroformate and subsequent distillation. L. S. T.

Reaction of some imino-ether hydrochlorides with alcohols. P. P. T. SAH (J. Chinese Chem. Soc., 1933, **1**, 100—105; cf. A., 1928, 394).—Prolonged interaction of acetimino-methyl (or -ethyl) ether hydrochloride with cold abs. Bu^{β} or *iso*amyl alcohol and K_2CO_3 affords, respectively, *Me*, b.p. 205—206°, and *Et diisobutyl*-, b.p. 208—210°; *Me*, b.p. 219—223°, and *Et diisoamyl-orthoacetate*, b.p. 236—238°.

$CH_2Ph{\cdot}CH_2{\cdot}CN$ and abs. EtOH in Et_2O containing HCl afford β-phenylpropioniminoethyl ether hydrochloride (I), which gives with excess of EtOH, *Et*$_3$ β-*phenylorthopropionate*, b.p. 242°. Me and Et ethers [analogous to (I)] from PhCN do not afford esters with many alcohols. J. L. D.

Insect wax. VI. Synthesis of triglycerides of palmitic and myristic acids. F. N. Schulz and M. Becker.—See this vol., 1066.

Branched-chain aliphatic acids. *iso*Myristic, *iso*palmitic, and *iso*stearic acids. C. R. Fordyce and J. R. Johnson (J. Amer. Chem. Soc., 1933, **55**, 3368—3372).—Sebacyl chloride (I), b.p. 155—156°/8 mm. (prepared by $SOCl_2$), and *n*-$C_8H_{13}{\cdot}MgBr$ in Et_2O at 25—26° give ι-ketopalmitic acid (28%), m.p. 75—75·8° (semicarbazone, m.p. 65—66°) [giving, when reduced (Clemmensen), palmitic acid], and a *substance*, m.p. 85·8—87°. The following were similarly prepared: from *n*-$C_8H_{17}{\cdot}MgBr$, ι-ketostearic acid (12%); from Mg *iso*hexyl bromide, *ι-keto-ν-methylpentadecoic* (*ι-ketoisopalmitic*) *acid* (24%), m.p. 68—69°, reduced to *ν-methylpentadecoic* (*isopalmitic*) *acid*, m.p. 61·8—62·4°; from Mg *iso*octyl bromide, *ι-keto-ο-methylheptadecoic* (*ι-ketoisostearic*) *acid* (11%), m.p. 71·2—72°, reduced to *ο-methylheptadecoic* (*isostearic*) *acid*, m.p. 67·6—68·2°. $MgBu^{\beta}Br$ and (better) *0-carbethoxynonyl chloride*, b.p. 158—160°/7 mm. [from (I) and EtOH], give a small amount of a *substance*, m.p. 43—44°, probably *δν-diketo-βο-dimethylhexadecane* (*semicarbazone*, m.p. 193—194°), and *ι-keto-λ-methyltridecoic acid* (43—47%), m.p. 52—53°, which is reduced to *λ-methyltridecoic* (*isomyristic*) *acid* (II), m.p. 50·5—51°. $MgPr^{\beta}Br$ and $(CH_2)_2O$ give *iso*amyl bromide, the Grignard reagent from which with Me η-aldehydooctoate gives *Me 0-hydroxyisomyristate* (30%), b.p. 146—153°/1 mm., oxidised by CrO_3 to *0-ketoisomyristic acid*, m.p. 58·2—59·5°, and converted by dehydration, reduction, and hydrolysis into (II). The *Et* ester, b.p. 140—142°/5 mm., of (II) with Na and EtOH gives *isomyristyl alcohol* (75—80%), b.p. 145—150°/6 mm. (*bromide*, b.p. 120—123°/3 mm.). $MgBu^{\beta}Br$ and $(CH_2)_2O$ give *iso*hexyl alcohol (40%), whence by $HBr–H_2SO_4$ the bromide was obtained in 90—92% yield, and thence similarly *iso*octyl bromide, b.p. 65—68°/10 mm. R. S. C.

Lycopodiumoleic acid. J. L. Riebsomer and J. R. Johnson (J. Amer. Chem. Soc., 1933, **55**, 3352—3357).—The acids of lycopodium oil are shown, mainly by fractionation of the Pb salts and esters and subsequent ozonolysis, to be chiefly oleic (55—60%) and Δ^{θ}-palmitoleic acid (30—35%), with a little linoleic, palmitic, 0ι-dihydroxystearic, and other acids. "Lycopodiumoleic acid" appears to be a mixture of these acids. R. S. C.

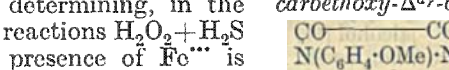
Reaction between pyruvic acid and hydrogen peroxide in presence of hydrogen sulphide. A. Wassermann (Biochem. Z., 1933, **263**, 1—8; cf. this vol., 789).—A method for determining, in the same solution, the velocity of the reactions $H_2O_2+H_2S$ and $H_2O_2+AcCO_2H$ (I) in the presence of $Fe^{\cdots}$ is described. The reactions do not interfere with each other. In (I) no $H_2C_2O_4$ or succinic acid can be detected. W. McC.

Lævulic acid. V. 2 : 4-Dinitrophenylhydrazones of its alkyl esters. M. A. Cowley and H. A. Schuette (J. Amer. Chem. Soc., 1933, **55**, 3463—3466; cf. this vol., 258).—Lævulic acid (I) in dil. HCl gives the 2 : 4-dinitrophenylhydrazone, m.p. 206·5° (lit. 92° and 203°); in EtOH the derivative of the Et ester may be formed. 2 : 4-*Dinitrophenylhydrazones* of the following esters of (I) are prepared: *Me*, m.p. 141·2°; *Et*, m.p. 101°; *Pr*$^{\alpha}$, m.p. 63°; *Bu*$^{\alpha}$, m.p. 65·8°; n-*amyl*, m.p. 84·2°; n-*hexyl*, m.p. 56·6°; n-*heptyl*, m.p. 79°. R. S. C.

Alkyl esters of lævulic acid. G. J. Cox and (Miss) M. L. Dodds (J. Amer. Chem. Soc., 1933, **55**, 3391—3394).—*Bu*$^{\gamma}$, b.p. 225·8°, dl-*amyl*, b.p. 248·8°, *CHMePr*, b.p. 239·6°, and *CHEt*$_2$ *lævulate*, b.p. 239°, are prepared, best from the crude acid. Physical consts. of these and other lævulates are recorded. The Bu$^{\alpha}$ ester was obtained in 11% yield from hot Bu$^{\alpha}$OH, sucrose, and HCl. Bu$^{\alpha}$OH extracts lævulic acid from solutions of the crude product. R. S. C.

Japanese beeswax. III. Composition of the "hydroxy-fatty acid." H. Ikuta (J. Soc. Chem. Ind. Japan., 1933, **36**, 444—447B; cf. B., 1933, 797).—A *hydroxypalmitic acid*, m.p. 73·8—74·2°, has been isolated from the fatty acids of Japanese beeswax, of which it constitutes about 20%, occurring partly in the free state. The "hydroxy-" and "*iso*hydroxymargaric" acids of Lipp and Kovacs (A., 1920, i, 140) probably consisted of mixtures of hydroxypalmitic and higher fatty (? hydroxylated) acids. E. L.

Ethyl oxalosorbate and oxalic ester condensations. W. Borsche and R. Manteuffel (Annalen, 1933, **505**, 177—194; cf. A., 1932, 721).—The K derivative of Et_2 oxalosorbate (I) is converted by prolonged action of cold 10% KOH into *oxalosorbic acid* (*Δ$^{\nu\epsilon}$-hexadiene-α-one-αζ-dicarboxylic acid*), m.p. 220—221° (decomp.) (*Me*$_2$ ester, m.p. 132—133°), and by Me_2SO_4 in boiling C_6H_6 into *Et*$_2$ *α-methoxy-Δ$^{\alpha\nu\epsilon}$-hexatriene-αζ-dicarboxylate* (II), b.p. 180—185°/15 mm. (I) is readily reduced (PtO_2–EtOH) to *Et*$_2$ *α-hydroxysebacate*, b.p. 167—170°/12 mm. (*Bz* derivative, b.p. 184—185°/2 mm., obtained by reduction of Et_2 benzoyloxyhexatrienedicarboxylate). Complete reduction of (II) (PtO_2–EtOH) leads to *Et*$_2$ *α-methoxysebacate*, b.p. 162—165°/12 mm., whereas partial reduction (Pd–EtOH) affords *Et*$_2$ *α-methoxy-Δ$^{\alpha}$-hexene-αζ-dicarboxylate*, b.p. 172—174°/12 mm., transformed by boiling EtOH–HCl into *Et*$_2$ *α-ketosuberate* (III), b.p. 174—175°/16 mm. (III) and $NHPh{\cdot}NH_2$ afford *2-carboxy-3-δ-indolylvaleric acid*, m.p. 193—195°. In presence of MeOH–HCl, (I) and *p*-$OMe{\cdot}C_6H_4{\cdot}N_2Cl$ yield *Et*$_2$ *αβ-diketo-Δ$^{\nu\epsilon}$-hexadieneαζ-dicarboxylate* β-p-*anisylhydrazone*, $CO_2Et{\cdot}C(OH){:}C(N{:}N{\cdot}C_6H_4{\cdot}OMe){\cdot}[CH{:}CH]_2{\cdot}CO_2Et$ (IV), m.p. 104—105° (or +1MeOH, m.p. 92—93°), and a small amount of 4 : 5-*diketo*-1-p-*anisyl*-3-δ-*carbethoxy-Δ$^{\alpha\gamma}$-butadienylpyrazoline*,



(V), m.p. 164—165° (or +1MeOH, m.p. 156—157°). The 2 : 4-*dinitrophenylhydrazone* of (V) has m.p. 258—259°. Treatment of (IV) or (V) with *p*-$OMe{\cdot}C_6H_4{\cdot}N_2Cl$ in

presence of MeOH–NH_3 gives *Et* δ-(pp′-*dimethoxyformazyl*)*butadienecarboxylate*, $OMe{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}C(N{:}N{\cdot}C_6H_4{\cdot}OMe){\cdot}[CH{:}CH]_2{\cdot}CO_2Et$, m.p. 136—137°. (I) and *p*-$C_6H_4Br{\cdot}N_2Cl$ yield *Et*$_2$ αβ-*diketo*-Δ$^{\gamma\epsilon}$-*hexadiene*-αζ-*dicarboxylate* p-*bromophenylhydrazone*, m.p. 126—127°, and 4 : 5-*diketo*-1-p-*bromophenyl*-3-δ-*carbethoxy*-Δ$^{\alpha\gamma}$-*butadienylpyrazoline*, m.p. 158—159°, or, +1EtOH, m.p. 117—118° (2 : 4-*dinitrophenylhydrazone*, m.p. 264°). (I) and $NO{\cdot}C_6H_4{\cdot}NMe_2$ in boiling EtOH afford the *anil* $NMe_2{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}[CH{:}CH]_2{\cdot}CO_2Et$, m.p. 187—188°.

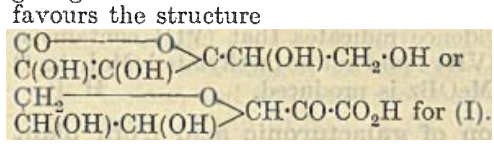
Et_2 oxalocrotonate (VI), m.p. 78° (2 : 4-*dinitrophenylhydrazone*, m.p. 117—118°), is converted into the K derivative and thence by Me_2SO_4 into *Et*$_2$ α-*methoxymuconate* (VII), b.p. 118—120°/2 mm. Hydrogenation of (VI) (PtO_2–EtOH) leads to *Et*$_2$ α-*hydroxyadipate*, b.p. 160—161°/17 mm. Complete reduction of (VII) (colloidal Pd–EtOH) yields *Et*$_2$ α-*methoxyadipate*, b.p. 142—144°/12 mm., whereas partial hydrogenation affords *Et*$_2$ α-*methoxy*-Δ$^{\gamma}$-*dihydromuconate*, b.p. 153—156°/15 mm., transformed by HCl–EtOH into *Et*$_2$ α-*ketoadipate*, b.p. 155—157°/16 mm. (semicarbazone, m.p. 118°). *Et*$_2$ α-*benzoyloxyadipate*, b.p. 160—162°/2 mm., is derived from the corresponding muconate. 4 : 5-*Diketo*-1-p-*bromophenyl*-3-β-*carbethoxyvinylpyrazoline* (+1EtOH), m.p. 91° after softening and darkening at 82° (2 : 4-*dinitrophenylhydrazone*, m.p. 237°), is formed in addition to Et$_2$ *p*-bromobenzeneazo-oxalocrotonate, m.p. 125°, from (VI) and *p*-$C_6H_4Br{\cdot}N_2Cl$. The p-*dimethylaminoanil*, m.p. 151·5—152·5°, and the 2 : 4-*dinitrophenylhydrazone*, m.p. 290—292°, of *Et* β-*formylacrylate* are described.

HCO_2Et under the influence of KOEt condenses with Et crotonate (VIII) to Et γ-aldehydocrotonate [2 : 4-*dinitrophenylhydrazone*, m.p. 147—148° (decomp.)] and with Et sorbate (IX) to Et ε-aldehydosorbate (2 : 4-*dinitrophenylhydrazone*, m.p. 148—150°). The primary stage of the condensation of (VIII) and (IX) is considered to consist in the production of the compounds $CH_2{:}CH{\cdot}CH{:}C(OK){\cdot}OEt$ and $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}C(OK){\cdot}OEt$, which undergo αδ and αζ addition with $CO_2Et{\cdot}C(ONa)(OEt)_2$. H. W.

Conjugated compounds. XIX. Michael reaction applied to a triene ester. E. H. Farmer and S. R. W. Martin (J.C.S., 1933, 960—962).—Addition of $CH_2(CO_2Me)_2$ to Me Δ$^{\alpha\gamma\epsilon}$-heptatriene-α-carboxylate gives about 67% of the αβ and at least 10% of the αζ additive products; αδ addition could not be detected. The resultant mixture, b.p. 154—159°/1—2 mm., of *Me* β-*methylheptadiene*-αα$_\eta$-*tricarboxylate* and *Me* Δ$^{\gamma\epsilon}$-*heptadiene*-α-*carboxylate*-β-*malonate* is reduced catalytically to a mixture, b.p. (mainly) 142—150°/1—2 mm., of *Me* β-*methylheptane*-αα$_\eta$-*tricarboxylate* and *Me heptane*-α-*carboxylate*-β-*malonate*, which on hydrolysis (aq. MeOH–NaOH), decarboxylation of the resulting acids at 170°, and subsequent dehydration (Ac_2O) gives β-n-*amylglutaric anhydride*, b.p. 138°/2 mm., and polymeric β-methylazelaic anhydride. *n*-Hexaldehyde and $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ give αα′-dicyano-β-*n*-amylglutarimide, which is hydrolysed (15% HCl) to β-n-*amylglutaric acid*, b.p. 208°/2 mm. β-n-*Amylglutaranilic acid* has m.p. 81°. H. B.

Vitamin-*C*. F. Micheel (Angew. Chem., 1933, 46, 533—536).—A lecture. H. W.

Structure of ascorbic acid (vitamin-*C*). P. A. Levene and A. L. Raymond (Science, 1933, 78, 64).—Ascorbic acid (I) absorbs 2 H on hydrogenation, giving an acid which forms a stable lactone. This favours the structure



L. S. T.

Synthesis of *d*- and *l*-ascorbic acid (vitamin-*C*). T. Reichstein, A. Grussner, and R. Oppenauer (Nature, 1933, 132, 280).—An improved method (this vol., 594) is described for the conversion of *d*- and *l*-xylosone, respectively, into *d*- and *l*- (I) -ascorbic acid, m.p. 186—189° (corr., decomp.) $[\alpha]_D^{23}$ ±48° in MeOH. Equal amounts of the *d*- and *l*-forms give crystals, m.p. 168—169° (corr.) $[\alpha]_D$ 0°. (I) is identical with natural ascorbic acid. L. S. T.

Biochemistry and physiology of glycuronic acid. I. Structure of glycuronic acid of animal origin. II. Methylation of glycurone of animal origin. III. Structure of benzoylglycuronic acid. J. Pryde and R. T. Williams (Biochem. J., 1933, 27, 1197—1204, 1205—1209, 1210—1215).—I. β-Bornyl-*d*-glycuronide (borneolglycuronic acid) (I), $C_{16}H_{26}O_7{,}1{\cdot}5H_2O$, m.p. 174—175°, isolated as its Zn salt (cf. Quick, A., 1927, 990) from the urine of dogs and human beings fed with borneol, is methylated (MeI, Ag_2O) to 2 : 3 : 4-*trimethyl*-β-*bornyl*-d-*glycuronide Me* ester, m.p. 92—93°, $[\alpha]_{5461}$ −30·7° in EtOH, which is hydrolysed (MeOH–0·2*N*-H_2SO_4 at 100°) to a *mixture* (II), b.p. 131°/4 mm., $[\alpha]_{5461}^{18}$ +98·9° in H_2O, of α- and β-2 : 3 : 4-trimethylmethyl-*d*-glycuronide Me ester. Oxidation (HNO_3, *d* 1·42) of (II) at 65—90° and subsequent esterification (MeOH–HCl) gives Me *d*-dimethoxysuccinate (small amount), Me *i*-xylotrimethoxyglutarate (III), and 2 : 3 : 4-trimethyl-δ-saccharolactone Me ester (IV). The isolation of (III) and (IV) establishes the pyranoid structure of the glycuronic acid residue of (I).

II. Hydrolysis of (I) (above) with boiling 0·2*N*-H_2SO_4, quant. removal of H_2SO_4 from the filtrate with $Ba(OH)_2$, evaporation of the resulting solution at 40°/vac. to a syrup, dissolution of this in the min. amount of H_2O, and subsequent addition of EtOH gives *d*-glycurone, m.p. 177—178°, $[\alpha]_{5461}^{15}$ +21·3° in H_2O. This is methylated (MeI, Ag_2O) (cf. A., 1931, 1036; this vol., 259) to trimethylglycurone (V), m.p. 131—132°, $[\alpha]_{5461}^{16}$ +197·5° in H_2O, the unsaturated *trimethylglycuralone* (VI), m.p. 88°, +110·8° in H_2O, and (mainly) a syrup [which is methylated further to (probably) 2 : 3 : 4-trimethyl-β-methyl-*d*-glycuronide Me ester]. Possible structures are suggested for (V) and (VI). The formation of a double linking [in (VI)] is ascribed to the mild oxidising action of Ag_2O.

III. Conjugated glycuronic acids are divided into three types: (*a*) glycoside-ether [as (I) (above)]; (*b*) glycoside-ester [as (VII) (below)]; (*c*) those containing two glycuronic acid residues, one being attached to a non-sugar group as in (*a*), the other attached by an ester linking as in (*b*). Benzoylglycuronide (benzoyl-

glycuronic acid) (VII) (improved method of prep. given; cf. Quick, A., 1926, 1056), m.p. 183° (lit. 170—172°), $[\alpha]_D$ −29·9° in H_2O, reduces sugar reagents owing to the ease of hydrolysis of the Bz group. Treatment of (VII) with aq. KCN causes hydrolysis and subsequent formation of glycuronic acid cyanohydrin (cf. Quick, *loc. cit.*). The above and other evidence indicates that (VII) contains a 1-Bz group. (VII) could not be methylated (MeI, Ag_2O or CH_2N_2); MeOBz is produced. H. B.

Preparation of galacturonic acid from plant materials and its derivatives. H. R. Nanji (Biochem. J., 1933, 27, 1163—1165).—Lemon peel is a more satisfactory source of *d*-galacturonic acid [cinchonine salt, m.p. 173° (decomp.); phenylhydrazine salt phenylhydrazone, m.p. 131° (decomp.)] than apple pomace or sugar-beet residues. H. B.

Composition of lemon albedo pectin. (Miss) C. M. Bridgham and C. G. King (J. Amer. Chem. Soc., 1933, **55**, 3319—3322).—Purified lemon albedo (white peel) pectin gives by hydrolysis *d*-galacturonic acid (4 mols.) (mostly present as the Me ester), galactose (1 mol.), and arabinose (1 mol.). R. S. C.

Bromometric determination of sulphido-acids. N. Hellstrom (Svensk Chem. Tidskr., 1933, **45**, 158—169).—Sulphido-acids are oxidised by a slight known excess of Br (in the form of $KBr+KBrO_3$) and back-titrated with $Na_2S_2O_3$ after adding KI. Alternatively, potentiometric titrations may be carried out directly with aq Br. Titrations must be rapid to avoid further oxidation. Typical reactions are: $\cdot CH_2\cdot S\cdot CH_2\cdot + 2Br + H_2O = \cdot CH_2\cdot SO\cdot CH_2\cdot + 2HBr$, $\cdot CH_2\cdot S\cdot S\cdot CH_2\cdot + 10Br + 6H_2O = 2\cdot CH_2\cdot SO_2\cdot OH + 10HBr$, $\cdot CH_2\cdot SH + 6Br + 3H_2O = \cdot CH_2\cdot SO_2\cdot OH + 6HBr$, $\cdot CH(S\cdot CH_2\cdot)_2 + 12Br + 7H_2O = \cdot CHO + 2\cdot CH_2\cdot SO_2\cdot OH + 12HBr$, $CH_2\cdot S(CH_2)_nS\cdot CH_2\cdot + 4Br + 2H_2O = \cdot CH_2\cdot SO(CH_2)_nSO\cdot CH_2\cdot + 4HBr$. Satisfactory results were obtained with the following acids: $S(CH_2\cdot CO_2H)_2$ (I), $NH_2\cdot CO\cdot CH_2\cdot S\cdot CH_2\cdot CO_2H$, $SMe\cdot CH_2\cdot CO_2H$, $CHMe(S\cdot CH_2\cdot CO_2H)_2$, $CO_2H\cdot CH(S\cdot CH_2\cdot CO_2H)_2$, $(\cdot CH_2\cdot S\cdot CH_2\cdot CO_2H)_2$, $CH_2(CH_2\cdot S\cdot CH_2\cdot CO_2H)_2$, $(\cdot S\cdot CH_2\cdot CO_2H)_2$ (II), and with $(S\cdot CH_2\cdot CO\cdot NH_2)_2$. $CH_2(S\cdot CH_2\cdot CO_2H)_2$ gave unsatisfactory results. The method was used to analyse a mixture of (I) and (II). R. P. B.

Stereochemistry of sulphur. I. Stereoisomeric αα′-dicarboxydipropyl disulphides. R. Ahlberg (J. pr. Chem., 1933, [ii], **138**, 128—144).—α-Thiodibutyric acid is prepared by interaction of aq. $CHEtBr\cdot CO_2Na$ and $OEt\cdot CS\cdot SK$, hydrolysis with aq. H_2SO_4, and air-oxidation of the resulting α-thiolbutyric acid in presence of $MnSO_4$ or Fe^{II} salts and $FeCl_3$. H_2O_2 may also be used as oxidising agent. With a slight deficit of NaOEt (? NaOH) in EtOH the *Na* salt ($+2H_2O$) of the racemic acid (I) separates; with excess of NaOEt more Na salt slowly forms, apparently by rearrangement of other racemic acids, as the *meso*-acid, separated as *cinchonine* salt, m.p. 67—68·5°, is unaffected by NaOEt. By optical resolution of (I) *cinchonidine* ($+4H_2O$) and *brucine* salts of the (+)-acid ($[\alpha]_I^5$ +427° in H_2O) and the *strychnine* salt ($+5H_2O$) of the (−)-acid are obtained. H. A. P.

Semi-acetal and hydrate formation of carbonyl and carboxyl derivatives. W. Herold (Z. Elektrochem., 1933, **39**, 566—571; cf. A., 1932, 982, 1188).—The change in absorption spectrum of aldehydes and ketones and their derivatives in alcoholic solvents is used to measure the extent of semi-acetal and hydrate formation. Data for many compounds containing the C:O group are discussed with reference to their stability and the influence of substituted groups. $CCl_3\cdot CHO$ has a strong tendency to semi-acetal formation. The kinetics of its reaction with EtOH in eight solvents were studied, and the influence of the solvent is discussed. H. J. E.

Colour reaction of aldehydes. P. Rumpf (Compt. rend., 1933, **197**, 337—339).—A cold, freshly-prepared solution of 2—3 mg. of rosaniline hydrochloride in 98—100% HCO_2H gives the following colours: (*a*) with CH_2O and $CCl_3\cdot CHO$ fuchsin-red (max. 5480 Å. for CH_2O); (*b*) with aromatic aldehydes and those having a *tert.* C atom, as (*a*), but brighter, and with αβ-unsaturated aldehydes [except acraldehyde (I)] as (*a*) with an orange shade (max. 4500 Å., possibly with a second max. at 4800 Å.); (*c*) with aldehydes having an α-CH_2 group, the colour changes more or less rapidly to green (max. 6270 Å.), and two substances, violet (max. 5600 Å.) and pure blue (max. about 5980 Å.), respectively, can be isolated by H_2O; (*d*) acraldehydes having no β-substituent and aldehydes having an α-CH< group, as (*c*) but more rapidly. Polymerides (*e.g.*, trioxymethylene), H sulphite and other compounds [*e.g.*, $(CH_2)_6N_4$, or acetal] which give the free aldehyde, even in traces, in anhyd. acid solution give the reaction. Certain terpenes give blue colours, thus preventing application of the reaction in this series. R. S. C.

Action of hydrogen peroxide on aldehydes. S. Bezzi (Gazzetta, 1933, **63**, 345—355).—The gaseous product from MeCHO and H_2O_2 in presence of H_2SO_4 at 95° is largely CH_4 and H_2; AcOH, HCO_2H, and CO_2 are also formed. Similarly EtCHO yields C_2H_6, H_2, $EtCO_2H$, etc. Mechanisms for such reactions proposed by Wieland (A., 1921, i, 889) and Fry and Payne (A., 1931, 819) are rejected. The mechanism $[CHR(OH)\cdot O\cdot]_2 \longrightarrow H_2 + 2RCO_2H$ and $\longrightarrow RH + HCO_2H + RCO_2H$ is suggested. E. W. W.

Thermal reaction between chlorine and formaldehyde. R. Spence and W. Wild (Nature, 1933, **132**, 170).—At 150°, in the dark, the rapid reaction $CH_2O + Cl_2 = CO + 2HCl$ occurs after a short induction period. A complex chain process is probably involved. No measurable reaction occurs at 100°. L. S. T.

ααβ-Trihalogenobutaldehydes. F. D. Chattaway, H. Irving, and G. H. Outhwaite (J.C.S., 1933, 993—995).—α-Chlorocrotonaldehyde (from $CHMeCl\cdot CHCl\cdot CHO$ and aq. NaOAc) and Br (1 mol.) at < 0° give α-chloro-αβ-dibromobutaldehyde (*monohydrate*, m.p. 45—50°), and α-bromocrotonaldehyde (I) similarly affords ααβ-tribromobutaldehyde (butyl bromal) [*monohydrate* (II), m.p. 42—45°]. αβ-Dichloro-α-bromobutaldehyde (*monohydrate*, m.p. 70°) is similarly prepared from (I) and Cl. Cautious fusion of (II) with $HCO\cdot NH_2$, NH_2Ac, and NH_2Bz gives

form-, m.p. 133° (decomp.), *acet-*, m.p. 140° (decomp.), and *benz-*, m.p. 142° (decomp.), *-ββγ-tribromo-α-hydroxybutylamide*, respectively; with $CO(NH_2)_2$, *ββγ-tribromo-α-hydroxybutylcarbamide*, m.p. 104° (decomp.), results. The following are similarly prepared: *form-*, m.p. 136° (decomp.), *acet-*, m.p. 142° (decomp.), and *benz-*, m.p. 144° (decomp.), *-β-chloro-βγ-dibromo-α-hydroxybutylamide*; *form-*, m.p. 140° (decomp.), *acet-*, m.p. 165° (decomp.), and *benz-*, m.p. 157° (decomp.), *-βγ-dichloro-β-bromo-α-hydroxybutylamide*; *β-chloro-βγ-dibromo-*, m.p. 112° (decomp.), and *βγ-dichloro-β-bromo-*, m.p. 153° (decomp.), *-α-hydroxybutylcarbamide*. The trihalogenobutaldehydes resemble butyl chloral in appearance and properties, give liquid alcoholates, and are oxidised (fuming HNO_3) to the trihalogenobutyric acids. H. B.

New ether-acetals and ether-aldehydes. M. Rotbart (Compt. rend., 1933, **196**, 2013—2015).—Na alkoxides are condensed with bromodiethylacetal by heating under pressure at ⩾190° to give ether-acetals, $OR{\cdot}CH_2{\cdot}CH(OEt)_2$ (75% yield), hydrolysed by 25% H_2SO_4 in aq. AcOH to ether-aldehydes, $OR{\cdot}CH_2{\cdot}CHO$, the yield reaching 90% when R is *n*-alkyl. The following are described: sec.-*octyloxy-diethylacetal*, b.p. 131—132°/14 mm., *-acetaldehyde*, b.p. 98—99·5°/15 mm. (*semicarbazone*, m.p. 78·5—79·5°), n-*decyloxy-diethylacetal*, b.p. 159—160°/14 mm., *-acetaldehyde*, b.p. 133—135°/15 mm., m.p. 19·5—20° (*semicarbazone*, m.p. 103—104°), *n*-dodecyloxy-diethylacetal, b.p. 150—151°/3 mm., *-acetaldehyde*, m.p. 18°, b.p. 118—119°/3 mm. (*semicarbazone*, m.p. 108°), n-*tetradecyloxy-diethylacetal*, m.p. 25°, b.p. 161—162°/2 mm., *-acetaldehyde*, m.p. 36°, b.p. 138—140°/4 mm. (*semicarbazone*, m.p. 97°), n-*hexadecyloxy-diethylacetal*, m.p. 37°, b.p. 192—194°/1 mm., and *-acetaldehyde*, m.p. 47° (*semicarbazone*, m.p. 102°). A. C.

Condensation of aldehydes with ketones and some of the products derived from the ketols. L. P. Kyrides (J. Amer. Chem. Soc., 1933, **55**, 3431—3435).—Gradual addition of a MeCHO–COMeEt (1 : 2) mixture to COMeEt at 8—9° in presence of a little NaOH gives a little crotonaldehyde and an 85% yield of γ-methylpentan-δ-ol-β-one, b.p. 95—96°/35 mm., dehydrated by distillation with a little HBr to γ-methyl-Δ$^{\gamma}$-penten-β-one, b.p. 139·5—141°, and reduced electrolytically in presence of $NaHCO_3$ to γ-methylpentane-βδ-diol (66% yield), whence by HBr a 64% yield of γ-methyl-Δ$^{\alpha\gamma}$-pentadiene, b.p. 75—80°, was obtained. PrCHO and COMeEt give similarly γ-methylheptan-δ-ol-β-one (78%), b.p. 105—120°/30 mm., dehydrated by distillation in partial vac. to γ-methyl-Δ$^{\gamma}$-hepten-β-one (95%), b.p. 174—176°. R. S. C.

Acyloins. V. Photochemical formation of acetoin, butyroin, and acetylphenylcarbinol. W. Dirscherl (Z. physiol. Chem., 1933, **219**, 177—190; cf. A., 1931, 1457).—The yield of acetoin formed by ultra-violet light from $AcCO_2H$ (I) in H_2O decreases from 100% at 0·2—3*M* to 12% at 11·4*M* [pure (I)]. In presence of PhCHO the formation of CHAcPh·OH was detected. PhCHO, C_6H_6, salts, and other dehydrating agents hinder acyloin formation. Irradiation of α-ketovaleric acid (0·5—2*M*) gives butyroin in 30—40% yield. In all cases where the acyloin yield is not quant. aldehyde is not detected in the products. J. H. B.

Removal of sugars from dilute solutions. J. L. Baker and H. F. E. Hulton (Biochem. J., 1933, **27**, 1040—1043).—Glucose (I) or maltose (II) in 0·2% aq. solution is completely fermented in 30 min. by 100 times its wt. of pressed brewer's yeast. Under similar conditions sucrose (III) and invert sugar are fermented to a slightly smaller degree, whilst galactose, lactose, and arabinose are unaffected. The rate of removal of up to 50% of (I), (II), or (III) from 0·2% aq. solution is dependent on the time of fermentation and on the relative amount of yeast present. The rate of CO_2 evolution indicates that such rapid disappearance of sugar is due to fermentation and not to adsorption (cf. A., 1928, 912). The presence of PhMe or 12% EtOH only partly inhibits fermentation. F. O. H.

Influence of hydrogen peroxide on determination of glucose by Bertrand's method. A. Malkov (J. Appl. Chem. Russ., 1933, **6**, 567).—H_2O_2 alone or together with Fe$^{\cdot\cdot}$ does not interfere with determination of glucose by Bertrand's method. R. T.

Biological reagents in sugar analysis. V. J. Harding and T. F. Nicholson (Biochem. J., 1933, **27**, 1082—1094).—A strain of *Proteus vulgaris* (I) has been found which removes glucose (II) from solution but leaves fructose (III), mannose (IV), and sucrose (V) intact; it may be employed in the determination of (II) in presence of (III), (IV), and (V). Mixtures of (II), (III), and (V) may be analysed by the removal of (II) by (I) and subsequent treatment with *Monilia krusei* (VI), which removes (III) but leaves (V). The presence of (IV) and maltose (VII) leads to erroneous results. (VII) may be removed by treatment with *M. penoyi* (VIII) previous to hydrolysis of (V). Application of (I) shows the presence of (II) in normal fasting urine. The method applied to the Folin–Wu blood filtrates gives results of the expected val. (I), (VI), *S. marxianus*, and *M. macedoninensis* do not act on (VII), whilst (VIII) and *M. tropicalis* remove (VII) completely. The removal of (VII) by brewer's or baker's yeast is somewhat variable. (VI) has no action on galactose (IX) and is therefore of use in the determination of this sugar in presence of (II), (III), and (IV). A scheme is given for the analysis of mixtures of (II), (III) or (IV), (IX), (V), (VII), and lactose. W. O. K.

Walden inversion in the glucose series. Derivatives of altrose. D. S. Mathers and G. J. Robertson (J.C.S., 1933, 1076—1081).—4 : 6-Benzylidene-α-methylglucoside 2 : 3-dibenzoate is hydrolysed (0·25% HCl in $COMe_2$) to *α-methylglucoside 2 : 3-dibenzoate*, $[\alpha]_D$ +154·4° in EtOH, which is methylated (MeI, Ag_2O) to an impure 4 : 6-Me_2 derivative. This is hydrolysed (aq. EtOH–KOH) to a product, b.p. 155° (bath)/0·03 mm., $[\alpha]_D$ +165·7° in $CHCl_3$, containing ⩽ 54% of 4 : 6-dimethyl-α-methylglucoside (isolated as the 2 : 3-di-*p*-toluenesulphonate); the remainder of the product probably consists of isomerides formed by the catalytic rearrangement of Bz groups during the methylation. *4 : 6-Benzylidene-α-methylglucoside 2 : 3-di-p-nitrobenzoate*, m.p. 169—170°, $[\alpha]_D$ +127·7°

in $CHCl_3$, is hydrolysed (as above) to *α-methylglucoside* 2 : 3-*di*-p-*nitrobenzoate*, m.p. 143—155°; methylation of this is complicated also. *α-Methylglucoside* 2 : 3-*di*-p-*toluenesulphonate*, $[\alpha]_D$ +58·5° in $CHCl_3$, prepared by hydrolysis of its 4 : 6-benzylidene derivative, is methylated (MeI, Ag_2O) to 4 : 6-*dimethyl-α-methylglucoside* 2 : 3-*di*-p-*toluenesulphonate* (I), m.p. 116—117°, $[\alpha]_D$ +54·7° in $CHCl_3$, which is hydrolysed (aq. EtOH–KOH) to 66% of a *dimethylanhydromethylhexoside* (II), m.p. 63—64°, $[\alpha]_D$ +188·9° in $CHCl_3$, and 26% of a syrup (III), b.p. 150—155° (bath)/0·8 mm., $[\alpha]_D$ +138·9° in H_2O. *p*-Toluenesulphonylation of (III) does not regenerate (I) but gives (probably) 4 : 6-*dimethyl-α-methylaltroside* 2 : 3-*di*-p-*toluenesulphonate*, m.p. 132—134°, $[\alpha]_D$ +103·3° in $CHCl_3$; methylation (MeI, Ag_2O) of (III) and subsequent hydrolysis of the glucosidic Me group affords (probably) 2 : 3 : 4 : 6-*tetramethylaltrose*, m.p. 76—78°, $[\alpha]_D$ +97·4° in EtOH. It is suggested that hydrolysis of (I) is accompanied by complete inversion of H and OH on C_2 (or C_3), simultaneously with a partial inversion on C_3 (or C_2), giving a mixture of mannose (or allose) and altrose derivatives; the former is then dehydrated. (II) is 4 : 6-*dimethyl*-2 : 3-*anhydro-α-methyl-mannoside* or *-alloside*. H. B.

Acetylation of galactoseoxime. V. Deulofeu, M. L. Wolfrom, P. Cattaneo, C. C. Christman, and L. W. Georges (J. Amer. Chem. Soc., 1933, **55**, 3488—3493).—The substance (A., 1932, 1237) called α-galactoseoxime hexa-acetate is a mixture. Galactoseoxime (I), C_5H_5N, and Ac_2O at 23—25° give *al*-galactoseoxime hexa-acetate (II), $[\alpha]_D$ +23·6° in $CHCl_3$, an *isomeride* (III), m.p. 106°, $[\alpha]_D^{25}$ −27·5° in $CHCl_3$, and galactonitrile penta-acetate (IV). Chiefly (IV) is obtained by acetylation at 100°. (I) with NaOAc and boiling Ac_2O forms (III) and (IV). (II), when melted or heated with NaOAc and Ac_2O, gives AcOH and (IV). (III) does not give (IV) when melted. *al-l*-Arabinoseoxime tetra-acetate gives the *oxime*, m.p. 137—139°, $[\alpha]_D^{20}$ −5·2° in $CHCl_3$, which with Ac_2O and C_5H_5N at 0° gives *l*-arabononitrile tetra-acetate. R. S. C.

Alleged production of polysaccharides in alkaline solutions of hexoses. H. A. Spoehr and H. H. Strain (Biochem. Z., 1933, **264**, 1—5).—Since aq. solutions of *d*-glucose, *d*-fructose, and *d*-galactose yield no polysaccharides after 2 months' contact with Na_2CO_3 or Ca, Pb, or uranyl acetate at 15·5—38·0° in the dark, Nef's conclusions (A., 1914, i, 490) must be rejected. W. McC.

Trianhydroperiplogenin. W. A. Jacobs and N. M. Bigelow (J. Biol. Chem., 1933, **101**, 697—700).—Periplogenin when heated with MeOH–HCl gives *trianhydroperiplogenin*, $C_{23}H_{28}O_2$, m.p. 191—193°, $[\alpha]^{24}$ −130° in C_5H_5N, reduced in AcOH (Pt–H_2) to the H_8-derivative, m.p. 176—177°, $[\alpha]_D$ +16·4° in $CHCl_3$. F. R. S.

Starch. Cinnamoyl esters. W. S. Reich and A. F. Damansky (Compt. rend., 1933, **197**, 275—277).—In anhyd. solvents natural starch (I) or amylopectin gives a *dicinnamoyl* ester, whereas amylose (II) gives a *tricinnamoyl* ester, $[\alpha]_D$ −187° in $CHCl_3$. Both esters give the original material when hydrolysed. In H_2O at 90° (II) gradually gives (I), as judged by the composition of the cinnamoylation products. R. S. C.

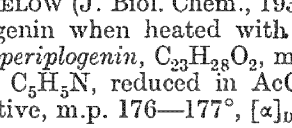
Additive compounds of cellulose. G. Champetier (Ann. Chim., 1933, [x], **20**, 5—96).—Cellulose immersed in aq. solutions yields the compounds $2C_6H_{10}O_5$,NaOH, $C_6H_{10}O_5$,NaOH, $3C_6H_{10}O_5$,2NaOH, $4C_6H_{10}O_5$,3NaOH, $3C_6H_{10}O_5$,H_3PO_4. No compounds are formed with AcOH or HCO_2H and in solutions of $Na_2S_2O_3$ and of C_5H_5N the hydrates $2C_6H_{10}O_5$,H_2O and $C_6H_{10}O_5$,H_2O are formed. The indications of *X*-ray diagrams require confirmation by experimental methods, and compounds with H_2O and with H_3PO_4 can be formed without change in the cellulose lattice. Cotton cellulose forms hydrates much more rapidly than does dried animal cellulose. A. G.

Nitration of cellulose. A. Bouchonnet, (Mme.) Trombe, and (Mlle.) Petitpas (Compt. rend., 1933, **197**, 332—334).—The solubilities of KNO_3, $NaNO_3$, and NH_4NO_3 in 97% HNO_3 are 50, 10, and 55%, respectively. These salts and 99·9% HNO_3 give pliable cellulose nitrates containing up to 13·87% N. R. S. C.

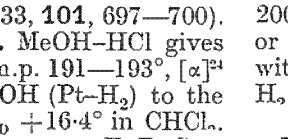
Nitration of cellulose fibres. I. Sakurada and M. Shōjino (J. Soc. Chem. Ind., Japan, 1933, **36**, 306B).—The views expressed previously (this vol., 788) fit the nitration of cellulose. A. G.

Introduction of amino-groups into cotton cellulose. E. Riesz (Bull. Soc. Ind. Mulhouse, 1933, **99**, 349—356).—Anilinetrisulphonyl chloride combines with cotton cellulose (1 mol. to about 24 $C_6H_{10}O_5$). The compound can be diazotised and coupled, but has no affinity for acid dyes. A. G.

Pentenylamine. H. Cottin (Compt. rend., 1933, **197**, 254—256).—Δ^γ-Pentenoic acid, NH_3, and SiO_2 at 500° give pentenonitrile, b.p. 142—143°/749 mm., 60—61°/40 mm. (also obtained from cyanopentenoic acid), reduced (Na–EtOH) to Δ^δ-pentenylamine, b.p. 105—106° (*hydrate*, b.p. 93°; *chloroplatinate*, decomp.; p-$C_6H_4Me{\cdot}SO_2$ derivative, an oil) (cf. lit.). Allyl halides and Et sodiocyanoacetate give Et diallylcyanoacetate (70% yield), b.p. 85°/25 mm., reduced to β-allyl-Δ^δ-pentenylamine, b.p. 57—58°/14 mm., which with HBr gives ε-bromo-β-(γ-bromopropyl)-amylamine, whence KOH forms a mixture of



2-methyl-4-allylpyrrolidine and



R. S. C.

Complexes of ethylenediamine with ferrous halides. R. E. Breuil (Compt. rend., 1933, **196**, 2009—2010).—The *compounds* $Fe\,en_3X_2$ (X=Cl, Br, or I) are obtained when the ferrous halide is treated with $(\cdot CH_2{\cdot}NH_2)_2$ (I) in anhyd. MeOH in a stream of H_2. They lose (I) when heated or exposed to air. A. C.

Red coloration of glycine with ferric chloride. J. V. Dubsky, M. Vitu, and A. Langer (Metallbörse, 1932, **22**, 1533—1534; Chem. Zentr., 1933, i, 1280).—The following *compounds* have been prepared (X= glycine): $FeCl_3$,$FeCl_2OH$,2X,3H_2O, decomp. 110°;
$FeBr_3$,$FeBr_2OH$,X,H_2O, decomp. 183°;
$FeCl_3$,$FeCl_2OH$,3X,2H_2O, decomp. 175°;
$FeBr_3$,$FeBr_2OH$,3X,H_2O, decomp. 181°;

$FeCl_3$,$FeCl_2OH$,4X,4H_2O, decomp. 123°;
$FeBr_3$,$FeBr_2OH$,4X,4H_2O, decomp. 112°;
$Fe(NO_3)_2OH$,2X,2H_2O, decomp. 183°. Similar compounds can be obtained with sarcosine and alanine. A. A. E.

Effect of p_H on the precipitation of arginine and histidine as the silver salts. J. Bussit (Bull. Soc. Chim. biol., 1933, **15**, 840—844).—A study of the influence of p_H on the pptn. of the Ag salts of arginine and histidine from their aq. solutions with aq. $Ba(OH)_2$ indicates that a complete separation by this method is impossible. A. L.

Preparation of ethyl *l*(+)-glutamate, *l*(−)-*iso*-glutamine, and ethyl *l*(−)-*N*-carbobenzyloxy-glutamate. E. Abderhalden and H. Nienburg (Z. physiol. Chem., 1933, **219**, 155—157).—Treatment of Et *l*(+)-glutamate, $CO_2H{\cdot}[CH_2]_2{\cdot}CH(NH_2){\cdot}CO_2Et$ (I), m.p. 194°, $[\alpha]_D$ +14·60° in H_2O, with 25% aq. NH_3 affords l(−)-iso*glutamine*, m.p. 160°, $[\alpha]_D$ −25·50° in H_2O (cf. Bergmann and Zervas, A., 1932, 935). The *carbobenzyloxy*-derivative of (I), m.p. 88—89°, $[\alpha]_D$ −9·31° in EtOH, is described. J. H. B.

Complex of cobalt and cysteine, and its behaviour with hydrogen peroxide. M. P. Schubert (J. Amer. Chem. Soc., 1933, **55**, 3336—3342).—Cysteine hydrochloride (I), $CoCl_3$, and KOH in complete absence of air give *K*, *cobaltodicysteinate*, $K_2(CoR_2)$,2H_2O [R=·S·CH_2·CH(NH_2)·CO_2], the reddish-violet colour of which with H_2O_2 fades but does not change to yellow (cf. A., 1931, 1403). More (I) and KOH lead to K_4 *cobaltotricysteinate*, $K_4(CoR_3)$,4H_2O, violet (corresponding *Ba*$_2$ salt, +4H_2O), which with air gives K_3 *cobaltitricysteinate* (II), $K_3(CoR_3)$,3H_2O, green (corresponding *Ba* salt, +7H_2O). (II) is very stable, but with H_2O_2 (not other oxidising agents) gives a yellow solution, from which K_3 *cobaltitri-*(α-*amino*-β-*sulphinopropionate*) (III), $K_3(CoR'_3)_3$,3H_2O [R'=·SO_2·CH_2·CH(NH_2)·CO_2] (corresponding *Ba* salt, +6H_2O, and *acid*, anhyd.), is obtained. With [·CH_2·NH_2]$_2$ at 40° (III) rapidly gives the *complex*, (Co en$_3$)(CoR'_3),7H_2O, and α-*amino*-β-*sulphinopropionic acid* (IV), $SO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$,+$H_2O$ (*Ba* salt, +H_2O). (IV) reduces $KMnO_4$ (2·2 O) to form the sulphonic acid (not isolated) and with $CoCl_3$,6NH_3 (V) gives the *complex*, $[Co(NH_3)_6]CoR'_3$,4H_2O, also obtained from (III) and (V). R. S. C.

Sources of error in the determination of cysteine and cystine in complex materials, using acid hydrolysis. J. W. H. Lugg (Biochem. J., 1933, **27**, 1022—1029).—When heated at 100° for 20 hr. in 5*N*-HCl alone or with $CO(NH_2)_2$ and stable NH_2-acids, cystine (I) is fairly stable, whilst approx. 1% decomp. occurs with cysteine (II). At 100° (I) is reduced to (II) by $SnCl_2$ in acid solution. In acid hydrolysates and in presence of carbohydrates and humin, considerable amounts of (I) and, more especially, of (II) are lost. Addition of $SnCl_2$ during hydrolysis not only fails to prevent loss of (II), but causes loss of (I) by reduction to (II). The presence of $Fe^{...}$ and other heavy-metal salts also results in low vals. for (I) and (II). F. O. H.

Interaction of halogenoacetates and thiol compounds. Reaction of halogenoacetic acids with glutathione and cysteine. Mechanism of iodoacetate poisoning of glyoxalase. F. Dickens (Biochem. J., 1933, **27**, 1141—1151).—Largely a more detailed account of work previously reviewed (this vol., 314). The reaction between glutathione (I) and $CH_2I{\cdot}CO_2Na$ (II) in dil. neutral solution is bimol.; a *thio-ether*, $C_{12}H_{19}O_8N_3S$,H_2O, is isolable. The respective velocity coeffs. for (I) and $CH_2Hal{\cdot}CO_2Na$ at 38° are of the relative order, I : Br : Cl=15 : 9 : 0·15. A similar reaction occurs with cysteine and (II); α-*amino*-β-(*carboxymethylthiol*)*propionic acid*, m.p. 84° (decomp.), is isolated. (II) inactivates the co-enzyme of glyoxalase; the enzyme is undamaged. H. B.

Aldehyde–imide condensation. I. Reactions between aldehydes and acetamide. W. A. Noyes and D. B. Forman (J. Amer. Chem. Soc., 1933, **55**, 3493—3494).—NH_2Ac, MeCHO, and a little AcOH under reflux give ethylidenediacetamide, CHMe($NHAc)_2$, m.p. 180° (lit. 169°). *Butylidene-*, m.p. 189°, iso*valerylidene-*, m.p. 184°, and *heptylidenediacetamide*, m.p. 171—172°, are described *inter al.* The compounds with mineral acids give NH_4, aldehyde, and AcOH. R. S. C.

Catalytic preparation of nitriles with Japanese acid clay. J. Abe (Bull. Waseda Appl. Chem. Soc., 1933, **19**, 8—14).—$EtCO_2H$ and NH_3 passed over Japanese acid clay, SiO_2 gel, or Al_2O_3 at 400° afforded PrCN in 95·5, 80·16, or 85·9% yield, respectively. Ch. Abs.

Brominated aliphatic nitriles and ketones. P. Trunel (Compt. rend., 1933, **197**, 453—456).—ε-Bromohexonitrile, b.p. 120—130°/11 mm., and MgMeI give η-*bromoheptan*-β-*one* (*semicarbazone*, m.p. 136°). Bromination of undecoic acid yields the κ-*Br*-derivative, m.p. 51°, converted successively into the acid *chloride*, *amide*, m.p. 88°, and *nitrile*, b.p. 184°/17 mm., which with MgMeBr forms μ-*bromododecan*-β-*one*, m.p. 22°, b.p. 153—154°/5 mm. (*semicarbazone*, m.p. 118°). λ-*Ketododecylphthalimide*, m.p. 69° (*semicarbazone*, m.p. 146°), yields μ-*aminododecan*-β-*one*, m.p. 93°. Undecenoic acid and HBr give ι-*bromoundecoic acid*, which is converted successively into the acid *chloride*, *amide*, m.p. 93·5°, and *nitrile*, b.p. 174°/15 mm. F. R. S.

Formation of methyl radicals in the decomposition of azomethane. J. A. Leermakers (J. Amer. Chem. Soc., 1933, **55**, 3499—3500).—Decomp. of NMe:NMe in H_2O vapour at 475° gives Me radicals, which remove a Pb mirror 10 cm. from the furnace. R. S. C.

Tertiary phosphines containing *sec.*-alkyl radicals. W. C. Davies (J.C.S., 1933, 1043—1044).—*Tri*iso*propylphosphine*, b.p. 81°/22 mm. (1 : 1-*compound*, m.p. 111°, with CS_2), and *tris*ec.-*butylphosphine*, b.p. 108°/11 mm. (1 : 1-*compound*, m.p. 66°, with CS_2), are prepared from PCl_3 and MgRBr. A large excess of Mg and *sec.*-bromide must be used, since the yield of MgRBr is low and a reaction can occur between PR_3 and, *e.g.*, PCl_3. p-*Phenoxyphenyldi*iso*propylphosphine*, b.p. 209°/13 mm. (*methiodide*, m.p. 203—204°; 1 : 1-*compound*, m.p. 46°, with CS_2), is similarly prepared from *p*-OPh·C_6H_4·PCl_2 and $MgPr^{\beta}Br$. *Methyltri*iso*propyl-* and *methyltri*sec.-*butyl-phosphonium iod-*

ides have m.p. $>360°$ and 149°, respectively. All b.p. and m.p. are corr. H. B.

Influence of poles and polar linkings on the course pursued by elimination reactions. XIX. Thermal decomposition of phosphonium chlorides. G. W. FENTON, L. HEY, and C. K. INGOLD. **XX. Elimination of saturated primary alcohols by thermal decomposition of sulphonium hydroxides.** C. K. INGOLD and K. I. KURIYAN (J.C.S., 1933, 989—991, 991—993).—XIX. Contrary to Collie *et al.* (cf. *ibid.*, 1888, **53**, 636, 714), thermal decomp. of PR_4Cl gives RCl and PR_3, which is in accordance with the theoretical considerations previously developed (A., 1929, 1431). Thus, PEt_4Cl gives EtCl and PEt_3; PMe_4Cl affords MeCl and PMe_3; PMe_3EtCl yields MeCl and PMe_2Et; benzyltriethylphosphonium chloride furnishes CH_2PhCl and PEt_3.

XX (cf. this vol., 701). $SR_3{\cdot}OH$ containing Me and Et (or Pr^α) groups undergo decomp. in all three possible directions [formation of MeOH, EtOH (or $Pr^\alpha OH$), and olefine]. The total alcohols (mols.-%) found are: Me_3, 100; Me_2Et, 73; $MeEt_2$, 45; Et_3, 14; Me_2Pr^α, 92; $MePr^\alpha_2$, 82; Pr^α_3, 64. $SR_3{\cdot}OH$ containing combinations of the groups Et and Pr^α, Pr^α and Bu^α, and Et and Bu^β give both alcohols and olefines; the proportions of the lower homologue in the olefine mixtures are determined and show the absence of any considerable mutual influence between the different alkyl groups. The following are described: *triethyl-*, m.p. 152—153°, *tri-n-propyl-*, m.p. 75—76°, *methyldiethyl-*, m.p. about 170°, *methyldi-n-propyl-*, m.p. 68°, *diethyl-n-propyl-*, m.p. 72—73°, *ethyldi-n-propyl-*, m.p. 73·5—74°, di-n-*propyl*-n-*butyl-*, m.p. 73°, n-*propyldi*-n-*butyl-*, m.p. 67—68°, and *ethyldiisobutyl-*, m.p. 75—76°, *-sulphonium picrates.* H. B.

Thermal decomposition of mercury dibutyl. F. E. FREY and H. J. HEPP (J. Amer. Chem. Soc., 1933, **55**, 3357—3361).—Quant. analysis of the decomp. products of $HgBu^\alpha_2$ in Pyrex at 350—450°/3 mm. proves formation of Bu^α radicals, which give mostly C_2H_4 and Et radicals and only a little C_8H_{10}; the free radicals then form C_2H_6, C_4H_{10}, and C_6H_{14}. $HgBu^\beta_2$ similarly gives $Bu^\beta{\cdot}$, which also ruptures only at one point to give C_3H_6 and Me·; the products are thus CH_4, $CHEtMe_2$, C_2H_6, C_3H_8, C_4H_{10}, and much C_8H_{18}. R. S. C.

Stereochemistry of platinum. H. D. K. DREW and F. S. H. HEAD (Nature, 1933, **132**, 210).—*iso*Butylenediamine and the mixed β-*diammine*, $Pt(NH_3)(NH_2Et)Cl$, give a mixture of two isomeric β-plato-tetrammines, $[Pt(NH_3)(NH_2Et)(NH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2)]Cl_2$, which are both of β-structure, and do not become interchanged; they give rise to different plato-salts. A similar pair of isomeric β-plato-tetrammines, $[Pt(NH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2)_2]Cl_2$, have been obtained in admixture and give rise to a mixture of two different plato-salts which are separable. The pairs of isomerides appear to represent *cis-* and *trans*-forms in each case, giving the first chemical evidence of planar structure among the plato-tetrammines. L. S. T.

Molecular structure of co-ordination compounds of platinum and palladium. E. G. Cox and G. H. PRESTON (J.C.S., 1933, 1089—1093; cf. A., 1932, 797; this vol., 41).—*X*-Ray examination of bisethylenediaminoplatinous chloride $[Pt\,en_2]Cl_2$, bisethylenediaminopalladous chloride, tetramminopalladous chloride $[Pd(NH_3)_4]Cl_2,H_2O$, and α- and β-diamminoplatinic tetrachlorides $[Pt(NH_3)_2Cl_4]$, and re-examination of tetramminoplatinous chloride and NH_4 chloropalladite (I) give further evidence of the planar distribution of Pt" and Pd" valencies. It is also concluded from the results that the valencies of the metal atom are not all crystallographically equiv., but are differentiated into pairs. Only those valencies which are *trans* to each other are equiv.; this applies to all the above compounds except (I), *i.e.*, to those compounds in which the metal atom is the centre of a positive or neutral complex. This supports the suggestion of paired valencies made by Drew *et al.* (A., 1932, 562) and also affords a physical basis for Werner's hypothesis of *trans*-elimination. H. B.

Complex compounds of iridium. II. Compounds of organic sulphides and pyridine. P. C. RAY, N. ADHIKARI, and R. GHOSH (J. Indian Chem. Soc., 1933, **10**, 275—279).—$IrCl_4$ and Et_2S in cold EtOH give (after 12 days) a brownish-red *compound*, $IrCl_3,3Et_2S$ (I), m.p. 171°, in addition to the orange isomeride (II), m.p. 131° (A., 1932, 1017); (I) and (II) are probably the *trans-* and *cis*-compounds, respectively. (II) and C_5H_5N in boiling C_6H_6 afford the *compound*, $IrCl_3,C_5H_5N,2Et_2S$, m.p. 171—172°, whilst (II) and C_5H_5N at 120—150° give the *compound*, $IrCl_3,2C_5H_5N,Et_2S$, m.p. 260°. NH_4 chloroiridate and aq. EtOH–Et_2S yield some (II) and the compound, $Ir_2Cl_5,4Et_2S$, m.p. 222° (decomp.) (lit. 207°). The *compound*, $IrCl_3,3S(CH_2Ph)_2$, m.p. 201°, is described. H. B.

Preparation of mono- and di-alkyl*cyclo*hexanes. F. K. SIGNAIGO and P. L. CRAMER (J. Amer. Chem. Soc., 1933, **55**, 3326—3332).—*cyclo*Hexanone or its Me derivatives yield by the Grignard reagent 1-n-*butyl-* (I), b.p. 88—91°/7 mm., 1-n-*amyl-* (II), b.p. 96—96·5°/5 mm., 2-*methyl*-1-n-*butyl-* (III), b.p. 76—80°/2 mm., 2-*methyl*-1-n-*amyl-* (IV), b.p. 89—90°/1·5 mm., 3-*methyl*-1-n-*butyl-* (V), b.p. 85—86°/2 mm., and 4-*methyl*-1-n-*butyl-* (VI), b.p. 74—76°/2 mm., -cyclo*hexanol*, together with some *cyclo*hexanol formed by simple reduction of the parent ketone. Thence distillation with $Al_2(SO_4)_3$ or (in the last four cases) I in EtOH at 100° affords the corresponding substituted cyclo*hexenes*, (I) b.p. 180·8—182·9°, (II) b.p. 203·4—205°, (III) b.p. 197·8—199·1°, (IV) b.p. 218·9—219·7°, (V) b.p. 195·2—195·7°, (VI) b.p. 196·3—197·1°. By hydrogenation (PtO_2; 45 lb.) in AcOH of these or similar *cyclo*hexenes were prepared 1-*methyl*-2-n-*propyl-*, b.p. 175·2—177°, -2-n-*amyl-*, b.p. 215·8—219·1°, -3-n-*butyl-*, b.p. 194·8—195·2°, -4-n-*propyl-*, b.p. 174·3—177·1°, and -4-n-*butyl-*, b.p. 195·9—196·6°, -cyclo*hexane*. The physical consts. of these and 57 other compounds of these series (similarly prepared) are recorded. R. S. C.

Constitution of α-carotene. P. KARRER, R. MORF, and O. WALKER (Nature, 1933, **132**, 171).—Ozonisation of α-carotene gives geronic and *iso*geronic acids and proves the correctness of the proposed formula (this vol., 733). L. S. T.

Nitration of *o*-dichlorobenzene. J. R. Ruhoff (J. Amer. Chem. Soc., 1933, **55**, 3470—3471).—Much 3 : 4- and a little 2 : 3-dichloronitrobenzene are formed. R. S. C.

Determination of aromatic nitro- and nitroso-compounds. S. Ueno and H. Sekiguchi (J. Soc. Chem. Ind. Japan, 1933, **36**, 410—412B).—NO_2- and NO-compounds containing SO_3H, CO_2H, or OH (as alkali salt if necessary) are reduced with Zn and cold HCl, and the amine is titrated with $NaNO_2$ (cf. A., 1920, ii, 331). Addition of KBr assists the titration. Other compounds are previously sulphonated, a method not applicable to *p*-$C_6H_4Cl{\cdot}NO_2$, *o*-$NO_2{\cdot}C_6H_4{\cdot}OH$, and *p*-$NO_2{\cdot}C_6H_4{\cdot}OMe$. A. A. L.

Mercury as sulphonation catalyst. K. Lauer (J. pr. Chem., 1933, [ii], **138**, 81—91).—As in the case of anthraquinone, Hg acts as a directive catalyst in the sulphonation of C_6H_6 derivatives. The mechanism involves formation of an organo-Hg compound and replacement of the Hg by SO_3H. The action may be obscured, however, by the poor solubility of $HgSO_4$ in H_2SO_4, the slow formation of the organo-Hg compounds, and their ready hydrolysis. Thus marked *op*-sulphonation occurs with $PhNO_2$, BzOH, and $PhSO_3H$, and 10—20% oleum previously saturated with $HgSO_4$, whereas in absence of Hg substitution is almost exclusively *m*-. That sulphonation occurs by replacement of Hg by SO_3H is shown by the fact that *o*- and *p*-mercuriphenols and the *m*-mercuri-derivatives of $PhNO_2$ and BzOH give the direct replacement products almost exclusively with 3—20% oleum (according to the example chosen), but mainly the normal sulphonation product of the Hg-free compound with 92% H_2SO_4. *o*-Xylene, *o*-$C_6H_4Cl_2$, *o*-$C_6H_4Br_2$, and phthalic anhydride, which with oleum alone give the 4-SO_3H, in presence of Hg give the 3-SO_3H in addition, but in the case of the last-named the 3 : 5-$(SO_3H)_2$ is formed by further sulphonation. 4-Sulphophthalic anhydride cannot be further sulphonated, and the use of stringent conditions results in destructive oxidation. *o-Xylene-3-sulphonic acid* [*Na* salt ($+1H_2O$); *chloride*, m.p. 46°; *amide*, m.p. 165°], 1 : 2-*dichlorobenzene-3-sulphonic acid* [*Na* salt ($+2H_2O$)], and 1 : 2-*dibromobenzene-3-sulphonic acid* [*Na* salt ($+1H_2O$); *chloride*, m.p. 31—32°; *amide*, m.p. 165°] appear to be new. H. A. P.

Catalytic oxidation of organic compounds in the vapour state. I. Toluene, its derivatives and homologues. II. Various compounds. G. Charlot.—See this vol., 1019.

Coupling action of the Grignard reagent. V. Influence of the halogen atom of the reagent. E. Ellingboe and R. C. Fuson (J. Amer. Chem Soc., 1933, **55**, 2960—2966).—CHPhCl, and MgMeCl in Et_2O give cumene (a little), *βγ-diphenylbutane* (I), two forms, m.p. 124—125° (also obtained from CHPhMeBr and Na or Mg in Et_2O), and an oil, b.p. 150—151°/20 mm., respectively, and *α-chloro-αγ-diphenylpropane* (II). (I) and (II) form solid solutions, separable by change of (II) by KOH–EtOH into *α-methylstilbene*, m.p. 48°. This with O_3 gives BzOH and COPhMe, and with a drop of HBr in AcOH gives an *isomeride*, m.p. 82—83°. *p*-$C_6H_4Cl{\cdot}CHCl_2$ and MgMeCl in Et_2O give *α-chloro-αβ-di-p-chlorophenylpropane*, m.p. 167°, *βγ-di-p-chlorophenylbutane*, m.p. 147—148°, *αδ-di-p-chlorophenyl-Δ$^{\alpha}$-propene*, m.p. 80°, and *p-chlorocumene*, b.p. 79—81°/15 mm., also prepared by hydrogenation of *β-p-chlorophenylpropene*, b.p. 89°/14 mm. (obtained from *p*-chloroacetophenone and MgMeI). Attention is directed to the marked difference in behaviour of benzylidene chlorides towards MgMeCl and MgMeI, respectively (cf. this vol., 385). R. S. C.

Conjugated systems. XIII. Preparation and properties of α-bromo-δ-phenylbutadiene. I. E. Muskat and L. B. Grimsley (J. Amer. Chem. Soc. 1933, **55**, 2860—2867; cf. A., 1929, 1170).—*cis-α-*Phenylbutadiene (I) reacts with Br more rapidly than the *trans*-form, giving, in both cases, only one γδ-dibromo-α-phenylbutene (II). This with more Br gives αβγδ-tetrabromo-α-phenylbutane, with Ag_2O affords (I), and with NH_2Ph (2 mols.) in C_6H_6 *δ-bromo-γ-anilino-α-phenyl-Δ$^{\alpha}$-butene*, m.p. 110° (*hydrobromide*, m.p. 124°; excess of Br in $CHCl_3$ affords *αβδ-tribromo-γ-tribromoanilino-α-phenylbutane hydrobromide*, m.p. 215°), with NH_2Ph (4 mols.) *γδ-dianilino-α-phenyl-Δ$^{\alpha}$-butene* (*dihydrochloride*, m.p. 113°), with NH_3–EtOH *γδ-diamino-α-phenyl-Δ$^{\alpha}$-butene* (*dihydrochloride*, m.p. 124°), and with KOH (1 mol.) in Et_2O–EtOH *δ-bromo-α-phenylbutadiene* (III), two forms, m.p. 52°, and an oil (formed also from the former, when kept) (giving a *dimeride*, m.p. 138°, when distilled at 137°/6 mm.), presumably *cis–trans* isomerides, isomerism being probably at the γδ-linking, since both forms give (II) with HBr. (III) liberates I from aq. KI, and with Br gives *γδδ-tribromo-α-phenyl-Δ$^{\alpha}$-butene*, m.p. 140—140·5°, which with O_3 affords BzOH. R. S. C.

Stereochemistry of the free triarylmethyl radical. Total asymmetric synthesis. G. Karagunis and G. Drikos (Naturwiss., 1933, **21**, 607).—By irradiating phenyl-*p*-tolyl-*p*-ethylphenylmethyl with circularly polarised light (4300 Å.) in presence of Cl_2 at 0°, an activity of 0·1° has been obtained and with phenyldiphenylyl-α-naphthylmethyl 0·2° has been measured. These results indicate that the three C valencies are not in one plane. F. R. S.

Photochemical production of triphenylmethyl. J. O. Halford and L. C. Anderson (Proc. Nat. Acad. Sci., 1933, **19**, 759—762).—CPh_3Br in *cyclo*hexane irradiated with sunlight is converted into a peroxide and unidentified products. The absorption spectrum suggests that CPh_3 is formed as an intermediary. E. S. H.

Addition of free radicals to dienes, pyrrole, and maleic anhydride. J. B. Conant and B. F. Chow (J. Amer. Chem. Soc., 1933, **55**, 3475—3479).—Diphenyldixanthyl and isoprene, best at 100°, give *αδ-di(phenylxanthyl)-β-methyl-Δ$^{\beta}$-butene*, m.p. 249—250°. Dibenzyldixanthyl gives similarly *αδ-di(benzylxanthyl)-β-methyl-Δ$^{\beta}$-butene*, m.p. 224°. CPh_3 (I) with butadiene in C_6H_6–PhMe at room temp. gives *ααζζζ-hexaphenyl-Δ$^{\gamma}$-hexene* (II), m.p. 224° (oxidised by O_3–Ag_2O to βββ-triphenylpropionic acid), and with piperylene in C_6H_6 *ααζζζ-hexaphenyl-β-methyl-Δ$^{\gamma}$-hexene*, m.p. 174°. (I) and pyrrole in C_6H_6 at room temp. give 2 : 5-*di(triphenylmethyl)-Δ^{3}-pyrroline*, m.p.

250° (decomp.), the *Bz* derivative, m.p. 265—266°, of which with PBr_5 in C_6H_6 gives PhCN and *βγδε-tetrabromo-ααα'ζζ'ζ'-hexaphenylhexane*, m.p. 168°, hydrogenated (PtO_2) to *ααα'ζζ'ζ'-hexaphenylhexane*, m.p. 189°, also obtained by hydrogenation of (II). 2 : 3-Dimethylpyrrole and (I) (2 mols.) give the *adduct*, $C_{43}H_{37}N$, m.p. 227°. Maleic anhydride and (I) give *s-di(triphenylmethyl)succinic acid*, m.p. 148° (decomp.) (*Me*$_2$ ester, m.p. 212—213°), and its *anhydride*, m.p. 232°. R. S. C.

Preparation of diphenyl. A. García Banus and J. Guiteras (Anal. Fis. Quím., 1933, **31**, 255—259).—A yield of 2 g. of Ph_2 per hr. per 100 g. C_6H_6 is obtained by the method of Lowe and James (A., 1924, i, 275), using nichrome wire of 0·25 mm. diam. at 1020—1030°. Deposition of graphite and accumulation of tarry products lower the rate of formation after 10—12 hr. R. K. C.

Diphenylindenes. II. Dehydration of benzylhydrobenzoin and formation of 1 : 2-diphenylindene. A. García Banus and E. de Salas (Anal. Fís. Quím., 1933, **31**, 378—389; cf. A., 1929, 688).—Benzylhydrobenzoin, $CH_2Ph{\cdot}CPh(OH){\cdot}CHPh{\cdot}OH$ (I) (modified prep.), and AcCl, either cold or boiled for a short time, yield the Ac derivative (II), but (II) is slowly converted into 1 : 2-diphenylindene (III) in presence of the HCl formed. This mechanism accounts for the varying proportions of (II) and (III) isolated when (I) is treated with hot AcCl, either alone or with added SO_2Cl_2 or $SOCl_2$. Treatment of (I) with Ac_2O and H_2SO_4 yields (II) or (III) with low or high proportions of H_2SO_4, respectively. Conc. H_2SO_4 and (I) yield $CH_2Ph{\cdot}CO{\cdot}CHPh_2$ (IV), whilst with dil. H_2SO_4 (III) and (IV) are formed. Treatment of (I) with AcOH and aq. HCl in a sealed tube at 140° yields 75% of (III). (II) is unchanged by P_2O_5, AcCl, or Ac_2O, but in Ac_2O with a little H_2SO_4, or in AcCl in presence of moisture, (III) is formed. Oxidation of (II) by CrO_3 in AcOH yields benzoin acetate. R. K. C.

1-Diphenylene-3-phenylindene. C. F. Koelsch (J. Amer. Chem. Soc., 1933, **55**, 3394—3399).—The Grignard reagent from ββ-diphenylvinyl bromide and fluorenone give α-diphenylene-γγ-diphenylallyl alcohol, m.p. 98—99° (this vol., 66, m.p. 139—140°), which at 225—230° gives a *substance*, $C_{27}H_{18}$, m.p. 308—311°, and with a little H_2SO_4 in hot AcOH affords 3-*phenyl*-1-*diphenyleneindene* (I), m.p. 140—141° (cf. *loc. cit.*). (I) with CrO_3–AcOH yields 9-*o-benzoylphenylfluorene*-9-*carboxylic acid*, m.p. 160—163° (decomp.) [decarboxylated by heat or by hot aq. K_2CO_3 to 9-*o-benzoylphenylfluorene* (II), m.p. 168—169°], *o*-benzoylbenzophenone-*o'*-carboxylic acid, and two *substances*, $C_{27}H_{18}O_2$ and $C_{26}H_{18}O_2$, respectively. (I) is nitrated to the (?2-)*NO*$_2$-derivative, m.p. 197—198°, and gives a (?2-)*Br*-derivative, m.p. 157—158°, which does not form a Grignard reagent, but with CuCN at 250—260° gives the (?2-)*CN*-derivative, m.p. 210—212° (resists hydrolysis). (I) with Na and hot amyl alcohol gives a *hydrocarbon*, $C_{27}H_{20}$, m.p. 125—127°, and with 40% Na–Hg yields an orange *Na* salt, giving with H_2O a *hydrocarbon*, $C_{27}H_{18}$, m.p. 213—215°, and with CO_2 an *acid*, $C_{28}H_{18}O_2$, double m.p. 187—190° (decomp.) and 203—206° (m.p. of pure decarboxylated *product*, 213—215°). The Grignard reagent from *o*-ω-ethoxytolyl bromide and fluorenone give 9-*hydroxy*-9-*o*-ω-*ethoxytolyl fluorene* (III), m.p. 102—103°, which with $SOCl_2$ forms the 9-*Cl*-compound, m.p. 113—114°. (III) is oxidised ($Na_2Cr_2O_7$–AcOH) to *diphenylenephthalide*, m.p. 219—220°, which is reduced by 8% Na–Hg to *o*-9-*fluorenylbenzoic acid*, m.p. 237—238°; this with MgPhBr gives *triphenyl*-*o*-9-*fluorenylcarbinol* (IV), m.p. 214°, also obtained from (II) and MgPhBr. (IV) gives with $SOCl_2$ *triphenyl*-*o*-9-*fluorenylmethyl chloride*, m.p. 242—248° (decomp. commencing at 220°), with AcOH and Zn *triphenyl*-*o*-9-*fluorenylmethane*, m.p. 258—260°, and with a drop of H_2SO_4 in hot AcOH a *substance*, $C_{32}H_{22}$, m.p. 215—220° (decomp.), probably 10 : 10-*diphenyl*-1 : 9-*diphenylene*-9 : 10-*dihydroanthracene*. The allene structure assigned (*loc. cit.*) to (I) is refuted by the above evidence. R. S. C.

Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones. I. 1 : 2-*cyclo*Pentenophenanthrene. J. W. Cook and C. L. Hewett (J.C.S., 1933, 1098—1111).—The additive compound from *cyclo*hexene and $CH_2Ph{\cdot}COCl$ in presence of $SnCl_4$ and CS_2 is converted by $NPhMe_2$ at 180° into 1-*phenylacetyl*-Δ^1-cyclo*hexene* (I), m.p. 46—48° (*semicarbazone*, m.p. 168—169°), which could not be transformed ($AlCl_3$ or conc. H_2SO_4) into the corresponding keto-octahydrophenanthrene. Clemmensen reduction of (I) gives an oil, b.p. 153—159°/12—15 mm., which is dehydrogenated (Se at 340°) to phenanthrene (II), showing that cyclisation occurs at some stage. 9-Methylphenanthrene is not formed by dehydrogenation of the product from (I) and MgMeI. The additive compound from 1-naphthylacetyl chloride (III) and 1-methyl-Δ^1-*cyclo*pentene is converted ($NPhMe_2$) into 1-α-*naphthylacetyl*-2-*methyl*-Δ^1-cyclo*pentene*, m.p. 32—33° (*picrate*, m.p. 130·5—131·5°). A pure product could not be obtained from (III) and *cyclo*pentene. *cyclo*Hexanone and $CH_2Ph{\cdot}CH_2{\cdot}MgCl$ give 1-β-*phenylethyl*cyclo*hexanol* (IV), m.p. 55—56°, dehydrated by $KHSO_4$ at 160° or short treatment with $SnCl_4$ in cold CS_2 to 1-β-*phenylethyl*-Δ^1-cyclo*hexene* (V), b.p. 145°/10 mm. (V) is converted by $AlCl_3$ in CS_2 or boiling AcOH–conc. H_2SO_4 into 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene, b.p. 159°/15 mm., also formed from (IV) and conc. H_2SO_4 at −5° to 0° or $SnCl_4$–CS_2 (prolonged treatment), which is dehydrogenated to (II). The Grignard reagent from β-1-*naphthylethyl chloride*, b.p. 167—168°/17 mm. (*picrate*, m.p. 67—68°) [the alcohol is prepared from α-$C_{10}H_7{\cdot}MgBr$ and $(CH_2)_2O$], and *cyclo*pentanone give 1-(β-1'-*naphthylethyl*)cyclo*pentanol* (VI), m.p. 59·5—60°, dehydrated by $KHSO_4$ at 160—170° to 1-(β-1'-*naphthylethyl*)-Δ^1-cyclo*pentene* (VII), b.p. 164°/4—5 mm. (*picrate*, m.p. 78—79°). (VII) is isomerised by $AlCl_3$ in CS_2 to trans-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (VIII), b.p. 160—161°/3—4 mm. (*picrate*, m.p. 128—129°), whilst (VI) or (VII) and AcOH–conc. H_2SO_4 at 100° give 1 : 2-cyclo*pentenophenanthrene* (IX), m.p. 134·5—135° (not 152—153° as stated in this vol., 710) (*picrate*, m.p. 134·5—135°). (VIII) is dehydrogenated (Se at 335—340°) to 1 : 2-cyclo-Δ$^{1'\cdot4'}$- or -*pentadienophenanthrene*, m.p. 142·5—143·5° (*picrate*, m.p. 192—

193°), and a little of an isomeride (?), m.p. 68—70° (picrate, m.p. 208—209°). Dehydrogenation (Se at 305—325°) of the mixture of hydrocarbons obtained from (VI) and $SnCl_4$ or of the saturated, non-picrate-forming constituents of the crude mixture containing (VIII) gives a mixture of hydrocarbons containing (IX) (which probably arises from *cis*-cyclopentanotetrahydrophenanthrene). (IX) could not be dehydrogenated. These results suggest that the course pursued by the dehydrogenation reaction is determined by the stereochemical configuration of the reduced ring system.

Cyclisation of 1-benzyl-Δ^1-*cyclo*hexene could not be effected with $AlCl_3$, $SnCl_4$, or AcOH–conc. H_2SO_4; with P_2O_5 at 140—150°, 1 : 2 : 3 : 4 : 10 : 11-*hexahydrofluorene*, b.p. 137°/15 mm., results. β-2-Naphthylpropionic acid (Mayer and Sieglitz, A., 1922, i, 740) [the intermediate β-naphthylmethylmalonic acid has m.p. 145° (lit. 94—95°)] and $SnCl_4$ at 120° give 4 : 5-benz-3-hydrindone, which could not be condensed ($AlCl_3$) with succinic anhydride and which is reduced (Clemmensen) to 4 : 5-benzhydrindene, b.p. 170°/15 mm.

Comparison [spectrum; m.p.; m.p. of picrate and compound with *s*-$C_6H_3(NO_2)_3$] of the hydrocarbon $C_{18}H_{16}$ (Diels *et al.*, A., 1928, 169; 1930, 470; Ruzicka and Thomann, this vol., 278), now prepared by dehydrogenation (Se at 320—340°) of cholesteryl chloride (X), with (IX) indicates that the former consists of (IX) contaminated with some persistent impurity. Dehydrogenation of (X) proceeds more rapidly at higher temp., but it is then difficult to isolate the $C_{18}H_{16}$ in a state approaching purity. Thus at 330—350°, the hydrocarbon, m.p. 123—124°, and the hydrocarbon $C_{25}H_{24}$ (now formulated as $C_{25}H_{22}$), m.p. 221—222·5° (1 : 1-*compound*, m.p. 239—240°, with 2 : 7-dinitroanthraquinone), of Diels *et al.* (A., 1928, 169) were isolated, whilst at 340—360°, impure chrysene probably results. The conclusions of Ruzicka *et al.* (this vol., 820) are criticised. H. B.

New route to chrysene and 1 : 2-benzanthracene. R. D. Haworth and C. R. Mavin (J.C.S., 1933, 1012—1016).—3-Phenanthryl CH_2Br ketone (from the Me ketone and Br in $CHCl_3$) and $CHNa(CO_2Et)_2$ in C_6H_6 give [after hydrolysis (10% MeOH–KOH) and decomp. of the resulting acid at 180—185°] 45% of β-3-*phenanthroylpropionic acid* (I), m.p. 157—158° [*oxime*, m.p. 169—170° (decomp.)], also obtained in 60% yield from phenanthrene, succinic anhydride, and $AlCl_3$ in $PhNO_2$. Clemmensen reduction of (I) affords γ-3-*phenanthrylbutyric acid*, m.p. 138—139°, converted by 85% H_2SO_4 at 100° into 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-5 : 6-*benzanthracene* (II), m.p. 179—180°, and a little of a *compound*, $C_{18}H_{14}O_2$, m.p. 246—248°. Clemmensen reduction of (II) and subsequent dehydrogenation (Se at 280—315°) gives 1 : 2-benzanthracene. β-2-*Phenanthroylpropionic acid*, m.p. 205—206°, prepared as above [$CHNa(CO_2Et)_2$ method] from 2-*phenanthryl* CH_2Br *ketone*, m.p. 140—142°, is similarly reduced to γ-2-*phenanthrylbutyric acid*, m.p. 134°, which is cyclised to 7-*keto*-4 : 5 : 6 : 7-*tetrahydrochrysene*, m.p. 124—125°. Clemmensen reduction of this affords an amorphous product (which is considered to be composed largely of 4 : 5 : 6 : 7-tetrahydrochrysene), readily dehydrogenated (Se at 290—310°) to chrysene (III). β-1-*Naphthylethyl bromide*, b.p. 145—148°/0·3 mm. [the alcohol is prepared from α-$C_{10}H_7$·MgBr and $(CH_2)_2O$], and Et potassio*cyclo*hexanone-2-carboxylate in C_6H_6 give *Et* 2-(β-1-*naphthylethyl*)cyclo*hexanone*-2-*carboxylate*, b.p. 210—215°/0·3 mm., which when heated with 85% H_2SO_4 at 100° undergoes ketonic hydrolysis and ring closure; the resulting oil is dehydrogenated to (III). Clemmensen reduction of 2- and 3-phenanthryl Me ketones gives 2-, m.p. 64—65° (*picrate*, m.p. 92—93°), and 3-*ethylphenanthrene*, an oil (*picrate*, m.p. 117—118°; *styphnate*, m.p. 114—116°).

Attempts to condense 1-keto- or 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene with $CH_2Br·CO_2Et$ (IV) or $CH_2Br·CH_2·CO_2Et$ (V) were unsuccessful; 2 : 6-dimethyl*cyclo*hexanone, (IV), and $NaNH_2$ in Et_2O give, however, *Et* 2 : 6-*dimethyl*cyclo*hexanone*-2-*acetate*, b.p. 132—134°/15 mm. Et sodio*cyclo*hexanone-2-carboxylate and (V) in C_6H_6 afford *Et* 2-*carbethoxy*cyclo*hexanone*-2-β-*propionate*, b.p. 199—202°/15 mm., hydrolysed (10% MeOH–KOH) to cyclo*hexanone*-2-β-*propionic acid*, b.p. 155—160°/0·2 mm., m.p. 65—66° [*Me* ester, b.p. 140—142°/15 mm., which with MgMeI gives a lactone, b.p. 155—160°/15 mm., and with (IV) and Zn affords an oil, b.p. 180—185°/15 mm.], and the *anhydride*, b.p. 250—260°/0·2 mm., m.p. 72—73°, of heptane-αγη-tricarboxylic acid. H. B.

Action of αγ-dichloropropylene on primary aromatic amines. C. Dorier (Compt. rend., 1933, **196**, 1677—1678).—The above reactants condense in C_6H_6 solution affording a secondary amine, $Ar·NH·CH_2·CH{:}CH_2Cl$. γ-*Chloroallyl-aniline*, b.p. 137°, -o-*toluidine*, b.p. 145°, and -m-*toluidine*, b.p. 148° (all at 13 mm.), are described. A. C.

Preparation of alkylanilines containing *tert.*-alkyl groups. W. J. Hickinbottom (J.C.S., 1933, 946—951).—The following are prepared by a modification of Nef's method (A., 1900, i, 4): *tert.*-butylaniline, b.p. 214—216°/753 mm. (corr.) {*hydrochloride*; *hydrobromide*; *sulphate*; *picrate*, m.p. 191—192° (decomp.); *Ac*, m.p. 55—56°, b.p. 124—125 /22 mm., p-*toluenesulphonyl*, m.p. 82—83°, m-*nitrobenzenesulphonyl*, m.p. 100—101°, *NO*-, m.p. 61—62°, and *Me*, b.p. 81—82°/39 mm. [*picrate*, m.p. 162—163° (decomp.)], derivatives; αβ-*diphenyl*-β-tert.-*butylcarbamide*, m.p. 81° (Ph·NCO)}; tert.-*amylaniline*, b.p. 227·5—229·5°/744 mm. (corr.) (*hydrochloride*; *NO*-, m.p. 47—48°, and p-*toluenesulphonyl* derivative, m.p. 73—74°); and tert.-*hexylaniline* (γ-*anilino*-γ-*methylpentane*), b.p. 253—254°/759 mm. (corr.) [*hydrochloride*; *picrate*, m.p. 133—135°; p-*toluenesulphonyl*, m-*nitrobenzenesulphonyl*, m.p. 85—86°, and *Me* (*picrate*, m.p. 127—128°) derivatives]. Separation from NH_2Ph is achieved by virtue of their resistance to acetylation. The *N*-Me derivatives do not react with HNO_2, and the nitrosoamines eliminate HNO_2 in the Fischer–Hepp reaction, no *p*-NO-derivative being formed. H. A. P.

Elimination of *tert.*-alkyl groups from alkylanilines by hydrolysis. W. J. Hickinbottom (J.C.S., 1933, 1070—1073).—*tert.*-Butyl- (I), -amyl-,

and -hexyl-anilines give NH_2Ph when heated with mineral acids (15*N*-H_2SO_4 at 110—140°, conc. HBr, HI, or H_3PO_4), but *n*-alkyl groups are unaffected, *e.g.*, $NHPhBu^{\alpha}$ is stable to 19*N*-H_2SO_4 at 120—140°, and NPhMe·CMe_3 gives only NHPhMe. The CMe_3 group is also eliminated from the $ArSO_2$ and NO-derivatives of (I) by aq. H_2SO_4, although in the case of the latter only a small amount of diazonium salt is formed, the main reaction being the elimination of HNO_2.

H. A. P.

p-Aminophenylurethanes as local anæsthetics. W. H. Horne, R. F. B. Cox, and R. L. Shriner (J. Amer. Chem. Soc., 1933, **55**, 3435—3439).—p-*Nitrophenylurethanes*, $NO_2·C_6H_4·NH·CO_2R$, were prepared in which R was (*a*) β-*diethylaminoethyl*, m.p. 59—60° [*hydrochloride*, m.p. 212° (block); *nitrate*, m.p. 192—193°], (*b*) β-*diisoamylaminoethyl*, m.p. 70—71° (*hydrochloride*, m.p. 129—130°), (*c*) γ-*di*-n-*amylaminopropyl*, an oil (*hydrochloride*, m.p. 153—154°), and (*d*) γ-*diisoamylaminopropyl*, an oil (*hydrochloride*, m.p. 150—151°; *nitrate*, m.p. 111—112°), hydrogenated (PtO_2–Pt black) in AcOH to the corresponding p-*aminophenylurethanes*, (*a*) [*hydrochloride*, an oil; *dihydrochloride*, m.p. 219—220°; (approx. *tri*-)*borate*, m.p. 368° (decomp.) (block)], (*b*) [*hydrochloride*, an oil; *dihydrochloride*, m.p. 212—214° (decomp.)], (*c*) (*hydrochloride*, m.p. 126°), and (*d*) (*hydrochloride*, an oil). Similarly were prepared *hydrochlorides* of p-*aminophenylurethanes* in which R was *Me*, m.p. 238°, *Et*, m.p. 238°, Pr^{α}, m.p. 221°, Pr^{β}, m.p. 228°, Bu^{α}, m.p. 219°, *sec.*-Bu, m.p. 241°, Bu^{β}, m.p. 225°, *amyl*, m.p. 215°, iso*amyl*, m.p. 230°, *hexyl*, m.p. 210°, and sec.-*octyl*, m.p. 195°. All the above are photosensitive. The pharmacological action of the *p*-aminophenylurethanes is described. R. S. C.

Reactivity of the chlorine atom in the benzene nucleus. B. B. Dey and Y. G. Doraiswami (J. Indian Chem. Soc., 1933, **10**, 309—320).—The activating influence of the *o*-NO_2, *o*-CN, and *o*-CO_2H groups on the case of replacement of the Cl atom in 1-chloro-2 : 4-dinitrobenzene (I), 2-chloro-5-nitrobenzonitrile (II), and 2-chloro-5-nitrobenzoic acid (III) during treatment with NH_2Ph and *o*-, *m*-, and *p*-$C_6H_4Me·NH_2$ is in the order $NO_2 > CO_2H > CN$, whilst for $NHEt_2$, $CO(NH_2)_2$ (IV), NaOMe, and NaOEt, the order is $NO_2 > CN > CO_2H$. (I) reacts only with $CHNa(CO_2Et)_2$ and CHNaAc·CO_2Et, whilst (I) and (II) react with CN·CHNa·$CO·NH_2$; reaction could not be effected with the Na derivatives of $MeNO_2$ or CN·$CH_2·CO_2Et$ even with Cu or $Cu(OAc)_2$ as catalysts. (II) reacts with *p*- but not with *o*- and *m*-$C_6H_4Cl·NH_2$ or $NO_2·C_6H_4·NH_2$. (III) does not react with NaOMe, NaOEt, or (IV), whilst (I) and (IV) at 160° give 2 : 4-dinitroaniline. The following appear to be new : 4-*chloro*-3-*cyanoaniline*, m.p. 133° (*Ac* derivative, m.p. 190°), prepared by reduction (Sn–conc. HCl) of the NO_2-derivative, which could not be hydrolysed; 4-*nitro*-2-*cyano*-, m.p. 171°, 4-*nitro*-2-*cyano*-3′-, m.p. 140°, and -4′-, m.p. 217°, -*methyl*- and 4′-*chloro*-4-*nitro*-2-*cyano*-, m.p. 282°, -*diphenylamines*; 5-*nitro*-2-*anilinobenzamide*, m.p. 190°; *Me* 5-*nitro*-2-*anilinobenzoate*, m.p. 100°; 4-*nitro*-2-*cyanodiethylaniline*, m.p. 88°; 5-*nitro*-2-*carbamidobenzamide*, m.p. 198°, from (II) and (IV) at 165—170°, which is hydrolysed by 15% KOH to 5-nitroanthranilic acid and by 20% KOH to 5-nitrosalicylic acid. H. B.

Saponification of nitrosodiarylamines and attempts to prepare a salt of aquoammononitrous acid. W. C. Fernelius and G. W. Watt (J. Amer. Chem. Soc., 1933, **55**, 3482—3485).—$NPh_2·NO$ (I) reacts quantitatively with $LiNH_2$, $NaNH_2$, KNH_2, and $Ca(NH_2)_2$, and $(p\text{-}C_6H_4Me)_2N·NO$ with $NaNH_2$ and KNH_2 in liquid NH_3, to give the metallic salt of the diarylamine, N_2, and NH_3. Salts of the type $NHR·NO$ are possible intermediates. $N(CH_2Ph)_2·NO$ (II) and NPhMe·NO react otherwise, no N_2 being evolved. (I) and (II) with $NaNH_2$ in PhMe give low yields of N_2 and tars. (I) is stable to KOH–EtOH.

R. S. C.

Substitution reactions of 4-aminodiphenylmethane. W. A. Waters (J.C.S., 1933, 1060—1064).—Halogenation of $CH_2Ph·C_6H_4·NH_2$-(*p*) and its Ac and Bz derivatives substitutes successively the 3, 5, and 4′ positions; nitration occurs 3, 4′. Orientation is established by deamination followed by oxidation to the known $COPh_2$ derivatives (cf. A., 1929, 1299), or by fission with Br to PhCHO or derivative and 2 : 4 : 6-$NH_2·C_6H_2Br_3$. The following are described : 4-*benzamidodiphenylmethane*, m.p. 161° (4′-*Br*-derivative, m.p. 181°); 3 : 5-*dibromo*-, m.p. 92° (*Ac*, m.p. 116°, and *Bz*, m.p. 222°, derivatives); 3 : 5 : 4′-*tribromo*-, m.p. 141° (*Ac* derivative, m.p. 209°); 3-*bromo*-, b.p. 204—208°/15 mm. [*hydrobromide*, m.p. 216° (decomp.); *Ac*, m.p. 91°, *Ac*$_2$, m.p. 112°, and *Bz*, m.p. 97°, derivatives]; 3 : 4′-*dibromo*- (*Bz* derivative, m.p. 135°); 3 : 5-*di*-*iodo*-, m.p. 137° (*Bz* derivative, m.p. 257°); 3-*bromo*-5-*iodo*-, m.p. 91°, and 3 : 4′-*dinitro*-4-*aminodiphenylmethane*, m.p. 122° (*Ac* derivative, m.p. 150°; 5-*Br* derivative, m.p. 181°) : (?) 2-*iodo*-, m.p. 201°, and (?) 3-*iodo*-4-*acetamidodiphenylmethane*, m.p. 113°; 3 : 5-*dibromo*-, m.p. 61°, b.p. 201°/15 mm., and 3 : 5-*di*-*iodo*-*diphenylmethane*, m.p. 73°. In one case by bromination of 4-$CH_2Ph·C_6H_4·NHAc$ at 100° the (?) 2-*Br*-derivative, m.p. 194° (*Bz* derivative of base, m.p. 166°), was obtained, but this prep. could not be repeated.

H. A. P.

Mechanism of aromatic rearrangements. II. Benzidine change. C. K. Ingold and H. V. Kidd (J.C.S., 1933, 984—988).—The conversion of 2 : 2′-di-methoxy- and -ethoxy-hydrazobenzenes into the corresponding benzidines by HCl in EtOH occurs at substantially the same rate, and when a mixture of the two is used leads only to the symmetrical benzidines, no 2-methoxy-2′-ethoxybenzidine being formed. Consequently the rearrangement is regarded as strictly intramol. The reaction is accompanied by disproportionation of the hydrazo-compound to amine and azo-compound. H. A. P.

Alkylation of α-naphthol-orange. K. H. T. Pfister (Ber., 1933, **66**, [*B*], 1052).—In consequence of the final acidity of the solution and the sensitiveness of the alkyl ethers of α-naphthol-orange to acids, the product obtained by Slotta (this vol., 270) is essentially initial material. H. W.

Synthesis of chloromethyl derivatives of phenols. M. Sommelet (Compt. rend., 1933, **197**, 256—257).—Ph Et carbonate, $CH_2Cl·OMe$, and $SbCl_5$

in CCl_4 at −15° give p-*chloromethylphenyl Et carbonate*, m.p. 25—26°, b.p. 163—166°/15 mm., hydrolysed by $(CH_2)_6N_4$ to *p*-OH·C_6H_4·CHO. Similarly were prepared the *chloromethyl* derivatives of *o*-, m.p. 35°, b.p. 162°/16 mm., *m*-, m.p. 29°, b.p. 165—167°/13 mm., and *p*-tolyl, b.p. 125—126°/2 mm., *thymyl*, b.p. 155—156°/3 mm., and *o*-chlorophenyl, b.p. about 162°/5 mm., Et carbonates. R. S. C.

Direct dibromination of *m*-bromophenol and an example of group migration. H. H. Hodgson, J. Walker, and [in part] J. Nixon (J.C.S., 1933, 1053—1056).—The orientation of 2 : 3 : 4- and 2 : 4 : 5-tribromo-, 3 : 4 : 6-tribromo-2-nitro-, and 2 : 3 : 4-tribromo-6-nitro-phenols and their Me ethers is established. Attempted dibromination of *m*-C_6H_4Br·OH in glacial AcOH (cf. A., 1925, i, 1264) gives a mixture containing 2 : 3 : 4 : 6-tetra- and 2 : 3 : 4-, m.p. 95°, and 2 : 4 : 5-tri-bromophenol, m.p. 87°, but in CCl_4 3 : 4-dibromo- and on long keeping (or better in $PhNO_2$) 2 : 4 : 5-tribromo-phenols are formed. Nitration of 2 : 5-dibromophenol (I) gives the 4- and 6-NO_2-derivatives, the latter of which with NaOBr gives 3 : 4 : 6-*tribromo*-2-*nitrophenol* (II), m.p. 127° [*Me ether*, m.p. 72° (CH_2N_2)], also obtained by bromination of 3-bromo-2-nitrophenol with NaOBr or in EtOH; Br in AcOH, however, gives 2 : 3 : 4-tribromo-6-nitrophenol (III), m.p. 123°, migration of the NO_2 having occurred. (III) is also obtained from 5-bromo-2-nitrophenol and NaOBr or by nitration of 2 : 3-$C_6H_3Br_2$·OH in AcOH and bromination of the resulting 2 : 3-*dibromo*-6-*nitrophenol*, m.p. 105°, in EtOH. Its orientation is confirmed by conversion of its Me ether through the anisidine into 2 : 3 : 4-*tribromoanisole*, m.p. 106°, identified by demethylation; the same method is applied to (II), which with Br in AcOH gives an unidentified substance, m.p. 220—225°. H. A. P.

Bromo-derivatives of thymoquinol. S. R. Chechik (J. Amer. Pharm. Assoc., 1933, **22**, 506—510).—Thymoquinol (2-methyl-5-*iso*propylquinol) treated with 3 or 4 mols. of Br yields a tribromide (not further characterised), m.p. 65°. 6-Bromothymoquinone, prepared by bromination of thymoquinone in $CHCl_3$ at 5°, yields 6-bromothymoquinol, m.p. 63—64° (cf. A., 1887, 1036), on reduction with SO_2 or semicarbazide +HCl but not with Zn+HCl. Reduction by Zn+HCl or SO_2 of a mixture of di- and tribromothymoquinone affords 3 : 6-*dibromothymoquinol*, m.p. 59—60° [diacetate, m.p. 96—97° (cf. A., 1882, 838)], whilst reduction with H_2S yields a substance, m.p. 118—119°. F. O. H.

Preparation of cryptophenols. L. H. Farinholt, W. C. Harden, and D. Twiss (J. Amer. Chem. Soc., 1933, **55**, 3383—3387).—CH_2PhCl and the appropriate phenoxide in hot PhMe give 2 : 4-dibenzylphenol, b.p. 238°/10 mm. (m.p. 111—112°), *o*-benzyl-, b.p. 147—148°/7 mm. (m.p. 144°), 3 : 5-dibenzyl-*p*-cresol, b.p. 205—207°/5 mm. (m.p. 129—130°), 2-*benzyl*-4-*propylphenol*, b.p. 186—187°/10 mm. (m.p. 92°), 2-benzyl-, m.p. 46—46·5°, b.p. 180—185°/8 mm. (m.p. 116°), and 2 : 6-*dibenzyl*-4-tert.-*amylphenol*, b.p. 225—230°/7 mm. (m.p. 146°), the m.p. in parentheses being those of the *phenylcarbamates*. Ph, o-, b.p. 245°, and p-*propyl*-, b.p. 254—256°, and 2 : 4-*dipropylphenyl propionate*, b.p. 277—279°, afford by the Fries reaction o-, b.p. 115°/15 mm., and p-*propionyl*-, m.p. 148°, p-*propionyl*-o-*propyl*-, m.p. 77°, o-*propionyl*-p-*propyl*-, b.p. 270°, and 6-*propionyl*-2 : 4-*dipropylphenol*, b.p. 295—298°, respectively, which are reduced to o-, b.p. 223—225°, and p-*propyl*-, b.p. 230—232°, 2 : 4-*dipropyl*-, b.p. 263°, and 2 : 4 : 6-*tripropyl*-*phenol*, b.p. 288—289°. PhOH, CH_2PhCl, and Zn at 70° give *tribenzylphenol*, b.p. 272°/10 mm. (*phenylcarbamate*, m.p. 120°). *o*-Propionylphenol and $AlCl_3$ give *o*-propionylphenol and $EtCO_2H$. R. S. C.

Organic reactions with boron fluoride. V. Rearrangement of phenyl, *o*- *m*-, and *p*-tolyl *iso*propyl ethers. F. J. Sowa, H. D. Hinton, and J. A. Nieuwland (J. Amer. Chem. Soc., 1933, **55**, 3402—3407).—Rearrangement of $PhOPr^{\beta}$ without external cooling by BF_3 gives 2-iso*propyl*- (I), b.p. 212—214° (this and other b.p. at 745 mm.), 2 : 4-*di*-iso*propyl*- (II), b.p. 228—230°, and 2 : 4 : 6-*tri*iso-*propyl*-*phenol* (III), b.p. 249°, and their *Pr*$^{\beta}$ *ethers*, b.p. 225—227°, 248°, and 263°, respectively, and PhOH. p-*Tolyl Pr*$^{\beta}$ *ether*, b.p. 197°, gives similarly *p*-cresol, 3-iso*propyl*-, b.p. 233—235°, and 3 : 5-*di*iso*propyl*-, b.p. 249—250°, -p-*cresol*, and their *Pr*$^{\beta}$ *ethers*, b.p. 241—243° and 257—259°, respectively. o-*Tolyl Pr*$^{\beta}$ *ether*, b.p. 191°, affords 5-iso*propyl*-, b.p. 231—235°, and 3 : 5-*di*iso*propyl*-, b.p. 253—256°, -o-*cresol*, and their *Pr*$^{\beta}$ *ethers*, b.p. 241—242° and 257—259°, respectively, and *o*-cresol. m-*Tolyl Pr*$^{\beta}$ *ether*, b.p. 197°, with slight cooling yields *m*-cresol, thymol, 6-*iso*propyl-*m*-cresol, *thymol Pr*$^{\beta}$ *ether* (IV), b.p. 233°, and 4 : 6-*di*iso*propyl*-m-*cresol* (V), b.p. 261°; without cooling, the *Pr*$^{\beta}$ *ether*, b.p. 262°, of (III) is also formed. (IV) and BF_3 give (V). Conductivity measurements of PhOH–BF_3 mixtures prove the existence of a *compound*, BF_3,2PhOH. PhOMe (stable to BF_3) gives with propylene and BF_3 2-iso*propylphenyl Me ether*, b.p. 200°. The Pr^{β} ether of (III) (also stable to BF_3) with PhOH and BF_3 gives (I) and (II). Most of the above ethers were also prepared from PhOH or the cresol, propylene, and BF_3. These results prove that the Pr^{β} migrates both by inter- and intra-molecular reactions. R. S. C.

Synthesis of fast-violet B base, its isomeride, and analogous compounds. N. Kishner and U. Krasova (Anilinokras. Prom., 1933, **3**, 179—184).—Fast-violet B base has been identified as 6-benzamido-4-methoxy-*m*-toluidine (I) by analysis and subsequent synthesis. *o*-Nitro-*p*-tolyl Me ether was reduced with NaCl and gun-metal filings to the NH_2-compound, m.p. 47°, the Ac compound, m.p. 95·5°, of which was nitrated with H_2SO_4–HNO_3 at < 3° to *5-nitro*-4-*methoxy*-o-*acetotoluidide*, m.p. 139°, hydrolysed by aq. NaOH to the free *base*, m.p. 166°. The *Bz* compound of this, m.p. 197°, was reduced with Zn and 5% HCl to (I), m.p. 189° (*Ac* derivative, m.p. 240°). Similarly, 6-nitro-4-methoxy-*m*-toluidine was converted into the *Bz* derivative, m.p. 123°, which was reduced to *5-benzamido*-4-*methoxy*-o-*toluidine* (II), m.p. 176°, giving slightly bluer shades than (I) in conjunction with Naphthol AS. 6-*Nitro*-4-*ethoxy*-m-*toluidine*, m.p. 93°, was converted into the *Bz* compound, m.p. 158°, and this reduced to 5-*benzamido*-4-*ethoxy*-o-*toluidine*, m.p. 126°, giving somewhat bluer

shades than (II) with Naphthol AS. 3-Chloro-4-nitro-6-methoxyaniline was converted into the *Bz* derivative, m.p. 142°, and this reduced to 2-chloro-4-benzamido-5-methoxyaniline, giving reddish-violet shades with Naphthol AS. 2 : 5-Dichloro-*p*-nitroaniline was converted into the *Bz* derivative, m.p. 151°, and this reduced to 2 : 5-dichloro-4-benzamidoaniline, m.p. 179·5°, which gives crimson shades with Naphthol AS (cf. B.P. 361,909; B., 1932, 337). G. A. R. K.

Condensation of formaldehyde, amines, and phenols. J. DECOMBE (Compt. rend., 1933, **197**, 258—260).—Contrary to patent lit., CH_2O and $NHMe_2$ do not condense with β-$C_{10}H_7$·OH (I) at 0°. CH_2O, piperidine, and (I) at 0° give N-2-*hydroxynaphthylmethylpiperidine*, m.p. 94—95° [*benzoate*, m.p. 115°, unstable (*hydrochloride*)], insol. in NaOH. *o*-, *m*-, and *p*-$C_6H_4(OH)_2$, and phloroglucinol (II) give resins with CH_2O and $NHMe_2$ at 0°, but with $NHMe_2$,HCl cryst. products are obtained, resinified by alkali. (II) gives single and double condensation products. Pyrocatechol Me ether with $NHMe_2$ and CH_2O gives 2-*hydroxy*-3-*methoxybenzyldimethylamine*, b.p. 127—129°/5 mm., m.p. 46—47° (*hydrochloride* of *Bz* derivative, m.p. about 160°). Similarly is obtained 2-*hydroxy*-5-*methoxybenzyldimethylamine*, b.p. 115—117°/2 mm. (*hydrochloride* of *Bz* derivative, m.p. 155—156°). Resorcinol Me ether and phloroglucinol Me and Me_2 ethers give resins. R. S. C.

Molecular dissymmetry and physiological activity [urethanes of α-*m*-hydroxyphenylalkyldimethylamines]. L. H. EASSON and E. STEDMAN (J.C.S., 1933, 1094—1098).—Interaction of *m*-OMe·C_6H_4·CHO with MgEtI gives m-*methoxyphenylethylcarbinol*, b.p. 135—138°/11 mm., the bromide from which with $NHMe_2$ in C_6H_6 gives α-m-*methoxyphenyl*-n-*propyldimethylamine*, b.p. 119°/11 mm. (*hydrochloride*, m.p. 149°; *methiodide*, m.p. 187°; *picrate*, m.p. 117°), hydrolysed by HBr to α-m-*hydroxyphenyl*-n-*propyldimethylamine*, m.p. 103°, b.p. 149—150°/8 mm. {*hydrochloride*, m.p. 163°; *methiodide*, m.p. 150°; *picrate*, m.p. 141°; *methylurethane* [*hydrochloride*, m.p. 153°; *methiodide* (+1H_2O), m.p. 111° (decomp.)] (MeNCO)}. The following are prepared similarly: α-m-*methoxyphenylisopropyldimethylamine* (I), b.p. 125—127°/13 mm. (*hydrochloride*, m.p. 96°; *methiodide*, decomp. 180°; *picrate*, m.p. 138°); α-m-*hydroxyphenylisopropyl*-, m.p. 129° {*methiodide*, m.p. 151°; *hydrochloride*, m.p. 213°; *methylurethane*, m.p. 96° [*hydrochloride*, m.p. 234° (decomp.); *methiodide*, m.p. 160° (rapid heating)]}; α-m-*methoxyphenyl*-n-*butyl*-, b.p. 129—130°/11·5 mm. (*methiodide*, m.p. 119·5°; *picrate*, m.p. 99—100°); α-m-*hydroxyphenyl*-n-*butyl*-, m.p. 107°, b.p. 170°/12 mm. {*hydrochloride*, (+1H_2O), m.p. 86°; *methiodide*, m.p. 191—192° (rapid heating); *picrate*, m.p. 154°; *phenylurethane*, m.p. 96° [*hydrochloride*, m.p. 201° (decomp.; rapid heating); *methiodide*, m.p. 146°]; *methylurethane* [*hydrochloride*, m.p. 143°; *methiodide*, m.p. 176° (decomp.)]; m-*methoxyphenyl*-n-*butylcarbinol*, b.p. 130—133°/3 mm.}; α-m-*methoxyphenyl*-n-*amyl*-, b.p. 146—148°/13 mm. (*hydrochloride*, m.p. 130·5°; *picrate*, m.p. 91°); α-m-*hydroxyphenyl*-n-*amyl*-, m.p. 91°, b.p. 173°/10 mm. [*methiodide*, m.p. 141°; *picrate*, m.p. 126°; *phenylurethane*, m.p. 103° (*hydrochloride*, m.p. 166°)]; m-*methoxydiphenylmethyl*-, b.p. 179°/12 mm. (*hydrochloride*, m.p. 182°); and m-*hydroxydiphenylmethyldimethylamine*, m.p. 94°, b.p. 205—207°/10 mm. {*hydrobromide* (+1H_2O); *picrate*, m.p. 129°; *phenylurethane*, m.p. 109° [*methiodide*, m.p. 186° (decomp.; rapid heating)]; *methylurethane*, m.p. 80° [*hydrochloride*, m.p. 204° (decomp.); *methiodide*, decomp. > 140°; *picrate*, m.p. 182°]. Attempted prep. of *m*-OMe·C_6H_4·CMe_2·OH from *m*-OMe·C_6H_4·COMe gave only *m*-methoxy*iso*propenylbenzene, from which (I) is obtainable in poor yield by successive action of HBr and $NHMe_2$. H. A. P.

Preparation of *p*-hydroxyphenylaminoacetic acid. A. TERENTIEV and S. CHERNIN (Khim. Farm. Prom., 1933, 18—19).—*p*-OH·C_6H_4·NH_2 (300 mol.) in boiling H_2O is treated with CH_2Cl·CO_2H (150 mol.), heated, stirred for 1 hr., and acidified with HCl; the centrifuged product is dissolved in aq. NH_3, treated with $Na_2S_2O_4$, and filtered through C. The ppt. obtained on addition of HCl is washed, and dried at 40—45°. CH. ABS.

Styphnic acid. II. Bromopicrin, the bromination product of sodium styphnate. H. H. LEI and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, **A**, **2**, 129—131).—Addition of Br to styphnic acid in 11% aq. Na_2CO_3 at 5° affords bromopicrin, b.p. 89—90°/20 mm., readily separated by steam distillation. When heated with NH_3–EtOH at 100° it explodes. J. W. B.

Styphnamic acid. P. P. T. SAH and C. T. HSIA (J. Chinese Chem. Soc., 1933, **1**, 92—95).—Reduction of styphnic acid (cf. A., 1909, ii, 487) with Na_2S_x in boiling H_2O affords styphnamic acid, m.p. 219° (lit., 190°), the diazonium compound of which is decomposed to 4 : 6-dinitropyrogallol (cf. A., 1904, i, 241). J. L. D.

Preparation, toxicity, and absorption of bismuth compounds. V. Pyrocatechol, pyrogallol, and gallic acid. W. M. LAUTER, A. E. JURIST, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1933, **22**, 531—534).—The prep. is described of Na Bi gallate, digallate (I), and methylgallate (II) and Bi pyrogalloxide and pyrocatecholoxide. These compounds are unstable in aq. solution and, whilst (I) and (II) are relatively low in toxicity, their absorption, tested on rats, is slow and incomplete. F. O. H.

Dehydrogenation of phenols. III. Transition from the dibenzyl to the phenanthrene series by dehydrogenation. H. ERDTMAN (Annalen, 1933, **505**, 195—202).—Reduction of veratril with Zn–Hg and conc. HCl in AcOH or hydrogenation (PtO_2) of 3 : 4 : 3′ : 4′-tetramethoxystilbene gives 3 : 4 : 3′ : 4′-*tetramethoxydibenzyl* (I), m.p. 109—110°, demethylated by 48% HBr to 3 : 4 : 3′ : 4′-*tetrahydroxydibenzyl* (II), m.p. 153—155° (Ac_4 derivative, m.p. 147—149°). In alkaline solution (I) readily absorbs O_2 giving an intense green colour; acids ppt. a violet mass probably containing a quinone, since reductive acetylation leads to 2 : 3 : 6 : 7-*tetra-acetoxy*-9 : 10-*dihydrophenanthrene* (III), m.p. 173—175°. Similar dehydrogenation is effected by $FeCl_3$ in neutral or slightly acid solution. The yield is poor, the main

product being a humus. (II) is very smoothly oxidised by tetrabromo-*o*-benzoquinone in Et_2O without production of a phenanthrene derivative. (I) is transformed by Br in AcOH into 6 : 6′-*dibromo*-3 : 4 : 3′ : 4′-*tetramethoxydibenzyl*, m.p. 157—159°, and by I and HgOAc followed by KI into 6 : 6′-*di-iodo*-3 : 4 : 3′ : 4′-*tetramethoxydibenzyl* (IV), m.p. 152—153° (transformed by AcOH–HNO_3 into 6 : 6′-dinitro-3 : 4 : 3′ : 4′-tetramethoxydibenzyl, m.p. 205—206°). (IV) and Cu powder at 220° yield 2 : 3 : 6 : 7-*tetramethoxy*-9 : 10-*dihydrophenanthrene*, m.p. 174—175·5°, demethylated and acetylated to (III). H. W.

Preparation of aminocycloheptanols **and their resolution into [optically] active components.** M. Godchot and M. Mousseron (Compt. rend., 1933, **196**, 1680—1682).—*cyclo*Heptene oxide and conc. aq. NH_3 at 120—130° give dl-trans-2-*amino*cyclo*heptanol* (I), m.p. 72—73°, b.p. 129—130°/16 mm. (*hydrochloride*, m.p. 115—116°; d-*H camphorate*, m.p. 176—177°, $[\alpha]_D$ +16·31°), converted by PCl_5 in $CHCl_3$ at 0° into 2-*chloro*cyclo*heptylamine*, b.p. 97—98°/16 mm. (I) is accompanied by some 2 : 2′-*dihydroxydi*cyclo*heptylamine*, b.p. 210°/16 mm. [*NO*-derivative, m.p. 220° (decomp.)]. Fractional crystallisation of the d-*H tartrate* of (I), m.p. 179—180°, $[\alpha]_D$ +14·20°, affords the d-*H tartrates* of l- and d-trans-2-*amino*cyclo*heptanols*, m.p. 197—198° and 152—153°, $[\alpha]_D$ +4·95° and +24·20°, respectively. The corresponding l-*H tartrates* have also been prepared. From these are obtained d- and l-trans-2-*amino*cyclo*heptanol*, m.p. 89—90°, $[\alpha]_D$ ±14·45° (*hydrochloride*, m.p. 124—125°).

Prolonged heating of *cyclo*heptene oxide with EtOH–NH_2Me at 130° affords dl-trans-2-*methylamino*cyclo*heptanol*, b.p. 121—122°/16 mm. The d-*H tartrate*, m.p. 129—130°, $[\alpha]_D$ +13·00°, is fractionated into the d-*H-tartrates* of *l*- and *d*-base, m.p. 156—157° and 115—116°, $[\alpha]_D$ +3·0° and +20·70°, respectively, which give d- and l-trans-2-*methylamino*cyclo*heptanol*, b.p. 118—119°/16 mm., $[\alpha]_D$ ±22·64°.

The low rotatory powers of the above bases compared with those of the corresponding 5- and 6-membered ring compounds may be due to the influence of the C_7 ring on the spatial relationship of the OH and NH_2. A. C.

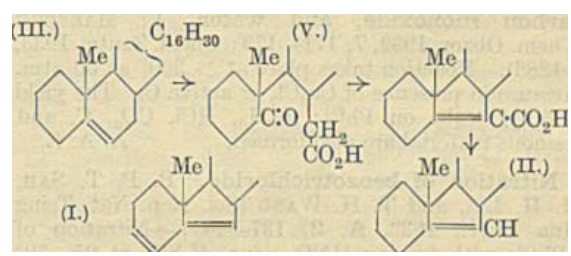
Preparation and resolution of aminocyclooctanols. M. Godchot, M. Mousseron, and R. Granger (Compt. rend., 1933, **196**, 2011—2013).—Prolonged heating of *cyclo*octene oxide (I) with NH_3 in H_2O–EtOH under pressure at 150—155° affords r-2-*amino*cyclo*octanol*, m.p. 77—78°, b.p. 132—133°/16 mm. (*hydrochloride*, m.p. 107—108°). The d-*H tartrate*, m.p. 195—196°, $[\alpha]_D$ +13·9°, is resolved into d-, m.p. 159—160°, $[\alpha]_D$ +22·85°, and l-2-*amino*cyclo*octanol* d-*H tartrates*, m.p. 205—206°, $[\alpha]_D$ +5·55°. These yield d- and l-2-*amino*cyclo*octanols*, m.p. 93—94°, $[\alpha]_D$ ±12·85°, respectively. r-2-*Methylamino*cyclo*octanol*, m.p. 25°, b.p. 123—124° [from (I) and NH_2Me] (*hydrochloride*), affords d-, m.p. 119—120°, $[\alpha]_D$ +27·6°, and l-2-*methylamino*cyclo*octanol* d-*H tartrates*, m.p. 160—161°, $[\alpha]_D$ +3·65°, which yield d- and l-2-*methylamino*cyclo*octanols*, b.p. 121—122°/16 mm., $[\alpha]_D$ ±19·9°, respectively. A. C.

Dehydrogenation of cholesterol. O. Diels (Ber., 1933, **66**, [*B*], 1122—1127).—The identity of the hydrocarbon obtained by dehydrogenation of cholesterol and cholic acid with chrysene is confirmed. Reply is made to Ruzicka *et al.* (this vol., 820) and Cook and Hewett (*ibid.*, 710). H. W.

Conversion of sterols into aromatic compounds. A. Windaus (Nachr. Ges. Wiss. Gottingen, Math.-Phys. Kl., 1932, 408—417; Chem. Zentr., 1933, i, 1296—1297).—The constitutions of Diels' hydrocarbons are discussed. A. A. E.

Dehydrogenation of cholesterol. E. Bergmann (Chem. and Ind., 1933, 681).—The identity of Cook's hydrocarbon, $C_{17}H_{14}$ (cf. this vol., 710), with that of Diels is questioned. F. R. S.

Degradation products of cholesterol. H. Lettré (Z. physiol. Chem., 1933, **218**, 67—73).—The dibromide of the doubly unsaturated hydrocarbon (I), m.p. 76°, of Windaus and Resau (A., 1915, i, 678) is $C_{26}H_{42}Br_2$. (I) is therefore $C_{26}H_{42}$ and the singly unsaturated hydrocarbon (II), m.p. 67° (A., 1914, i, 682), is $C_{26}H_{44}$. The non-cryst. acid oxidation products of cholestene (III) yield a cryst. *Me* ester (IV), $C_{28}H_{48}O_3$, m.p. 102—103°, $[\alpha]^{20}$ +103·8° in $CHCl_3$, which gave no typical :CO derivative. Treatment of (IV) with AcOH and conc. HCl or distillation of the free acid (V) gives (II). Distillation in vac. of the acid products obtained by the action of CrO_3 on cholesteryl chloride affords (I). The reactions are formulated :



The ultra-violet spectrum shows that the double linkings in (I) are probably conjugated. J. H. B.

Number of members in ring B of cholesterol. O. Stange (Z. physiol. Chem., 1933, **218**, 74—76).—Thermal decomp. of the Ba salt of the acid $C_{27}H_{46}O_4$, obtained from cholestan-6(or 7)-one, affords a *ketone*, $C_{27}H_{44}O$, m.p. 93°, $[\alpha]^{20}$ +35·7° in $CHCl_3$ (*oxime*, m.p. 186°), thereby proving that ring B is six-membered. J. H. B.

Cholestanols. G. Vavon and (Mlle.) B. Jakubowicz (Bull. Soc. chim., 1933, [iv], **53**, 581—588).—The prep. of β-cholestanol (I) [*benzoate*, m.p. 135° (clears at 155°), $[\alpha]_{5780}$ +19·3° (this and other $[\alpha]$ in $CHCl_3$); iso*valerate*, m.p. 110—111°, $[\alpha]_{5780}$ +14·7°] and β-cholestanone (II) is modified. Hydrogenation (very active Pt-black) of (II) in Bu_2O–HCl gives mostly ε-cholestanol (III), $[\alpha]_{5780}$ +25° (*benzoate*, m.p. 102—103°, $[\alpha]_{5780}$ +24°; iso*valerate*, m.p. 79—80°, $[\alpha]_{5780}$ +26°). Esterification and hydrolysis of its esters are more rapid, dehydration and oxidation by CrO_3 are slower, for (I) than for (III), whence it is concluded that the OH group and *cyclo*pentane ring

are in *trans*- and *cis*-positions in (I) and (III), respectively. R. S. C.

Nomenclature of the œstrin group. N. K. Adam, J. F. Danelli, E. C. Dodds, H. King, G. F. Marrian, A. S. Parkes, and O. Rosenheim (Nature, 1933, **132**, 205—206).—It is suggested that the parent saturated hydrocarbon of the œstrin group, $C_{18}H_{20}$, containing the sterol skeleton with one Me but without the side-chain, be termed "œstrane." Systematic names for the principal compounds of this group are tabulated on this basis and with the same numbering as in Rosenheim and King's formula for the sterols. L. S. T.

Identification of β-phenylethyl alcohol as oxalate. L. Palfray, S. Sabetay, and D. Sontag (Ann. Chim. Analyt., 1933, [ii], **15**, 338—339).—The oxalate, m.p. 51—51·5°, of $CH_2Ph{\cdot}CH_2{\cdot}OH$ (I) is formed by boiling (I) for 1—2 min. with anhyd. $H_2C_2O_4$ and crystallising from 60% EtOH. E. C. S.

Law of periodicity. VIII. Theory of coloured inorganic and organic compounds. P. Petrenko-Kritschenko (Ber., 1933, **66**, [*B*], 1049—1051).—The dependence of intensity of colour of inorg. compounds on valency, accumulation of similar and dissimilar groups, mol. wt., and temp. can be represented by graphs which in some cases can be united to graphs with inflexions apparently representing a portion of the periodic curve. The formulation of aminotriphenylmethyl salts is discussed. H. W.

Synthesis of benzoic acid from chlorobenzene, carbon monoxide, and water. V. Marecek (Chem. Obzor, 1932, **7**, 171—173; Chem. Zentr., 1933, i, 1286).—Reaction takes place at > 300° at 50 atm. pressure in presence of Cu_2Cl_2 or active C. The yield is 3·9%, calc. on PhCl; C_6H_6, HCl, CO_2, C, and resinous material are also formed. A. A. E.

Nitration of benzotrichloride. P. P. T. Sah, H. H. Lei, and T. H. Wang (Sci. Rep. Nat. Tsing Hua Univ., 1933, **A**, **2**, 137—141).—Nitration of $CPhCl_3$ with fuming HNO_3–conc. H_2SO_4 at 25—30° gives an 85% yield of m-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, 3 : 5-dinitrobenzoic acid being obtained with excess of HNO_3 at 185°. J. W. B.

New class of "free" radicals. A. Schonberg and E. Rupp (Naturwiss., 1933, **21**, 561).—Solutions of $(PhS{\cdot})_2$ and $(\alpha\text{-}C_{10}H_7{\cdot}CS{\cdot}S{\cdot})_2$ in inert solvents do not obey Beer's law and are thermochromic. They contain "thiyl" radicals, R·S·, and react with heavy metals, CPh_3, and aliphatic diazo-compounds. Diphenylene disulphide solutions obey Beer's law, since dissociation entails no increase in no. of mols. R. K. C.

2 : 5-Dibromo-*p*-toluic acid. A. Marzin (J. pr. Chem., 1933, [ii], **138**, 103—106).—The 5-Br atom in 2 : 5-dibromo-*p*-toluic acid (I) is readily replaced. With NaOH–MeOH in presence of Cu, 2-*bromo*-5-*methoxy*-p-*toluic acid*, m.p. 130—133°, is formed, demethylated by HI to 2-*bromo*-5-*hydroxy*-p-*toluic acid*, m.p. 205—208°, and oxidised by alkaline $KMnO_4$ to 2-*bromo*-5-*methoxyterephthalic acid*, m.p. 265—268° [-5-*hydroxy-acid* (HI)]. The Na salt of 2 : 5-dibromoterephthalic acid, prepared from (I), is converted by hot aq. NaOAc in presence of Cu into 2 : 5-dihydroxyterephthalic acid, m.p. > 300°. H. A. P.

Cleavage of carbonyl compounds by alkalis. X. Trihalogenomethylketonic acids. B. A. Bull and R. C. Fuson (J. Amer. Chem. Soc., 1933, **55**, 3424—3428; cf. this vol., 956).—4-Carbomethoxy-2 : 6-dimethylbenzoic acid and $SOCl_2$ give the *acid chloride*, b.p. 147—150°/8 mm., which with ZnMeI gives 4-*acetyl*-3 : 5-*dimethylbenzoic acid* (I), m.p. 160—161°, yielding with cold 10% NaOCl and NaOBr solutions 4-*trichloro*-, m.p. 165—166°, and 4-*tribromoacetyl*-3 : 5-*dimethylbenzoic acid*, m.p. 161—162°, both fairly stable to 5% NaOH at 0°, but less stable at room temp. Solubility, therefore, plays little part in determining the stability of these compounds. 2 : 6-Dimethylterephthalic acid and PCl_5–$POCl_3$ give the *di-acid chloride*, b.p. 124—138°/20 mm., giving with ZnMeI a poor yield of 2 : 5-*diacetyl*-m-*xylene*, m.p. 61·5—62° (4-*phenylhydrazone*, m.p. 154—156°), whence by NaOBr impure (I) was obtained. R. S. C.

Reactions of olefinic compounds. III. Orienting influence of Ph group. E. H. Farmer and C. G. B. Hose (J.C.S., 1933, 962—968).—The direction of addition of HOCl to $CHPh{:}CH{\cdot}CO_2H$ (I), $CHPh{:}CMe{\cdot}CO_2H$ (II), and δ-phenyl-Δ^{α}-, -Δ^{β}- (III), and -Δ^{γ}- (IV) -pentenoic acids is studied. The influence of the Ph group, contrary to that of phenylalkyl, is overwhelmingly in favour of the orientation ····OH·CPh—CCl····, and is referred to its absorption of the negative charge normally expected in the β-position. The Δ^{α}-acids [(I) and (II)] react much less readily than do the Δ^{β}- or Δ^{γ}-acids. With HOCl (I) in Et_2O gives exclusively α-chloro-β-hydroxy-β-phenylpropionic acid, the constitution of which is proved by its reduction with Na–Hg in neutral (H_2CO_3) solution to β-hydroxy-β-phenylpropionic acid [*Et* ester, b.p. 154—156°/13 mm. (synthesis by Andrievski's method improved)], and dehydration with Ac_2O at the b.p. to α-chlorocinnamic acid. Condensation of PhCHO with $CHMeBr{\cdot}CO_2Et$ and Zn in C_6H_6 gives *Et* β-*hydroxy*-β-*phenyl*-α-*methylpropionate*, b.p. 157—158°/11 mm., dehydrated by $SOCl_2$ and C_5H_5N to (II). This with HOCl gives α-*chloro*-β-*hydroxy*-β-*phenyl*-α-*methylpropionic acid*, m.p. 156° (approx. 60%), and β-*chloro*-α-*phenyl*-Δ^{α}-*propylene*, b.p. 118—123°/28 mm.; the former is reduced by Na–Hg to an oily acid which on oxidation gives BzOH.

δ-*Phenyl*-Δ^{α}-*pentenoic acid*, m.p. 103°, prepared from $CH_2Ph{\cdot}CH_2{\cdot}CHO$ (V) and $CH_2(CO_2H)_2$ in C_5H_5N (Δ^{α} structure proved by oxidation to $CH_2Ph{\cdot}CH_2{\cdot}CO_2H$ and $H_2C_2O_4$), gives with HOCl α-*chloro*-β-*hydroxy*-δ-*phenylvaleric acid*, reduced by Na–Hg in acidified aq. EtOH at 0° to β-hydroxy-δ-phenylvaleric acid, m.p. 130° (*Et* ester, b.p. 178—182°/12 mm.), synthesised for comparison from (V) and $CH_2Br{\cdot}CO_2Et$ by the Reformatsky reaction. (III) was obtained together with some (IV) by reduction of $CHPh{:}CH{\cdot}CH{:}CH_2{\cdot}CO_2H$ (cf. A., 1931, 233) and in poor yield from (II) and $CH_2(CO_2H)_2$ in presence of strong bases. With HOCl it gives β-*chloro*-γ-*hydroxy*-δ-*phenylvalerolactone*, liquid, and a small amount of (?) *isomeride*, m.p. 113°; the former on distillation/vac. loses all its Cl as HCl to give a liquid lactone oxidised by $KMnO_4$ to $H_2C_2O_4$

and a neutral substance and converted by KOH in aq. EtOH into *γ-hydroxy-δ-phenyl-Δ$^{\alpha}$-pentenoic acid*, m.p. 57°. Addition of HOCl to (III) (prep. improved) gives a cryst. *chlorohydroxy-δ-phenylvalerolactone* and a liquid *lactone*, b.p. 180—190°/6 mm., probably an isomeride. Both readily lost HCl on heating and gave BzOH and $(CH_2{\cdot}CO_2H)_2$, but no $CHPhCl{\cdot}CO_2H$ on oxidation with $KMnO_4$ or CrO_3 under varied conditions, hence are regarded as stereoisomeric γ-chloro-δ-hydroxy-δ-phenylvalerolactones. H. A. P.

Synthetic substances with œstrogenic activity O. Blum-Bergmann (Naturwiss., 1933, **21**, 578).—Definite but slight activity is shown by 1-hydroxy-1-allyl- and 2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, but 1 : 2-*dihydrophenanthryl*-4-*acetic acid*, m.p. 153—155°, and its Δ$^{\alpha}$-isomeride, 1 : 2 : 3 : 4-*tetrahydrophenanthryl*-4-*methylenecarboxylic acid*, m.p. 215—217°, are inactive. H. A. P.

Perceric salicylate. A. Fouchet (Bull. Soc. chim., 1933, [iv], **53**, 570—571).—The compound described as perceric salicylate, obtained by addition of H_2O to a dry mixture of Na_2CO_3, $Ce(NO_3)_4$, and Na salicylate, is shown to be a mixture of $Ce_2(CO_3)_3$ and decomp. products of salicylic acid. A. S. C. L.

Phenolic acids. IV. Benzyl salicylate and its derivatives. T. S. Ma, V. Hoo, and P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1933, **A**, **2**, 133—136).—CH_2Ph salicylate, b.p. 211°/20 mm. (p-*nitrobenzyl ether*, charring at 260°), is best prepared by addition of CH_2PhCl to Na salicylate in boiling EtOH. With fuming H_2SO_4–HNO_3 at 0° it gives a $(NO_2)_4$-derivative, m.p. 156—158°. J. W. B.

Hydrolysis of 2-chloro-, -ethoxy-, and -methoxy-5-nitrobenzonitriles. B. B. Dey and Y. G. Doraiswami (J. Indian Chem. Soc., 1933, **10**, 353—359).—2-Chloro-5-nitrobenzonitrile is hydrolysed by hot slightly diluted H_2SO_4 to the amide, which is further hydrolysed (conc. HCl) to 2-chloro-5-nitrobenzoic acid (*ethylamide*, m.p. 148°; *propylamide*, m.p. 142°; *diethylamide*, m.p. 72°; *ethylenediamide*, m.p. 310°). 5-*Nitro*-2-*methoxy*-, m.p. 212°, and -2-*ethoxy*-, m.p. 176°, *-benzamides* are obtained similarly from the nitriles and are hydrolysed further (conc. HCl) to the corresponding acids. All the above nitriles, amides, and acids are converted by aq. or EtOH–KOH into 5-nitrosalicylic acid. 2-*Chloro*-5-*nitrobenzoylcarbamide* has m.p. 216°. H. B.

Structure of α-benzoyl-α-bromo-esters. B. W. Howk and S. M. McElvain (J. Amer. Chem. Soc., 1933, **55**, 3372—3380).—Et α-bromo-α-benzoylpropionate, b.p. 144—145°/1 mm., and MgPhBr give PhBr (81%) and $CHMeBz{\cdot}CO_2Et$ (85%). Et α-bromo-α-benzoylacetate, however, gives C_6H_6 (20%), PhBr (56%), Ph_2 (11·3%), $CH_2Bz{\cdot}CO_2Et$ (56·5%), and $(\cdot CHBz{\cdot}CO_2Et)_2$ (10·8%), whilst 14·5% was unchanged. Study of the rate of reaction of these Br-esters with KI and N_2H_4 indicates partial reaction which is of a complicated order. It is concluded that the esters exist partly in the $\cdot C(OBr){:}C$ form. R. S. C.

Syntheses of cyclic compounds. X. Thermal decomposition of substituted glutaric acids. I. αβ-Dimethylglutaric, *cyclo*pentane- and *cyclo*hexane-1 : 1-diacetic acid; mechanism of reaction. A. I. Vogel (J.C.S., 1933, 1028—1031).—The principal products at 290—>370° are unsaturated ketone and hydrocarbon (I) according to the scheme (cf. A., 1929, 700) $>C{:}CH{\cdot}COMe+CO_2 \leftarrow$ $>C(CH_2{\cdot}CO_2H)_2 \longrightarrow >C{:}CH_2+AcOH+CO_2$, except in the case of ββ-dimethylglutaric acid, which is unchanged. The yield of (I) from *cyclo*hexane-1 : 1-diacetic acid (33%) is higher than from the *cyclo*pentane acid in agreement with the smaller tendency to ring formation. In presence of Fe and a little $Ba(OH)_2$ (*loc. cit.*) both products were formed in every case, although in very poor yield from the glutaric acid, which also gave some *iso*phorone. H. A. P.

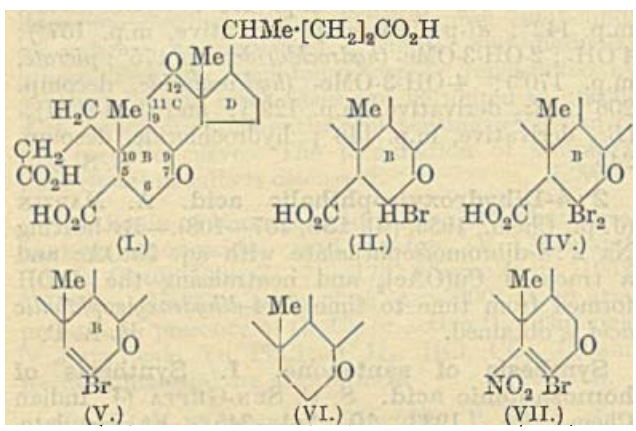
Reduction of hydroxymandelonitriles. Synthesis of tyramine. J. S. Buck (J. Amer. Chem. Soc., 1933, **55**, 3388—3390).—The following substituted *mandelonitriles* were prepared: 3-, m.p. 110°, and 4-*OH*-, m.p. 98°, 2-*OH*-3-*OMe*-, m.p. 85°, 4-*OH*-3-*OMe*-, m.p. 83°, and 3 : 4-$(OH)_2$-, m.p. 95°. When hydrogenated (PtO_2) these give 31—77% yields of the following substituted phenylethylamines: 3-OH- (*picrate*, m.p. 170°; *hydrochloride*, m.p. 142°; *di*-p-*nitrobenzoyl* derivative, m.p. 157°); 4-OH-; 2-OH-3-OMe- (*hydrochloride*, m.p. 175°; *picrate*, m.p. 170°); 4-OH-3-OMe- (*hydrochloride*, decomp. 206°; Bz_2 derivative, m.p. 129°); and 3 : 4-$(OH)_2$- (Bz_3 derivative, m.p. 140°; hydrochloride, decomp. 245°). R. S. C.

2 : 4-Dihydroxy*iso*phthalic acid. A. Marzin (J. pr. Chem., 1933, [ii], **138**, 107—108).—By heating Na 2 : 4-dibromo*iso*phthalate with aq. NaOAc and a trace of $Cu(OAc)_2$ and neutralising the AcOH formed from time to time 2 : 4-*dihydroxy*i*sophthalic acid* is obtained. H. A. P.

Synthesis of santenone. I. Synthesis of homosantenic acid. S. C. Sen-Gupta (J. Indian Chem. Soc., 1933, **10**, 341—345).—Et lævulate, $CHBrMe{\cdot}CO_2Et$, and Zn in C_6H_6 give the *lactone*, b.p. 148—149°/8 mm., of α-Et H β-hydroxy-αβ-dimethyladipate, which when heated with KCN at 200—220°, then hydrolysed (conc. HCl), and subsequently esterified (EtOH vapour; conc. H_2SO_4) affords *Et γ-methylpentane-αγδ-tricarboxylate*, b.p. 147—152°/5 mm. This is converted by Na in C_6H_6 into *Et* 2 : 3-*dimethyl*cyclo*pentanone*-3 : 5-*dicarboxylate*, b.p. 145—150°/5 mm., hydrolysed (dil. HCl) to 2 : 3-*dimethyl*cyclo*pentanone*-3-*carboxylic acid*, b.p. 150—153°/5 mm. (*semicarbazone*, m.p. 208°), the *Et* ester, b.p. 105—106°/5 mm. (*semicarbazone*, m.p. 191°), of which with $CH_2Br{\cdot}CO_2Et$ and Zn in C_6H_6 gives (after complete dehydration with $POCl_3$ in C_6H_6) *Et dehydrohomosantenate* (*Et* 3-*carbethoxy*-2 : 3-*dimethyl*-cyclo*pentylideneacetate*), b.p. 125—130°/4 mm. This is reduced (H_2, PtO_2, Et_2O) to *Et homosantenate* (*Et* 3-*carbethoxy*-2 : 3-*dimethyl*cyclo*pentylacetate*), b.p. 130—135°/5 mm. (free *acid*, m.p. 170°). H. B.

Constitution of bile acids. LI. Bromination of bilianic acid and of some other keto-acids. H. Wieland and M. A. Kennelly (Z. physiol. Chem., 1933, **219**, 138—147; cf. this vol., 609).—Bromination of bilianic acid (I) in AcOH gives *bromobilianic acid* (II), m.p. 180—190° (decomp.) (+AcOH, froths at

125—127°), which, on oxidation with HNO_3, affords biloidanic acid (III). At 65° bromination of (I) yields *dibromobilianic acid* (IV), m.p. 208—209° (decomp.) (*Me* ester, m.p. 133°). When warmed with C_5H_5N, (IV) gives an unsaturated *Br-acid* (V), $C_{23}H_{31}O_6Br$, m.p. 213°, which is very resistant to hydrolysis. Catalytic hydrogenation eliminates Br from (V), affording a saturated *diketocarboxylic acid* (VI), $C_{23}H_{34}O_6$, m.p. 221—222° (*Me* ester, m.p. 109—110), readily oxidised to (III). Reduction of (V) with Zn dust and acid gives a *ketodicarboxylic acid*, $C_{23}H_{36}O_5$, m.p. 198—200°. Oxidation of (V) directly with fuming HNO_3 yields the unsaturated *bromonitrodiketodicarboxylic acid* (VII), $C_{23}H_{30}O_8NBr$, m.p. 215°. Bromination of (I) sometimes yields a mol. *compound* (VIII), m.p. 180°, of a *mono-* (IX) and *di-bromobilianic acid*. Hydrolysis of (IX) with 0·1*N*-KOH gives a *hydroxyketodicarboxylic acid*, $C_{23}H_{34}O_7$, m.p. 222—223° (*Me* ester, m.p. 105°). The C_5H_5N reaction with (VIII) gives a resinous product, which, when heated with *N*-KOH, affords an unsaturated *acid*, $C_{23}H_{30}O_6$, m.p. 151—152°. The reactions are formulated :



Bromination of 3 : 6-diketo*allo*cholanic acid gave the *Br-*, m.p. 164—165°, *Br*$_2$-, m.p. 194—195°, and *Br*$_3$-, m.p. 219—220°, *-acids*. 3-Hydroxy-6-ketocholanic acid (*Me* ester, m.p. 140—142°) gave the *Br-*, m.p. 193° (*Me* ester, m.p. 108—109°), and *Br*$_2$-, m.p. 175°, *-acids*. 3-Hydroxy-6-keto*allo*cholanic acid afforded the *Br-acid*, m.p. 162°. J. H. B.

Lichen substances. XXVIII. Occurrence of stictic acid in various lichens. Y. Asahina, M. Yanagita, T. Hirakata, and M. Ida (Ber., 1933, **66**, [*B*], 1080—1086).—Stictic acid (I) is converted by Ac_2O containing a drop of H_2SO_4 into a *tetra-acetate*, m.p. 221—222°, in which 2 Ac are in the form of aldehyde diacetate. (I) and boiling Ac_2O afford the *diacetate* (II), $C_{19}H_{12}O_9Ac_2$, m.p. 235—236°, probably identical with Zopf's compound from *ψ*-psoromic acid. Since (II) gives an *oxime*, m.p. 213° (decomp.), the CHO group is intact. (I) is hydrolysed by conc. NaOH to MeOH and atranol. Catalytic reduction of (I) (Pd–C) leads to a *compound* (III), $C_{19}H_{16}O_8$, m.p. 265° (decomp.), transformed by CH_2N_2 into the substance $C_{18}H_{11}O_5(OMe)_3$, m.p. 165°, identical with the *Me*$_3$ *ether* of the first reduction product of salazic acid (III). Reduction of (III) with Zn dust and AcOH gives the *compound* $C_{19}H_{16}O_7$, m.p. 263° (decomp.), transformed by CH_2N_2 into a substance, m.p. 283°, identical with the Me_2 ether of the second reduction product of (IV). Extraction of *Stereocaulon nabewariense*, A. Zahrbruckner, with Et_2O and $COMe_2$ yields atronorin (V) and (I). (V), (I), and lobaric acid are obtained from *Stereocaulon japonicum*, Th. Fr.; *Parmelia pertusa* (Schrank), Schaier, yields (V) and (I). The probable identity of (I) with physodalic, scopuloric, and *ψ*-psoromic acids is indicated. H. W.

Action of phosphoryl chloride on aldehydes. M. Backes (Compt. rend., 1933, **196**, 1674—1675; cf. this vol., 376).—Equimol. mixtures of PhCHO (I) and MeCHO afford cinnamaldehyde when treated with $POCl_3$ at 30—35°. (I) and heptaldehyde give α-amylcinnamaldehyde. In the absence of H attached to the C adjacent to the ·CHO group, chlorination occurs. Thus, (I) alone gives BzCl and $CHPhCl_2$, and CH_2O gives $(CH_2Cl)_2O$. SO_2Cl may be used instead of $POCl_3$. A. C.

Isomerism of the oximes. XXXVIII. Constitution of the acetyl derivatives of α- and β-aldoximes. O. L. Brady and H. J. Grayson (J.C.S., 1933, 1037—1038).—Comparison of absorption spectra of the α- and β-Ac derivatives of anisaldoxime and *p*-nitrobenzaldoxime with those of the α- and β-*O*-Me ethers and of the *N*-Me ether of the oximes indicates that the two Ac derivatives are similarly constituted and have the Ac attached to O. F. R. S.

Anishydroxamyl chloride. C. R. Kinney, E. W. Smith, B. L. Woolley, and A. R. Willey (J. Amer. Chem. Soc., 1933, **55**, 3418—3424).—α- or β-Anisaldoxime (I), best with Cl_2 (1 mol.) in cold dry Et_2O, gives anishydroxamyl chloride (II), m.p. 88—89°, in 45% yield, which, when kept, gives dianisenylazoxime oxide, m.p. 179°, and anisoylanishydroxamic acid. With hot 6*N*-HCl or NaOH (II) gives anisic acid, with $AgNO_3$ dianisylfurazan oxide (III), with AgOBz in Et_2O anishydroxamic acid benzoate and (III), and with NH_3–Et_2O anisohydroxamamide. With more Cl_2 (I) gives 3-*chloro-*, m.p. 106·5°, and 3 : 5-*dichloro-*, cryst., *-4-methoxybenzhydroxamyl chloride*, hydrolysed to the corresponding chloroanisic acids and affording the *di*-3-*Cl-* and *di*-3 : 5-*Cl*$_2$-derivatives of (III), m.p. 165° and 146°, respectively. (I) and NOCl in Et_2O give an intermediate *compound*, m.p. about 50°, readily passing into (II). Rheinboldt's compound, m.p. 120° (A., 1927, 245), was not obtained; it was probably a mixture of (II) and anisic acid. R. S. C.

Behaviour of vanillin substitution products : (*a*) Perkin reaction ; (*b*) preparation of substituted vanillic acids. L. C. Raiford, V. S. Webster, and D. J. Potter (Proc. Iowa Acad. Sci., 1931, **38**. 171).—The Cl and Br substitution products of vanillin previously described (A., 1931, 90) have been converted by the Perkin reaction into the corresponding cinnamic acids. The latter with alkaline $KMnO_4$ afford the original vanillin derivatives; the vanillic acids were obtained by hydrolysis of the nitriles prepared from the oximes. Ch. Abs.

Jute-lignin. II. Potassium hydroxide fusion of lignin. P. B. Sarkar (J. Indian Chem. Soc., 1933,

10, 263—270).—Fusion of jute-lignin (I) with KOH at 220—230° in air gives lignic acid (II) [24·6% of (I) used], $PrCO_2H$ (9·13%), $H_2C_2O_4$ (18·72%), protocatechuic acid (III) (12·1%), and o-$C_6H_4(OH)_2$ (IV) (3·5%); at 280—300°, $H_2C_2O_4$ (20·3%) is the sole product. (II) is the precursor of (III) and (IV). The production of $PrCO_2H$ and (III) shows that Cross and Bevan's formula (J.C.S., 1882, **41**, 90) for (I) is untenable. Delignified jute-fibre does not yield $PrCO_2H$ or aromatic compounds; the latter must arise from aromatic groupings in the mol. of (I). Synthetic lignin, prepared from delignified jute by Hawley and Harris' method (B., 1932, 836), does not give any of the above products. H. B.

Lignin. VIII. Oxidation of alkali-lignin. M. Phillips and M. J. Goss (J. Amer. Chem. Soc., 1933, **55**, 3466—3470; cf. A., 1932, 1032).—Alkali-lignin (I) from corn cobs with Me_2SO_4–NaOH gives a product (OMe, 27·2%) (II), which with hot 5N-HNO_3 gives an amorphous NO_2-compound [oxidised by $KMnO_4$ to anisic acid (III)], (III), and $H_2C_2O_4$. The ethylation product (similarly prepared) gives p-OEt·C_6H_4·CO_2H. (I) with O_3 gives $H_2C_2O_4$, but (II) gives also (III). (I), therefore, contains p-HO·C_6H_4·C groups. R. S. C.

Lignin and its derivatives. II. L. Lemmel (Anal. Fís. Quím., 1933, **31**, 50—52; cf. A., 1932, 1296).—*Orcinol-lignin*, m.p. 250—257° after darkening at 180° and softening at 225°, is prepared by fusion of pine sawdust with orcinol. The *Ac* derivative is formulated: $\{(C_8H_7)(OMe)(OAc)[C_6H_2Me(OAc)_2]\}_x$. R. K. C.

Hydroaromatic compounds of the *cyclo*octane series. M. Godchot and (Mlle.) Cauquil (Chim. et Ind., 1933, Spec. no., 1019—1023; cf. A., 1930, 596).—2-Methyl*cyclo*octanone (I), b.p. 74—75°/7 mm. (*oxime*, b.p. 115°/7 mm., and its *phenylurethane*, m.p. 117—118°), is oxidised by dil. $KMnO_4$ to *η-keto-n-nonoic acid* (*semicarbazone*, m.p. 116—117°). Treatment of (I) with $NaNH_2$ and MeI leads to 2 : 2-*dimethyl*cyclo*octanone* (II), b.p. 88—90°/12 mm. (which does not react with NH_2OH or NH_2·CO·NH·NH_2), containing a little of the 2 : 8-isomeride (III). *Me* 1-*hydroxy*cyclo*heptyl*-1-*carboxylate*, b.p. 117—118°/11 mm., m.p. 24°, and MgMeI in Et_2O yield α-cyclo*heptyl*-β-*methylpropane*-αβ-*diol*, b.p. 128—130°/7 mm., m.p. 45°, dehydrated by aq. $H_2C_2O_4$ at 135—140° or conc. H_2SO_4 at 0° to the ethylenic *hydrocarbon* $C_{10}H_{16}$, b.p. 68°/7 mm., 188—190°/760 mm., containing small amounts of (II) and (III). Reduction of (I) (Pt-black–AcOH) gives exclusively 2-*methyl*cyclo*octanol* A, b.p. 100—101°/16 mm., 201—202°/760 mm. (*H phthalate*, m.p. 104°; *phenylurethane*, m.p. 137°), whereas treatment with Na and EtOH leads almost exclusively to 2-*methyl*cyclo*octanol* B, b.p. 103—104°/16 mm. (*H phthalate*, m.p. 119—120°; *phenylurethane*, m.p. 154°). (II) with Na and EtOH affords 2 : 2-*dimethyl*cyclo*octanol*, b.p. 91—92°/6 mm., 219—220° (corr.)/754 mm. (*H phthalate*, m.p. 110—113°; *phenylurethane*, m.p. 147°). *cyclo*Octanol is readily transformed into *cyclo*octyl bromide and thence through the Mg derivative into cyclo*octanecarboxylic acid*, b.p. 150°/19 mm. (*chloride*, b.p. 110°/19 mm.; *amide*, m.p. 191°). H. W.

Behaviour of keten in the Friedel–Crafts reaction. K. Packendorff, N. D. Zelinski, and L. Leder-Packendorff (Ber., 1933, **66**, [*B*], 1069—1073).—Keten is passed into a mixture of C_6H_6 and $AlCl_3$, whereby HCl is freely evolved. The crude ketones are hydrogenated (Pt–C+Pd) giving PhEt and (?) 2-ketotetrahydronaphthalene [*semicarbazone*, m.p. 212°; oxime, m.p. 74° (lit. 77·5—78°)]. It appears probable that 1 : 3-diketotetrahydronaphthalene is present in the mixture of ketones. Its formation is not due to intermediate production of *cyclo*butanedione, which ultimately yields only PhEt when similarly treated with C_6H_6 and $AlCl_3$. PhMe similarly affords p-ethyltoluene and a semicarbazone, m.p. 219°. H. W.

Side-chain chlorination of *pp'*-dimethylbenzophenone. I. 4 : 4'-Dichlorodimethylbenzophenone. E. Connerade (Bull. Soc. chim. Belg., 1933, **42**, 311—329).—4 : 4'-Dimethylbenzophenone (improved separation from the 4 : 2'-compound described) with Cl_2 (slightly > 2 mols.) at 130—135° affords the 4 : 4'-*di*(*chloromethyl*) compound (I), m.p. 110·5°, mixtures of Cl_2- and Cl_3-, and of Cl_3- and Cl_4-derivatives being removed by C_6H_6–ligroin (5 : 20). With KOH in aq. MeOH at 65° (I) affords the 4 : 4'-*di*(*hydroxymethyl*) derivative (II), m.p. 51°, b.p. 197—203°/Hg vac. (oxime, not pure), readily polymerised by light to a resin which affords (p-CO_2H·C_6H_4·)$_2$CO by oxidation with CrO_3, the corresponding Ac_2 derivative, m.p. 42—48°, Me_2 [contaminated with (II)] and Et_2, b.p. 267—270°/high vac., *ether* being obtained from AgOAc–AcOH, and NaOR–ROH, respectively, and (I). Oxidation of (II) with 65% HNO_3 in 60% AcOH gives *benzophenone*-4 : 4'-*dialdehyde*, partial fusion at 180° to a plastic which liquefies at 265° [*diphenylhydrazone*, m.p. 234—235° (decomp.); *dioxime*, partial fusion at 150—152°, liquid at 190°]. With 3% NH_3 in EtOH at 80—82° (I) gives a *polymeride* NH_2·CH_2·R·CH_2·[NH·CH_2·R·CH_2]$_n$·NH·CH_2·R·CH_2·NH_2 [R=C_6H_4·CO·C_6H_4; n=10(?)], similar treatment with $NHEt_2$ giving 4 : 4'-*tetraethyldiaminodimethylbenzophenone*. Reduction of (II) in 90% EtOH with Na–Hg gives a theoretical yield of *di*-ω-*hydroxy*-p-*tolylcarbinol* (Ac_3 and Cl_3-derivatives not characterised). The reactions of these compounds are discussed on an electronic basis. J. W. B.

2 : 4-Dinitrobenzophenone. I. Tanasescu and (Mme.) M. Macarovici (Bull. Soc. chim., 1933, [iv], **53**, 597—599).—2 : 4-Dinitrobenzyl chloride, $AlCl_3$, and C_6H_6 give a viscous mass (*A*), whence a substance (*B*), m.p. 190°, is obtained. (*A*), but not (*B*), with CrO_3–AcOH gives 2 : 4-dinitrobenzophenone, m.p. 167° R. S. C.

Substitution in compounds containing two or more phenyl groups. IV. Nitration of diphenyl derivatives containing *m*-directing substituents. W. S. M. Grieve and D. H. Hey (J.C.S., 1933, 968—972).—Mononitration occurs when a negatively 2- or 4-substituted Ph_2 derivative is added to well-stirred HNO_3 (d 1·46) at −5° to 0°; under other conditions either dinitration or no reaction occurs. It is exclusively heteronuclear. The reaction is applied to the prep. of 4'-, m.p. 152—153°, and 2'-*nitro*-4-*diphenylyl Me ketone*, m.p. 110°, 4'-, m.p.

127°, and 2′-*nitrodiphenyl-4-aldehyde*, m.p. 101°, and 4′- (*Et* ester, m.p. 112°) and 2′-nitrodiphenyl-4-carboxylic acid. Under the same conditions quant. mononitration of 2- and 4-NO_2·C_6H_4Ph and dinitration of Ph_2 occur. The nitro-4-diphenylyl Me ketones are also obtained (the 4′-compound in 55% yield) from the NO_2·C_6H_4Ph, AcCl, and $AlCl_3$. 2 : 4′-*Dinitro-4-diphenylyl Me ketone* has m.p. 155—146°. H. A. P.

Organic molecular compounds of titanium tetrachloride. F. Evard (Compt. rend., 1933, **196**, 2007—2009).—Treatment of $TiCl_4$ with an excess of an aromatic ketone (I) in anhyd. C_6H_6 affords halochromic compounds, the colour deepening as the no. of double linkings in (I) increases. The *compounds* $TiCl_4$,$COPh_2$, and $TiCl_4$,$(COPh·CH:CHPh)_2$ are described. A. C.

Isomerism of halochromic compounds. I. P. Pfeiffer and H. Kleu (Ber., 1933, **66**, [*B*], 1058—1063).—Dissolution of Ph *p*-dimethylaminostyryl ketone in 70% $HClO_4$ yields the colourless *salt* (I), $HClO_4$,NMe_2·C_6H_4·CH:CH·COPh, m.p. 165° after becoming brown at 140° and softening at 155°, slowly hydrolysed by H_2O. Dissolution of (I) in molten $CH_2Cl·CO_2H$ (III) followed by rapid cooling and removal of (III) with anhyd. Et_2O leads to the pinkish-violet *salt* (II), NMe·C_6H_4·CH:CH·CPh:O·$HClO_4$, immediately hydrolysed by H_2O. Similarly, *p*-dimethylaminostyryl Me ketone, m.p. 135·5°, gives a colourless *perchlorate*, slowly hydrolysed by cold H_2O, and a blue *perchlorate*, rapidly hydrolysed. Ph styryl ketone affords a canary-yellow *perchlorate*. H. W.

Preparation of azines by means of hydrazine hydrochloride. N. Schapiro (Ber., 1933, **66**, [*B*], 1103—1107).—Fluorenone and N_2H_4,HCl (I) in hot EtOH afford fluorenoneketazine, m.p. 266°. *p*-Tolilketazine (II), m.p. 248—249° after softening at 247°, and 4 : 4′-*diphenoxybenzilketazine*, m.p. 228—229° after softening at 226°, are similarly prepared, whereas *p*-toluoin affords (II) and a small amount of (?) tetra-*p*-tolylpyrazine, m.p. > 250°. Di-2-tetrahydronaphthyl diketone, anthraquinone, carvone, camphor, and lævulic acid do not react with (I). Similarly are prepared aldazines of PhCHO, m.p. 92—93°, *o*-OH·C_6H_4·CHO, m.p. 214—215°, *o*-OMe·C_6H_4·CHO, m.p. 139·5—140°, *p*-OMe·C_6H_4·CHO, m.p. 179—179·5° after softening at 168°, *piperonal*, m.p. 202—203° (decomp.), vanillin, m.p. 231—232°, *ψ*-cumaldehyde, m.p. 168°, *p*-NO_2·C_6H_4·CHO, m.p. 307° (partial decomp.), *o*-NO_2·C_6H_4·CHO, m.p. 204·5° after softening at 203·5°, m-NO_2·C_6H_4·CHO, m.p. 193—194° after softening at 193°, and 2-*methoxynaphthaldehyde*, m.p. 265—266° (decomp.) after softening. Furfuraldehyde yields a dark brown powder, apparently neither ketazine nor hydrazone. Citral does not react. CCl_3·$CH(OH)_2$ at 20° yields a brownish-red *substance*, m.p. ≯ 300° after changing at 230°. H. W.

Phenanthrene series. V. 9-Acetylphenanthrene. Reduction products of 2-, 3-, and 9-acetylphenanthrenes. VI. ω-Aminoacetylphenanthrenes and aminomethylphenanthrylcarbinols. E. Mosettig and J. van de Kamp (J. Amer. Chem. Soc., 1933, **55**, 3442—3448, 3448—3452; cf. this vol., 951).—V. Me phenanthrene-9-carboxylate, much EtOAc, and Na at 170° give an ester, which, when hydrolysed, affords 9-*acetylphenanthrene* (I), m.p. 74—74·5° (*semicarbazone*, m.p. 199—201°; *oxime*, m.p. 154—154·5°; *picrate*, m.p. 107—108°), giving with CrO_3 phenanthraquinone and with NaOCl phenanthrene-9-carboxylic acid. 2-, 3-, and 9-Acetylphenanthrene with $(NH_4)_2S$ gives 2- m.p. 181—183° (*Me* ester, m.p. 78—78·5°), 3-, m.p. 175—177° [*Me* ester, an oil (*picrate*, m.p. 103·5—104°), and 9-*phenanthrylacetic acid*, m.p. 219—221° (*Me* ester, m.p. 75—75·5°); they are hydrogenated very slowly in presence of PtO_2, and much better in presence of Cu–Cr–BaO at 100° or 140°/1200—1900 lb., to α-2-, m.p. 135—135·5°, α-3-, m.p. 83—83·5° (*picrate*, m.p. 118—119°; also a *by-product*, m.p. 109—109·5°), and α-9-*phenanthrylethyl alcohol*, m.p. 135—136°, and at 150° to 2-, m.p. 67—68° (*picrate*, m.p. 95—96°), 3-, an oil (*picrate*, m.p. 121·5—122°), and 9-*ethylphenanthrene*, m.p. 62·5—63° (*picrate*, m.p. 123—124°), also obtained by Clemmensen reduction in 5—10% yield. The nature of Willgerodt's supposed (I) (A., 1911, i, 882) is not clear.

VI. The acetylphenanthrenes and Br–Et_2O at 0° afford 2-, m.p. 142·5—143°, 3-, m.p. 87—88° (*picrate*, m.p. 104·5—105·5°), and 9-ω-*bromoacetylphenanthrene*, m.p. 93—93·5° (*picrate*, m.p. 122—122·5°) (oxidised to the corresponding halogen-free acids), whence by the appropriate base the following substituted *acetylphenanthrenes* were prepared, the m.p. in parentheses being those of the *hydrochlorides* and *picrates*, respectively: (*a*) 2-ω-*dimethylamino-*, an oil (227—228°; 198—199°), (*b*) 2-ω-*diethylamino-*, an oil (—; 176·5—178°; *perchlorate*, m.p. 182—182·5°), (*c*) 2-ω-*piperidino-*, m.p. 94—95° (276—277°; 192—193°), (*d*) 3-ω-*dimethylamino-*, an oil (228—230°; 189—189·5°), (*e*) 3-ω-*diethylamino-*, an oil (231—232°; 181—182°), (*f*) 3-ω-*piperidino-*, an oil (259·5—261°; 189—190°), (*g*) 9-ω-*dimethylamino-*, an oil (199—201°; 189—190°), (*h*) 9-ω-*diethylamino-*, an oil (158—159°; 138—139°), and (*i*) 9-ω-*piperidino-*, an oil (250—251°; 150—151°). These give by hydrogenation (PtO_2) in EtOH the corresponding substituted β-*amino*-α-*phenanthrylethyl alcohols*, the m.p. in parentheses being those of the *hydrochlorides* and *picrates*, respectively: (*a*) m.p. 100—101° [222—223°; 235—236°; *benzoate*, m.p. 108·5—109° (*hydrochloride*, m.p. 244—245°)], (*b*) m.p. 75—76° (194—195°; 154—155°), (*c*) m.p. 126—127° (254·5—255·5°; 180·5—181·5°), (*d*) m.p. 76—76·5° (179·5—180·5°; 218—218·5°; *hydrochloride* of *benzoate*, m.p. 223—224°), (*e*) m.p. 59—60° (168—169°; 163—164°), (*f*) m.p. 108—109° (242—243°; 174—175°), (*g*) m.p. 93—94° (211—211·5; 210—211°; *hydrochloride* of *benzoate*, m.p. 228—229°), (*h*) m.p. 87—88° (—; 178·5—179·5°), and (*i*) m.p. 111·5—112° (216—216·5°; 196—196·5°). Phenanthrene and $CH_2Cl·COCl$ give a mixture of 2- and 3-ω-*chloroacetylphenanthrene*, m.p. 139—139·5° and 93·5—94°, respectively, identified by condensation with piperidine. R. S. C.

Alkyl*cyclo*pentanones. III. Synthesis of 3-methyl*cyclo*pentane*spirocyclo*hexane-3 : 5-dione. R. D. Desai (J. Indian Chem. Soc., 1933, **10**, 257—261).—Et 3-methyl*cyclo*pentan-1-ol-1-acetate (A.,

1932, 740) is dehydrated ($POCl_3$–C_6H_6 or $SOCl_2$–C_5H_5N) to the *Et* ester, b.p. 94—95°/10 mm., of 3-*methyl*cyclo*pentenylacetic acid*, b.p. 127—128°/12 mm., the chloride of which with ZnMeI gives 3-*methyl*cyclo*pentenylacetone*, b.p. 93—94°/18 mm. [*semicarbazone*, m.p. 185° (decomp.)]. Condensation of this with $CHNa(CO_2Et)_2$ and hydrolysis (KOH) of the resulting ester gives 3′-*methyl*cyclo*pentane*spirocyclo*hexane*-3 : 5-*dione* (I), m.p. 127—128° [condensation *product*, $C_{23}H_{32}O_4$, m.p. 161—162°, with CH_2O; *anil*, m.p. 156°]. The chloride from Et H 3-methyl-*cyclo*pentane-1 : 1-diacetate and ZnMeI give *Et* 1-*acetonyl*-3-*methyl*cyclo*pentane*-1-*acetate*, b.p. 152—155°/14 mm. {145°/14 mm., when prepared from the free *acid*, b.p. 181—182°/12 mm. [*semicarbazone*, m.p. 182° (decomp.)]} (*semicarbazone*, m.p. 87—88°), converted by EtOH–NaOEt into (I). The latter method is recommended. H. B.

Identification of carbonyl compounds by 2 : 4-dinitrophenylhydrazine. J. Ferrante and A. Bloom (Amer. J. Pharm., 1933, **105**, 381—384).—EtOH contains traces of aldehydes. 2 : 4-Dinitrophenylhydrazine is, therefore, best used in MeOH solution. 2 : 4-*Dinitrophenylhydrazones* of the following substances are described: $CO(CH_2Ph)_2$, m.p. 238°; *o*-, *m*-, and *p*-methoxy*cyclo*hexanone, m.p. 135°, 135·5°, and 150°, respectively; COPhEt, m.p. 187·5°; *p*-OMe·C_6H_4·CHO, m.p. 253·5°; *o*-C_6H_4Cl·CHO, m.p. 213·6°; *p*-OMe·C_6H_4·COPh, m.p. 180°; *p*-OH·C_6H_4·COPh, m.p. 242·4°; $CO(C_6H_4Me\text{-}p)_2$, m.p. 229·4°; COPhPr, m.p. 188°; *o*-OH·C_6H_4·CHO, m.p. 258·3° (lit. 237°); *p*-C_6H_4Me·COPh, m.p. 202·4°; *p*-C_6H_4Me·COMe, m.p. 260·4°; furfurylidene-, m.p. 241°, vanillylidene-, m.p. 229°, di-*p*-tolylidene-, m.p. 165·5°, dipiperonylidene-, m.p. 238·2°, dicinnamylidene-, m.p. 195·7°, and dianisylidene-acetone, m.p. 82—83°; furfurylidene-, m.p. 169°, *p*-methoxy-, m.p. 231·8°, *p*-hydroxy-, m.p. 261·5°, cinnamylidene-, m.p. 222°, 2-methyl-5-*iso*propyl-, double m.p. 140—142° (turbid) and 160° (clear), and *p*-bromo-acetophenone, m.p. 237°. M.p. above 195° are corr. Allen's method of analysis is best for these substances. R. S. C.

Reaction of diazonium salts with open-chain hydroxymethyleneketones. S. N. Roy and H. K. Sen (J. Indian Chem. Soc., 1933, **10**, 347—351; cf. A., 1928, 185).—Hydroxymethylenedeoxybenzoin (Ph β-hydroxy-α-phenylvinyl ketone) and PhN_2Cl in cold aq. EtOH–NaOAc (excess) give the monophenylhydrazone of benzil (*phenylhydrazone*-p-*nitrophenylhydrazone*, m.p. 255°); the mono-*p*-nitrophenylhydrazone is similarly obtained using *p*-NO_2·C_6H_4·N_2Cl. Reaction probably occurs thus: OH·CH:CPh·COPh $\rightleftharpoons$ CHO·CHPh·COPh $\longrightarrow$ NPh:N·CPh(CHO)·COPh $\longrightarrow$ HCO_2H + NPh:N·CHPh·COPh $\longrightarrow$ NHPh·N:CPh·COPh. Ph β-hydroxy-α-methylvinyl ketone and PhN_2Cl afford the *monophenylhydrazone*, m.p. 146—147°, of PhMe diketone (*phenylhydrazone*-p-*nitrophenylhydrazone*, m.p. 230°). H. B.

Cleavage of carbonyl compounds by alkalis. XI. Action of hypobromite solutions on β-diketones. C. F. Woodward and R. C. Fuson (J. Amer. Chem. Soc., 1933, **55**, 3472—3475; cf. this vol., 1048).—*p*-Bromobenzoylacetone and NaOBr give C_6H_4Br·CO_2Na, NaOAc, and CBr_4. Acetomesitylene, EtOAc, and NaOEt give *acetylacetomesitylene*, m.p. 45—46° (gives with NH_2·NHPh the *phenylhydrazone*, m.p. 128·5—129·5°, and *phenylpyrazolone* derivative, m.p. 86—87°), which with NaOBr gives NaOAc and ωωω-tribromoacetomesitylene. 2-Methoxy-1-naphthoylacetone, m.p. 71—72·5° (from 1-aceto-2-methoxynaphthalene), with NaOBr gives 1-tribromoacetyl-2-methoxynaphthalene. NaOBr is thus shown to cleave CO compounds by preliminary attack on the active CH_2 group. R. S. C.

Synthesis of an isomeride of plumbagin. J. S. de Buruaga (Anal. Fís. Quím., 1933, **31**, 185—188).—Oxidation of 8-acetoxy-2-methylnaphthalene by CrO_3 in AcOH and hydrolysis yields 8-*hydroxy*-2-*methyl*-α-*naphthaquinone*, m.p. 158°, which resembles plumbagin (A., 1928, 1376) except in m.p. Plumbagin is probably the 3-Me derivative. R. K. C.

Biochemistry of micro-organisms. XXXII. Cynodontin (1 : 4 : 5 : 8-tetrahydroxy-2-methylanthraquinone), a metabolic product of *Helminthosporium cynodontis*, Marignoni, and *H. euchlœnæ*, Zimmermann. H. Raistrick, R. Robinson, and A. R. Todd.—See this vol., 1082.

Conversion of phthaloylnaphthalenes and naphthoyl-2-benzoic acids into benzanthraquinones. L. F. Fieser and (Mrs.) M. Fieser (J. Amer. Chem. Soc., 1933, **55**, 3342—3352).—Quinones are formed from naphthoylbenzoic acids more smoothly by H_2SO_4 than by $AlCl_3$, migration of both acyl and alkyl groups sometimes occurring with the latter reagent. The following are obtained by means of phthalic anhydride and $AlCl_3$ in $C_2H_2Cl_4$ at 0°: from 2 : 6-$C_{10}H_6Me_2$, 2′ : 6′- (I) (47%) and 3′ : 7′- (II) (20%) -*dimethyl*-1′-*naphthoyl*-2-*benzoic acid*, m.p. 225° (*Me* ester, m.p. 110°; *Na* salt); from 1 : 6-$C_{10}H_6Me_2$, 4′ : 7′- (III), m.p. 189°; from 2 : 3-$C_{10}H_6Me_2$, 2′ : 3′- (IV) (35%), m.p. 229°, and 6′ : 7′- (V) (17%), m.p. 234° (*Me* ester, m.p. 125°) -*dimethyl*-1′-, and 6′ : 7′-*dimethyl*-2′-*naphthoyl*-2-*benzoic acid* (VI), m.p. 193° (*Me* ester, m.p. 145°) (7·3%); from 2 : 7-$C_{10}H_6Me_2$, 2′ : 6′-dimethyl-1′- (75%) and 3′ : 6′-*dimethyl*-1′- or -2′-*naphthoyl*-2-*benzoic acid*, m.p. 193° (*Me* ester, m.p. 85°; *Na* salt) (1%); from 2-$C_{10}H_7Me$, 2′-methyl-1′-, m.p. 197° (lit. 190—191°) (Me ester, m.p. 112°) (> 47%), and 7′-*methyl*-1′- or -2′-*naphthoyl*-2-*benzoic acid*, m.p. 190° (*Me* ester, an oil) (> 3%) (gives 2′-methyl-1 : 2-benzanthraquinone with H_2SO_4). The following 1 : 2-*benzanthraquinones* were obtained by ring-closure with hot H_2SO_4: from (II) 2′ : 4-Me_2-, m.p. 173°, also obtained from 1 : 8-phthaloyl-2 : 6-dimethylnaphthalene (VII) by 82% H_2SO_4; from (III) 2′ : 3-Me_2- (VIII), m.p. 203° (previously considered to be 2′ : 4-), also obtained from 1 : 8-*phthaloyl*-2 : 5-*dimethylnaphthalene* (IX), m.p. 140°; from (V) 2′ : 3′-Me_2- (X), m.p. 247°, also obtained from (VI) and 1 : 8-phthaloyl-2 : 3-dimethylnaphthalene. The substance, m.p. 195°, previously called 4 : 3′-*dimethyl*-1 : 2-*benzanthraquinone*, is of unknown orientation, the substance really having this structure having m.p. 175°. By $AlCl_3$–NaCl fusion were obtained: from (II), (VII) and (VIII);

from (I), (VIII); from (III), (VIII) and (IX); from (IV), (X); from (V), (X) and 1 : 8-*phthaloyl*-?·?-*dimethylnaphthalene*, m.p. 182° (*quinone*, m.p. 223°); from (VI), (X) and two ?·?-*dimethyl*-2 : 3-*benzanthraquinones*, m.p. 230° and 296°, respectively. 1 : 8-Phthaloyl-2-methylnaphthalene and H_2SO_4 give 2′-methyl-1 : 2-benzanthraquinone. 1 : 8-Phthaloyl-β-naphthol gives similarly 2′-*hydroxy*-1 : 2-*benzanthraquinone*, m.p. 253° (*Ac* derivative, m.p. 255°), and 1 : 8-phthaloyl-2-chloronaphthalene gives 2′-*chloro*-1 : 2-*benzanthraquinone*, m.p. 233—234°, probably identical with the substance described by Heller (A., 1913, i, 631) as the 2 : 3-benzanthraquinone. Decarboxylation of (II) gives 1-benzoyl-2 : 6-dimethylnaphthalene. R. S. C.

Use of acenaphthene in the production of dyes of the anthanthrone series. II. New synthesis of naphthastyryl. A. Corbellini and L. Barbaro (Giorn. Chim. Ind. Appl., 1933, **15**, 335—337).—Naphthastyryl may be synthesised according to the scheme: acenaphthene ⟶ 8-hydroxymercuri-1-naphthoic anhydride ⟶ 8-bromo(or chloro)-1-naphthoic acid ⟶ naphthastyryl. 4 : 9-Dibromoanthanthrone, m.p. above 350°, has been prepared by diazotisation of 5-bromo-8-amino-1-naphthoic acid, reduction to 4 : 4-dibromo-1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid, and cyclisation of the latter. It has approx. the same properties as the isomeride already described (B., 1931, 623), but the Me_2 ester of the acid from which it is derived is not identical with the isomeric ester obtained by dibromination of Me_2 1 : 1′-dinaphthyl-8 : 8′-dicarboxylate. Hence the dibromoanthanthrone derived from the latter, and also the corresponding diamino- and dinitroanthanthrones, cannot be 4 : 9-derivatives. T. H. P

Oxidation of theelin and some theelol derivatives. D. W. MacCorquodale, L. Levin, S. A. Thayer, and E. A. Doisy (J. Biol. Chem., 1933, **101**, 753—761).—Quant. oxidation ($KMnO_4$) of theelin (I), its Me ether, and theelol (II) shows that, except with the Me ether, the reaction varies with the temp. and concn. of $KMnO_4$. Methylation of the phenolic OH stabilises the aromatic nucleus, but reduction of the CO of (I) does not affect the oxidation val. Oxidation of the Me ether of (II) in $COMe_2$ affords a *OMe-lactone*, $C_{18}H_{22}O_3$, m.p. 182°, and an *acid*, $C_{19}H_{24}O_5$, m.p. 192°, identical with the Me ether of the acid obtained by fusion of (II) with KOH, and oxidised by $KMnO_4$ to a dibasic *acid*, $C_{19}H_{22}O_5$, m.p. 234—235°, and by CrO_3 to a dilactonic *acid*, $C_{18}H_{18}O_5$, m.p. 243—244°. Fusion of (I) (from either mare's or human urine) with KOH yields a phenolic monobasic *acid*, $C_{17}H_{22}O_3$, m.p. 195°. The oxidation products have several times the œstrogenic potency of (I). F. R. S.

Aspergillin, the spore pigment of *Aspergillus niger*. III. A. Quilico (Gazzetta, 1933, **63**, 400—410; cf. this vol., 536, 751).—The acid character of aspergillin (I) is due to CO_2H groups, since at 150—250° CO_2 is evolved and the product is insol. in alkali. Oxidation by H_2O_2 yields mellitic, without oxalic, acid; both are formed by HNO_3 oxidation. The presence of a hexagonal nucleus $\left[C(OH)<\begin{matrix}CO\cdot CH-\\CH\cdot CH-\end{matrix}\right]_3$ is suggested; (I) is regarded as a humic acid in pure form. E. W. W.

***iso*Pulegone. Pyrolysis of *iso*amyl*iso*pulegol.** J. Dœuvre (Bull. Soc. chim., 1933, [iv], **53**, 589—596).—*d*-Citronellal (I), $[\alpha]_{20}^{20}$ +13·45° [containing 90% of the *iso*propylidene form], and $MgPr^{\beta}Br$ form βε*ι*-*trimethyl*-Δ^{δ}-*decen*-γ-*ol*, b.p. 126—127°/12 mm., $[\alpha]_{5780}$ +5·28°, giving with O_3 $COMe_2$ (96), CH_2O (1), and HCO_2H (7%). (I) and boiling Ac_2O give a little diacetate of (I) and much *iso*pulegol acetate, b.p. 105—108°/14 mm., hydrolysed to *iso*pulegol (II), b.p. 93—94°/14 mm., $[\alpha]_{5780}$ +0·04°, $[\alpha]_{4360}$ −0·02° [giving with O_3 CH_2O (55), HCO_2H (37), and $COMe_2$ (3%)]. This with CrO_3–H_2SO_4 at < 40° gives *iso*pulegone (III), $[\alpha]^{23}_{5780}$ −0·66°, $[\alpha]^{23}_{4360}$ −2·06°. (II) and (probably) (III) are mixtures of stereoisomerides. The latter gives two *semicarbazones*, m.p. 172—173° (block) and 156° (lit. 155—157° form only), $[\alpha]^{23}_{5780}$ −29·96° and +4·50° in C_6H_6, respectively, both giving with O_3 only traces of $COMe_2$. (III) and *iso*-C_5H_{11}·MgBr give < 35% of iso*amyl*iso*pulegol* (IV), b.p. 139—141°/15 mm., $[\alpha]^{16}_{5780}$ +14·01°, probably formed mostly from the *d*-isomeride of (III), the *l*-isomeride being supposed to enolise more rapidly and thus give very little (IV). (IV) at 540—550°/50 mm. gives βηλ-*trimethyl*-Δ^{κ}-*dodecen*-ε-*one* (V), b.p. 148—150°/16 mm., $[\alpha]^{16}_{80}$ +2·34°, giving with O_3 93% of $COMe_2$, and with O_3–CrO_3 ε-*keto*-γ0-*dimethyldecoic acid* [*semicarbazone* (VI), m.p. 140—141° (block)]. (I) and *iso*-C_5H_{11}·MgBr give a 50% yield of βηλ-*trimethyl*-Δ^{κ}-*dodecen*-ε-*ol*, b.p. 153—154°/15 mm., $[\alpha]^{16}_{5780}$ +1·80°, yielding with Cu at 250°/20 mm. (V) and thence (VI). Pyrolytic fission of (IV) is probably preceded by formation of an O-ring between C3 and C8. R. S. C.

Caoutchouc. XV. Polymerisation of caoutchouc, isoprene, and styrene by light in presence of sensitising agents. R. Pummerer and H. Kehlen (Ber., 1933, **66**, [*B*], 1107—1122).—Sol caoutchouc (I) in Et_2O is converted by sufficiently prolonged exposure to sunlight into a material (II) completely insol. in Et_2O; incidence of the reaction is somewhat uncertain. The I val. of (II) is 94—98% of that of (I). The conception that the action is polymerisation is strengthened by the analogous behaviour of isoprene (III) and styrene (IV). Gel formation of caoutchouc solutions is caused with certainty by CO compounds. Eosin renders good service, whereas methylene-blue and malachite-green present no advantages and bleach more easily. $COPh_2$ and benzanthrone are serviceable. PhCHO yields gels, but, as with MeCHO, the relationships appear less simple than with ketones. COPhMe and $COEt_2$ are active. Moderate action is shown by AlkOBz, whereas aliphatic esters and coloured hydrocarbons such as perylene and carotene are inactive. The use of sensitisers permits the utilisation of light of longer wave-length. Polymerisation of (III) as liquid or in soap emulsion is similarly accelerated by CO compounds, the synthetic isoprene-caoutchouc having an I val. of 94—99% (with evolution of halogen acid). Polymerisation of (IV) to styrene-resin is

readily effected by CO compounds in glass vessels at room or raised temp. The view that the action of sensitisers is due to traces of activated O (V) is supported by the observation that polymerisation is inhibited by antioxidants, *e.g.*, quinol. The formation of (V) during irradiation of CO compounds is detected by benzidine solutions containing NaCl. Heavy metals, particularly Fe, appear without influence. H. W.

Synthesis of camphor. J. J. RITTER (J. Amer. Chem. Soc., 1933, **55**, 3322—3326).—In the reaction of bornyl chloride with NH_2Ph, excess of the latter increases the amount of *iso*bornylamine (I) and decreases the amount of camphene formed, indicating an equilibrium between the two products. (I) with S at 215—220° (75% yield) or Ni (better with a little KOH) at 340° gives camphoranil, whence camphor is obtained by dil. HCl slowly at room temp. and in a few min. at 100°. R. S. C.

Azulene. J. MELVILLE (J. Amer. Chem. Soc., 1933, **55**, 3288—3292).—Azulene (I), b.p. 169°/12 mm. (from guaiacum wood oil and S), probably Ruzicka's "sulphur-guaiazulene," gives with O_3 in CCl_4 CH_2O, HCO_2H, and $COMe_2$. The rate of its hydrogenation (Pd) in EtOH decreases greatly after reduction of 3·5—3·7 ethylenic linkings (55% saturation); the mixture thus obtained gives with O_3 no CH_2O, HCO_2H, or $COMe_2$, but a *ketone* [*semicarbazone*, m.p. about 234° (decomp.)], a non-ketonic *substance*, b.p. 125—145°/3 mm., $Pr^{\beta}CO_2H$, and an *acid*, $C_{14}H_{21}\cdot CO_2H$, b.p. about 180°/1·5 mm. (*p-phenylphenacyl* ester, m.p. 144·5°). (I) gives a Na-derivative, unstable, whence CO_2 yields an *acid*, $C_{30}H_{36}(CO_2H)_2$, m.p. about 100°, which with O_3 gives CH_2O and HCO_2H, but no $COMe_2$. O_3 attacks the CH_2, Na the CMe_2 group. R. S. C.

Terpenoid ring systems. I. Synthesis of a substance with blue antimony trichloride reaction. H. VOGEL and M. STOHL (Ber., 1933, **66**, [*B*], 1066—1069).—β-Ionone is converted by moderately dil. H_2SO_4 at room temp. into a *substance* $C_{20}H_{28}O_2$, m.p. 216—217° (corr.) after softening at 188° (corr.). Its colour reactions resemble those of the sterols; the very intense blue colour with $SbCl_3$ in $CHCl_3$ is particularly characteristic. Carotene yields a similar product. H. W.

Constitution of carlina oxide. H. GILMAN, P. R. VAN ESS, and R. R. BURTNER (J. Amer. Chem. Soc., 1933, **55**, 3461—3463).—Furfuryl chloride and CPh·C·MgBr give *phenyl-2-furfurylacetylene* (I), b.p. 160—161° [different from carlina oxide (II)], reduced by Na–EtOH to α-phenyl-γ-2-furylpropane [5-*HgCl*-derivative, m.p. 94—95°, also obtained by reduction and mercuration of (II)]. (II) with O_3 in AcOH gives $CH_2Ph\cdot CO_2H$. (I), but not (II), with maleic anhydride gives an *adduct*, m.p. 112°. (II) is, therefore, benzyl-2-furylacetylene. R. S. C.

New condensing agent for the preparation of benzo-γ-pyrones and their derivatives. Mode of action of sulphoacetic acid during acetylation. E. GOTTESMANN (Ber., 1933, **66**, [*B*], 1168—1177).—The following condensations (yields in parentheses) are rapidly effected by AcCl containing 1/40th of its weight of conc. H_2SO_4 or $HClO_4$; Ac_2O, $(EtCO)_2O$, or BzCl may replace AcCl, but are less volatile. Phenylsalicylic acid to xanthone (100%); *o*-methoxyphenylsalicylic acid to 4-methoxyxanthone (100%); β-naphthylsalicylic acid to 1 : 2-benzoxanthone (100%); 4 : 6-diphenoxy*iso*phthalic acid to dixanthone (100%); dihydroxy-*p*-diphenoxyterephthalic acid to 9 : 10-dihydroxyxanthone (60%); *cis*-β-phenoxyacrylic acid, m.p. 129° (from NaOPh and Et propiolate in Et_2O) (*K* salt), to chromone (100%); *phenoxyfumaric acid*, m.p. 216° (from Me bromofumarate and NaOPh in Et_2O), to *chromone-2-carboxylic acid*, m.p. 260° (100%); β-phenoxypropionic acid to chromanone (25%); *quinol-O-propionic acid* (I), m.p. 168—169° [from quinol, KOH, and $CH_2Cl\cdot CH_2\cdot CO_2K$ (II)], to *6-hydroxychromanone*, m.p. 134—135° (25%); *quinol-OO′-dipropionic acid*, m.p. 200° [from the K salt of (I) and (II)], to *dichromanone*, decomp. 200° (10%). *o*-$C_6H_4Bz\cdot CO_2H$ is not converted into anthraquinone by AcCl–H_2SO_4. AcCl without catalyst produces only traces of xanthones from arylsalicylic acids. It is considered that the primary product of the xanthone synthesis is a mixed anhydride and that reaction between the anhydride group and the heteronuclear H atom is induced by sulphoacetic acid (III). The action of (III) does not differ widely from that of $AlCl_3(FeCl_3)$ in the Friedel–Crafts reaction. H. W.

Pigment of birch buds. K. H. BAUER and H. DIETRICH (Ber., 1933, **66**, [*B*], 1053—1054).—Successive extraction of the buds with light petroleum and EtOH yields 1-hydroxy-3 : 4′-dimethoxyflavone, m.p. 174—174·5° (Ac derivative, m.p. 199°), demethylated to apigenin, m.p. 347°. H. W.

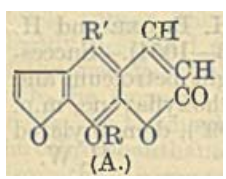
Chromone group. IX. Synthesis of 5 : 7 : 4′-trihydroxy-3′ : 5′-dimethoxyflavone, believed to be identical with tricin. K. C. GULATI and K. VENKATARAMAN. **VIII. Derivatives of *o*-hydroxy-, 2 : 5-dihydroxy-, and 2 : 4 : 5-trihydroxyacetophenone.** T. C. CHADHA and K. VENKATARAMAN (J.C.S., 1933, 942—943, 1073—1076).—IX. Phloroacetophenone, *O*-benzylsyringic anhydride, and Na *O*-benzylsyringate afford 5 : 7-*dihydroxy-3′ : 5′-dimethoxy-4′-benzyloxyflavone*, m.p. 234°, which with HCl–AcOH forms 5 : 7 : 4′-trihydroxy-3′ : 5′-dimethoxyflavone, probably identical with tricin. 5 : 7 : 3′ : 4′ : 5′-Penta-acetoxyflavone has m.p. 241—242° (cf. Anderson, A., 1932, 1256).

VIII. *o*-Hydroxyacetophenone with Bz_2O gives a small yield of flavone (cf. A., 1931, 963), and with trimethylgallic anhydride (I) affords 3′ : 4′ : 5′-trimethoxyflavone. 2 : 5-Dihydroxyacetophenone with anisic anhydride and Na anisate forms 6-*hydroxy-4′-methoxy-*, m.p. 249° (*Ac* derivative, m.p. 161°), and with (I) yields 6-*hydroxy-3′ : 4′ : 5′-trimethoxy-*, m.p. 232—233° (*Ac* derivative, m.p. 185°), demethylated to 6 : 3′ : 4′ : 5′-*tetrahydroxy-flavone*, m.p. 347° (*Ac* derivative, m.p. 258—259°). 6 : 7-Dihydroxyflavone has m.p. 254° (lit. 135°, 250°). F. R. S.

Rotenone. XXVII. Hydrogenation of rotenone. H. L. HALLER and P. S. SCHAFFER (J. Amer. Chem. Soc., 1933, **55**, 3494—3495; cf. this vol., 955).—Hydrogenation of rotenone with a freshly-prepared PtO_2 catalyst gives mostly rotenonic acid (I); use of the same catalyst a second time leads chiefly to

dihydrorotenone (II), in presence or absence of a little C_5H_5N (cf. *ibid.*, 512). With Pd–$BaSO_4$ in C_5H_5N only (I) is formed. Raney's catalyst (Ni–Al) in neutral solution at room temp. and atm. pressure gives 90% of (II), but with a special Ni catalyst in BuOAc at 90—105°/35—60 lb. dihydrorotenol is quantitatively obtained. R. S. C.

Vegetable fish poisons. V. Constitution of imperatorin (from *Imperatoria Ostruthium*). E. Späth and H. Holzen. **VI. Constitution of *iso*imperatorin (from *I. Ostruthium*).** E. Späth and L. Kahovec. **VII. Constitution of ostruthol (from *I. Ostruthrum*).** E. Späth and A. von Christiani (Ber., 1933, **66**, [*B*], 1137—1145, 1146—1150, 1150—1156).—V. *Imperatorin* (I), $C_{16}H_{14}O_4$, m.p. 102°, [α] ±0° in C_5H_5N, does not contain OH, OAlk, or CO. Its solubility in cold MeOH–KOH indicates the presence of a lactone group. Catalytic hydrogenation of (I) (Pd–C) leads to a *substance*, $C_{11}H_{10}O_4$, m.p. 128° [*Me ether*, b.p. 150° (bath)/0·004 mm.], and *hexahydroimperatorin*, m.p. 85°, oxidised by HNO_3 (*d* 1·4) to $H_2C_2O_4$ and succinic acid, showing the adherence of the lactone ring to a coumarin system. Oxidation of (I) with H_2O_2 in AcOH yields furan-2 : 3-dicarboxylic acid (II), showing the presence of the furan ring. Treatment of (I) with AcOH containing a little conc. H_2SO_4 at room temp. yields the *substance* (A) (R=R′=H), m.p. 244° (*Ac* derivative, m.p. 174—175°), converted by CH_2N_2 into xanthotoxin and by KOH–NaOH at 205—210° into 2 : 3 : 4-trihydroxybenzoic and 4 : 5 : 6-trihydroxy*iso*phthalic acid. A volatile alcohol (and its acetate) obtained during hydrogenation is hydrolysed, hydrogenated, and the product is identified as γ-methylbutanol by conversion into the trinitrobenzoate, m.p. 125—126°. Since oxidation of (I) by $KMnO_4$ and CrO_3 yields α-hydroxy*iso*butyric acid and $COMe_2$, respectively, (I) is (A) (R=CH_2·CH:CMe_2; R′=H). Small amounts of (I) can be distilled in high vac. Under rather higher pressure (0·5 mm.) (I) is isomerised to allo*imperatorin* (III), m.p. 233°, oxidised by H_2O_2 to (II) and converted by CH_2N_2 into the *Me ether*, m.p. 113·5°. Hydrogenation of (III) in AcOH (Pd–C) affords *hexahydro*allo*imperatorin*, m.p. 129°, oxidised by HNO_3 to $C_2H_4(CO_2H)_2$ and γ-methyl-*n*-valeric acid, identified as the phenylhydrazide, m.p. 140°. (III) is oxidised by CrO_3 to $COMe_2$. Hence (III) is (A) (R=H; R′=CH_2·CH:CMe_2).



(A.)

VI. iso*Imperatorin* (II), $C_{16}H_{14}O_4$, m.p. 109°, [α] ±0°, does not contain OH, OMe, or CO. Catalytic hydrogenation leads to the absorption of 3 H, and the product is oxidised by HNO_3 (*d* 1·4) at room temp. to $H_2C_2O_4$ and $C_2H_4(CO_2H)_2$. Treatment of (IV) with NaOMe and Me_2SO_4 and subsequent hydrolysis leads to a *OMe-acid*, $C_{17}H_{18}O_5$, m.p. 117·5°, showing the presence of a lactone group. Oxidation of (IV) by H_2O_2 in alkaline solution leads to (II). Treatment of (IV) with AcOH containing a little conc. H_2SO_4 gives a *phenol*, m.p. 277° (decomp.), transformed by CH_2N_2 into bergapten, m.p. 188—189°, and an unsaturated alcohol (or its acetate), which is hydrogenated and hydrolysed, thus yielding *iso*amyl alcohol, identified as the trinitrobenzoate. $COMe_2$ is produced when (IV) is oxidised by CrO_3 in AcOH. (IV) is therefore (A) (H for OR; R′=·O·CH_2·CH:CMe). Treatment of (IV) with BzO_2H in $CHCl_3$ leads to oxypeucedanin.

VII. Ostruthol (V), $C_{21}H_{22}O_7$, has m.p. 136—137°, $[\alpha]^{22}$ +8·36° in $COMe_2$, $[\alpha]_D^{15}$ −18·3° in C_5H_5N. It does not contain OH or CO_2H, but behaves as a lactone. It is hydrolysed by KOH–MeOH to α-methyl-Δ^{α}-butenoic acid, m.p. 43° (hydrogenated to α-methyl-*n*-butyric acid, identified as the phenylhydrazide, m.p. 103—104°), and (+)-*oxypeucedanin hydrate* (VI), m.p. 131°, $[\alpha]_D^{21}$ +18·9° in $COMe_2$. (V) is converted by H_2O_2 in alkaline solution into (II) and with Ac_2O yields *acetylostruthol*, m.p. 125°. Catalytic hydrogenation of (V) in AcOH (Pd–C) yields *hexahydro-ostruthol*, m.p. 139—140°, oxidised by HNO_3 to $C_2H_4(CO_2H)_2$. Oxidation of (V) by $KMnO_4$ in alkaline solution yields α-hydroxy*iso*butyric acid. Bergapten is formed from (V) by treatment with boiling AcOH containing a little conc. H_2SO_4, and subsequently with CH_2N_2. (VI) is converted by P_2O_5 in PhMe into *iso*oxypeucedanin. (V) is therefore (A) with H for OR and R′=·O·CH_2·CH(CMe_2·OH)·O·CO·CMe:CHMe. H. W.

Thionaphthen series. III. G. Komppa and S. Weckman (J. pr. Chem., 1933, [ii], **138**, 109—127).—The Mg compound of bromothionaphthen (I) (*picrate*, m.p. 114—114·5°) (A., 1929, 1077) gives with O_2 in dry Et_2O the known 2-hydroxythionaphthen, m.p. 69—70°, and some thionaphthen (II); it is therefore the 2-Br-derivative. With CO_2 the main products are thionaphthen-2-carboxylic acid (III), m.p. 174—175° [*Ag*, *Cu*, and *Ba* salts; *Me*, b.p. 165—166°/17 mm., 285—287°/750 mm., and *Et*, b.p. 172—173°/17 mm., 304—306°/750 mm., esters; *chloride* (IV), m.p. about 50°, b.p. 296—298°/758 mm.; *amide*, m.p. 197—198°; *anilide*, m.p. 172—173°] (cf. *loc. cit.*), and 2 : 2′-*dithionaphthenyl ketone*, m.p. 167—167·5°, which is better prepared from the Mg compound and (IV); this ketone does not give an oxime or semicarbazone. With $CH(OEt)_3$ or, better, with OEt·CH:NPh the Mg compound of (I) gives *thionaphthen-2-aldehyde*, m.p. 58°, b.p. 149—150°/10 mm. (*semicarbazone*, m.p. 235—235·5°; *phenylhydrazone*, m.p. 115°; p-*nitrophenylhydrazone*, m.p. 232—233°), which is oxidised to (III) by $KMnO_4$. Action of KOH in MeOH at 200—220° on (I) gives (II), 2-hydroxythionaphthen (V), m.p. 46·5°, and o-*methylthiolphenylacetic acid* (VI), m.p. 128° (*amide*, m.p. 164—165°), identified by synthesis by methylation of o-SH·C_6H_4·CH_2·CO_2H; in EtOH under the same conditions no product corresponding with (VI) is formed, but mainly (II) and some (V). At 200—220° KOH in MeOH has no action on (II) or (VI), but with (V) some *diphenyl disulphide*-2 : 2′-*diacetic acid* (VII), m.p. 147—148°, is formed. (VI) was not demethylated by HI (*d* 1·96) or by heating its chloride in xylene, but its chloride with $AlCl_3$ in CS_2 gives some (V), the cyclisation product of the SH-acid. The last-named readily cyclises with boiling dil. HCl, some (VII) being formed at the same time. The occurrence of the labile form of (V), m.p. 34—34·5° (cf. Marschalk,

A., 1913, i, 1088), in a single experiment is recorded; it could not be obtained under Marschalk's conditions, and rapidly changes into the stable form on keeping. No interaction was observed between the latter and PhNCO; it is therefore probably the keto-form. Benzamidothionaphthen has m.p. 152° (not 132°; cf. *loc. cit.*). H. A. P.

2-Methylpiperidinopropyl thiol- and thionbenzoates. S. A. KARJALA and S. M. MCELVAIN (J. Amer. Chem. Soc., 1933, **55**, 2966—2973).—γ-Thiolpropyl alcohol, b.p. 81—82°/10 mm., and 48% HBr or PBr_3 give *γ-thiolpropyl bromide* (*A*), b.p. 55—56°/12 mm., which with BzCl and aq. Na_2CO_3 form *γ-bromopropyl thiolbenzoate*, b.p. 148—149°/1 mm., whence by 2-methylpiperidine (I) at 100° *γ-2-methylpiperidinopropyl thiobenzoate hydrochloride*, $SBz\cdot[CH_2]_3\cdot NH\cdot C_5H_{10}\}Cl$, m.p. 137—138°, was obtained. PhCN and $CH_2Cl\cdot CH_2\cdot CH_2\cdot OH$ give *γ-chloropropylbenzimino-ester hydrochloride*, $CPh(:NH_2Cl)\cdot O\cdot[CH_2]_2\cdot CH_2Br$, m.p. 122—123°. Similarly was prepared the *γ-Br*-compound, m.p. 115—116°, the free base from which with H_2S in Et_2O gives crude *γ-bromopropyl thionbenzoate* (III), $CPhS\cdot O\cdot[CH_2]_2\cdot CH_2Br$, b.p. 148—150°/1 mm., and *2-phenyl-4 : 5-dihydro-1 : 3-oxazine hydrobromide*, m.p. 139—140°. *γ-Chloropropyl thionbenzoate* (IV), similarly prepared, has b.p. 145—146°/1 mm. (III) or (IV) with (I) gives mostly (II) and some *γ-2-methylpiperidinopropyl thionbenzoate* (V), which is, however, best prepared from PhCN and γ-2-methylpiperidinopropyl alcohol and then has m.p. 149—149·5°. (V) rapidly gives (II) at 175° or when distilled. (*A*), PhCN, and HCl give *γ-bromopropyl thiolbenziminoester hydrochloride*, m.p. 157—158°, whence by evaporation in Et_2O *2-phenyl-4 : 5-dihydro-1 : 3-thiazine hydrobromide*, m.p. 171—172°, is obtained, and by H_2S *γ-bromopropyl dithiobenzoate*, m.p. 112—114°, which with (I) in hot, dry C_6H_6 gives a resin. (V) is active as a surface anæsthetic or when injected, (II) only when injected; the former is more efficient than the *O*-analogue. Thion S can be determined by $AgNO_3$ in the dark at room temp. Thiol S reacts only when heated. R. S. C.

Structure of ammines of platinous chloride. F. W. PINKARD, H. SAENGER, and W. WARDLAW. —See this vol., 1001.

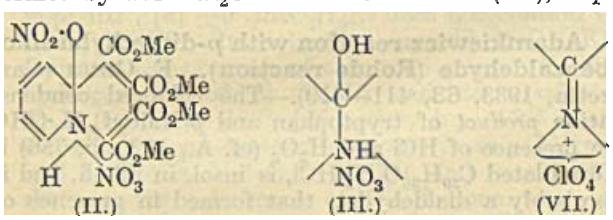
Additive reactions of the indole nucleus. S. G. P. PLANT and (MISS) M. L. TOMLINSON (J.C.S., 1933, 955—960).—Nitration of 2 : 3-dimethylindole (I) gives the 5-NO_2-derivative, m.p. 188°, also obtained (Fischer reaction) from the *p*-nitrophenylhydrazone of COMeEt. *1-Acetyl-2 : 3-dimethylindole* (II), m.p. 74°, is nitrated to the 4(or 6)-NO_2-derivative, m.p. 170°, deacetylated to the 4(or 6)-NO_2-derivative of (I), m.p. 142°, similarly obtained from the *m*-nitrophenylhydrazone of COMeEt. *1-Benzoyl-2 : 3-dimethylindole*, m.p. 98°, and HNO_3 form an additive compound, *3-nitro-2-hydroxy-1-benzoyl-2 : 3-dimethyl-2 : 3-dihydroindole*, m.p. 125° (decomp.), debenzoylated to the corresponding *-dihydroindole*, m.p. 103°. (I) and Br–AcOH give *2-methyl-3-hydroxymethylindole*, m.p. 225°, the dibromide not being isolated. Similarly (II) yields *1-acetyl-3-methyl-2-hydroxymethylindole*, m.p. 90—91°, deacetylated to the *2-hydroxymethyl* compound, m.p. 122°; with less AcOH, *1-acetyl-3-methyl-2-bromomethylindole*, m.p. 92—94°, is obtained. 2 : 3-Diphenylindole and Br give after ethylation *Et* 4(or 6)-*bromo-2 : 3-diphenylindole-1-carboxylate*, m.p. 110°. 1-Acetyl-2 : 3-diphenylindole is brominated to the 4(or 6)-*Br*-compound, m.p. 141—142°, also obtained with the 6(or 4)-*Br*-derivative, m.p. 223—225°, from the *m*-bromophenylhydrazone of COPhBz. 4(or 6)-*Bromo-1-benzoyl-*, m.p. 174—176°, and *-1-cinnamoyl-2 : 3-diphenylindole*, m.p. 176°, are similarly obtained. The *p*-bromophenylhydrazone of $COPh\cdot CH_2Ph$ gives 5-bromo-2 : 3-diphenylindole, m.p. 148° (1-*Ac* derivative, m.p. 218°). Bromination of 2-phenyl-3-methylindole affords the 4(or 6)-*Br*-derivative, m.p. 147°; COPhPr, *p*-bromophenylhydrazine, and HCl–EtOH give the 5-*Br*-compound, m.p. 141°. F. R. S.

Adamkiewicz reaction with *p*-dimethylaminobenzaldehyde (Rohde reaction). E. GHIGI (Gazzetta, 1933, **63**, 411—419).—The coloured condensation *product* of tryptophan and $-NMe_2\cdot C_6H_4\cdot CHO$ in presence of HCl and H_2O_2 (cf. A., 1920, ii, 786) is formulated $C_{29}H_{25}O_2N_3,HCl$, is insol. in alkali, and is probably a dialdehyde; that formed in presence of $NaNO_2$ (cf. Neri, Biochim. Ter. Sper., 1932, **19**, 49) is formulated $C_{31}H_{29}O_6N_3,HCl$, and is probably a OH-acid; the *product* formed in presence of $K_2Cr_2O_7$ is colourless. E. W. W.

Heterocyclic acetylcholines. E. MACOVSKI and E. RAMONTEANU (J. pr. Chem., 1933, [ii], **138**, 92—98).—The following quaternary salts from heterocyclic bases and $CH_2Cl\cdot CH_2\cdot OAc$ or $CH_2I\cdot CH_2\cdot OAc$ are described: β-*acetoxyethylpyridinium chloride* ("pyridine acetylcholine chloride") [*iodide*; chloroplatinate, m.p. 183—186° (decomp.) (lit. 193—194°)]; β-*acetoxyethyl-2-methylpyridinium chloride* [*iodide*, m.p. 117—118°; *chloroplatinate*, m.p. 196—199° (decomp.)]; β-*acetoxyquinolinium iodide*, m.p. 122—123° [*chloroplatinate*, m.p. 202—203° (decomp.)]; and β-*acetoxyethyl-2-methylquinolinium iodide*, m.p. 137° (diffuse). H. A. P.

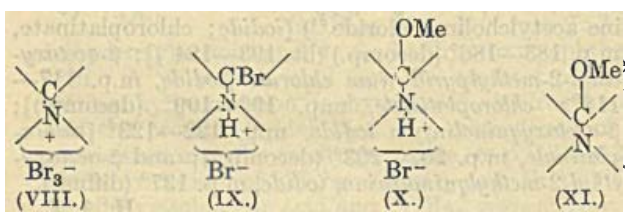
2-Anilinolepidine derivatives. O. G. BACKEBERG (J.C.S., 1933, 1031—1032).—The following are prepared from 2-chlorolepidine etc. (cf. A., 1932, 951): 2-anilino- (*picrate*, m.p. 228°), 2-o-, m.p. 140° (*picrate*, m.p. 223°), and 2-p-*anisidino-*, m.p. 129° (*picrate*, m.p. 190°), 2-o-, m.p. 127° (*picrate*, m.p. 226°), and 2-p-*phenetidino-lepidine*, m.p. 165° (*picrate*, m.p. 215°); *2-anilino-*, m.p. 139° (*picrate*, m.p. 213°), 2-o-, m.p. 151° (*picrate*, m.p. 228°), and 2-p-*anisidino-*, m.p. 137° (*picrate*, m.p. 216°), 2-o-, m.p. 119° (*picrate*, m.p. 237°), and 2-p-*phenetidino-6-methoxylepidine*, m.p. 149° (*picrate*, m.p. 183°); *2-anilino-*, m.p. 127° (*picrate*, m.p. 236°), 2-o-, m.p. 158° (*picrate*, m.p. 241°), and 2-p-*anisidino-*, m.p. 172° (*picrate*, m.p. 203°), 2-o-, m.p. 141° (*picrate*, m.p. 224°), and 2-p-*phenetidino-6-ethoxylepidine*, m.p. 128° (*picrate*, m.p. 218°). The following are prepared by cyclisation of the corresponding acetoacetarylamides with conc. H_2SO_4 at 100°: 2-hydroxy-6-methoxy-, m.p. 272° (picrate, m.p. 204°) (cf. A., 1931, 1433), and *2-hydroxy-6-ethoxy-lepidine*, m.p. 232° (*picrate*, m.p. 179°; *2-chloro-6-ethoxylepidine*, m.p. 123°). Acetoacet-*o*-anisidide and *-o*-phenetidide were not cyclised by H_2SO_4, HCl, H_3PO_4, P_2O_5, $POCl_3$, or Ac_2O. H. A. P.

Syntheses in the hydroaromatic series. XVIII. "Diene" syntheses with heterocyclic nitrogen compounds. VI. "Diene" syntheses of pyridine, quinolizine, indolizine, norlupinane, and ψ-lupinine. O. DIELS and K. ALDER [with FRIEDRICHSEN, KLARE, WINKLER, and SCHRUM] (Annalen, 1933, **505**, 103—150; cf. A., 1932, 1144).—Further examination of the acid $C_9H_7O_5N$ (*loc. cit.*) establishes the formula $C_6H_5O_3N$ and its identity with 2-*carboxypyridine* 1-*oxide* prepared from pyridine-2-carboxylic acid and H_2O_2 in AcOH at 100°. Me quinolizine-1 : 2 : 3 : 4-tetracarboxylate (I) is converted by conc. HNO_3 under specified conditions into the *ester nitrate* (II), m.p. 110—111° (decomp.), described (*loc. cit.*) as $C_{17}H_{17}O_8N,2HNO_3$, transformed by warm H_2O into the *OH-nitrate* (III), m.p.



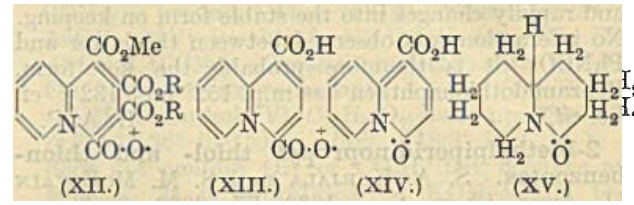
(II.) (III.) (VII.)

92—93° (decomp.). (III) is converted by boiling C_5H_5N into the compound $C_{16}H_{13}O_8N$ (IV), by dil. HNO_3 or H_2SO_4 into Me indolizinetricarboxylate (V), by HBr in $COMe_2$ into the dibromide (VI), m.p. 102°, and by dil. $HClO_4$ into the *perchlorate* (VII), m.p. 201° (decomp.). (I) is transformed by an excess of Br in AcOH or MeOH into the *perbromide* (VIII), decomp. 129—130°, in which Br is entirely in ionic



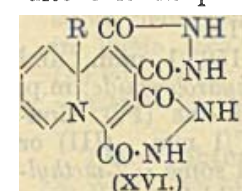
(VIII.) (IX.) (X.) (XI.)

union, since (VIII) is transformed by aq. $HClO_4$ into (VII). Hydrolysis of (VIII) with KOAc, Na_2CO_3, or H_2O leads very readily to (V). (VIII) is converted by $COMe_2$ (owing to liberated HBr) into the colourless *bromide* (IX), decomp. 100—102°, obtained also by the action of 1 mol. of Br on (I) in $CHCl_3$. (IX) is re-converted into (I) by reduction (Pd–$CaCO_3$) in alkaline solution. Treatment of (IX) with cold MeOH yields the *substance* (X), decomp. about 102—103°, transformed by Ag_2CO_3 into the free *base* (XI), m.p. 160°, from which (X) is regenerated by HBr. Warm C_5H_5N converts (IX) into (IV). Direct or indirect hydrogenation of (I) appears to lead invariably to (IV), which is best prepared as above, but is also obtained as by-product in the prep. of (I) and from (I) by means of PbO_2 or Et azodicarboxylate. Oxidation of (IV) shows it to retain the substituted C_5H_5N nucleus. Hydrolysis occurs with difficulty under the influence of boiling HCl, leading to the dicarboxylic acid (XII; R=H) [re-converted into (IV) by CH_2N_2] and thence through the *acid* (XIII), m.p. 272° (decomp.) after darkening at 250°, into the monocarboxylic *acid* (XIV), m.p. about 295° (decomp.) after darkening at 280° [obtained directly from (IV) and conc. H_2SO_4 at 90—130°]; the *hydrochloride* and *Me* ester, m.p. 148—149°, are described.



(XII.) (XIII.) (XIV.) (XV.)

(XIV) does not react with the customary reagents for OH or CO and is not reduced by Zn–Hg and conc. HCl or by Zn dust. The presence of amide-like CO is therefore postulated and the structure (XIV) is supported by the prep. of an H_8-derivative, m.p. 189°, not affected by Ac_2O (*Me* ester, m.p. 76—77°, does not react with NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$). Distillation of (XIV) with CaO leads to the *substance* (XV), b.p. 250—260°. The production of octahydroindolizine instead of octahydroquinolizine (norlupinane) by treatment of (XV) with Na and amyl alcohol is unexplained. Confirmation of the structure of (IV) (XII, R=Me) is found in its transformation by N_2H_4,H_2O into the *hydrazinodihydrazide* (XVI) (R=NH·NH_2), m.p. > 350°, converted by boiling dil. HCl into the *dihydrazide* (XVI; R=OH) and by hot conc. H_2SO_4 into the *substance* $C_{12}H_6O_4N_5$, m.p. > 350°. Treatment of (IV) with NaOMe and subsequently with $HClO_4$ leads to (VII).



(XVI.)

Repetition of the alkaline hydrolysis and subsequent decarboxylation of (I) shows that the product, provisionally regarded as quinolizine (*loc. cit.*), consists mainly of indolizine. Hydrolysis of (I) with PhOH leads to the Me_3 ester, m.p. 75°, identical with that obtained by use of HCO_2H (*loc. cit.*), converted by acids into the Me H_2 ester, m.p. 235—236° (decomp.), which when heated in phenanthrene affords the *Me H* ester of the dicarboxylic acid (XVII), m.p. 201—202°, and transformed by alkali into the dicarboxylic acid obtained directly from (I) and alkali. Since this product is obtained by devious routes, it is probable that isomerisation does not occur during hydrolysis and initial loss of CO_2, but during decarboxylation of (XVII). Hydrogenation of the products of decarboxylation and treatment with picric acid leads to octahydroindolizine picrate, and the picrate, m.p. 193°, of a base $C_9H_{17}N$, which, provided isomerisation has not occurred at any stage, must be identical with norlupinane. The picrates have identical m.p. and do not give depression when mixed, but the method of mixed m.p. has restricted val. with these substances and the chloroaurates do not appear identical. Hydrolysis of (I) with aq. HCl leads to the hydrochloride of a monocarboxylic acid (XVIII), hydrogenated to the acid $C_{10}H_{17}O_2N$ [*Me* ester (XIX), b.p. 135—136°/20 mm., its *picrate*, m.p. 161—162°, and *methiodide*, m.p. 179—181°]. Oxidation of (XVIII) affords only pyridine-2-carboxylic acid. Reduction of (XIX) by Na and EtOH gives the primary *alcohol* $C_{10}H_{19}ON$, m.p. 75—76° (*H phthalate*, m.p. 229°; *phenylurethane*, m.p. 110—111°; *methiodide*, m.p. 149—150°), not identical with lupinine

or *iso*lupinine. If the acid belongs to the quinolizine group, the CO_2H is not in the β-position.

LiPh, 2-methylpyridine, and $Pr^{\beta}Br$ yield 2-*iso*butylpyridine, b.p. 180—185° (*chloroplatinate*, m.p. 193°), hydrogenated (PtO_2 in AcOH) to 2-*iso*butylpiperidine, b.p. 177—179° (hydrochloride, m.p. 203°; *picrolonate*, m.p. 208—209° after darkening at 198°). 2-Acetylpyridine is transformed by MgEtI into 2-α-*hydroxy*-α-*methylpropylpyridine*, b.p. 93°/10 mm. (*chloroplatinate*, m.p. 190°), transformed by successive treatment with HI (*d* 1·7) and red P and Zn dust into 2-α-*methylpropylpyridine* (2-ψ-butylpyridine), b.p. 174—175° (*chloroplatinate*, m.p. 166°), whence (PtO_2 in AcOH) 2-α-*methylpropylpiperidine*, b.p. 179—181° (*hydrochloride*, m.p. 169°; *picrolonate*, m.p. 209°).

H. W.

Separation and purification of organic bases by means of metalammines. I. *o*-Phenanthroline. II. Pyridine, α-picoline, and *iso*quinoline. G. Tartarini and T. Samaja (Annali Chim. Appl., 1933, **23**, 351—356, 356—362).—I. When *o*-phenanthroline is synthesised from *o*-$C_6H_4(NH_2)_2$ and is extracted from the acidified products, either much tar is extracted as well or, if little acid is used, a large proportion of the product remains unrecovered in the viscous mass. This difficulty is removed by treating the product of the reaction with $FeSO_4$, precipitating the complex as *mercurichloride*, $[Fe^{II}(C_{12}H_8N_2)_3]Hg_2Cl_6,4H_2O$ (*perchlorate* also described), decomposing this with NaOH, evaporating, and extracting the free base with light petroleum.

II. Similarly, C_5H_5N may be separated from homologous bases by means of its $Cu(ClO_4)_2$ compound; α-picoline from crude picoline by means of the *compound*, $Ag_2S_2O_8$, $4C_6H_7N$, and *iso*quinoline from quinoline by means of its insol. *compound*, $Ni(SCN)_2,4C_9H_7N$.

T. H. P.

Acridol [5-hydroxyacridine]. A. Marzin (J. pr. Chem., 1933, [u], **138**, 99—102).—5-Chloroacridine (I) in boiling $PhNO_2$ gives a red *substance*, m.p. 250°, regarded as 5-hydroxyacridine. It does not depress the m.p. of acridone, being converted into it at 250°, and gives *N*-methylacridone, m.p. 203—204°, with Me_2SO_4 and KOH and (I) with PCl_5+POCl_3.

H. A. P.

Canavanine, an amino-acid. III. Canaline, a decomposition product of canavanine. M. Kitagawa and H. Yamada (J. Agric. Chem. Soc. Japan, 1932, **8**, 1201—1208).—*Canaline*, $C_4H_{10}O_3N_2$, m.p. 214° (decomp.), α_D −8·31° [*picrate*, m.p. 192—193° (decomp.); *flavianate*, m.p. 211° (decomp.); *Cu* salt; *hydrochloride*, m.p. 166°; *Bz* derivative, m.p. 99°], is formed in 75% yield on decomp. of canavanine by liver extract. It has one (probably α-) NH_2-N, is pptd. by $HgNO_3$ and Nessler's solution, and has no reducing power.

Ch. Abs.

***p*-Xylylmethylpyrazolones and [their] derivatives.** R. C. Huston, H. M. Sell, and H. R. Brigham (J. Amer. Chem. Soc., 1933, **55**, 3407—3408).—*p*-Xylylhydrazine (modified prep.; 68% yield), b.p. 120°/4 mm., m.p. 76—77°, and its Ac derivative, m.p. 104—106° (lit. 196°), give, 1-*p*-xylyl-3-methyl-, m.p. 164° (5-*Bz* derivative, m.p. 119°), and -2 : 3-dimethyl-5-pyrazolone, m.p. 97·5°, and 1-*p*-xylyl-5-methyl-3-pyrazolone (3-*Bz* derivative, m.p. 74°).

R. S. C.

Naphthyl derivatives of barbituric acid. De W. T. Keach (J. Amer. Chem. Soc., 1933, **55**, 2975—2979).—1-$C_{10}H_7$·CH_2Br and 5-alkylbarbituric acids give 5-α-*naphthylmethyl*-5-*ethyl*-, m.p. 247°, -n-*butyl*-, m.p. 214°, and -*allyl*-, m.p. 212°, -*barbituric acids*. α-Naphthylethyl derivatives could not be so obtained. 1-$C_{10}H_7$·CH_2·CH_2Br affords *Et*$_2$ α-*naphthylethylmalonate*, b.p. 198—203°/4 mm., whence *Et*$_2$ α-*naphthylethyl-ethyl*-, b.p. 188—193°/3—4 mm., -n-*butyl*-, b.p. 202—206°/3—4 mm., and -*allyl*-, b.p. 212—213°/5—6 mm., -*malonate* were prepared. With $CO(NH_2)_2$ these led to 5-α-*naphthylethyl*-, m.p. 196—198°, 5 : 5-α-*naphthylethyl-ethyl*-, m.p. 178°, -n-*butyl*-, m.p. 187°, and -*allyl*-, m.p. 169°, -*barbituric acid*. These compounds have relatively weak hypnotic properties.

R. S. C.

Synthesis of 5-α-naphthyl-5-ethylbarbituric acid. De W. T. Keach (J. Amer. Chem. Soc., 1933, **55**, 3440—3442).—α-$C_{10}H_7$·CH_2·CO_2Me, $Me_2C_2O_4$, and NaOMe give an oxalo-ester, which at 150°/5—6 mm. gives CO and *Me*$_2$ α-*naphthylmalonate*, b.p. 160—173°/5—6 mm., m.p. 104°, whence by prolonged alkylation at 100° *Me*$_2$ α-*naphthylethylmalonate*, m.p. 109—110°, b.p. 168—175°/5—6 mm., is obtained. This with $CO(NH_2)_2$ and NaOEt gives 5-α-*naphthyl*-5-*ethylbarbituric acid*, m.p. 254—255°, the hypnotic val. of which for white rats is inferior to that of luminal.

R. S. C.

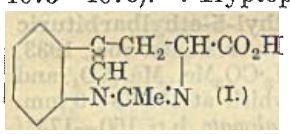
Pyrimidines. CXXXIV. Reaction of phenylacetaldehyde and acetophenone with carbamide. K. Folkers and T. B. Johnson (J. Amer. Chem. Soc., 1933, **55**, 3361—3368; cf. this vol., 957).—CH_2Ph·CHO, $CO(NH_2)_2$, and a little HCl in hot EtOH (with or without CH_2Ac·CO_2Et) give 2-*keto*-5-*phenyl*-4-*benzyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine* (I), m.p. 214—216°, hydrogenated (PtO_2; 3 atm.) in AcOH to 2-*keto*-4-cyclo*hexylmethyl*-5-cyclo*hexylhexahydropyrimidine*, m.p. 267·5—269·5°. 2-Keto-4 : 6-diphenyl-4-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine (II) (improved prep.), m.p. 179·5—180°, previously considered to be *s*-di-(α-methylbenzylidene)carbamide (A., 1915, i, 846), is hydrogenated to 2-*keto*-4 : 6-*di*cyclo*hexyl*-4-*methylhexahydropyrimidine*, m.p. 262—263°, which is stable to hot NaOH–EtOH and phthalic anhydride at 250—300°. Similarly, the substance considered (*loc. cit.*) to be *s*-di-(α-ethylbenzylidene)carbamide is 2-keto-4 : 6-diphenyl-5-methyl-4-ethyl-1 : 2 : 3 : 4-tetrahydropyrimidine (III). The structures of (I), (II), and (III), based on the stability and hydrogenation of the compounds, are supported by the absorption spectra. Et acetoacetate, $CO(NH_2)_2$, and a little HCl in hot EtOH give a little Et β-aminocrotonate.

R. S. C.

New reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. XI. Constitution of the phthalazine derivatives. F. M. Rowe and A. T. Peters (J.C.S., 1933, 1067—1070).—Methylation (Me_2SO_4–KOH) of 1-*hydroxy*-3-*aryl*-3 : 4-*dihydrophthalazine*-4-*acetic acids*, obtained by hydrolysis of Na 3-aryl-3 : 4-dihydrophthalazine-1-sulphonate-4-acetates (cf. A., 1926, 625), gives 1-*keto*-3-*aryl*-2-*methyltetrahydrophthalazine*-4-*acetic acids*,

which form Me esters: (aryl group) 4′-*nitrophenyl*, m.p. 207° (*Me* ester, m.p. 188°), 3′-*nitrophenyl*, m.p. 235° (*Me* ester, m.p. 180°), -*nitro*-2′-*methylphenyl*, m.p. 211° (*Me* ester, m.p. 201°), 2′-*chloro*-4′-*nitrophenyl*, m.p. 218° (*Me* ester, m.p. 210—211°), 2′ : 6′-*dichloro*-4′-*nitrophenyl*, m.p. 216° (*Me* ester, m.p. 186°), 2′ : 6′-*dibromo*-4′-*nitrophenyl*, m.p. 240° (*Me* ester, m.p. 215°), *benzeneazophenyl*, m.p. 189°, and 4′-*nitrobenzeneazophenyl*, m.p. 246°. Reduction products (*loc. cit.*) are 1-*hydroxy*-3-(4′-*aminophenyl*)-, m.p. 239°, -(3′-*aminophenyl*)-, m.p. 252°, and -(4′-*amino*-2′-*methylphenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid*, m.p. 217° The constitution of "Soluble Yellow-I" and "-II" products (cf. Bucherer and Frohlich, A., 1931, 1409) are discussed. F. R. S.

Reaction of tryptophan and acetyl chloride. F. Wrede and G. Feuerriegel (Ber., 1933, **66**, [*B*] 1073—1076).—*l*-Tryptophan is converted by AcOH and AcCl at 100° into NN′-



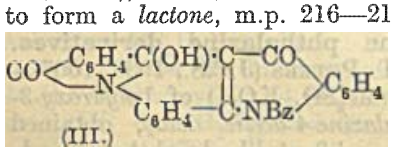
(I.)

ethenyltryptophan (I), m.p. 202°, $[\alpha]_D$ ±0° (*Ag* salt; *chloroaurate*, m.p. 179°; *chloroplatinate*, decomp. about 240°; non-cryst. *Me* ester; corresponding *amide*, decomp. about 180°). H. W.

Attempts to prepare nitrogenous derivatives of bivalent carbon. D. Wood, jun., and F. W. Bergstrom (J. Amer. Chem. Soc., 1933, **55**, 3314—3319).—Attempts to prepare Scheibler's $C(OEt)_2$, Pinner's compound, $(C_{10}H_{21}N_3,HCl)_2,PtCl_4$ (A., 1884, 724), $C(OK)_2$, and C(OK)·OEt failed. Diphenylmethylformamidine, b.p. 335—340°, 215·5—216·5°/24 mm. [*picrate*, m.p. 152—152·5° (decomp.)], with an excess of the appropriate metal amide in liquid NH_3 gives NHPhMe, a *substance* [*picrate*, m.p. 146·5° (decomp.)], and *salts*, NHPh,CHR·NM, in which R=NPhMe·, and M=Ba, Ca, Na_2, and Ag_2 (from KNH_2 and AgI), and $NPhBa_{0·5}$·CHR·NBa. Glyoxaline affords similarly the *Na*, Li (+0·5, 1, and $2NH_3$), and Ba (+0 and $1NH_3$) salts; the *K* salt was prepared by using only 1 mol. of KNH_2. *N*-Methylglyoxaline and $NaNH_2$ give the *compound*,

$C_6H_4<\begin{matrix}NNa\\NMe\end{matrix}>CH\cdot NHNa$. R. S. C.

Benzoyl derivatives of indigotin. E. Hope, R. W. R. Kersey, and D. Richter (J.C.S., 1933, 1000—1003).—Höchst Yellow R and 15% KOH at 100° (autoclave) give BzOH, anthranilic acid, and a *substance*, $C_{16}H_{11}O_3N$ (I), m.p. 237°, whilst 10% KOH at atm. pressure gives the *lactam*, $C_{16}H_9O_2N$ (II), m.p. 232°. (I) forms *Ac*, m.p. 199°, and *Bz* derivatives, m.p. 236°, and is methylated to *Me*, m.p. 183—184°, and *Me*$_2$ derivatives, m.p. 98°. (II) is oxidised ($KMnO_4$) to phthalic acid and an *acid*, $C_{16}H_{11}O_6N$, m.p. 135—138° (efferv.) (*Ag*$_2$ salt; *Me*$_2$ ester), which, when heated, loses H_2O and CO_2 to form a *lactone*, m.p. 216—217°, hydrolysed to a



(III.)

hydroxy-acid (*Me* ester, m.p. 207°), and subsequently methylated to a *methoxymonobasic acid*, m.p. 172—173°. The formula (III) is suggested for Höchst Yellow R (all $C_6H_4<$ are *o*). F. R. S.

Bilirubinoid pigments. V. Chromoproteins of red algæ. III. Phycobilins of red algæ. Transformation into mesobilirubin and dehydromesobilirubin. R. Lemberg [with, in part, G. Bader] (Annalen, 1933, **505**, 151—177; cf. A., 1930, 488; 1932, 1266).—Proof that the phycobilins are bile pigments is found in the transformation of phycoerythrin (I) by boiling KOH–MeOH into dehydromesobilirubin (glaucobilin) (II), isolated as the Me$_2$ ester, m.p. 218—218°, and mesobilirubin (III); the total yield is 1·53%, whereas 1·69% is calc. for a mol. of wt. 34,500. *c*-Phycocyan from *Nori* yields (II) but not (III). The work of Levene *et al.* (A., 1931, 1436) is criticised. The behaviour of (I) towards MeOH–HCl is described and also the oxidation of phycoerythrobilin Me ester to phycocyanobilin Me ester. Mesobiliviolin is shown to be a mixture of a blue mesobilicyanin corresponding with the unsaturated bilicyanin and identical with phycocyanobilin and a red pigment spectroscopically similar to phycoerythrobilin and probably composing the pigment constituent of (I) for which the name mesobilierythrin is proposed. Reply is made to Siedel and Fischer (this vol., 405). H. W.

Magnetic behaviour of hæmoglobin derivatives. F. Haurowitz and H. Kittel (Ber., 1933, **66**, [*B*], 1046—1049).—Mesoporphyrin Me$_2$ ester and protoporphyrin are diamagnetic; the two radical positions are therefore so arranged that their magnetic moments neutralise one another as indicated in the formula of Clar and Haurowitz (this vol., 404). Chlorohæmin I and II and oxyhæmin are strongly paramagnetic. It must be assumed that the Fe atom in them retains the high paramagnetism of Fe^{III}; the apparent contradiction in the chemical properties of the hæmins is explained by assuming that in them Fe is attached by weak forces but is sterically sheltered from the dissociating action of H_2O and the influence of acids and alkalis by the peculiar structure of the porphyrin skeleton. The diamagnetic susceptibility of Fe$^{\cdot\cdot}$ in hæmoglobin is the same as that of Fe$^{\cdot\cdot}$ in hæmin. H. W.

4 : 5′-Di*iso*xoazoloyl ketone. II. M. Freri (Gazzetta, 1933, **63**, 419—425; cf. A., 1931, 968).—This substance (I) when isolated in EtOH or *iso*amyl alcohol is reduced to s-4 : 5′ : 4″ : 5‴-*tetraisooxazolylpinacol*, m.p. 195—196°, which with BzCl gives (I) and the carbinol. (I) forms a single *oxime*, m.p. 155° (*Bz* derivative, m.p. 121°), which when heated decomposes slowly to a *product*, m.p. 135—140°. E. W. W.

Quinoline derivatives. I. Furanoquinolines. M. A. Haq, M. L. Kapur, and J. N. Rây (J.C.S., 1933, 1087—1089).—α-*Piperonylidene*-, m.p. 226° (*lactone*), α-2-*nitrobenzylidene*-, m.p. 262° (*lactone*, m.p. 200°, reduced to the *furanoquinoline*, m.p. 172°), *lactone* of α-6-nitro-3 : 4-methylenedioxybenzylidene-, m.p. 232° (reduced to the *base*, m.p. 262°), and the *lactone* of α-6-nitroveratrylidene-β-3 : 4-dimethoxybenzoylpropionic acid, m.p. 206° [reduced to the *base*, m.p. 245° (*picrate*, m.p. 241°)], are prepared by condensing β-3 : 4-dimethoxybenzoylpropionic acid with the appropriate aldehyde. β-6-*Nitro*-3 : 4-*dimethoxybenzoylpropionic acid*, m.p. 212° (*Me* ester, m.p. 118°), is

reduced to the NH_2-compound, m.p. 118° (*Bz*, m.p. 225°, and *Ac* derivative, m.p. 187°; *Me* ester, m.p. 127°), which gives 6 : 7-*dimethoxy*-3-*acetyl*-2-*methylquinoline*, m.p. 245° (decomp.) (with acetylacetone), -3-*benzoyl*-2-*phenylquinoline*-, m.p. 229° (decomp.) (with dibenzoylmethane), 6 : 7-*dimethoxy*-2-*phenylquinoline*-, m.p. 231—232° (with COPhMe), and 6 : 7-*dimethoxyquinoline*-4-*propionic acid*, m.p. 120—121° (with MeCHO). F. R. S.

Alkaloid cuprichlorides. Specific precipitation by cupric chloride of cinchona alkaloids containing the vinyl group. A. Cohen (J.C.S., 1933, 996—1000).—The *cuprichlorides* of *quinine*, m.p. 210° (decomp.), *quinidine*, m.p. 208—209° (decomp.), *cinchonine* (+1·5H_2O), m.p. 130—132° (decomp.), and *cinchonidine* (+2H_2O), m.p. 128—129° (decomp.), Q,2HCl,$CuCl_2$, have been obtained; they are recryst. from HCl and decomposed by H_2O. The corresponding dehydro-bases do not form complex salts and hence the salts may be used for purification of alkaloidal derivatives. The constitution of the salts is discussed. *Quinene*, decomp. 125—130°, *cinchene*, decomp. 185—187°, and *dihydroquinene cuprichloride*, decomp. 195°, are also obtained. 5-*Nitro*-6-*methoxy*- (+H_2O), efferv. 187—189°, and 2-*methyl*-*quinoline*, m.p. 175—178° (decomp.), and *quinoline cuprichloride*, decomp. > 185°, and a *compound* of 6-methoxyquinoline cupri-tri- and -tetra-chloride, m.p. 157—159°, are described. F. R. S.

Constitution of strychnine. I. M. Kotake and T. Mitsuwa (Annalen, 1933, **505**, 203—208).—Dihydrostrychnine and PhCHO in EtOH containing NaOEt give *benzylidenedihydrostrychnine* (I), m.p. 255° (*picrate*, m.p. 230°). Oxidation of (I) in $COMe_2$–AcOH leads to the *substance*, $C_{28}H_{28}O_5N_2$, m.p. 280° [*picrate*, m.p. 215°; *chloroaurate*, m.p. 214—217° (decomp.); *chloroplatinate*, decomp. 233°). Treatment of (I) in $COMe_2$–H_2O with $KMnO_4$ leads to the *compound*, $C_{21}H_{22}O_3N_2$, m.p. 263°, and an *acid*, $C_{20}H_{22}O{\cdot}N_2$, m.p. 300°, decarboxylated to the *substance* $C_{19}H_{22}O_3N_2$, m.p. 268° (*hydrochloride*, m.p. 286°), and transformed by Br–H_2O into the *compound*, $C_{19}H_{20}O_3N_2Br$, isolated as the *acetate*, m.p. 235°. Strychnine methiodide in EtOH–AcOH is converted by H_2O_2 into the periodide, m.p. 245°, and a yellow liquid which yields strychnine methochloride. H. W.

***Strychnos* alkaloids. LXXV. Reduction and oxidation of brucinesulphonic acids III and IV and of strychninesulphonic acid III.** H. Leuchs and A. Dornow (Ber., 1933, **66**, [*B*], 1159—1165).—Hydrogenation of brucinesulphonic acid III (PtO_2) gives a H_4-derivative, $[\alpha]_D^{20}$ +77·3°/*d* in H_2O, whereas oxidation with CrO_3 affords the substance $C_{16}H_{20}O_7N_2S$, $[\alpha]_D^0$ −193·2°/*d* in H_2O (H_4-derivative, $[\alpha]_D^{20}$ −56·8°/*d* in H_2O), identical with that obtained from aminostrychnine- and brucine-sulphonic acid II. Brucinesulphonic acid III smoothly gives a H_2-derivative, $[\alpha]_D^{20}$ +88·5°/*d* in 0·1*N*-NaOH, whereas oxidation leads to ill-defined products even when conducted through the aminoquinol hydrate [*perchlorate* (+H_2O), $[\alpha]_D^0$ +3·0°/*d* in H_2O]. Hydrogenation of strychninesulphonic acid III leads to partly unchanged material, whilst oxidation with CrO_3 yields little cryst. material. Oxidation with 14*N*-HNO_3 in presence of $CO(NH_2)_2$ at 0° gives the *substances* $C_{21}H_{23}O_7N_3S$ and $C_{21}H_{24}O_7N_2S$ (I), darkens without melting at 260—290°. (I) is transformed by HCl into the *salt* $C_{21}H_{22}O_6N_2S$,HCl,3H_2O. Hydrogenation of (I) leads to the compound $C_{21}H_{24}O_6N_2S$, $[\alpha]_D^{20}$ +16°/*d* in 0·1*N*-NaOH, identical with strychninesulphonic acid hydrate IV. Nitration gives the *compound* $C_{21}H_{22}O_{11}N_4S$. The *substance* $C_{21}H_{24}O_{11}N_4S$ is obtained by nitration of the acid $C_{21}H_{24}O_6N_2S$. H. W.

Metathebainone. R. S. Cahn (J.C.S., 1933, 1038—1040).—Thebaine in conc. HCl is reduced (Pd–H_2) to 85% metathebainone and some dihydrocodeine and other non-phenolic bases. This result cannot be reconciled with Schopf's speculations (A., 1931, 1313). F. R. S.

Solanidine and solanthrene. F. Bergel and R. Wagner (Ber., 1933, **66**, [*B*], 1093—1096).—Treatment of solanine with 2% HCl leads to solanidine (I), m.p. 219°, for which the formula $C_{27}H_{43}ON$ is confirmed (*benzoate*, m.p. 214°; acetate, m.p. 207°), and solanthrene (II), $C_{27}H_{41}N$, m.p. 167° (identical with the solanidene of Schopf). Catalytic hydrogenation of (I) in AcOH (PbO_2) leads only to the absorption of 2H with production of dihydrosolanidine, m.p. 222° (*acetate*, m.p. 195°). The conception that (II) is formed by loss of H_2O from (I) is strengthened by the observation that it absorbs $2H_2$ (PtO_2 in AcOH) with production of tetrahydrosolanthrene, $C_{27}H_{45}N$, m.p. 164°. Thermal decomp. of dihydrosolanidine palmitate hydrochloride, m.p. 225°, leads to *dihydrosolanidene*, $C_{27}H_{43}N$, m.p. 165°, not identical with Schopf's solanidane. H. W.

Decomposition of the arsinic acids. B. Englund (Svensk Kem. Tidskr., 1933, **45**, 170—172).—Benzylarsinic acid (I) and H_2O slowly give $CH_2Ph{\cdot}OH$ +As_2O_3. The hydrolysis is catalysed by HCl, and is then unimol. with respect to (I). The velocity is approx. proportional to the activity of HCl. The temperature coeff. is normal. Arsinoacetic acid (II) in H_2O, EtOH, or AcOH takes up 2 mols. of Br per mol., the velocity being proportional to the concn. of (II) and to $[Br]^{1/2}$. Distilling the product in vac. gives $CHBr_3$, $AsBr_3$, and $CBr_3{\cdot}CO_2H$. R. P. B.

New derivatives of *p*-arsanilic acid. V. *p*-Arsinomethylmalonanilic acid and related compounds. G. T. Morgan and E. Walton (J.C.S., 1933, 1064—1067).—Me methylmalonate (improved prep.) is hydrolysed (KOH–MeOH) to *Me H methylmalonate*, b.p. 131°/16 mm., which with $SOCl_2$ gives *α-carbomethoxypropionyl chloride*, b.p. 73°/16 mm. α-Carbethoxypropionyl chloride, from Et methylmalonate (improved prep.), and atoxyl form *Et* p-*arsinomethylmalonanilate* [*Na* salt; *Me* ester and its *Na* salt (+H_2O)], which with the corresponding amine yields *methylmalon-anilamide*- [NH_3; *Na* salt (+H_2O)], -*anilomethylamide*- (NH_2Me; *Na* salt), -*anilethylamide*- [NH_2Et; *Na* salt (+H_2O)], and -*anilo*-n-*propylamide*-p-*arsinic acid* [NH_2Pr; Na_2 salt (+H_2O)]. The ester gives p-*dichloroarsino*- (I), m.p. 158—160° (decomp.), which in $NaHCO_3$ is acidified to p-*oxyarsini*-, oxidised (H_2O_2) to p-*arsino-methylmalonanilic acid*. (I) in $SOCl_2$ and NH_2Ph form p-*oxyarsinomethylmalonanilide*, oxidised (H_2O_2) to

methylmalonanilide-p-*arsinic acid* [*Na* salt ($+2H_2O$)]. Atoxyl and methylmalonyl dichloride yield *methylmalonanilide*-pp'-*diarsinic acid*. Many of the compounds show marked trypanocidal activity. F. R. S.

Constitution of sulpharsphenamine. W. J. C. Dyke and H. King (J.C.S., 1933, 1003—1012).—When CH_2O and $NaHSO_3$ are added to salvarsan the methylenesulphite groups are attached to the phenolic groups, but when preformed Na formaldehyde H sulphite (I) is used they become attached to the NH_2. *p*-Aminophenylarsinic acid in NaOH and (I) form *Na* p-*aminophenylarsino*-N-*methylenesulphite* ($+2{\cdot}5H_2O$). (I) and 3-amino-4-hydroxyphenylarsonic acid give Na_2 3-*amino*-4-*hydroxyphenylarsino*-N-*methylenesulphite* ($+6H_2O$), or in neutral solution, the *Na* salt ($+4H_2O$); and the acid with CH_2O and $NaHSO_3$ successively forms a *substance*, containing two differing methylenesulphite groups. Samples of commercial sulpharsphenamine have been analysed for total and oxidised S (Elvove's method); it is the Na salt of 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene-*OO'N*-trimethylenesulphurous acid. F. R. S.

Organic compounds of germanium. II. H. Bauer and K. Burschkies (Ber., 1933, **66**, [*B*], 1156—1158).—Ge aryl trihalides are quantitatively prepared from arylgermanic anhydrides and conc. HCl, HBr, or HI in sealed vessels at 100°. The following *compounds* are described: $GePhCl_3$, b.p. 102—103°/13 mm.; $GePhBr_3$, b.p. 120—122°/13 mm.; $GePhI_3$ (III), m.p. 55—56°: *p*-$C_6H_4Me{\cdot}GeCl_3$ (II), b.p. 115—116°/12 mm.; *p*-$C_6H_4Me{\cdot}GeBr_3$, b.p. 155—156°/13 mm.; *p*-$C_6H_4Me{\cdot}GeI_3$, m.p. 72°. MgMeI and MgEtI convert (I) into $GePhMe_3$, b.p. 182—183°, and $GePhEt_3$, b.p. 116—117°/13 mm. The *compound* -$C_6H_4Me{\cdot}GeEt_3$, b.p. 125—126°/12 mm., results from (II) and MgEtI. H. W.

Action of copper on some aromatic mercuriaceto-compounds. A. Contardi and B. Ciocca (Annali Chim. Appl., 1933, **23**, 362—366).—$HgPh_2$ and Hg bis-*p*-diethylaminophenyl are conveniently prepared by heating the corresponding mercuriacetocompounds in PhMe or C_6H_6 solution in presence of Cu (cf. A., 1925, i, 1341). T. H. P.

Furan mercurials. H. Gilman and G. F. Wright (J. Amer. Chem. Soc., 1933, **55**, 3302—3314).—Furan, $HgCl_2$, and NaOAc give 2-*chloromercuri*- (I), m.p. 151°, and 2 : 5-*dichloromercuri-furan*, and the mother-liquors with KI_3 give tetra- and 2 : 5-di-iodofuran. (I) and BzCl in Et_2O give a little dibenzoylfuran. (I), with AcCl in $COMe_2$, gives furyl Me ketone (21%), with furfuryl chloride in Et_2O *difurylmethane* (II), b.p. 94°/22·5 mm., with I 2-iodofuran (5-*HgCl*-derivative, m.p. 173°), with Me_2SO_4 at 160—170° furan, with $Na_2S_2O_3$ *Hg difuryl*, m.p. 114°, b.p. 156°/7 mm. [also prepared from (I) and I in $COMe_2$, or N_2H_4, and from Mg 2-furyl iodide and $HgCl_2$ in Et_2O], with HCl–H_2O–EtOH at 100° furan (82%), and with $SOCl_2$ in Et_2O at 20° a little 2-chlorofuran. (II) is stable to $KMnO_4$ and $EtNO_3$–NaOMe, and gives the 5-*HgCl*-derivative, m.p. 149·5°, which regenerates (II) with hot acid and with aq. I (best with $CaCO_3$) gives a 70% yield of 5-*iodo*-2 : 2'-*difurylmethane*, b.p. 123°/9 mm. 2-Furonitrile and Mg 2-furyl iodide in Et_2O give 2-*furoyl*-2-*furylmethane*, m.p. 33°, b.p. 113°/6 mm. (73·3% yield), which with N_2H_4 and KOH–MeOH gives (II) in 92% yield. Mg 5-iodo-2-furyl iodide and Me_2SO_4 give a 72% yield of 2-iodofuran, also obtained in 60% yield from 2 : 5-di-iodofuran and Al–Hg. 2-Methylfuran gives the 5-*HgCl*-derivative (III), m.p. 127°, by way of an intermediate compound (IV), $C_5H_6O{\cdot}Hg(OH)Cl,HgCl_2$. (IV) with KI_3 gives 5-*iodo*- (V), b.p. 59°/18 mm., and (?-)*di-iodo*-2-*methylfuran* (unstable). The latter with Al amalgam in Et_2O–MeOH gives β-(? 3-)*iodo*-2-*methylfuran*, b.p. 57°/28 mm. (5-*HgCl*-derivative, m.p. 193·5°). (III) with KI_3 gives (V) (48%), the Grignard reagent from which affords 5-methyl-2-furoic acid (33%) and *o*-*methyl*-2-*furoyl*-α-*naphthalide*, m.p. 149·5° (also obtained from α-$C_{10}H_7{\cdot}NH_2$ and 5-*methyl*-2-*furoyl chloride*, b.p. 93°/20 mm.). Na furoate and hot aq. $HgCl_2$ give 2-chloromercuri- and 2 : 5-dichloromercuri-furan; the appropriate Na salts give similarly good yields of 5-iodo-, 5-*bromo*- (VI), m.p. 177°, and 5-*methyl*-2-*chloromercurifuran*, m.p. 134°; the 5-NO_2-compound (VII), m.p. 208°, was obtained in 25% yield at 150—160°. (VI) and (VII) with aq. HCl give quant. yields of 2-bromo- and 2-nitro-furan, respectively. Furoic acid (VIII), its 5-Br- and other α-substituted derivatives (but not the 5-NO_2-acid) are decarboxylated by hot, aq. $HgCl_2$ to furan etc. (VII) and NaI_3 give 2-*iodo*-5-*nitrofuran*, m.p. 76°, lachrymatory, also obtained from 2 : 5-di-iodofuran and HNO_3 (*d* 1·52) in Ac_2O at −5° to −10°. Similar nitration of 2 : 5-dibromofuran gives a quant. yield of fumaric acid. (VIII) and aq. $Hg(OAc)_2$ give *acetoxymercury furoate*, which at 110—135° gives a mixture whence AcOH and NaCl yield 3-*chloromercurifuran*, m.p. 184·5°. This with hot HCl–aq. EtOH gives (I) (63% yield), with $Na_2S_2O_3$ *Hg* 3 : 3'-*difuryl* (72%), m.p. 73°, and with KI_3 3-*iodofuran*, b.p. 132·2°/732 mm. (62%) (also obtained from tetraiodofuran and Al–Hg in Et_2O–MeOH). Mercurials could not be obtained from 2 : 5-di-iodo- or 2-nitrofuran, or 2-nitrothiophen. In general α- are more reactive than β-mercurials. R. S. C.

Organic derivatives of silicon. XLVIII. Steric effects of the *cyclo*hexyl group. N. W. Cusa and F. S. Kipping (J.C.S., 1933, 1040—1043).—$SiPhCl_3$ and $C_6H_{11}{\cdot}MgBr$ give cyclo*hexyloxydi*cyclo*hexylphenylsilicane*,, m.p. 103—104°, and, in absence of O_2, *di*cyclo*hexylphenylsilicane*, b.p. 180—185°/4 mm. The non-formation of quaternary hydrocarbon is probably due to steric hindrance. Di*cyclo*hexylphenylsilicyl bromide and MgEtBr form *di*cyclo*hexylphenylethylsilicane*, b.p. about 370°, decomposed by Br to a mixture of condensation products of di*cyclo*hexylsilicanediol. F. R. S.

Hydrolysis of proteins during denaturation. M. A. Lissitzin and N. S. Alexandrovskaja (Biochem. Z., 1933, **264**, 35—39).—The chemical changes which occur in proteins (legumin, phaseolin, glycinin) on denaturation (acid and alkali) do not go beyond a certain point and are not continued on repeating the treatment. The denatured products closely resemble Hammarsten's caseinogen. W. McC.

Dipeptide phosphoric acid from caseinogen. P. A. Levene and D. W. Hill (J. Biol. Chem., 1933,

101. 711—718).—*Brucine glutamylserinephosphate* (I), $C_{31}H_{39}O_{13}N_4P$, m.p. 171—172° [*Ba* salt, $(C_8H_{10}O_9N_2Ba)_2Ba$], is isolated from the brucine salt of the ppt. obtained by hydrolysing caseinogen-phosphopeptone with 2*N*-HCl and treatment with $Ba(OH)_2$. Two possible structures are suggested for (I). A. L.

Reversibly oxidisable substance from irradiated protein. P. Wels [and M. Jokisch] (Arch. exp. Path. Pharm., 1933, **171**, 480—495).—Ultraviolet irradiation of aq. ovalbumin in N_2 gives a reversibly oxidisable substance containing SH (possibly glutathione). F. O. H.

Isolation of tyrosylserylprolyltyrosine in the stepwise degradation of silk-fibroin (*Bombyx mori*). E. Abderhalden and A. Bahn (Z. physiol. Chem., 1933, **219**, 72—81).—Tyrosylserylprolyltyrosine [Bz_4 and Bz_3 (by loss of serine-Bz) derivatives] was isolated from the fraction of the hydrolysis products of silk-fibroin pptd. by Hopkins' reagent. Tryptic hydrolysis gave tyrosine, *serylproline*, froths at 110—150°, solidifies, m.p. 215—225°, and *tyrosylserylproline* [*dibenzenesulphonyl* and *phenylcarbimido*- (I) -derivatives; benzylamine derivative of (I)]. l-*Tyrosylglycine*, froths at 150—170°, solidifies, m.p. 255—265° (decomp.), $[\alpha]_D^{20}$ +69·7° in H_2O, was synthesised from *dicarbobenzoyloxytyrosine chloride*, m.p. 73°, by interaction with glycine to give *dicarbobenzoyloxytyrosylglycine*, m.p. 168°. J. H. B.

Cleavage of nitrogen linkings in protein and peptides by the light of the quartz lamp. H. C. Eckstein and F. Lieben (Biochem. Z., 1933, **263**, 366—370).—Irradiation of feebly acid solutions of globin, gelatin, and caseinogen by means of the quartz lamp causes an increase of NH_2-N (Van Slyke) partly due to the formation of NH_3 and partly of free NH_2 groups. This is not due either to the hydrolysis of the peptide linking nor to arginine, and it appears probable that the newly-formed NH_2 groups and NH_3 are derived from the N-containing nuclei of histidine, proline, and hydroxyproline. P. W. C.

Viscosity of ovalbumin and hæmoglobin in carbamide solutions. C. S. Liu (Chinese J. Physiol., 1933, **7**, 107—116).—In 40% $CO(NH_2)_2$ solution, η of ovalbumin (I) increases with denaturation: this is not due to p_H change. (I) shows a min. at p_H 5·7 and hæmoglobin at p_H 7·4, the isoelectric points of the denatured proteins. By determining the shift of p_H by citrate buffers these vals. were calc. to be 5·2 and 6·9. H. G. R.

Formation of carbamide from prolysin, citrullin, hydantoins, and protein by the action of hydrogen sulphide. M. Wada and N. Hayama (Proc. Imp. Acad. Tokyo, 1933, **9**, 305—308).—$CO(NH_2)_2$ (I) results when prolysin, citrullin, and other hydantoins are treated with H_2S and weak alkali. The amounts of (I) so obtained from some proteins are reported. A. L.

Dilatometric studies of the fission of proteins and dipeptides. P. Rona and Fischgold (Klin. Woch., 1933, **12**, 113; Chem. Zentr., 1933, i, 1953).—Vol. changes on fission of proteins with pepsin at 37° and of peptides with conc. HCl at 50° or 1·5*N*-NaOH at 37° have been determined. The diminution in vol. on fission of ovalbumin (but not of caseinogen) is proportional to the degree of degradation. A similar proportionality holds for the cleavage of dipeptides; NaOH causes an increase, and HCl a decrease, in vol. Hence vol. changes are considerably influenced by the different ionic conditions of the amphoteric dipeptides or NH_2-acids. A. A. E.

Semimicro-determination of carbon and hydrogen. E. P. Clark (J. Assoc. Off. Agric. Chem., 1933, **16**, 414—418).—Procedure, using an electric combustion furnace and a CeO_2 catalyst, is described. J. S. A.

Rapid colorimetric determination of total carbon and nitrogen in the same sample. E. M. Emmert (J. Assoc. Off. Agric. Chem., 1933, **16**, 424—427).—The substance is oxidised by heating with $NaClO_3+H_2SO_4$, C being oxidised to CO_2, and N to HNO_3 which is distilled over. CO_2 is determined colorimetrically by means of Na phenolphthalein (cf. A., 1931, 1142), and HNO_3 by means of phenoldisulphonic acid (cf. B., 1930, 372). J. S. A.

Micro-determination of sulphur and phosphorus in organic compounds. A. Elek and D. W. Hill (J. Amer. Chem. Soc., 1933, **55**, 3479—3482).—This is effected by fusion with Na_2O_2 in a micro-bomb and subsequent determination as $BaSO_4$ and NH_4 phosphomolybdate, respectively, 3·5 mg. of substance being required. R. S. C.

Determination of aldehydes by quantitative application of Cannizzaro's reaction. L. Palfray, S. Sabetay, and (Mlle.) D. Sontag (Chim. et Ind., 1933, Spec. no., 1037—1038; cf. A., 1930, 318; 1931, 856; 1932, 867).—The Cannizzaro change is quant. with aromatic but only with certain aliphatic aldehydes (*e.g.*, heptaldehyde). The method is applicable to mixtures (oils of bitter almond, cumin). H. W.

Determination of cholesterol. I. Colorimetric methods. A. S. Ruiz and I. Torres (Anal. Fís. Quím., 1933, **31**, 370—377).—The methods of Myers and Wardell (I), Grigaut (II), Bloor (III), and Autenrieth and Funk (IV) are compared. Preference is given to (I), and (II) is satisfactory, but (III) gives high vals. and in (IV) extraction is incomplete. R. K. C.

[Organic] colour reactions. II. I. M. Korenmann (Z. anal. Chem., 1933, **93**, 438—447; cf. A., 1932, 717).—The influence of temp. and concn. on various org. colour reactions with conc. H_2SO_4 or HCl has been investigated, the importance of these factors being emphasised. The following colour reactions are considered: vanillin test for phloroglucinol, $COMe_2$, and pinene; Schryver's test for CH_2O; the $K_2Cr_2O_7$ test for NH_2Ph and NHAcPh; the $KClO_3$ test for NH_2Ph; the KNO_3 test for *m*-$C_6H_4(OH)_2$; the brucine test for HNO_3. D. R. D.

Bromometric determination of novocaine and anæsthesin by Fijalkow's method. W. Hoffmann (Apoth.-Ztg., 1932, **47**, 686—687; Chem. Zentr., 1932, ii, 3925).—Sources of error are discussed. L. S. T.

Volumetric potassium bromate–bromide titration of furfuraldehyde. Effect of temperature.

O. C. MAGISTAD (Ind. Eng. Chem. [Anal.], 1933, 5, 253).—Theoretical results are obtained at 18°, but not at higher temp. E. S. H.

Antimony trichloride reaction with compounds containing 5-membered monoheterocyclic rings. V. E. LEVINE and E. RICHMAN.—See this vol., 987.

Micro-determination of proline and oxyproline. K. LANG (Z. physiol. Chem., 1933, 219, 148—154).—Proline and oxyproline are oxidised to pyrroline (I) and hydroxypyrroline (II) by means of OCl′. (I) and (II) are isolated by steam distillation and determined together by *p*-$NMe_2 \cdot C_6H_4 \cdot CHO$. (II) is determined separately by condensation with isatin in dil. H_2SO_4. J. H. B.

Volumetric determination of very small amounts of nicotine. L. NAGY and A. DICKMANN (Z. anal. Chem., 1933, 94, 12—17).—Nicotine is pptd. by silicotungstic acid. The ppt. is dissolved in a known amount of 0·01*N*-NaOH and excess of NaOH is titrated with 0·01*N*-HCl in presence of Me-red. The procedure can be carried out in presence of C_5H_5N. E. S. H.

Spectrophotometric investigation of the Jaffe-Folin reaction for creatinine. H. MOHLER and F. ALMASY (Z. anal. Chem., 1933, 94, 17—18).—The absorption spectra of solutions of creatinine (I), $K_2Cr_2O_7$ (II), and Na picrate (III) have been compared. Those of (I) and (III) are identical in the ultra-violet. (II) is most suitable as a colour comparison at 4650—5100 Å. E. S. H.

Identification of organic compounds. XIV. Gen-alkaloids [*N*-oxides of alkaloids]. L. ROSENTHALER (Pharm. Ztg., 1933, 78, 926—928; cf. this vol., 844).—Pptn. tests are described for the *N*-oxides of atropine (orange), hyoscyamine (pale orange), eserine (very pale yellow), scopolamine (orange), strychnine (yellow), and morphine (yellow). The colours in parentheses are those given in boiling Ac_2O (cf. lit.). R. S. C.

Concentrated sulphuric acid without and with addition of other substances as reagents for colour reactions of alkaloids. R. LILLIG (Pharm. Ztg., 1933, 78, 910—913, 921—926).—Lists of the reactions are given and various corrections of lit. statements are made. R. S. C.

Biochemistry.

Method of gas analysis for respiration trials. M. KLEIBER (J. Biol. Chem., 1933, 101, 583—594).—To avoid the error, in the Haldane apparatus, due to effusion of O_2 from the KOH to the sample, determinations of CO_2 and CO_2+O_2 are carried out simultaneously in two separate apparatus. In the determination of O_2, distillation of H_2O from the measuring pipette to the pyrogallol is decreased to a min. H. G. R.

Precise analysis of air from respiration chambers. T. M. CARPENTER (J. Biol. Chem., 1933, 101, 595—601).—The accuracy of the author's modification (A., 1929, 1113) of the Haldane apparatus is demonstrated. No evidence of the diffusion of gases through KOH solution was obtained. H. G. R.

Continuous recorder of respiratory metabolism. H. REIN (Arch. exp. Path. Pharm., 1933, 171, 363—402).—The apparatus, which is electrically controlled, records the % O_2 consumption, the % CO_2 of the expired air, the vol. of inspired air, and the frequency of respiration. Its application to men and animals is described. F. O. H.

Mammalian life without red blood-corpuscles. W. R. AMBERSON, A. G. MULDER, F. R. STEGGERDA, J. FLEXNER, and D. S. PANKRATZ (Science, 1933, 78, 106—107).—Experiments which show that hæmoglobin (I) can perform its respiratory function in solution much as it does within red corpuscles are described. The chief function of the vertebrate red corpuscles is to keep (I) in the blood-stream by means of impermeable membranes. L. S. T.

Diet and its effect on blood formation. F. S. ROBSCHEIT-ROBBINS (J. Amer. Dietet. Assoc., 1933, 8, 387—395).—The increase in hæmoglobin produced in dogs by various foods has been determined. CH. ABS.

Combination of methæmoglobin with hydrogen sulphide. D. KEILIN (Proc. Roy. Soc., 1933, B, 113, 393—404).—The necessity of O_2 for the formation of sulphohæmoglobin (I) (A., 1926, 314) from hæmoglobin (II) and H_2S is confirmed. (I) appears to be an irreversible Fe^{II} derivative of (II) + an oxidation product of H_2S. (II) cannot be recovered from (I). Acid methæmoglobin (III) and H_2S [1 mol. per atom of Fe of (III)] combine to form "H_2S-hæmoglobin" (IV), distinct from (I), with absorption bands at 578 (weak) and 545 mμ (stronger), and a dissociation const. of approx. $1{\cdot}3 \times 10^{-5}$. Treatment of (IV) with $Pb(OAc)_2$ yields (III), reduction gives (II). A. C.

Preparation of hæmatoporphyrin. M. A. KAPLAN (J. Lab. Clin. Med., 1932, 18, 309—312).—Oxalated blood is mixed with an equal vol. of conc. H_2SO_4, cooled, and diluted with 4 vols. of H_2O. The filtrate is neutralised with NaOH and the brown ppt. repeatedly dissolved and repptd. until the filtrate gives no biuret test. The ppt. is then suspended in H_2O and dialysed until free from Fe and SO_4″. CH. ABS.

Lipin content of white blood-cells in normal young women. E. M. BOYD (J. Biol. Chem., 1933, 101, 623—633).—The total lipin content (I) is 1—3%, composed of phospholipin 47, neutral fat 31, free cholesterol 11, and cholesteryl ester 11%; the total fatty acid is approx. 2/3 of the total lipin. White blood-cells are intermediate between body-tissues and blood-plasma with respect to (I). H. G. R.

Determination of serum-cholesterol adapted to the Man and Gildea fatty acid method. Determination of lipin-phosphorus. E. B. MAN and J. P. PETERS (J. Biol. Chem., 1933, 101, 685—695).—Serum-cholesterol is determined in the solution

from the determination of serum-fatty acids by the Man and Gildea method (this vol., 295). Lipin-P is determined in an aliquot of the EtOH–Et_2O extract of serum by a modification of the Fiske and Subbarow method (A., 1926, 443). H. G. R.

Hourly and daily variations in the blood-cholesterol [of dogs]. J. M. Muñoz (Rev. Soc. Argentina biol., 1932, **8**, 595—603).—The average hourly variation was 6·5%; daily variations (11 or 18%) depended on the diet. Ch. Abs.

Determination of the ratio cholesteryl esters to total cholesterol in blood-serum. L. Velluz (Bull. Soc. Chim. biol., 1933, **15**, 845—846).—A modification of the method of Bloor (A., 1916, ii, 650) in which a more conc. final solution facilitates the colorimetric determination. A. L.

Effect of the removal of lipins on the precipitability of serum-proteins by neutral salts. H. Wu (Chinese J. Physiol., 1933, **7**, 125—134).—The proteins are more easily pptd. by Na_2SO_4 and $MgSO_4$ from the reconstituted lipin-free serum than from the original serum. H. G. R.

Determination of serum-proteins. S. L. Malowan (Biochem. Z., 1933, **264**, 224—227).—At the isoelectric point the proteins of human and animal blood-serum (I) are quantitatively pptd. by heating to 75—80°. The (I) from tumours in rats and mice contains only half as much protein as does that from the healthy animals. In guinea-pigs the colloidal nature of the (I) is altered and pptn. of protein made difficult by life in a low-pressure (260—630 mm.) atm., but such life results in slight increase in the protein content of the (I). W. McC.

Distribution of indole between plasma and red corpuscles. J. García-Blanco and O. Vidal (Anal. Fís. Quím., 1933, **31**, 392—393).—Greater adsorption of indole (I) by red corpuscles occurs when the latter are suspended in 0·95% NaCl containing (I) than when (I) is added to whole blood. R. K. C.

Micro-determination of indole in blood-plasma. J. García-Blanco and O. Vidal (Anal. Fís. Quím., 1933, **31**, 390—391).—Least indole (I) is removed by adsorption on pptd. protein when the latter is pptd. by EtOH. 1 c.c. of oxalate plasma, treated with 4·5 c.c. of EtOH, is centrifuged, and to 4 c.c. of the liquid are added 10 drops of 5% p-$NMe_2 \cdot C_6H_4 \cdot CHO$ and 2 c.c. of conc. HCl. In a concn. of 0·01—0·04 mg. per c.c. 65% of added (I) is accounted for in the colorimetric determination. R. K. C.

Glutathione and the non-glucose reducing substances of blood. M. Rawson and J. Pickard (Bull. Soc. Chim. biol., 1933, **15**, 781—789; cf. A., 1932, 960).—There is no relationship between the non-glucose reduction (I) and the amount of hæmoglobin. (I) is due to unknown substances the amount of which increases in pathological blood and to glutathione (II) which represents approx. half of (I) in normal blood. The (II) is present only in the corpuscles. A. L.

Creatinine as a source of error in blood-sugar determination by the Crecelius–Seifert method. G. Gruber and A. F. Pellegrini (Wien. med. Woch., 1932, **82**, 1253—1255; Chem. Zentr., 1932, ii, 3923—3924).—Owing to the high creatinine content of blood, this method for blood-sugar yields results which are much too high. L. S. T.

Physiology, pathology, and pharmacology of blood-magnesium. K. Lang (Z. klin. Med., 1932, **122**, 206—243; Chem. Zentr., 1933, i, 797—798).—A survey. L. S. T.

Electrodialysis of the electrolytes of blood-serum. E. Di Benedetto (Rev. Soc. Argentina biol., 1932, **8**, 497—504).—From horse and dog serum all the Cl, 97% of the Na, 80—83% of the K, and 55—63% of the Ca were separated. Ch. Abs.

Determination of iodine in blood. H. J. Perkin (Biochem. J., 1933, **27**, 1078—1081).—Blood (10 c.c.) is heated with K_2CO_3 (2 g.) in a 50-c.c. Ni crucible for 4 hr. at 500°; the ash, made into a paste with H_2O, is extracted 4 times with EtOH (7 c.c. of 95%) and the extracts are filtered and evaporated to dryness without boiling. The residue, dissolved in H_2O (1 c.c.), is treated with Br in slightly acid solution to oxidise I′ to IO_3', excess of Br removed by boiling, and IO_3' determined by addition of I′ and micro-titration of the liberated I. The error is $< 10\%$. Rabbit's blood contains $8{\cdot}0 \times 10^{-6}$ g. and human blood 6·5—$9{\cdot}0 \times 10^{-6}$ g. of I per 100 g. W. O. K.

Rapid method for obtaining protein-free ultra-filtrates of blood and plasma. C. Wilson and E. R. Holiday (Biochem. J., 1933, **27**, 1095—1098).—An ultra-filtration apparatus suitable for obtaining protein-free filtrates from blood, plasma, and serum is described. The prep. of two types of collodion membrane for the apparatus is given. A. W.

Loss of weight of fibrinogen on coagulation. C. H. Hsu and H. Wu (Chinese J. Physiol., 1933, **7**, 117—124).—The fibrin obtained on coagulation is approx. 6·7% $<$ the fibrinogen from which it is derived. H. G. R.

Thrombin. I. Fractionation and purification. II. Components. III. Coupling of the components. A. Fischer (Biochem. Z., 1933, **264**, 169—177, 178—183, 184—191; cf. this vol., 522).—I. A method for the determination of thrombin (I) is described. (I) is pptd. by half-saturation with $(NH_4)_2SO_4$, is very sol. in acids, has its isoelectric point near neutrality, and is rapidly denatured by acidifying or heating. Fifty-fold purification of the (I) in muscle extract is attained by acidifying, rapidly neutralising, and centrifuging, or by heating at 50° for 1 min. The coagulating power of (I) so purified differs from that of the original material in being only slightly sensitive to the action of heparin (II). The difference is probably due to partial denaturation.

II. (I) has two components: a protein and an Et_2O-sol substance (III). The ultra-violet absorption spectrum of (III) from purified (I) exhibits a band at 250—260 mμ, the degree of activity of (I) being proportional to the magnitude of the absorption in this region. Blood-serum exhibits an absorption min. at 255 mμ, but the greater is the activity of (I) the less pronounced is this min.

III. Although neither the protein component nor (III) has any coagulating power, they combine to

produce an active coagulant which is very sensitive to the action of (II), but is rendered insensitive by treatment for a short time with acid. (I) is a lipo-protein containing Ca and (III) is possibly cephalin. The activity of samples of (I) is proportional to their content of (III). W. McC.

Stability of glycerinated hæmolysin. R. A. KILDUFFE (J. Lab. Clin. Med., 1933, **18**, 571).—Anti-sheep hæmolysin with an equal vol. of glycerol showed practically no loss in titre after 16 years. CH. ABS.

Effect of organ extracts on hæmolysis. L. PINCUS (Z. klin. Med., 1933, **123**, 55—62; Chem. Zentr., 1933, i, 1469).—Hæmolysis is inhibited by thymus, heart, and liver extracts. A. A. E.

Isolation of antibodies from immunised serum-globulin. T. ASABA (Arb. med. Fak. Okayama, 1933, **3**, 467—486).—Pptn., electrodialysis, and the biological method are discussed. CH. ABS.

Relationship between structure of antigen and specificity of antibody. VI. Relation between mol. wt. of haptenes and their affinity for antibodies. E. BERGER and H. ERLENMEYER (Biochem. Z., 1933, **264**, 113—119; cf. this vol., 846).—The power of antigens (I) (aromatic sulphonic acids) containing the same active group (SO_3H) to bind antibodies *in vivo* (rabbits) does not increase with increasing mol. wt. of (I), but increases suddenly when a certain mol. wt. (tyrosinebisazosulphanilic acid) is reached. W. McC.

Parallel action of neutral salts on the inhibition of complement and on the dispersion of gelatin. J. GORDON and F. C. THOMPSON (Brit. J. Exp. Path., 1933, **14**, 33—42).—The action of neutral, non-hydrolysable Na and K salts on the inhibition of complement is in the order: $CNS' > I' > Br' = NO_3' > \frac{1}{2}SO_4'' > Cl'$; this is the lyotropic series for the salt effects in the swelling of purified gelatin at low concns. of salts. Dispersion of the serum-proteins is probably the cause of the observed inhibition. CH. ABS.

Physico-chemical properties and solubility in ethyl alcohol of egg-yolk oil. M. G. VITA and C. L. BRACALONI (J. Pharm. Chim., 1933, [viii], **18**, 104—108). H. D.

Elementary composition and caloric value of the fatty acids of the phospholipins of human skeletal muscle. D. P. CUTHBERTSON (Biochem. J., 1933, **27**, 1099—1102).—Phospholipins derived from the skeletal muscle of normal men yielded fatty acids which gave C 76·03, H 11·98, O 11·99%. The average R.Q. of the acids was 0·709 and the average caloric val. 9·521 g.-cal. per g. at const. pressure. The equiv. of 1 litre of O_2 at const. pressure was 4·75 g.-cal. and the I val. was 111. These vals. are similar to those previously recorded for the triglycerides of subcutaneous fat, and differ from those for the triglycerides of skeletal muscle. A. W.

Degree of unsaturation of the fats of human adipose tissue in relation to depth from skin surface. D. P. CUTHBERTSON and S. L. TOMPSETT (Biochem. J., 1933, **27**, 1103—1106).—The fats of the panniculus adiposus abdominalis, omental, perinephric, epicardial, and liver tissues of three normal human cadavers gave average I val. of 70, 63·5, 63, 63·5, and 127, respectively. The corresponding average vals. for the fats of six obese female cadavers were 70, 69, 63, —, and 89, respectively. Distinct differences in the composition of the storage fat at different depths from the skin surface are not found in man. A. W.

Insect wax. VI. Synthesis of di-acid triglycerides of palmitic and myristic acids. F. N. SCHULZ and M. BECKER (Biochem. Z., 1933, **264**, 87—93; cf. this vol., 736).—*α-Palmito-α β-dimyristin* and *α-myristo-α'β-dipalmitin*, prepared from $COMe_2$-glycerol, have m.p. 53·2° and 56·5°. *β-Palmito-αα'-dimyristin* and *β-myristo-αα'-dipalmitin*, from α-iodohydrin, have m.p. 54·8° and 56·8°. The mixtures of acids obtained from the triglycerides by hydrolysis have m.p. 45—46°, 53·5°, 45—46°, and 44°, respectively. *β-Lauro-αα'-dimyristin* has m.p. 47·6°. *αβ-Dimyristoiodohydrin* and *αα'-dimyristin* have m.p. 42·5° and 63·8°, respectively. A mixture of 2 mols. of myristic and 1 mol. of palmitic acid has m.p. 45—46°, whilst the acid obtained from *Schizoneura* wax by hydrolysis has m.p. about 38°. The wax is consequently not identical with any of these glycerides. W. McC.

Determination of the total carbohydrate content of the liver tissue in the fasting rabbit. C. TSAI (Chinese J. Physiol., 1933, **7**, 91—102).—Total carbohydrate (I) is determined by determination of the reducing sugar, after HCl hydrolysis and removal of non-carbohydrate reducing substances by $HgSO_4$. Under fasting conditions (I) and glycogen (II) vary considerably, whereas the non-(II) fraction is approx. const. H. G. R.

Determination of total sugar in liver tissue. Reply to C. Tsai. A. CARRUTHERS (Chinese J. Physiol., 1933, **7**, 103—106; cf. preceding abstract).—The supernatant fluid, obtained by centrifuging a boiling H_2O extract of ground liver tissue, is in equilibrium with the sugar in the tissue residue. H. G. R.

Determination of lactic acid. I. Comparison of the method of Furth and Charnass with the modification of Friedemann, Cotonio, and Shaffer. II. Determination in urine, milk, blood, and organs. J. A. COLLAZO and A. S. RUIZ (Anal. Fís. Quím., 1933, **31**, 458—493).—The presence of $MnSO_4$ is necessary in the oxidation of lactic acid to MeCHO, and the MeCHO–H sulphite compound is best determined by Clausen's method, but direct distillation of MeCHO is simplest, and the aeration method is unnecessary (cf. Friedemann *et al.*, A., 1927, 800; 1929, 677; this vol., 488). R. K. C.

Occurrence of a substance resembling acetylcholine in skeletal muscle. III. F. PLATTNER (Pfluger's Archiv, 1932, **230**, 705—716; Chem. Zentr., 1933, i, 1969).—EtOH extracts of the muscle of various animals contained detectable quantities of a substance resembling acetylcholine (I) which does not originate in the (I)-sensitive apparatus. A. A. E.

Tissue-acetylcholine. I. Origin, significance, and fate of acetylcholine in human placenta.

H. C. Chang and A. Wong. **II. Acetylcholine content of Collip's œstrogenic placental extract.** H. C. Chang (Chinese J. Physiol., 1933, **7**, 151—169, 171—178).—I. The amount of acetylcholine (I) in placenta appears to be directly related to the activity of the uterus (II). (I)-like substance of human placenta is not liberated into the natural circulation in any appreciable quantity.

II. Collip's extract (A., 1930, 646) exhibits (I)-like action in addition to its œstrogenic effect. H. G. R.

Approximate determination of spermine in single human organs. G. A. Harrison (Biochem. J., 1933, **27**, 1152—1156).—The dry organ is freed from fat (Et_2O) and then extracted with 2·5% $CCl_3{\cdot}CO_2H$; the clear extract is treated with picric acid and the pptd. spermine picrate converted through the hydrochloride into the phosphate. The amounts of spermine (I) in individual normal prostates obtained *post mortem* vary enormously and are probably fortuitous. The approx. amounts of (I) in testes, pancreas, and other human organs are reported; they are of the same order as found in all organs other than the prostate. H. B.

A constituent of adrenal cortex. E. Schmitz and G. Hilgetag (Naturwiss., 1933, **21**, 626—627).—By a modification of the method described previously (this vol., 642), a cryst. neutral *substance*, $C_{35}H_{74-76}O_8N_2S$, m.p. 242° (decomp., brown at 200°), is obtained which depresses blood-cholesterol in dogs. R. K. C.

Salmenic acid, a carotenoid of the salmon. H. von Euler, H. Hellstrom, and M. Malmberg (Svensk Kem. Tidskr., 1933, **45**, 151—152).—Et_2O extracts of salmon muscle or roe yield on hydrolysis the sparingly sol. *Na* salt of *salmenic acid*, with absorption bands at 485 mμ and 525 mμ. R. K. C.

I. Carotenoids of marine invertebrates. II. Carotenoid pigments of fishes. E. Lonnberg (Ark. Zool., 1933, **25A**, No. 1, 1—17; No. 2, 1—8).—I. Carotene and xanthophyll were detected spectroscopically and with the $SbCl_3$ test in certain echinoderms and molluscs. In the crustacea, polychæta, nemertines, and anthozoa examined, xanthophyll appeared to predominate.

II. Xanthophyll appeared to be widely distributed in the skin and fins of various fishes, being also, apparently, the predominant carotenoid in the bodies of the prey. Nutr. Abs. (*b*)

A lyochrome from ova of *Myxine glutinosa*. H. von Euler and H. Hellstrom (Svensk Kem. Tidskr., 1933, **45**, 180).—A yellow, fluorescent colouring-matter, with absorption from 500 mμ into the ultra-violet, and a band at 275 mμ, is obtained by extracting the fat-free ova with H_2O. It gives the murexide reaction and oxidises leucomethylene-blue. R. K. C.

Enzymes of the skin. X. Catalase of human skin. J. Wohlgemuth and E. Szorenyi (Biochem. Z., 1933, **264**, 94—103; cf. A., 1925, i, 203).—The decomp. of H_2O_2 at 0° (but not at higher temp.) by catalase (I) from human skin is a unimol. reaction. The activity (II) of (I) alters only slightly between p_H 6·5 and 8·0, the optimum being at neutrality. Low concn. of $FeSO_4$ partly and of NaCN completely inhibits (II), but, although probably identical with them, (I) differs from blood- and liver-catalase in that its (II) is not affected by O_2, CO, or CO_2. The preps. used contained Cu, but it is possibly not a constituent of (I). W. McC.

Chloride and water in the constitution of tissues. H. G. Close (Biochem. J., 1933, **27**, 967—975).—At room temp. the Cl′ and H_2O contents of human *post-mortem* tissue remain const. for at least 24 hr. The tissues form three groups according to their H_2O content: (I), body-fluids (90—99%); (II), nuclear tissues (75—85%); and (III), anuclear tissues (10—73%). (I) have an average Cl′ content > that of (II) or (III). The tissues arranged in order of descending p_H give a series almost identical with that of descending Cl′ content. The chief characteristics, including metabolic rate and the Na, K, and protein contents, of the three groups are discussed. F. O. H.

Micro-determination of calcium in tissues rich in iron. R. Wolff (Bull. Soc. Chim. biol., 1933, **15**, 814—819).—The method is a modification of that of Guillaumin (A., 1931, 248), the Ca being pptd. as oxalate at p_H 5·0. Fe does not interfere provided there are < 6 mg. per 10 c.c. of solution, and the determination can be made when the amount of Fe is 50 times that of Ca. A. L.

Micro-determination of magnesium in animal tissues. R. Wolff and M. Train (Bull. Soc. Chim. biol., 1933, **15**, 820—832).—The tissue is ashed and extracted with aq. HCl. Ca is pptd. at p_H 5·0 as oxalate and Mg as $MgNH_4PO_4$ in presence of NH_4 citrate. After washing with aq. EtOH, the NH_4 in the ppt. is determined by the Kjeldahl method. The separation of Ca is necessary only when the amount present is > thrice that of the Mg, and the method can be used to determine 0·02 mg. A. L.

Vanadium in certain organisms. A. P. Vinogradov (Trav. lab. biogeochim. acad. sci. U.R.S.S., 1932, **2**, 1—7).—*Ciona intestinalis*, L., and *Ascidiella aspersa*, Müll., contained, respectively, $1{\cdot}3\times10^{-3}$ and $4{\cdot}9\times10^{-3}$% V. V was detected in ash of *Sarcobotryloides aurea*, but not in that of *Pyura*, *Styela*, *Molpadia affinis*, or *Cucumaria frondosa*. Ch. Abs.

Daily variations in the f.p. of milk. H. A. Schuette and E. O. Huebner (Trans. Wisconsin Acad. Sci., 1933, **28**, 267—274).—The f.p. of the milk, determined by the Hortvet method (cf. B., 1933, 40), of a well-fed cow over a period of 30 days does not vary individually or from that of the herd. With two cows, the vals. 0·542—0·563° (average 0·551°) and 0·542—0·557° (average 0·549°) were obtained. The presence of colostrum depresses the f.p., due to increased salt concn. and probably also to retardation of freezing by the high protein content. With the approach of parturition there is a decrease in the lactose content and a corresponding increase in the inorg. salts. F. O. H.

Amount and properties of fat-globules in Siberian cow's milk at different periods of lactation. A. Ghurauskaya (Trans. Omsk Inst. Dairving, 1931, **1**, 60). Nutr. Abs. (*b*)

Peroxidase reaction. XLII. Arakawa's reaction and toxicity of human milk. K. Asakura and H. Ohsako (Tôhoku J. Exp. Med., 1933, **20**, 429—433).—Although human milk (I), negative to Arakawa's reaction, is deficient in vitamin-B_1, this deficiency is not the cause of death when (I) is injected into mice receiving a diet of H_2O and well-polished rice, since milk with a positive Arakawa reaction, in which the vitamin has been destroyed by heat or oxygenation, has no toxic effect when injected. Nutr. Abs. (*m*)

Action of sodium thiocyanate on milk. II. Bactericidal action of NaCNS. W. Wittholz (Milch. Forsch., 1933, **15**, 315—320).—In acid solution *B. bulgaricum*, *S. thermophilus*, and *Diploc. lacticus* were destroyed. The destruction of *B. bulgaricum* required least NaCNS, whilst *D. lacticus* required most. E. B. H.

Inorganic constituents of cerebrospinal fluid. IV. Potassium in serum, serum-ultra-filtrate, and cerebrospinal fluid. E. Watchorn and R. A. McCance (Biochem. J., 1933, **27**, 1107—1112).—Serum-K is wholly ultra-filterable, and thus the agreement between this val. and the K level of hydrocele, pleural, and ascitic fluids is explained. The K level of cerebrospinal fluid (I) is, at the most, only 65—70% of the serum-K, and this suggests that (I) does not, as far as K is concerned, represent a serum-ultra-filtrate. A. W.

Correlation of the p_H of the cerebrospinal fluid and blood in rabbits. A. M. Petrunkin, M. L. Petrunkin, and A. P. Zavyalova (Arch. Sci. biol., U.S.S.R., 1932, **32**, 61—67).—Vals. are parallel normally and during Et_2O anæsthesia. Ch. Abs.

Reducing property of aqueous humour. H. K. Müller (Nature, 1933, **132**, 280).—The reduction of methylene-blue by the aq. humour (I) of the rabbit and of cattle depends, not on an enzyme, but on a reducing substance (II) present in the $CCl_3{\cdot}CO_2H$ filtrate [1 c.c. of (I) = 1 c.c. 0·002*N*-I, approx.]. (II) is sensitive to O_2 only in alkaline solution, and the reduction of the dye by (I) is accelerated by increased alkalinity and addition of NaCN. Substances containing SH are not demonstrable in (I). (II) is probably vitamin-*C* which is closely related to the metabolism of the lens and to the genesis of cataract. L. S. T.

Determination of cholesterol in bile and duodenal fluid. V. Deulofeu and J. E. Bavio (Anal. Fís. Quím., 1933, **31**, 206—209).—The fluid is dried on plaster of Paris, which is then extracted with Et_2O, and the cholesterol is determined in the extract by Grigaut's method, using the Liebermann–Burchard reaction. R. K. C.

Gastric mucus. I. Determination. F. Baltzer (Biochem. Z., 1933, **264**, 28—34).—Ultra-filtration, treatment with colloidal $Fe(OH)_3$, determination of N (total, NH_2, NH_3), and observation of changes in viscosity due to alteration in reaction show that the mucus probably consists of mucins containing NH_2-compounds in colloidal solution. W. McC.

Inverse concentration ratios for sodium and potassium in gastric juice and blood-plasma. R. C. Ingraham and M. B. Visscher (Proc. Soc. Exp. Biol. Med., 1933, **30**, 464—466).—The Na content of blood-plasma of etherised or amytalised dogs is 1·6 times that of their gastric juice secreted after histamine injection; the K content is < half that in the gastric juice. Nutr. Abs. (*m*)

Gastric pepsin. I. Methods of measurement and factors which influence it. A. E. Osterberg, F. R. Vanzant, and W. C. Alvarez (J. Clin. Invest., 1933, **12**, 557—556).—Gilman and Cowgill's method gives accurate vals. Blood, mucin, blood-proteins, peptones, and alkalis markedly reduce peptic activity. Ch. Abs.

[H·] of gastro-intestinal contents of vegetarian and omnivorous rats. S. Wan (Chinese J. Physiol., 1933, **7**, 179—184).—No significant difference was found in the p_H of fæces and gastro-intestinal contents of rats on omnivorous and vegetarian diets. H. G. R.

Gastric secretion and alkaline tide in urine. R. S. Hubbard, S. A. Munford, and J. Tyner (J. Biol. Chem., 1933, **101**, 781—785).—A comparison of the p_H of urine from patients with normal gastric juice with that from patients with achlorhydria indicates that the secretion of HCl by the stomach is the main cause of the alkaline tide. The urine of the last-named group showed a regular increase in acidity after the meal. A. L.

Chloride content of glomerular urine and plasma of frogs. B. B. Westfall and A. N. Richards (Amer. J. Med. Sci., 1933, **185**, 148).—The max. difference in Cl content is 6% (average 2%). As regards Cl′, glomerular urine of frogs is an ultra-filtrate from plasma. Ch. Abs.

Glyoxaline derivatives in urine. O. Fürth and E. H. Majer (Biochem. Z., 1933, **264**, 142—156; cf. A., 1932, 1056).—Glyoxaline derivatives (I) in urine are best pptd. with Hopkins' reagent and are then colorimetrically determined (as histidine) by the method of Weiss and Sobolev (A., 1914, ii, 155) using histidine (II) as standard. Other otherwise satisfactory methods are untrustworthy when applied to urine. Normal human urine contains 8—18 mg. of (I) per 100 c.c. In tuberculosis, diseases of the liver, and pregnancy the amounts are respectively 10—32, 13—16, and 14—53 mg. Only exceptionally does (II) constitute the chief part of the (I) of pregnancy urine. W. McC.

Detection of protein in human urine. R. Hirohata, H. Shimokawa, and O. Kamizawa (Biochem. Z., 1933, **264**, 126—130).—Filtered urine (5 c.c.) is acidified if necessary with AcOH and 10% aq. flavianic acid (0·5—1·0 c.c.) is added. Presence of protein (I) is indicated by production of a turbidity or ppt. insol. in excess. 0·003% of (I) can be detected. All usual constituents of urine do not interfere, and a ppt. due to substances other than (I) (quinine, K, Ca) is dissolved by diluting or heating. W. McC.

Determination of indican in urine. J. Broekmeyer (Klin. Woch., 1932, **11**, 1713—1715; Chem. Zentr., 1932, ii, 3924).—A modification of Obermeyer's method is described. L. S. T.

Blood in unexplained gastric anacidity. W. S. POLLAND (J. Clin. Invest., 1933, **12**, 599—611).—No abnormalities were observed. CH. ABS.

Electrolyte balance studies in adrenalectomised dogs with particular reference to the excretion of sodium. R. F. LOEB, D. W. ATCHLEY, E. M. BENEDICT, and J. LELAND (J. Exp. Med., 1933, **57**, 775—792).—Blood-Na, -Cl, and -HCO_3' decrease in Addison's disease, and in adrenalectomised animals. Blood-K increases after adrenalectomy. Loss of Na from the body results from increased urinary excretion of Na, vomiting, and diarrhœa. CH. ABS.

Influence of iodine, and its mode of action, in experimental adrenaline arteriosclerosis. I, II. K. KAGAWA (Folia Pharmacol. Japon., 1933, **15**, No. 4, 309—320, 321—331).—Small doses of KI prevent adrenaline arteriosclerosis in normal, but not in thyroidectomised, rabbits. CH. ABS.

Effect of thyroid preparations on experimental hypercholesterolæmia and atherosclerosis. I. B. FRIEDLAND (Z. ges. exp. Med., 1933, **87**, 683—702).—Administration of cholesterol to rabbits leads to rapid development of atherosclerosis (I) which does not run parallel with the degree of hypercholesterolæmia (II). Simultaneous administration of thyreoidin (III) (50—250 mg. per kg. per day) reduces or prevents the (II) and development of (I) even when large doses of cholesterol (IV) are given for long periods. When the blood-(IV) is normal (III) has little effect on it. Male rabbits are more susceptible than females to the action of (III). NUTR. ABS. (*m*)

Anæmia of infancy from maternal iron deficiency in pregnancy. M. B. STRAUSS (J. Clin. Invest., 1933, **12**, 345—353).—Fe given during pregnancy to mothers with hypochromic anæmia prevents the development of anæmia in infants during the first year of life. Apparently the fœtus of Fe-deficient mothers does not store sufficient Fe to carry the infant through this period. CH. ABS.

Cholesterol and lecithin-phosphorus in the plasma of anæmia other than pernicious anæmia. G. L. MULLER and C. W. HEATH (Arch. Int. Med., 1933, **52**, 288—305).—In anæmia (I) due to chronic loss of blood the plasma-cholesterol (II) and the lecithin-P (III) decrease with increasing severity of (I), whilst in (I) due to acute loss of blood the (II) and (III) remain normal or increase. In (I) associated with cancer of the stomach the (II) and (III) tend to be low. In chronic myologenous leucæmia (II) is usually below normal, whilst (III) is normal. In aplastic (I) (II) and (III) are high. Irregular results are obtained in ideopathic hypochromic (I). W. O. K.

Glycolysis in the blood of patients with pernicious anæmia. S. M. GOLDHAMER (J. Clin. Invest., 1933, **12**, 538—588).—Retarded glycolysis is proportional to red-cell decrease. CH. ABS.

Gastro-intestinal studies. II. Pancreatic enzymes in pernicious anæmia. O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (J. Clin. Invest., 1933, **12**, 519—532).—Pancreatic enzymes were present in the duodenum. Determination of these enzymes in gastric contents during fasting is of no val. in estimating pancreatic activity. There is no impairment of functional secretion of enterokinase in pernicious anæmia. Liver feeding had little effect on the activity of the pancreatic enzymes. CH. ABS.

Relationship between anti-anæmic principles in stomach and liver. J. F. WILKINSON and L. KLEIN (Lancet, 1933, **125**, 629—632).—The prep. of different concentrates containing hæmopoietin (I), the active anti-anæmic substance in hog's stomach, is described. (I) is less stable than, and has different properties from, the anti-anæmic principle in liver (II). When stomach fractions containing the thermo-labile (I) are incubated with beef or stomach muscle, a relatively heat-resistant, hæmopoietically-active material is obtained; a substance similar to or identical with (II) is probably synthesised. The enzyme (I), by acting on some substance present in protein food, may produce *in vivo* a substance which is stored as (II) until it is required for red-cell formation. (I) is present in the normal stomach of man, of carnivorous and omnivorous animals, but not in those of herbivorous animals. Pernicious anæmia is a type of deficiency disease characterised by absence of a sp. enzyme, (I), and pepsin and HCl from gastric secretion. Experimental evidence for the enzymic nature of (I) is adduced. L. S. T.

Increased potency of liver-extract by incubation with human gastric juice. O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (Proc. Soc. Exp. Biol. Med., 1933, **30**, 775—778).—One case of pernicious anæmia showed no response when treated daily for 10 days with liver-extract No. 343 (I), derived from 100 g. liver. Another showed no improvement during a 10-day control period in which 150 c.c. of normal human gastric juice (II) were taken by mouth daily. Both cases responded well when treated daily for 10 days with (I), from 100 g. of liver, after incubation of the extract at 40° for 4 hr., with 100 c.c. of (II). NUTR. ABS. (*b*)

Effect of injected liver-extracts on blood-cholesterol and -cholesteryl esters. F. GEBHARDT and J. KLEIN (Klin. Woch., 1933, **12**, 494—497).—The concn. of free cholesterol and of cholesteryl esters in the blood was raised by the injection of liver-extract in all cases investigated, including patients with pernicious and secondary anæmia, liver disease, and healthy subjects. NUTR. ABS. (*b*)

Biochemistry of asthmatic conditions with special reference to the urinary "proteose." G. H. ORIEL (Lancet, 1933, **125**, 406—409).—The differences in biological activity of urinary proteose in different phases of asthma are described. Normal proteose gives one fraction only, whilst asthmatic proteose can be separated into three fractions. L. S. T.

Arterial and venous blood-sugar response to adrenaline in normal individuals and in biliary tract disease. A. CANTAROW (Amer. J. Med. Sci., 1933, **185**, 449—450). CH. ABS.

Influence of the endocrine system in blood disorders. D. HUBBLE (Lancet, 1933, **125**, 113—119).—Evidence relating to the effect of the thyroid, the adrenals, and the pituitary on hæmopoiesis is

reviewed. The thyroid hormone stimulates the production of red cells (I) and lymphocytes, and depresses the formation of granular leucocytes (II); the adrenal cortical hormones stimulate the production of (II), and possibly of (I), whilst the basophile cells of the anterior lobe of the pituitary stimulate all types of circulating cells. Blood disorders are discussed in relation to disorders of the endocrine system. L. S. T.

Cancer : application of the Rupp–Schied–Thiel thiocyanate reaction to urine. M. X. SULLIVAN and W. C. HESS (J. Washington Acad. Sci., 1933, 23, 378—380).—The test, which consists in the determination in the 24-hr. urine of the apparent CNS′, is not sp. for, or necessarily positive in, cancer. W. O. K.

Metabolism of normal and tumour tissue. IX. Ammonia and urea formation. X. Effects of lactate, pyruvate, and deprivation of substrate. F. DICKENS and D. G. GREVILLE (Biochem. J., 1933, 27, 1123—1133, 1134—1140).—X. Aerobic formation of NH_3 by kidney, spleen, Jensen sarcoma, and embryo tissue was large, but was completely inhibited by glucose or fructose. Anaerobic elimination of NH_3 is generally < aerobic. Judged by NH_3+urea formation, protein oxidation, in a glucose medium, is so small as to have no influence on the R.Q.

X. The inhibitory effect of *l*-lactate on anaerobic glycolysis (I) is about half that of *d*-lactate. After preliminary substrate-deprivation, (I) recovers completely with tissue other than brain, which recovers to only 12% of the normal val. Pyruvate tends to keep the glycolysis of tissues at max. H. G. R.

Phosphatase content of the muscle of animals with tumours. J. WIENBECK (Z. physiol. Chem., 1933, 219, 164—172).—Striped muscle of rats with tumours can liberate H_3PO_4 from thymonucleic acid, although in normal animals the power is lacking (cf. Edlbacher and Kutscher, A., 1931, 1180). In mice the difference is less marked, since muscle of the normal animal shows nucleophosphatase action. After 4 hr. products are formed which favour a synthetic PO_4''' metabolism, and hence mask the phosphatase effect. J. H. B.

Enzymes in tumours. I. E. WALDSCHMIDT-LEITZ, E. MCDONALD, and collaborators (Z. physiol. Chem., 1933, 219, 115—127).—The amount of cathepsin (I), phosphatase (II), and deamidase in experimental tumours falls, but of arginase (III) rises, with increasing necrosis. The amounts of amino- and dipeptidase are independent of the ageing of the tumour. The (I) and (III) of the liver are diminished, the kidney-(II) is increased, in the diseased animals. Generally the enzyme content of the tumour is similar to that of normal organs, but differs from that of muscle-tissue, although the high catalase content of the liver forms an exception. The degree of activation of (I) in tumours, independent of ageing, is similar to that of the liver, but whilst active (III) in tumours alters only slightly with age, the total enzyme, determined after cysteine–Fe activation, increases greatly. The incomplete activation, like the lowered respiration, is attributed to a lack of heavy metal. J. H. B.

Alleged activators of proteolysis in tumours. L. POZZI (Atti R. Accad. Lincei, 1933, [vi], 17, 865—868).—Aq. and EtOH extracts of liver have no accelerating effect on proteolysis, but, on the contrary, an inhibitory action. Similar extracts of rat tumours have neither accelerating nor inhibitory effects. Liver and tumour extracts mixed together appear to exert a mutual inhibition. R. N. C.

Activation of fructose fermentation by Jensen sarcoma with pyruvic acid and various oxidising agents. O. ROSENTHAL (Z. Krebsforsch., 1932, 38, 216—240; Chem. Zentr., 1933, i, 1475).—$AcCO_2H$, methylene-blue, Lauth's violet, Capri-blue, $K_3Fe(CN)_6$, and $C_5H_{11}\cdot NO_2$, which activate lactic acid fermentation of fructose in Jensen rat sarcoma, are reduced by the tissues and act as H acceptors. A. A. E.

Action of chlorophyll on blood-corpuscles normally and in cancer. A. H. ROFFO (Z. Krebsforsch., 1933, 38, 312—325; Chem. Zentr., 1933, i, 1469).—In cancer, red blood-corpuscles are hæmolysed more readily than normally by irradiated chlorophyll. A. A. E.

Is methylene-blue anti-carcinogenic? M. COPISAROW (Science, 1933, 78, 212).—A discussion. L. S. T.

Treatment of cancer with connective tissue extracts. H. S. BAKER (Lancet, 1933, 125, 643—645).—Intravenous administration of an extract, presumed to contain a principle inhibiting cell overgrowth, of connective tissue from an area in the pig or cow corresponding with that of the primary growth, diminishes the size and vigour of carcinomata in human beings. L. S. T.

Potassium content of benign uterine tumours. L. C. SCOTT (Amer. J. Cancer, 1933, 17, 924—931).—The average val. is 0·166 (normal, 0·188) g. per 100 g. of moist tissue. Tumour-K decreases as growth progresses. CH. ABS.

Heat cramps. J. H. TALBOTT and J. MICHELSEN (J. Clin. Invest., 1933, 12, 533—549).—Cramp is probably caused by loss of base, Cl′, and H_2O, principally from the sweat glands. CH. ABS.

Substances formed in decay of dental pulp (gangrene). I. H. SCHMALFUSS and G. FISCHER [with W. MORING] (Zahnarztl. Rund., 1932, 41, No. 28, 6 pp.; Chem. Zentr., 1933, i, 1144).—Indole substances and volatile bases are present in decayed, but not in normal, dental pulp. A. A. E.

Quebrachitol as a sweetening agent for diabetics. R. A. MCCANCE and R. D. LAWRENCE (Biochem. J., 1933, 27, 986—989).—Whilst quebrachitol (*l*-methylinositol) has a sweetness approx. $\frac{1}{3}$ that of sucrose, it has no influence on insulin hypoglycæmia and neither raises the blood-sugar nor causes deposition of liver-glycogen in normal animals. That it readily produces colic or diarrhœa, however, militates against its use in diabetes. F. O. H.

Post-insulinic blood-sugar levels. I. F. FERNANDEZ and J. M. CLAVERA (Anal. Fís. Quím., 1933, 31, 364—369).—In 22 patients, contrary to Burger, there was no relation between initial post-insulinic hypoglycæmia and functional state of the liver. R. K. C.

Virus obtained from influenza patients. W. SMITH, C. H. ANDREWS, and P. P. LAIDLAW (Lancet, 1933, **125**, 66—68).—Filtrates of throat washings from influenza patients produce a disease (I) in ferrets. Human sera, especially those from influenza convalescents, contain antibodies which neutralise the virus of (I). Swine influenza virus produces in ferrets a disease indistinguishable from (I), and the pig and human viruses have close antigenic relationships.

L. S. T.

Low excretion of nitrogen and rise of basal metabolic rate in hypertonus. A. HELD (Z. ges. exp. Med., 1933, **87**, 578—584).—In patients (I) with high blood-pressure (II) who are pale, the urinary output of N on a diet containing min. amounts of protein is > in patients who are florid. In (I) the basal metabolism was high, especially when the high (II) was fixed. *X*-Ray irradiation of rabbits leads to an increase of protein decomp. products in the blood and a rise of (II). The output of creatinine accounts for a large part of the urinary N but does not run parallel with it. NUTR. ABS. (*m*)

Relation of liver function to the amount of guanidine and sugar in the blood. N. ARAKAWA (Nagoya J. Med. Sci., 1932, 6, 96—99).—Blood-sugar was inversely, and -guanidine directly, proportional to the severity of hepatic injury in rabbits.

CH. ABS.

Hæmorrhagic tendency in jaundice. Blood-fibrin, sedimentation rate, coagulation time, and other blood factors. C. F. BURKE and J. F. WEIR (J. Lab. Clin. Med., 1933, **18**, 657—668).—Blood-fibrin and -protein, serum viscosity, and sedimentation rate of erythrocytes are normal in obstructive or intrahepatic jaundice. Increase in serum-bilirubin and prolongation of coagulation time are the best criteria of hæmorrhagic tendency. CH. ABS.

Determination of amino-nitrogen in endocrine and joint disease. G. PEREMY and K. FELEDY (Magyar Orvosi Arch., 1932, **33**, 296—302; Chem. Zentr., 1932, ii, 3907).—Blood- and urinary NH_2-N were determined fasting and after a meat meal.

A. A. E.

Quinoline derivatives for the treatment of malaria. O. MAGIDSON, I. STRUKOV, N. DELEKTORSKAYA, and I. LIPOVICH (Khim. Farm. Prom., 1933, 9—14).—Of the derivatives synthesised 6-methoxy-8-*N*-dimethylaminopropylquinoline was the most efficient. CH. ABS.

Changes in distribution ratio of constituents of blood and cerebrospinal fluid in meningitis. S. J. KOPETZKY and E. H. FISHBERG (J. Lab. Clin. Med., 1933, **18**, 796—801).—Cerebrospinal fluid (I)-lactic acid is increased; (I)-Cl : blood-plasma (II)-Cl, and (I)-CO_3 : (II)-CO_3 are decreased.

CH. ABS.

Irradiation treatment in mongolism; effect on the cholesterol of blood-serum. E. BINGENHEIMER (Z. ges. exp. Med., 1933, **87**, 592—612).—The blood-cholesterol (I) has a higher val. in warm- than in cold-blooded animals. In man it is lowest at birth, rises quickly until the third month, and then gradually reaches the adult val. at puberty; it is lower and shows a slower rise in the premature than in the full-term infant. In normal children the val. varies between 120 and 170 mg. per 100 c.c., whilst in children with mongolism it is much less, the lowest normal (120) figure being reached in the tenth year. Children with other types of mental deficiency have normal (I) val. *X*-Ray irradiation of the skull or trunk of mongols leads to an increase in (I) and perhaps to a decrease in susceptibility to infection, but otherwise causes no improvement clinically. The typical (I) curve found after irradiation of the skull suggests that the pituitary may influence cholesterol metabolism. NUTR. ABS. (*m*)

Experimental muscle degeneration. IV. Carbohydrate metabolism in muscle repair. V. Nitrogen metabolism of degenerated muscle in acute injury and repair. D. K. FISHBACK and H. R. FISHBACK (J. Lab. Clin. Med., 1933, **18**, 777—781, 781—788).—IV. The lactic acid (I) content of striated muscle in rabbits increases rapidly during acute mol. degeneration, and diminishes after 4 hr. Glycogen (II) decreases during 48 hr. and then tends to become normal. There is no const. ratio between the changes in (I) and (II). A decrease in the phosphocreatine content and a retarded increase in inorg. P are observed throughout degeneration and repair.

V. The decrease in total N in mol. degeneration is approx. proportional to the degree of œdema. Diminished non-protein- and NH_2-N increase rapidly during repair. Variations in urea-N are not const.

CH. ABS.

Urine- and serum-proteins in nephritis. E. M. WIDDOWSON (Biochem. J., 1933, **27**, 1321—1331).—Determination of the N distribution, optical rotation and racemisation, osmotic pressure, and sp. refraction of the urine- and serum-albumin and -globulin of nephritics shows no difference between the proteins from the two sources. H. D.

Cystine and nephrotoxicity. M. E. BELL (Biochem. J., 1933, **27**, 1267—1270).—The feeding of young rats with synthetic diets containing 1—2% of free cystine failed to produce acute nephrosis (cf. A., 1929, 720). The condition is probably due to an infection which is partly dependent on the altered oxidation–reduction potential in the intestines.

F. O. H.

Urea secretion. VIII. Effects on urea clearance of changes in protein and salt contents of the diet. C. L. COPE (J. Clin. Invest., 1933, **12**, 567—572).—NaCl, or increase in protein intake from 75 to 120 g., had little effect on urea clearance in normal or nephritic patients. Depressed clearance followed a decrease in protein intake to 40 g.

CH. ABS.

Biochemical changes in the blood in intestinal obliteration. J. GARCÍA-BLANCO and F. COMESANA (Anal. Fís. Quím., 1933, **31**, 394—398).—In rabbits blood-sugar increased very rapidly after ligature of the gut below the pylorus (I), but changed little after ligature below the duodenum (II) or at the rectum. The non-protein-N increased rapidly after ligature below (I) or (II), and less rapidly after rectal ligature.

R. K. C.

Ætiology of pellagra. H. CHICK (Lancet, 1933, **125**, 341—346).—A discussion. The hypothesis that

pellagra is caused by a toxic substance derived from maize and can be corrected by foodstuffs such as meat, milk, eggs, and green vegetables, or perhaps by sufficient vitamin-B_2, is advanced. L. S. T.

Plasma-protein changes and suspension stability of the blood in lobar pneumonia. J. K. Moen and H. A. Reimann (J. Clin. Invest., 1933, **12**, 589—598).—Plasma-total protein is usually decreased during the febrile period; the fibrinogen and globulin fractions are increased. Ch. Abs.

Excretion of sodium thiosulphate during uncomplicated human pregnancy after intravenous administration in large amounts. A. Bolliger and M. S. S. Erlam (J. Obstet. Gynæcol., 1933, **40**, 289—298).—The % excretion was subnormal in the later months of pregnancy and during the puerperium. Ch. Abs.

Effect of pregnancy and lactation on blood-serum of cattle, with remarks on milk fever. W. Frei and M. Demmel (Schweiz. Arch. Tierheilk., 1932, **11**, 525—538).—A small decrease in serum-glucose was observed during pregnancy (86—91 mg.) as compared with œstrus and interœstrus (99—110 mg. per 100 c.c.). The *n* of the serum was not significantly different in lactating cows as compared with non-lactating animals. The composition of the blood is not materially altered in normal cows during lactation. Milk fever, associated with hypocalcæmia or hypoglycæmia, arises more from disturbances of the endocrine and vegetative nervous system associated with parturition than from the onset of lactation. Nutr. Abs. (*b*)

Relation between pancreas and eclampsia. Significance of diastase in normal and pathological pregnancy, birth, and confinement. W. Spitzer (Arch. Gynakol., 1932, **150**, 681—685; Chem. Zentr., 1932, ii, 3899).—No increase in the diastase content of blood or urine was detected during normal pregnancy, parturition, and confinement. In many pathological cases the diastase val. is raised. L. S. T.

Nitrogen metabolism in pituitary insufficiency. B. Braier (Anal. farm. bioquim., 1932, **3**, 61—76, 97—106).—Normal dogs eliminate 0·24 and hypophysectomised 0·14 g. N per kg. per day. Equilibrium through gradual elimination of N from the diet is reached at 0·30 and 0·20 g., respectively. Fasting dogs eliminate 0·36 and 0·25 g. N per day. Vals. for creatinine elimination are also given. Ch. Abs.

Magnesium rickets. G. M. zu Horste (Klin. Woch., 1932, **11**, 1796; Chem. Zentr., 1932, ii, 3910).—Addition of $MgCO_3$ to a non-rachitic diet causes a P-deficiency rachitis in rats and rabbits, as does an excess of $CaCO_3$. L. S. T.

Factors involved in malformation of the bones of growing chickens. I. Value of egg-yolk and chicken fat. E. W. Henderson (Poultry Sci., 1933, **12**, 91—96).—The type of rickets not cured by these additions probably results from high dietary Ca and/or P. Ch. Abs.

Trypanosomiasis and avitaminosis. I. Rickets and *T. lewisi*. II. Scurvy and *T. brucei*. B. Borghi (Atti R. Accad. Lincei, 1933, [vi], **17**, 574—577, 665—671).—I. The symptoms of rickets in rats are greatly aggravated by infection with *T. lewisi*, death being hastened. The splenomegalic effect of *T. lewisi* is not shown.

II. Scurvy is aggravated in guinea-pigs by infection with *T. brucei*, whether applied at early or late stages of the avitaminosis, but death is not hastened. The splenomegalia produced by the trypanosome in normal animals does not appear. R. N. C.

Proteolytic enzymes in the organs of scorbutic guinea-pigs. L. Pozzi (Atti R. Accad. Lincei, 1933, [vi], **17**, 583—586).—Extracts of the liver and kidneys of scorbutic guinea-pigs showed a catheptic activity (I) > those of normal animals; the activity of the liver extract was > that of the kidney extract, which is the reverse of the normal condition. Extracts from scorbutic animals cured with adrenal cortex extract showed a decrease in (I). The dipeptidase activity of such extracts was unaltered in scurvy. R. N. C.

Oxygen consumption of scorbutic and normal guinea-pigs. N. Soderstrom and N. Tornblom (Upsala Lakareforenings Forhandl., 1932, **38**, 1—6).—Five out of six guinea-pigs on a scorbutic diet showed a lower O_2 consumption than controls on an antiscorbutic diet. Nutr. Abs. (*b*)

Seborrhœa in the rat caused by feeding with whale oil. E. Somekawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 149—157).—Rats fed on a diet containing 15% of sperm-head oil or arctic-sperm oil developed seborrhœa (I), growth was retarded, and death occurred in a few weeks. Additions of yeast prolonged the life of the animals, but (I) was even more conspicuous. The saponification products of the whale oil were toxic, but caused no (I). Synthetic oleyl oleate produced (I); oleyl palmitate and cetyl oleate were without effect. A. L.

Treatment of parathyroid tetany with calcium chloride, parathyroid extract, and vitamin-*D*. P. Schultzer (Acta med. scand., 1932, **79**, 11—22; Chem. Zentr., 1933, i, 797).—The fallen Ca-level in parathyroid tetany was raised by administration of parathyroid hormone, vitamin-*D*, and $CaCl_2$. L. S. T.

Behaviour of the anterior pituitary hormone in a case of teratoma testis. R. S. Ferguson (Amer. J. Roentgenol., 1933, **29**, 443—449).—In testicular teratoma the hormone is excreted in the urine. Irradiation of the tumour with *X*- or γ-rays diminishes the output. Ch. Abs.

Blood in tuberculosis. D. M. Telang (J. Univ. Bombay, 1933, **1**, No. 5, 181—201).—The sedimentation rate (I) of the red blood-corpuscles is faster in acute stages of osteomyelitis, pneumonia, amœbic dysentery, and malaria than in all tuberculous conditions (II) and the rate in (II) is > that in normal health. (I) is faster in pulmonary and bone tuberculosis than in glandular or intestinal types, the rate increasing as the disease progresses and *vice versa*. In pulmonary tuberculosis systolic and diastolic blood-pressure and blood-Ca are lower than normal, whilst blood-sugar, -urea, and -Cl′ show no deviation from normal. A. L.

Accumulation of iron in tuberculous areas. III. V. MENKIN (Amer. J. Med. Sci., 1933, **185**, 40—49).—Repeated intravenous injection of $FeCl_3$ is followed by accumulation of Fe in caseous areas of tubercles. CH. ABS.

Gastric pepsin. II. Secretion of pepsin in cases of duodenal ulcer and pseudo-ulcer. F. R. VANSANT, A. E. OSTERBERG, W. C. ALVAREZ, and A. B. RIVERS (J. Clin. Invest., 1933, **12**, 557—565).—Pepsin is increased in peptic ulcer; high vals. are also found in certain nervous patients who present some of the symptoms of ulcer. CH. ABS.

Protein content of normal and pathological serum in cattle. M. DEMMEL (Münch. tierärztl. Woch., 1932, **83**, 457—460).—The n of serum is taken as a measure of its protein (I) content, calculations being made from Reiss tables on the assumption of 0·00277 as index component for the non-protein constituents and 0·00172 for each 1% of (I). Comparative figures are thus provided for healthy and diseased cattle. Chronic infections and chronic organic disorders cause a rise in (I). In diseases associated with nutritional disturbance and poor condition, and in inflammatory conditions with œdema, there is a distinct decrease in (I). In general (I) is raised in cases of sterility. NUTR. ABS. (*b*)

Some chemical aspects of life. (SIR) F. G. HOPKINS (Nature, 1933, **132**, 381—394).—Presidential address to the British Association, 1933. L. S. T.

Intracellular oxidation-reduction studies. V. Comparison of intact and cytolysed starfish eggs by the immersion method. R. CHAMBERS, L. V. BECK, and D. E. GREEN (J. Exp. Biol., 1933, **10**, 142—152).—The aerobic apparent oxidation-reduction potential for intact and cytolysed starfish eggs at p_H 6·8—7·0 is approx. −0·06 volt; the anaerobic val. is $<$ 0·167 volt. Cytolysis results in a lowered reduction rate. Et_2O and phenylurethane do not affect the reduction rate of intact eggs; EtOH and Et_2O inhibit that of cytolysed eggs. KCN has no effect; $HgCl_2$ destroys the reducing power. $PbCO_3$ retards the reducing power of intact eggs and destroys that of cytolysed eggs. CH. ABS.

Manometric analysis of the metabolism in avian ontogenesis. III. Respiratory quotient of the yolk-sac and allantois during the last two weeks of development. J. NEEDHAM (Proc. Roy. Soc., 1933, **B**, **113**, 429—459; cf. this vol., 87).—The R.Q. of the allantois (I) falls from 0·95 on the fifth to 0·82 on the twentieth day of development; that of the yolk-sac (II) from 0·9 on the second to 0·6 on the seventh, remaining at 0·56 until the fourteenth day. The vals. for (I) are reduced by 0·1 if glucose is absent from the medium. The low vals. for (II) at mid-development are not due to (*a*) tissue damage, (*b*) conversion of fat into carbohydrate, (*c*) desaturation of fatty acids, or (*d*) ketogenic processes, but probably to the low R.Q. of protein catabolism ending in uric acid and to synthetic use of C and O_2. During the last week of development respiration of (II) is irreversibly inhibited by $CH_2I{\cdot}CO_2H$, but is unaffected by quinine or atoxyl. A. C.

Metabolism of tissues. H. LASER (Biochem. Z., 1933, **264**, 72—86; cf. A., 1932, 1058; Lipmann, this vol., 741).—The metabolism of hen fibroblast *in vitro* is similar to that of surviving tumour tissue. Extensive glycolysis takes place under anaerobic conditions (I) and also under aerobic conditions when respiration is strong and unaffected. Embryonic connective (II) and epithelial tissue and leucocytes live and grow for several days under (I). The increase in wt. of (II) in 4—6 days under (I) is the same as in O_2. W. McC.

Physiology of normal and Frizzle fowl: basal metabolism. F. G. BENEDICT, W. LANDAUER, and E. L. FOX (Storrs Agric. Exp. Stat. Bull., No. 177, April 1932).—In fowls, parts of the body without feathers lose heat as much as do the feathered areas. Observations of the course of the R.Q. and the total metabolism immediately following the ingestion of food indicate that the fowl must fast 48 hr. before the fat quotient is reached and its metabolism is basal. When the fat quotient obtains, the total metabolism reaches a const. level for at least 24 hr. more of fasting. The heat production of normal fasting hens (between 15 and 28°) averages 866 g.-cal. per sq. m. body-surface (K—10) per 24 hr. and that of normal cocks 838 g.-cal. At night metabolism is much lower. The heat production of normal moulting hens at 28° is 844 g.-cal. and at 17—19° 1291—1611 g.-cal. In the Frizzle fowl (a type characterised by very scanty feathering), even at 28° fasting heat production is $>$ in the normal, and nearly in proportion to the defective nature of the plumage. At about 17° the Frizzles have much greater heat production (twice normal). Metabolism is lower at night, and night measurements only are valid in determinations of basal metabolism in the fowl. The heat lost in the form of H_2O vapour is 49% in the normal and 17% in the Frizzle. NUTR. ABS. (*m*)

α-Oxidation of fatty acids. H. FASOLD (Klin. Woch., 1932, **11**, 1151; Chem. Zentr., 1932, ii, 3912).—Ingestion of $NaHCO_3$ increases, and of free org. acids decreases, urinary org. acids. A. A. E.

Specificity of cholesterol resorption and its biological significance. R. SCHOENHEIMER (Klin. Woch., 1932, **11**, 1793—1796; Chem. Zentr., 1932, ii, 3913).—Cholesterol, but not sitosterol, is resorbed by rabbits. A. A. E.

Liver-lipins after splenectomy. S. MARINO (Arch. Farm. sperim, 1933, **56**, 327—342).—Following splenectomy in dogs the level of the lipins of the liver fluctuates considerably; this is most marked with the total sterols and the phosphorylated fatty acids. Thus the liver, in common with other organs (cf. this vol., 304, 739), can partly replace the spleen, the function of which in fat metabolism is discussed. F. O. H.

Lipin metabolism. V. Blood-lipase of Carnivora and Herbivora during experimental lipæmia. VI. Effect of cholesterol on secretion of pepsin. I. REMESOV, N. TAVASTSTYERNA, and D. MATROSSOVITSCH (Z. ges. exp. Med., 1933, **87**, 613—622, 623—634).—V. Hypercholesterolæmia in dogs leads to a reduction of blood-lipase activity (I) due to adsorption of the lipase by the colloidal

cholesterol (II) particles, the ester being more powerful than free (II). Mn sol and to a greater extent Ni sol partly prevent the reduction of (I), whilst addition of Ca oleate has little effect. Lecithin, which *in vitro* has no action on blood-lipase, reduces its activity when present in excess in the blood-stream. Injection of insulin leads to an increase in (I) which reaches its max. when the blood-sugar and (II) are at their lowest. Injection of adrenaline or nicotine reduces (I), an effect possibly only partly due to increase of (II). (II) is an important regulator of enzyme action in the body owing to its property of adsorbing enzymes.

VI. Investigation of peptic activity of the gastric juice obtained from dogs with a gastric fistula shows that max. peptic activity occurs just before the stomach is emptied; this has the purpose of clearing the stomach of undigested food. Oral administration of (II) with meat broth reduces peptic activity; the effect is more marked when sunflower oil is given with (II). When a colloidal solution of (II) in bouillon is given, peptic activity increases. The toxic effect of high (II) feeding may be primarily due to its action on alimentary enzymes. NUTR. ABS. (*m*)

Induction substance in the development of the embryo. F. G. FISCHER and E. WEHMEIER (Naturwiss., 1933, **21**, 518).—The substance which in amphibian embryos controls the induction of the medulla plate is probably glycogen. W. O. K.

Glycogen metabolism of the organisation centre in amphibian gastrula. I. C. P. RAVEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 566—569).—The decrease in glycogen content of invaginating cells during gastrulation of the axolotl embryo is a direct result of the involution process.

Site of formation of the principal glycogen reserve on ingestion of carbohydrate. I. S. SCHWARTZ (Arch. sci. biol., U.S.S.R., 1932, **32**, 68—71).—In dogs, glycogen is synthesised largely in the liver and to only a small extent in the intestinal wall. CH. ABS.

Pentose metabolism. III. Absorption of *l*-rhamnose and formation of glycogen in the rat. A. K. SILBERMAN and H. B. LEWIS (J. Biol. Chem., 1933, **101**, 741—751).—The absorption coeffs. of *l*-rhamnose (I) administered orally from the gastro-intestinal tract of the rat were found to be 41, 20, and 12 mg. per 100 g. of rat per hr. for 1, 2, and 3 hr. absorption periods, respectively. As these results indicate that no significant absorption took place after the first hr., a mixture of glucose and (I) was fed with a view to find if (I) had a toxic effect. The absorption of glucose, however, was normal. The absorption of (I) fed to phloridzinised animals decreased to about 50% of the above vals., and in no case after (I)-ingestion was glycogen deposition apparent in the liver. A. L.

Fate of pentose in the healthy and the diabetic system. E. GRAFE (Klin. Woch., 1932, **11**, 1742—1744; Chem. Zentr., 1933, i, 805).—The effect of *l*-xylose (I), especially, on dogs and diabetic men, has been investigated. 20—60% of added pentose appears in the urine without distinction between men and dogs or normal and diabetic cases. Diuresis is markedly increased. Glucose never appears or increases in the urine. Glucose and pentose metabolism proceed independently. Blood-sugar always increases after addition of (I), depending mainly on the dose and conditioned only by excess of pentose. L. S. T.

Diuretic action and elimination of intravenously injected pentoses. P. THOMAS and A. GRADINESCU (Compt. rend. Soc. Biol., 1933, **112**, 415—416).—In dogs with catheterised ureters, injection of pentose (0·4 g. per kg. body-wt.) first results in a transitory increase in arterial blood-pressure. Diuresis commences as soon as the blood pressure rises by 10 mm. Hg. Xylose (I) has a greater effect than arabinose (II). The urine contains 3—5% of sugar in 15 min. and up to 8% in 1 hr. (II) is eliminated more quickly than (I). NUTR. ABS. (*m*)

Relation of lactic acid and alanine to glycogen formation. T. H. HODGSON (Biochem. J., 1933, **27**, 1158—1162).—Young rabbits form liver-glycogen from Na *dl*-lactate injections, but not from *dl*-alanine. H. G. R.

Lactic acid of the blood during experimental glycæmia due to ingestion of glucose. J. A. COLLAZO, J. PUYAL, and I. TORRES (Anal. Fís. Quím., 1933, **31**, 454—457).—In 20 healthy, fasting, human subjects given 50 g. of glucose the rise and fall of the lactic acid and glucose of the blood in the next 2 hr. was parallel. R. K. C.

Intermediate products and the last stages of carbohydrate breakdown in the metabolism of muscle and in alcoholic fermentation. O. MEYERHOF (Nature, 1933, **132**, 337—340, 373—375).—A lecture. L. S. T.

Absorption of glucose by rectum. W. S. COLLENS and L. C. BOAS (Arch. Int. Med., 1933, **52**, 317—324).—When glucose, dissolved in distilled H_2O, is administered, per rectum, to normals or diabetics, resorption (up to 90% in 2 hr.) takes place and a rise in blood-sugar usually occurs. W. O. K.

Absorption of glucose from intestinal loops. I. S. RAVDIN, C. G. JOHNSTON, and P. MORRISON (Amer. J. Med. Sci., 1933, **185**, 303). CH. ABS.

Metabolism of amino-acids in animal tissues. H. A. KREBS (Klin. Woch., 1932, **11**, 1744—1748; Chem. Zentr., 1933, i, 806—807).—Large amounts of NH_2-acids (I) obtained by keeping tissues of man, dogs, rats, and cats in physiological saline in presence of O_2 at 37·5° are decomposed under suitable conditions with formation of NH_3. Deamination occurs mainly in the kidneys, and these (I) are the chief source of urine-NH_3. Keto-acids, which result from deamination of the natural α-(I), have been isolated. Oxidative deamination is practically the only way in which deamination of (I) occurs in animal organisms. L. S. T.

Growth-promoting properties of homocystine and proof of the structure of homocystine. V. DU VIGNEAUD, H. M. DYER, and J. HARMON (J. Biol. Chem., 1933, **101**, 719—726).—The structure of homocystine (I) suggested by Butz and Vigneaud (this vol., 151) is proved by its conversion into meth-

ionine (II) by reduction in liquid NH_3 with Na and subsequent methylation. Feeding experiments in which additions of (I) were made to a basal diet containing caseinogen 5·0, dextrin 38·0, sucrose 15·0, lard 19·0, cod-liver oil 5·0, salt mixture 4·0, agar 2·0, and milk vitamin concentrate 12·0, showed that (I) could support the growth of rats in lieu of (II). A. L.

Cystine and wool production. C. Rimington, J. G. Bekker, and J. Kellerman (Nature, 1933, **132**, 63—64).—A reply to criticism (cf. A., 1932, 646). L. S. T.

Metabolism of sulphur. XX. Rate of absorption of *dl*-methionine from the gastrointestinal tract of the rat. B. W. Chase and H. B. Lewis (J. Biol. Chem., 1933, **101**, 735—740).—The absorption coeff. of *dl*-methionine (I) from the gastro-intestinal tract of the rat was 53 mg. per hr. per 100 g. of rat, slightly > the rate observed for cystine by other workers. No deposition of glycogen in the liver was observed after absorption of (I) for 3 hr. The urines of rats receiving (I) gave the cyanide–nitroprusside test for the ·S·S· linking. A. L.

Absorption of certain sulphur compounds from intestinal loops of dogs. J. C. Andrews and C. G. Johnston (J. Biol. Chem., 1933, **101**, 635—640).—Relative rates of absorption from isolated jejunal loops (I) of the dog were: cysteic acid> cysteine>*dl*-cystine>*l*-cystine and Na_2SO_4. No reduction of cystine occurred during 4 hr. in (I). H. G. R.

Relation of thiol concentration to size inheritance in the rabbit. P. W. Gregory and H. Goss (Amer. Naturalist, 1933, **67**, 180—185).—Average glutathione concns. (mg. per 100 g.) were 43·78 (large race) or 30·8 (small race). Ch. Abs.

Energy of urea synthesis. II. Effect of varying hydrogen-ion concentration with different metabolites. H. Borsook and G. Keighley (Proc. Nat. Acad. Sci., 1933, **19**, 720—725).—1 mol. of O_2 is required for every mol. of urea synthesised. In absence of NH_3, the rate of respiration, with lactate or succinate as metabolite, was > when no metabolite or glucose was added. H. G. R.

Uric acid excretion on diet low in purines. J. Melka (Pflüger's Archiv., 1933, **232**, 61—65).—The summer and winter excretion of uric acid (I) was determined when the subject was on a diet containing 87 mg. of purine substances daily. There was a reduction of (I) within 2 days of the commencement of the diet; 6 weeks later the output increased. It is concluded that man can synthesise nucleoprotein over long periods. The output of (I) was relatively higher in winter. Nutr. Abs. (*b*)

Variations in the plasma- and blood-potassium during alimentation and fasting. R. Gerschman and A. D. Marenzi (Anal. farm. bioquim., 1932, **3**, 128—133).—For dogs, starvation vals. are approx. const., whilst on a meat diet they vary considerably from day to day. Ch. Abs.

Fasting and specific dynamic action [of meat proteins] in dogs with lesion of the tuber cinereum or in hypophysectomised dogs. P. Mazzocco (Rev. soc. argentina biol., 1932, **8**, 621—627). Ch. Abs.

Changes in body composition with various diets and with starvation. Dittmar (Arch. exp. Path. Pharm., 1933, **171**, 496—518).—With starved rats the ratio body-wt./organ-wt. varies considerably. Thus the liver suffers a relatively greater loss in wt., whilst the heart decreases proportionately with the body. With carbohydrate-fed rats, starvation for 1—2 days produces a rapid diminution in liver-glycogen (I) and -sugar formation, an increased amount of fat and protein being used for production of sugar. Fat deposition also occurs, a process which in phloridzinised animals is therefore due to rapid deprivation of (I). With 3 days' starvation, storage of (I) and decomp. of fats are increased. The periodic variations in (I) and liver-fat occur also with rats fed on a fat and protein diet. Prolonged starvation diminishes the fat content of all the organs and of the muscle. F. O. H.

Bacteria as food for vertebrates. V. Burke (Science, 1933, **78**, 194—195).—Common H_2O bacteria contain all the food factors, including vitamins, necessary for normal development of the larval stage of *Rana pretiosa*. Bacteria also serve as direct and indirect factors in determining the food supply of higher animals. L. S. T.

Detoxication of phenylacetic acid. A. M. Ambrose, F. W. Power, and C. P. Sherwin (J. Biol. Chem., 1933, **101**, 669—675).—About 95% is detoxicated with glutamine and about 5% with glycuronic acid; on continued ingestion the ratio is shifted in favour of the latter. H. G. R.

Growth of pigs. I. Calcium and phosphorus metabolism in young growing pigs. L. S. Spildo (Rep. Res. Lab. Roy. Vet. Agric. Coll., Copenhagen, 1933, No. 151).—Pigs 6—8 weeks old were fed on a basal ration of barley, maize, soya-bean meal, and dry or skimmed milk. With a high P_2O_5 : CaO ratio (above 2·5) blood-Ca fell and -P rose, change in composition of the blood always being the first sign of an abnormal ration. The skeleton showed osteoporotic changes ("osteitis fibrosa") and tetany occurred. With a low P_2O_5 : CaO ratio (about 0·4) reverse changes in the blood were noted and osteoporosis with rickets developed. Tetany did not occur. The Ca : P ratio appeared to be the most important factor governing metabolism, but if the total CaO intake fell below 0·2% of the dry matter of the ration, normal growth and composition of the blood were not maintained even with a good ratio of Ca : P. The utilisation of CaO in the ration was about 60% and that of P_2O_5 50%. For 100 g. growth, 1·4 g. CaO and 2·6 g. P_2O_5 were required. Addition of inorg. salts to a ration of cereals and skimmed milk to make the P_2O_5 : CaO ratio about 1·6 and the Ca intake about 4·6 g. per kg. of dry matter gave excellent results. Without vitamin additions and without direct light the pigs remained normal. Administration of vitamin-*D* with a high P_2O_5 : Ca ratio improved the absorption of Ca, but did not greatly affect the composition of the blood; with a low

P_2O_5 : Ca diet, it was definitely unfavourable. Addition of vitamin-*A* had no definite effect. Light had a beneficial action, but could not altogether counteract the effect of a badly balanced ration.
NUTR. ABS. (*b*)

Calcium and phosphorus metabolism of normal pre-school children. I. T. PORTER-LEVIN (J. Amer. Dietet. Assoc., 1933, **8**, 482—488).—The increase in mineral retention from the use of irradiated cereals was within experimental error. CH. ABS.

Toxicity of methyl alcohol. I. Comparison with formaldehyde and formic acid on the isolated frog's heart. II. Comparison with formaldehyde and formic acid on the posterior vessels of the frog. U. SAMMARTINO (Arch. Farm. sperim., 1933, **56**, 311—319, 320—326).—I. The toxicities of HCO_2H, CH_2O, and MeOH as shown by the isolated frog's heart are in the mol. ratio of 1430 : 187 : 1.

II. All three substances in extreme dilution ($1 : 10^6$) produce vasodilation, whilst with larger doses HCO_2H and CH_2O, but not MeOH, produce vasoconstriction.
F. O. H.

Toxicity of methyl alcohol. III. Minimum delayed [lethal] intravenous dose of methyl alcohol, formaldehyde, and formic acid. IV. Critical review; mode of action of methyl alcohol. U. SAMMARTINO (Arch. Farm. sperim., 1933, **56**, 351—363, 364—371; cf. preceding abstract).—III. In rabbits the min. lethal doses and times of death after intravenous injection are: MeOH, 4·2 g., 104 hr.; CH_2O, 0·7 g., 8 hr.; HCO_2H, 0·24 g., 21 hr. The paralysis caused by MeOH is preceded by convulsions, whilst CH_2O and HCO_2H are consistently depressant. MeOH alone causes ocular lesions.

IV. Experiments on the isolated frog's heart, on the posterior venous system of the frog, and on rabbits, indicate that the toxicity of MeOH is due to the alcohol itself and not to its oxidation products.
R. K. C.

Epivan : an intravenous anæsthetic. R. JARMAN and A. L. ABEL (Lancet, 1933, **125**, 18—20).—Epivan, the Na salt of *CC-cyclo*hexenylmethyl-*N*-methylbarbituric acid, produces all stages of general anæsthesia in a few sec. when intravenously injected into human beings. L. S. T.

Determination of toxicity constants and activity of some barbituric derivatives. L. LAUNOY (J. physiol. path. gen., 1932, **30**, 364—378).
CH. ABS.

Habituation and accumulation phenomena. II. Phanodorm, luminal, and prominal. M. R. BONSMANN (Arch. exp. Path. Pharm., 1933, **171**, 612—618).—Daily administration of phanodorm (I) to dogs produces a continuous inhibition of the secretion of urine, whilst with prominal (II) or luminal (III) the inhibition is only temporary. Preliminary treatment with (II) inhibits the diminution of urine due to (III) and *vice versa*, whilst that due to (I) is inhibited by (II) or (III), but not *vice versa*. Dogs become habituated to the narcotic effects of (I) and (II). Whilst the inhibition of diuresis rapidly follows administration in each case, the onset of the effects on the nervous system varies with the three narcotics. F. O. H.

Narcotic potency in paraldehyde series. P. K. KNOEFEL (J. Pharm. Exp. Ther., 1933, **48**, 488—491).—Paraldehydes produced by the polymerisation of CH_2O, EtCHO, $Pr^{\alpha}CHO$, and $Pr^{\beta}CHO$ are unsuitable as narcotics. H. D.

Influence of iodoacetic acid on the blood-sugar level. J. T. IRVING (Nature, 1933, **132**, 315).—Perfusion experiments with rabbit's legs show that Na iodoacetate (1 in 2000 to 1 in 6000, calc. as free acid) impairs the utilisation of blood-sugar both in presence and absence of insulin. L. S. T.

Vesicant action of halogenated sulphides. W. R. KIRNER (J. Amer. Chem. Soc., 1933, **55**, 3501—3502).—Dawson's conclusion (this vol., 709) is not new (cf. A., 1928, 1214). R. S. C.

Vesicant action of chloroalkyl sulphides. T. P. DAWSON (J. Amer. Chem. Soc., 1933, **55**, 3506).—Kirner's priority (cf. preceding abstract) is admitted.
R. S. C.

Action of furfuraldehyde on respiratory and blood gas. I. HAYASHI, Z. KANDA, T. SATO, and I. MATSUMIYA (Nagoya J. Med. Sci., 1932, **6**, 141—149).—In rabbits the CO_2 in the expired air was decreased and the O_2 increased. The CO_2-combining power of the blood was decreased. CH. ABS.

Inhibition of esterification by phloridzin. E. LUNDSGAARD (Biochem. Z., 1933, **264**, 209—220; cf. Wilbrandt and Laszt, this vol., 630).—Phloridzin (I) in concn. of 0·005—0·02*M* inhibits phosphorylation (II), dephosphorylation (III), and production of lactic acid from glucose or glycogen. Since (I) likewise inhibits glycolysis in brain, the views of Ashford and Holmes (A., 1929, 1124) receive no support. In rabbits receiving injections of (I) in doses required to result in diabetes the concn. of (I) necessary for causing inhibition of (II) and (III) is reached in the kidneys only. The diabetes caused by (I) which acts by inhibiting the (II) believed to accompany reabsorption of glucose in the tubuli of the kidneys is probably a purely renal disease. W. McC.

Effect of phloridzin on the absorption of glucose. E. LUNDSGAARD (Biochem. Z., 1933, **264**, 221—223).—Phloridzin (0·02*M*), injected directly into the intestine of the rabbit or cat, specifically inhibits resorption of glucose, but does not affect resorption of NH_2-acids (glycine, glutamic acid). W. McC.

Biological determination and standardisation of some cardiac glucosides. Ouabain, digitalin, scillaren, and cymarin. J. LEVY and R. CAHEN (Bull. Sci. pharmacol., 1932, **38**, 23—37, 85—108; Chem. Zentr., 1932, ii, 3926).—Min. lethal doses for dogs are recorded. Ouabain, international standard, is the cryst. glucoside of *Strophanthus gratus*, 19·94% H_2O, α_D −30·6° for the anhyd. substance.
L. S. T.

Cumulative poisoning by squill derivatives and ouabain. E. W. WALLACE and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1933, **48**, 430—444).—In the dog scillonin (I) is cumulatively < half as potent as ouabain (II), and < as toxic as scillaren-*A* and -*B*,

scillicin, and digitalis. The lethal doses of (I) and (II) are approx. the same for mammals, whereas in the frog (I) was the least toxic. H. D.

Pharmacological action of peimine and peiminine. K. K. CHEN, A. L. CHEN, and T. Q. CHOU (J. Amer. Pharm. Assoc., 1933, **22**, 638—641; cf. A., 1932, 178).—Both peimine and peiminine when perfused through the inferior vena cava in frogs produce the same effect and in the same degree, *i.e.* decrease in heart rate, complete A-V block, and periodicity. They cause a fall of blood-pressure (cats) and inhibit the activity of rabbits' isolated intestine (concn. 1 : 10,000). There is a moderate hyperglycæmic action in rabbits. The min. lethal dose to white mice is 9 mg. per kg. E. H. S.

Relation between tetanus symptoms and the calcium and inorganic phosphorus content in the serum of parathyroidectomised dogs. A. BEZNAK (Magyar Orvosi Arch., 1932, **33**, 253—262; Chem. Zentr., 1932, ii, 3907).—Strychnine convulsions raise the inorg. P of blood-serum in normal and in parathyroidectomised dogs. The increase comes from the contracted muscles. In tetanus the creatine-P of muscle decreases, whilst the inorg. P increases. The Ca concn. in blood-serum decreases in tetanus convulsions, but increases in those produced by strychnine. L. S. T.

Modification in the lipin content of the central nervous system in the convulsive state. V. SANGIRARDI (Atti R. Accad. Lincei, 1933, [vi], **17**, 861—864).—The convulsive state produced by strychnine, nicotine, picrotoxin, PhOH, $BaCl_2$, etc. is accompanied by a fall in the lipin content of the spinal cord, the extent of which varies with the lipin concerned, and in the cholesterol content. R. N. C.

Enteral absorption of ergot alkaloids and their specific action on the circulation. E. ROTHLIN (Arch. exp. Path. Pharm., 1933, **171**, 555—591).—Direct duodenal or jejunal administration of ergot alkaloids (I) is followed after a latent period of approx. 10 min. by rapid absorption, a max. effect being attained after 40 min. With 0·25 and 0·50 mg. per kg. the action persists for 2—4 and 4—6 hr., respectively. Aq. ergotamine is readily absorbed from the rectum. Following intestinal administration, (I) are absorbed from both normal and defatted ergot preps. F. O. H.

Detection of morphine in urine of addicts. F. PANSE (Fort. Therapie, 1932, **8**, 629—633; Chem. Zentr., 1932, ii, 3924).—Urine is treated with NaOH and $NaHCO_3$, and an EtOAc extract is evaporated to 1—2 c.c. and fractionally sublimed for the identification of morphine. L. S. T.

Detection of quinine in urine by erythroquinine reaction. R. MONNET (J. Pharm. Chim., 1933, [viii], **18**, 94—96).—0·01 mg. of quinine (I) per c.c. of urine is detected by the addition of 1% aq. AcOH to a $CHCl_3$ extract of urine made alkaline with aq. NH_3, shaking, and adding successively $Br\text{-}H_2O$, aq. $K_4Fe(CN)_6$, and dil. aq. NH_3. The red colour in the $CHCl_3$-layer indicates the presence of (I). H. D.

Action of ultra-violet rays of various frequencies on solutions of alkaloids. Q. MINGOIA (Annali Chim. Appl., 1933, **23**, 318—330).—The behaviour of certain alkaloid salts, alterable by heating, is recorded. Wood's light (I) does not affect aq. solutions of heroine, cocaine, or codeine hydrochloride, or atropine sulphate, when exposed either freely or in quartz tubes. Moreover, the same solutions, when inoculated with *Aspergillus fumigatus*, *B. tumefaciens*, *B. coli*, etc., are not sterilised by (I). Hence, ultra-violet rays (II) offer no advantage over other sterilising agents for the sterilisation of solutions used in hypodermo-therapy, as the more refractive (II) usually change the solutions and (I) does not ensure asepsis. T. H. P.

Pharmacology of substances from yeast. K. ZIPF and J. BRAKLING (Arch. exp. Path. Pharm., 1933, **171**, 603—611).—Abs. EtOH, $COMe_2$, or Et_2O extracts of pressed or dried brewer's yeast contain no substance acting on the rabbit's blood-vessels or intestine or on the guinea-pig's uterus. Aq. and aq.-EtOH extracts have an action characteristic of the adenosine and/or the choline type of substances; acetylcholine, histamine, and the depressor substance of Euler and Gaddum (A., 1932, 1061) are not detectable. F. O. H.

Inactivation of biogenic amines etc. by formaldehyde. K. ZIPF and E. BARTSCHER (Arch. exp. Path. Pharm., 1933, **171**, 592—602).—The following are inactivated by CH_2O: histamine, posterior pituitary gland extract, tyramine, phenylethylamine, *iso*amylamine, muscle- and yeast-adenylic acid, acetylcholine, carbamylcholine chloride (A., 1932, 301), pilocarpine, and $BaCl_2$. Inactivation is due to actual combination of $\cdot NH_2$ or $:NH$ with CH_2O and/or to intracellular action of CH_2O on the substrate concerned. The detection of histamine by CH_2O is applicable only to tissue extracts. F. O. H.

Relationship between chemical constitution and physiological action. V. Molecular dissymmetry and physiological activity. L. H. EASSON and E. STEDMAN (Biochem. J., 1933, **27**, 1257—1266).—The miotic action, the degree of inhibiting the hydrolysis of $PrCO_2Me$ by liver-esterase (cf. A., 1931, 1190), and the action on the intestine of a no. of methylurethanes of the type $m\text{-}NHMe\cdot CO_2\cdot C_6H_4\cdot CRR'\cdot NMe_2$ (R=H, Me, and R′=H, Me, Et, Pr^a, Ph) and similar compounds (this vol., 1046) support the theory that, assuming that three of the groups linked to the asymmetric C in an optically active drug are concerned in its attachment to its sp. receptor in the tissues, mol. dissymmetry and its associated optical activity have no direct influence on the magnitude of the physiological activity of a drug. This theory is further supported by the fact that *d*-adrenaline has approx. the same pressor activity as 3 : 4-dihydroxy-β-phenylethylmethylamine. F. O. H.

Dinitro-*o*-cresol as a stimulator of metabolism. E. C. DODDS and (SIR) W. J. POPE (Lancet, 1933, **125**, 352—353).—Subcutaneous injection and oral administration of dinitro-*o*-cresol (I) increase the

O_2 consumption of guinea-pigs. (I) is three times as active as 2 : 4-dinitrophenol in this respect. L. S. T.

[Pharmacological] actions of dinitrophenol. M. L. TAINTER and W. C. CUTTING (J. Pharm. Exp. Ther., 1933, 48, 410—429).—Administration of 2 : 4-dinitrophenol to rabbits, cats, dogs, rats, pigeons, and men, in doses from 3 to 40 mg. per kg. body-wt., produces an increase in body-temp. up to 7°; this increase is independent of the central nervous system and of contractions of the skeletal muscles, and is not prevented by ergotamine, adrenalectomy, or thyroidectomy. Death may result from direct circulatory depression, hyperpyrexia, or acidosis and anoxæmia. H. D.

Experimental apiol poisoning in animals. L. KALBFLEISCH (Arch. exp. Path. Pharm., 1933, **171**, 439—442).—The toxicity of apiol is at least partly due to $(o\text{-}C_6H_4Me)_3PO_4$ (I). That the latent period between the time of administration of (I) to rabbits is hyperbolically related to the dose and that (I) produces neuritis indicate a combination occurring with certain phosphorylated lipins of the body at a rate dependent on the concn. of (I) in the blood. F. O. H.

Chemicals active in increasing tissue permeability and enhancing certain infectious processes. A. CLAUDE (Science, 1933, **78**, 151—152).—Diazo-compounds are the only synthetic substances so far discovered which are able to increase tissue permeability, and to enhance the lesions resulting from infectious agents, thus resembling certain tissue extracts and virulent bacteria. p-Ph·N_2·SO_3H, but not sulphanilic acid, is suddenly and completely diffused when intradermally injected; coupling with serum- or ov-albumin gives an active prep. of greater spreading power, and one which enhances infectious processes. L. S. T.

Efficiency of intravenously injected medicaments as a function of time. W. GEHLEN (Arch. exp. Path. Pharm., 1933, **171**, 541—554).—Mathematical considerations indicate that a max. content of an intravenously injected drug is attained after a period which is characteristic for the drug and is independent of the dose. A characteristic period also occurs with continuous administration. F. O. H.

Action of lymphagogues of the first class. Y. TAKAYANAGI (Nagoya J. Med. Sci., 1932, **6**, 113—131).—In narcotised dogs peptone, Na nucleate, and adrenaline increased the d, vicosity, and total solids. CH. ABS.

Changes in blood concentration incident to shock. V. H. MOON and P. J. KENNEDY (Amer. J. Med. Sci., 1933, **185**, 447—448).—In dogs, determinations of d, erythrocytes, and hæmoglobin indicate increase in blood concn. CH. ABS.

Blood-potassium and -calcium in electric shock. I. R. PETROV and S. F. LIBIKH (Arch. Sci. Biol., U.S.S.R., 1932, **32**, 229—239).—In most rabbits (surviving) blood-serum-K is greatly increased and -Ca decreased; in dogs and some rabbits (killed) -Ca was increased whilst -K was unchanged or slightly decreased. In man (one experiment) -K was slightly increased and -Ca was decreased. CH. ABS.

Influence of variations in systematic acid–base balance on carbohydrate tolerance in normal subjects. G. THOMPSON, D. M. MITCHELL, and L. C. KOLB (Biochem. J., 1933, **27**, 1253—1256).—Ingestion of 15—25 g. of NH_4Cl by men reduces the alkali reserve of the blood-plasma to a level comparable with that found in diabetic coma and raises the urinary excretion of acid by 100—200% and of NH_3 by 300%. The acidosis is accompanied by a failure in glucose tolerance, but administration of glucose does not produce any trace of glycosuria even when the blood-sugar level exceeds the normal threshold val. Ingestion of 20—70 g. of $NaHCO_3$ reduces the urinary excretion of acid and NH_3 to zero, but does not produce a marked increase in the CO_2-combining power of the plasma. Such alkalosis causes only a slight variation in the blood-sugar response to ingestion of glucose. F. O. H.

Effect of feeding fluorides on the composition of the teeth and bones of rats. M. C. SMITH and E. M. LANTZ (J. Biol. Chem., 1933, **101**, 677—683).—With 0·05% NaF in the diet there was no significant alteration in the composition of teeth and bones. With 0·1% NaF, ash and P were lower, Ca was higher, and Ca : P ratio increased. H. G. R.

Effect of fluorine on the nutrition of swine, with special reference to bone and tooth composition. C. H. KICK, R. M. BETHKE, and B. H. EDGINGTON (J. Agric. Res., 1933, **46**, 1023—1037).—Administration to pigs of $<$ 0·3% F as natural phosphate rock or as NaF reduced growth, food consumption, and the efficiency of utilisation of the ration. The femurs of the pigs showed an increased diam., decreased breaking strength, and loss of normal colour and lustre. Affected bones contained normal proportions of ash, Ca, and P, increased Mg and F, and decreased CO_3''. These changes were directly correlated with the amount of F fed. Enlargement of the mandibles following F feeding was due to an increase in the diam. of the marrow cavity rather than to thickening of the walls. The type of marrow was also changed. Prolonged feeding of excessive amounts of F caused softening of the teeth. The % of ash, Ca, P, Mg, and CO_3'' was not appreciably affected, but the F content was directly proportional to the amount consumed. The F of natural phosphate rock and of NaF produced similar physiological effects except that the former induced certain pathological changes in the kidneys. A. G. P.

Biochemistry of silicic acid. I. Micro-determination of silica. E. J. KING and H. STANTIAL. II. Presence of silica in tissues. III. Excretion of administered silica. E. J. KING, H. STANTIAL, and M. DOLAN. IV. Relation of silica to the growth of phytoplankton. E. J. KING and V. DAVIDSON (Biochem. J., 1933, **27**, 990—1001, 1002—1006, 1007—1014, 1015—1021).—I. A method is described based on the formation of a silicomolybdic acid complex (I) (A., 1923, ii, 507), reduced by 1 : 2 : 4-aminonaphtholsulphonic acid giving a blue colour which is compared with suitable standards. Form-

ation of (I) is max. at an acidity of 0·08*N*. PO_4''' and Fe''' interfere with the reaction and are removed by $CaCl_2+CaCO_3$ (A., 1932, 34). Blood (2 c.c.) is deproteinised by basic Fe^{III} acetate. Typical data for blood, urine, and tissues are given.

II. The SiO_2 content of the urine of carnivorous and omnivorous animals is < that of herbivorous animals; in all cases it is markedly influenced by the diet. Human urine contains 0·7—2·2 mg. per 100 c.c., a level considerably increased by silicosis. Human blood has an average content only approx. $\frac{1}{10}$ that found by Kraut (A., 1931, 378). Small but significant amounts occur in fœtal tissues, whilst with adult tissues wide variations occur, the highest content being found in the lungs.

III. Introduction of finely-ground SiO_2 or of gelatinous H_2SiO_3 into the stomachs of dogs produces an increase in the urinary excretion (I) of SiO_2 without any concomitant increase in the blood level (II). Intravenous injection of aq. Na_2SiO_3 produces a large increase in (I) and a moderate increase in (II). The amount excreted is < that injected. With suspensions of finely-divided SiO_2, intravenous injection causes death, there occurring only a slight increase in (I). The highest val. of (II) is attained by injection of "silistren" (a glycol silicate), death ensuing within 5 days. Spraying of aq. Na_2SiO_3 into the lungs appears to lead to increased (I). Animals possess a very low renal threshold for SiO_2.

IV. The addition of Na_2SiO_3 (up to 100 mg. of SiO_2 per litre) to diatoms growing in sea-H_2O containing an abundance of nutrient salts causes increased growth, whilst higher concns. have an unfavourable effect. That dissolution of SiO_2 appears to be more rapid in an autolysing suspension of diatoms containing $CHCl_3$ than in one which has been boiled indicates the probability of the existence of a silicatase.

F. O. H.

Silica content of lungs. A. F. Sladden (Lancet, 1933, **125**, 123—125).—The SiO_2 contents (I) of the lungs of 60 industrial workers are recorded. When (I) is > 1·0% of dried lung substance, extensive fibrosis (II) is usually present. When (I) is > 1·6%, (II) is severe. L. S. T.

Toxicity of arsenious oxide. L. Cohen (Rep. Austral. Assoc. Adv. Sci., 1933, **21**, 42—46).—The solubility of relatively pure commercial As_2O_3 in 5—7% glucose or sucrose is about ¼ (or less) of its solubility in H_2O. The variable toxicity to animals of As_2O_3 may be due to differences in the concn. of sugars in the alimentary tract. W. O. K.

Toxicity of neoarsphenamine. I. Increase on exposure to air. II. Characteristic curve for rats. C. A. Morell and C. W. Chapman (J. Pharm. Exp. Ther., 1933, **48**, 375—390, 391—409).—I. Solutions of neoarsphenamine (I) in glass-distilled H_2O, kept in air for 20 min., increase in toxicity by 107% > those kept under oil. The latter show no increase in toxicity after 2½ hr.

II. A characteristic curve for the toxicity of (I) for rats is constructed. Individual variations of 211% in one colony of rats were observed. H. D.

Dissociation and local irritating effects of calcium salts. B. Behrens and J. Wajzer (Biochem. Z., 1933, **264**, 120—125; cf. Weilguny, A., 1932, 964).—The degrees of local irritation produced by org. Ca salts (propionate, lactate, valerate, hexoate, gluconate) on injection are to some extent related to the degree of their dissociation. W. McC.

Toxicity and deposition of thallium in birds. P. A. Shaw (J. Pharm. Exp. Ther., 1933, **48**, 478—487).—The lethal doses of Tl for quail, geese, and ducks are respectively 12, 15, and 30 mg. per kg. body-wt. Tl accumulates in the muscles. In the dog > 100 days are required for the complete elimination of a dose of Tl. H. D.

Mercury poisoning. II. Influence of diuretin and theocin. M. Kuse (Folia Pharmacol. Japon., 1933, **15**, No. 4, 333—340).—When administered to rabbits with novasurol, diuretin and theocin have a favourable effect. Ch. Abs.

Antidotal action of sodium thiosulphate and dihydroxyacetone in cyanide poisoning, and alleged antidotal action of glucose. B. B. Turner and H. R. Hulpieu (J. Pharm. Exp. Ther., 1933, **48**, 445—469).—The fatal dose of NaCN for rabbits is approx. 2 mg. per kg. body-wt. The blood-sugar curve of rabbits given NaCN is of the same form as one of severity of symptoms plotted against time; no antagonistic action of glucose to NaCN is observed. $Na_2S_2O_3$ and dihydroxyacetone (I) administered together enable the rabbit to recover from thrice the lethal dose of NaCN, whereas the action of $Na_2S_2O_3$ alone is too slow to be effective and that of (I) is of too brief duration. H. D.

Sodium tetrathionate and methylene-blue in cyanide and carbon monoxide poisoning. J. H. Draize (Science, 1933, **78**, 145).—$Na_2S_4O_6$ (I) and methylene-blue (II) are both effective antidotes for CN' or CO poisoning in rabbits. (I) is more effective than (II) in each case. L. S. T.

Sodium nitrite and sodium hyposulphite in potassium cyanide poisoning. A. Buzzo and R. E. Carratala (Semana med., 1933, i, 1224—1229). Ch. Abs.

Chronic radium poisoning in rats. H. E. Thomas and F. H. Bruner (Amer. J. Roentgenol., 1933, **29**, 641—663).—Injection of $RaCl_2$ leads to decrease in calcification of the central portions of all bones, and a concn. of Ca salts in the parts of bones nearest the joints. > 99% of the retained Ra is present in the bones. Organs dealing with Ca metabolism contained more Ra than did other soft tissues. Ch. Abs.

Action of radium emanation on single cells or groups of cells. A. Foa (Atti R. Accad. Lincei, 1933, [vi], **17**, 578—582).—Cells exposed to Ra needles undergo a series of irreversible changes, involving increased refractivity of the nuclear membrane, granulation and shrivelling of the protoplasm, and ending in complete fracture of the cell. The effects are due entirely to the α-particles. R. N. C.

Reaction in the skin occurring during the latent period following *X*-radiation. J. C. Mottram (Nature, 1933, **132**, 317).—Some hr. after exposure

of the skin of rats, inoculated with pyrrole-blue, to X-rays a blue colour appears at the area of irradiation. L. S. T.

Chemical nature of enzymes. E. Waldschmidt-Leitz (Science, 1933, **78**, 189—190).—A discussion. L. S. T.

Respiration co-enzyme. F. E. Allison, S. R. Hoover, and D. Burk (Science, 1933, **78**, 217—218).—A factor, designated co-enzyme *R* (I), which is sp. and essential for respiration has been obtained by extracting commercial sucrose with abs. EtOH. Certain organisms fail to reproduce or grow in absence of (I) because of inability to respire; adequate addition of (I) causes respiration to reach the normal max. in $\Rightarrow$ 1 hr. (I) is sol. in H_2O and in abs. EtOH, but insol. in the ordinary fat solvents; it is readily dialysable and heat-stable, and contains no inorg. element. *Azotobacter vinelandii* synthesises (I), which is discharged into the culture medium. (I) appears to be widely distributed throughout the animal and vegetable kingdoms. L. S. T.

Peroxidase reaction and metals. W. Grimmer and S. Rauschning (Milch. Forsch., 1933, **15**, 381—383).—The effect of the presence of Cu, Fe, Ni, and Mn on the various types of peroxidase reactions was studied. Apparent positive results were obtained in all cases with p-$C_6H_4(NH_2)_2$ and Rothenfusser's reagent, whilst with guaiacol, benzidine, and guaiacum tincture results were negative. E. B. H.

Catalase. VII. Synthetic hæmin-catalases. K. G. Stern (Z. physiol. Chem., 1933, **219**, 105—114; cf. this vol., 862).—The parahæmatins (I) and hæmochromogens (II) of various NH_2-acids and proteins show a lower catalase activity (III) than free hæmin. Piperazine, on the other hand, especially in the Fe^{III} complex, activates strongly, although quinoline and isatin inhibit. (II) are almost always less active than (I), and have a lower optimum p_H. Adsorption of the (I) and (II) of arginine, histamine, and nicotine on animal charcoal affects the p_H max., but not the (III). J. H. B.

Digestion of raw starch. E. Pozerski (Bull. Soc. sci. Hyg. aliment., 1933, **21**, 1—29).—Starch dissolved by heat, or broken up mechanically, is digested *in vitro* by saliva and pancreatic juice, crude starch only slightly. Pre-treatment with dil. HCl aids digestion by enzymes. Starch in the form of cereal grains is completely digested by fowls and pigeons, but when given as a powder with non-carbohydrates is scarcely digested at all. Nutr. Abs. (*b*)

Amylase and sisto-amylase in malts from various grains. T. Chrzaszcz and J. Janicki (Biochem. Z., 1933, **264**, 192—208; cf. this vol., 749, 982).—Malt from various grains (barley, wheat, rye, millet, buckwheat, oats, and maize) contains greatly varying amounts of sisto-amylase (I) and of eleuto-substances (II). The amount of amylase (III) which passes into aq. malt extracts (IV) depends on the amounts of (I) and (II) present, on the concn. of (IV), and on the manner in which they are diluted. The different powers (*e.g.*, liquefying) of (IV) vary independently and are affected in different degrees by the type of malt, the concn. of (IV), and the amounts of (I) and (II) present. W. McC.

Barley diastase. R. H. Hopkins, G. F. Cope, and J. W. Green (J. Inst. Brew., 1933, **39**, 487—493).—Barley diastase, either EtOH-pptd. (I) or barley extract (II), has the most rapid saccharifying action on Lintner sol. starch (III) at p_H 4·5—4·7 for range of action within 45% conversion at 37°. The p_H–activity curve resembles that of malt diastase at the same temp. The normal limit of maltose production, 60—65%, is not substantially modified between p_H 4·3 and 7·5. The enzyme is not activated by Meyerhof's activator (A., 1927, 590) or Pringsheim's complement (A., 1923, i, 965), but both (I) and (II) are activated in the presence of living yeast. (I) degrades glycogen 1/3 as rapidly as it does (III). (III) was degraded to 3% of the original dry wt. by the repeated addition of large doses of (I) to the redispersed undegraded dextrin. R. H. H.

Biolase. R. Weidenhagen and B. Korotkyj (Z. Ver. deut. Zucker-Ind., 1933, **83**, 262—272).—The authors failed to confirm the statement of Pringsheim and Schapiro (A., 1926, 715) that the main product of starch conversion by biolase at 70° is a trisaccharide (I). The main fractions were dextrinous and had < half the reducing power of maltose. Small quantities of glucose and probably *iso*maltose were isolated as osazones, but no (I). J. H. L.

β-*h*-Fructosidase [invertase]. II. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1933, **83**, 376—389).—A further study of the method of prep. already described (A., 1932, 91). Products 1000 times as active as the original yeast can be obtained. By the use of large amounts of the enzyme, irisin, like inulin (*ibid.*, 543; B., 1933, 280), has been quantitatively converted into fructose. J. H. L.

Production of lactic acid in liver pulp. J. S. L. Browne and R. Grant (Biochem. Z., 1933, **264**, 163—168).—When liver pulp (I) is digested at 37—38° its lactic acid content (II) increases only slightly and its total carbohydrate content does not decrease. When (I) contains many blood-corpuscles the increase in (II) is > when it contains few. Possibly (I) itself exerts no glycolytic action. W. McC.

Production and transformation of α-glycerophosphoric acid during enzymic hydrolysis of carbohydrates. O. Meyerhof and W. Kiessling (Biochem. Z., 1933, **264**, 40—71; cf. this vol., 528, 742).—α-Glycerophosphoric acid (I) and $AcCO_2H$ (II) are produced in equiv. amounts in muscle extracts (rabbit, frog) when enzymes and sulphite are present. The detection, determination, and isolation of (I) are described. The Me_3 ester of its Me_2 ether has $[\alpha]_D^{20}$ −4·46°. Lactic acid (III) is produced from (I) and (II) according to the scheme proposed by Embden *et al.* (Klin. Woch., 1933, **12**, 213). In presence of NaF the yield of (III), which is not decreased, is equiv. to the amount of (II) consumed, but in absence of NaF this yield is equiv. to twice the amount of (II) consumed. Since NaF inhibits the hydrolysis of phosphoglyceric acid (IV), $H_2PO_3{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, it appears that (I) and (II) react to produce an acid probably identical with glyceraldehyde-γ-phosphoric acid. The -form

only of (I) reacts thus. $CH_2I{\cdot}CO_2H$ does not inhibit the hydrolysis of (IV) to (II) and H_3PO_4, but inhibits the reaction between (I) and (II). When adenyl pyrophosphate is absent this reaction produces only half the usual amount of (III), which is equiv. to the amount of (II) consumed. In yeast maceration juice similar changes occur. W. McC.

Phosphatase activity of tissue extracts. H. Bakwin and O. Bodansky (J. Biol. Chem., 1933, **101**, 641—656).—In rat-bone extracts the reaction velocity (I) of phosphatase activity is proportional to the enzyme concn. In intestinal extracts of cattle and rats there is < direct proportionality, due to the presence of proteolytic autolysis products. In cattle-bone extracts there is > direct proportionality, due to insufficient concn. of Mg and other accelerants. H. G. R.

Glucosulphatase. VI. Natural substrates of the enzyme. T. Soda and J. Yamazaki (Bull. Chem. Soc. Japan, 1933, **8**, 207—212; cf. this vol., 749).—The distribution of org. sulphates in various parts of *Viviparus japonicus*, Martens, and the total org. sulphates in four other shell-fish, are recorded. The substrate of glucosulphatase exists in sol. and insol. form in some shell-fish. R. S. C.

Comparison of the choline-esterase activities of the blood-sera from various species. E. Stedman, (Mrs.) E. Stedman, and A. C. White (Biochem. J., 1933, **27**, 1055—1060).—Choline-esterase (I), determined by a new modification of the method previously described (this vol., 315), could not be detected in sera (II) of tortoise, frog, hedgehog, goose, rat, rabbit, goat, ox, sheep, and ferret. A small but definite amount was detected in (II) from pig, fowl, mouse, pigeon, and duck, whilst relatively large quantities existed in (II) from cat, fox, guinea-pig, dog, man, horse, and monkey (order of increasing amount). The (I), Me butyrate esterase (III), or tributyrin lipase (IV) activities of these (II) showed no relationship. (I) and (III) are distinct enzymes, although their action may not be absolutely sp. Certain (II) probably also contain (IV) as a third enzyme. W. O. K.

Digestibility of proteins *in vitro*. V. Rate of liberation of cystine on hydrolysis of caseinogen. Observations on colorimetric tests for cystine when applied to peptic and acid digests of caseinogen. D. B. Jones and C. E. F. Gersdorff (J. Biol. Chem., 1933, **101**, 657—667).—After 30 min. hydrolysis with 20% HCl, 20% of the cystine (I) content of caseinogen was liberated, as determined by Sullivan's method (II) (A., 1930, 1604), and after 3½ hr. 50%. No increase was obtained after 6 hr. Folin and Marenzi's method (III) (A., 1929, 1039) first gives abnormally high vals. (0·55% after 15 min. hydrolysis) which slowly decrease, becoming 0·33% after 18 hr. hydrolysis. Using (II) on peptic digests no appreciable quantity of (I) was detected; using (III) an early rise and fall, becoming const. at 0·25% after 5 hr., was observed. The colour obtained with peptic digests is not due to free NH_2-acid. H. G. R.

Rate of ammonia liberation in tryptic and peptic digestion of caseinogen. I. Kraus-Ragins (Proc. Soc. Exp. Biol. Med., 1933, **30**, 452—457).—Liberation of NH_3 in tryptic digestion of caseinogen (*in vitro*) is due to the action of the enzyme, but in peptic digestion NH_3 is liberated by HCl without pepsin. Nutr. Abs. (*m*)

Activation of propepsin. R. Ege and P. Menck-Thygesen (Biochem. Z., 1933, **264**, 13—23).—Pepsin is determined by measuring its coagulating effect on caseinogen in circumstances where no activation (I) of propepsin occurs. (I) becomes measurable at 40° when the p_H exceeds 5·1. A change of p_H from 5 to 4 results in a ten-fold increase in the rate of (I) and a temp. rise of 10° doubles the rate. W. McC.

Antipepsin; determination. A. Slive (J. Lab. Clin. Med., 1933, **18**, 801—805).—Rabbit's blood and tissues, particularly the liver, often contain an antipeptic substance. Antipeptic activity is produced by intravenous injection of pepsin. The detection and determination of antipepsin is described. Ch. Abs.

Cathepsin and papain. E. Maschmann and E. Helmert (Z. physiol. Chem., 1933, **219**, 99—104).—The inactivation of cathepsin (I) and papain (II) by $CH_2I{\cdot}CO_2H$ is due to a sp. action on the enzyme and not to oxidation of the thiol activator (cysteine). When HCN is added to (I) or (II) solutions a Na nitroprusside reaction develops. The activating power of HCN may be due to its power of converting ·S·S· into ·SH groups. Fully active (I) giving a negative test for thiol is inhibited by O_2. J. H. B.

Aminopolypeptidase. II. A. K. Balls and F. Kohler (Z. physiol. Chem., 1933, **219**, 128—137; cf. A., 1932, 543).—When aminopolypeptidase (I) solution is dialysed against H_2O, activity and P are lost at the same rate. Against 0·005*M*-PO_4''' the loss of activity is much slower. The partly inactivated enzyme is incompletely reactivated on addition of the evaporated dialysate, but not by PO_4''' or P_2O_7''''. (I) is not attacked by phosphatase. Preps. of (I) obtained by different methods show the same affinity relations towards various polypeptides, indicating the homogeneity of the enzyme. J. H. B.

Action of polyhydric phenols on urease; influence of thiol compounds. J. H. Quastel (Biochem. J., 1933, **27**, 1116—1122).—*o*- (I) and *p*- (II) $-C_6H_4(OH)_2$ are very toxic to jack-bean or soya-bean urease, but *m*- is not. Adrenaline, protocatechuic acid, protocatechualdehyde, gallic acid, and pyrogallol are toxic, but less so than (I); phloroglucinol is inactive. CN′ and NH_2-acids do not protect urease against (I) or (II), and thus this toxicity differs from that of metals or of dyes. Serum or egg-white gives no protection, but boiled egg-white does, probably due to liberated SH groups. SH compounds (cysteine, glutathione, thiolacetic acid, H_2S) and $Na_2S_2O_4$ reduce or eliminate the toxic action of (I) etc. It is suggested that the high toxicity of (I) and (II) is probably due to the presence in these solutions of the corresponding quinone; benzoquinone is more toxic than (II). Protection by SH

compounds is probably due to the reduction of the quinone to the dihydric phenol. A. W.

Proteolytic enzymes of yeast. T. F. MACRAE (Biochem. J., 1933, **27**, 1229—1236).—By a modification of Willstatter's method (A., 1926, 321) preps. of (*a*) dipeptidase (I) free from proteinase (II) with traces of aminopolypeptidase (III) and (*b*) (III) free from (I) and (II) have been obtained from top yeast (IV). (II) free from (I) but not (III) has been obtained from (IV) and Dutch bakers' yeast. H. G. R.

Molasses-fermenting yeasts. *Saccharomyces formosensis*, nov. sp. R. NAKAZAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 285—291).—The yeast was isolated from Formosan fermented molasses. CH. ABS.

Relation between alcohol fermentation, yeasts, and fermentation temperature. III. R. NAKAZAWA, Y. TAKEDA, and M. ASHIKAGA (J. Agric. Chem. Soc. Japan, 1933, 9, 260—272).—The best source of N for *S. formosensis*, Nakazawa (nov. sp.), was asparagine. The optimum p_H for EtOH fermentation was 5·0—6·0. Fermentation by various species of *Saccharomyces* is classified in three types according to the relation between max. fermentation temp. and time taken to reach the max. temp. CH. ABS.

Cozymase of yeast. K. MYRBACK (Z. physiol. Chem., 1933, **219**, 173—176).—Kidney-phosphatase [glycerophosphate activity (I)=1] is about 6 times as active towards cozymase (II) as bone-phosphatase [(I)=0·4]. Heat-inactivated (II) is deaminated by HNO_2 at the same rate as active (II). The NH_2-group is probably free in both cases. J. H. B.

Production of glycogen by yeast. F. T. BRUCKE (Biochem. Z., 1933, 264, 157—162).—Yeast produces 2—3 times as much glycogen (I) from glucose (II) as from a quantity of EtOH containing an equal amount of C. In concn. of 1 : 5000 $CH_2I{\cdot}CO_2H$ (III) inhibits the production of (I) from (II), the inhibition being dependent on p_H in the same way as is the inhibition of the fermentation by (III). (III) also inhibits the production of (I) from EtOH to the same extent as from (II). W. McC.

Cell-nucleus of yeast and Feulgen's reaction. E. J. ROCHLINA (Bull. Acad. Sci. U.S.S.R., 1933, 855—858).—A technique is described by means of which the presence in yeast (Berlin Race XII) of a nucleic acid of the thymonucleic type may be demonstrated. T. H. P.

Agglutination of yeast. A. MALKOV, A. PETINA, and N. ZWETKOVA (Zentr. Bakt. Par., 1933, **88**, II, 193—200).—Agglutination is influenced solely by the p_H of the medium. The optimum for non-fermenting yeast is within the p_H range 2·85—3·15. A. G. P.

Combined action of coal tar and ultra-violet light on the development of yeast. M. N. MEISEL (Bull. Acad. Sci. U.S.S.R., 1933, 849—853).—The toxicity towards yeasts of coal tar dispersed in a solid or liquid medium increases with the degree of dispersion. *S. cerevisiæ* is less sensitive to the tar than *S. Ludwigii*, and when grown for a long time (2 years) on tar-containing media, undergoes morphological changes with formation of "saltants." This effect becomes more pronounced if the cultures are simultaneously exposed to ultra-violet light and results in the appearance of mycelial forms. T. H. P.

Decomposition of polyuronides by fungi and bacteria. I. Decomposition of pectin and pectic acid by fungi and formation of pectolytic enzymes. S. A. WAKSMAN and M. C. ALLEN (J. Amer. Chem. Soc., 1933, **55**, 3408—3418).—*Penicillium*, *A. niger*, and *Fusarium* sp., isolated from soil, decompose pectin and polygalacturonic acids, simple uronic acids being first formed and then decomposed. The three organisms differ in the speed with which they effect each reaction; they produce pectolytic enzymes responsible for these hydrolyses. The amount of enzyme which will hydrolyse 1 mg. of polygalacturonic acid in 1 hr. at 40° and p_H 4·0—6·0 is termed a pectolytic unit. 1 g. of the dry enzyme used contained 4000 such units. A sediment of uncertain nature is formed during the hydrolyses. R. S. C.

Production of acids by *Aspergillus niger*. X. Production of oxalic acid from formic acid. K. BERNHAUER and F. SLANINA (Biochem. Z., 1933, **264**, 109—112; cf. A., 1932, 1168).—*A. niger* converts up to 41% of HCO_2Na into $Na_2C_2O_4$, CO_2 being produced simultaneously. $(HCO_2)_2Ca$ likewise yields CaC_2O_4, but in poorer yield. The results confirm the theory of Chrzaszcz and Zakomorny (this vol., 536). W. McC.

Biochemistry of micro-organisms. XXXII. Cynodontin (1 : 4 : 5 : 8-tetrahydroxy-2-methylanthraquinone), a metabolic product of *Helminthosporium cynodontis*, Marignoni, and *Helminthosporium euchlœnœ*, Zimmermann. H. RAISTRICK, R. ROBINSON, and A. R. TODD (Biochem. J., 1933, **27**, 1170—1175).—The mycelia of *H. cynodontis* (I) and *H. euchlœnœ* (II), when grown on a synthetic culture medium containing glucose as the sole source of C, give *cynodontin* (III), $C_{15}H_{10}O_6$, m.p. 260° (*Ac*$_4$ derivative, m.p. 224—225°), when extracted with $CHCl_3$. (III) is probably 1 : 4 : 5 : 8-*tetrahydroxy-2-methylanthraquinone*, since it is formed from helminthosporin (IV) (this vol., 752), MnO_2, and conc. H_2SO_4 at 50—60°. A little (IV) is also produced from (I) but not from (II). H. B.

Biochemistry of micro-organisms. XXXIII. Mycelial constituents of *Penicillium brevi-compactum*, Dierckx, and related species. I. Ergosteryl palmitate. A. E. OXFORD and H. RAISTRICK (Biochem. J., 1933, **27**, 1176—1180).—*Ergosteryl palmitate* (I), m.p. 106—108°, $[\alpha]_{5461}^{20}$ −67° in $CHCl_3$, has been isolated (usually in yields of 0·02%) from the dry mycelia of 14 out of 15 species and strains of *P. brevi-compactum* and from *P. italicum*, Wehmer. The mycelium of *P. aurantio-griseum*, Dierckx (var. *Poznaniensis*, Zaleski), contains as much as 0·5% of (I). All the moulds were grown on Raulin–Thom medium and incubated at 24° for 20—30 days; (I) is extracted by light petroleum. H. B.

Bacterial production of amyl alcohol. S. FORSSMAN (Biochem. Z., 1933, **264**, 228—230)—Lindner's *Termobacterium mobile* converts *dl*-valeraldehyde quantitatively into amyl alcohol (67% in the *d*-form). MeCHO is produced simultaneously in traces. W. McC.

Enzyme system of Lindner's *Termobacterium mobile*. S. FORSSMAN (Biochem. Z., 1933, **264**, 231—236; cf. Tanko, A., 1932, 651).—Glucose and, more slowly, sucrose are fermented to the extent of 70% by the fresh bacterium (I), which also converts raffinose (II) (60%) into fructose and melibiose and hydrolyses lactose (93%). The decomp. of (II) by dried (I) reaches 83%. Glucosides (α- and β-methylglucosides, α-methylmannoside, amygdalin) are not attacked by (I). W. McC.

Fermentation of cellulose by thermophilic bacteria. IV. Products of fermentation. Y. TOMODA and H. YAMAURA (J. Soc. Chem. Ind. Japan, 1933, **36**, 436B).—The amounts of EtOH, AcOH, CH_4, H_2, CO_2, butyric and lactic acid formed are recorded. A. A. L.

Fermentation of polyhydric alcohols by the colon and aerogenes groups of bacteria. I. *d*-Sorbitol. C. F. POE, J. T. FIELD, and N. F. WITT (Univ. Colorado Bull. Studies, 1933, **20**, No. 2—3, 165—171).—The latter group showed greater total acidity and gave greater amounts of org. acids. CHAcMe·OH was not formed. CH. ABS.

Extracellular fat-formation by a lime-assimilating bacillus. A. BRUSSOFF (Naturwiss., 1933, **28**, 528—529).—From the Aix medicinal springs there has been isolated a CaO-assimilating bacillus the development of which is associated with the extracellular production of fat. There is probably some connexion between the amounts of CaO assimilated and fat produced. R. N. C.

Lipins of tubercle bacilli. XXXIV. Isolation of a pigment and anisic acid. R. J. ANDERSON and M. S. NEWMAN (J. Biol. Chem., 1933, **101**, 773—779).—The $COMe_2$-sol. fat of the tubercle bacillus (strain H-37) was hydrolysed and the fatty acids were removed as Pb salts. The amyl alcohol solution of the residue after extraction with aq. KOH, acidification, and extraction with Et_2O gave a mixture which was treated with KOH and dried. From this residue $COMe_2$ extracted the K salt of a *pigment*, $C_{11}H_8O_3$, m.p. 173—174°, and left K anisate. A. L.

Water-soluble proteins of the tubercle bacillus. G. A. C. GOUGH (Biochem. J., 1933, **27**, 1049—1054).—The bacilli were suspended in abs. EtOH at −10°, transferred to EtOH–Et_2O mixtures at −3° containing increasing amounts of Et_2O, and finally extracted with Et_2O. An aq. extract of the product yielded a globulin- (I) and an albumin-fraction (II) on treatment with $(NH_4)_2SO_4$ to half- and full-saturation, respectively. Whilst (I) gave a positive and (II) a negative tryptophan response, the carbohydrate content of (II) (11·7% as glucose) is much > that of (I) (0·3%). Differences also occurred in their immunological reactions. A certain similarity appears to exist between the protein constitution of the tubercle bacillus and that of the *Salmonella* group. F. O. H.

Chemical composition of the active principle of tuberculin. XVII. Nitrogen partition values of proteins from different acid-fast bacilli and the relationship to biological activity. F. B. SEIBERT and B. MUNDAY (J. Biol. Chem., 1933, **101**, 763—771).—Three different protein preps. made from tuberculin of the human tubercle bacillus and containing almost identical amounts of total N gave similar N partition vals. No significant differences were detected between the above preps. and those similarly made from avian and bovine tubercle bacilli and timothy-grass bacilli filtrates. Using two proteins made from Koch's "old tuberculin" and two denatured protein preps., high vals. for basic N were obtained, but these fractions were less potent in giving the skin reaction on tuberculous guinea-pigs. The presence of much polysaccharide caused an increase in the amide-N vals. A. L.

Effect of tuberculin on spermatozoa from normal and tuberculous guinea-pigs. L. C. DONALDSON and A. J. VORWALD (Amer. Rev. Tuberc., 1933, **27**, 401—410).—The spermatozoa method is not suitable for testing the potency of tuberculin. CH. ABS.

Sensitisation of guinea-pigs and the production of allergy and anaphylaxis to tuberculoprotein. H. S. REICHLE and H. GOLDBLATT (Amer. Rev. Tuberc., 1933, **27**, 291—307). CH. ABS.

Effect of the reaction of the medium on the characteristics of bacteria. I. General. Results obtained with *B. coli comm.*, *S. enteritidis*, and *Ps. pyocyanea*. II. Behaviour of *B. subtilis*. III. *B. cereus*. E. W. STEARN and A. E. STEARN (J. Bact., 1933, **26**, 9—35, 37—55, 57—75).—I. Differences in growth and appearance of colonies grown in media of different p_H persist in certain cases after repeated subculturing in a neutral medium.

II. In media having $p_H <$ a fairly definite crit. val. a variant "acid strain" develops. By modifying cultural conditions a reversal to the "alkaline" strain may be induced.

III. Characteristic differences in colonies grown on media having $p_H < 6·0$ are described. A. G. P.

Use of reduced iron for the cultivation of anaerobic organisms. J. P. SCOTT and C. A. BRANDLY (J. Bact., 1933, **26**, 1—7).—Typical fermentation reactions of anaerobes occur in media containing reduced Fe in place of the customary vaseline seal. Fe causes active partial reduction of methylene-blue. A. G. P.

Vitamin necessary for the growth of *B. sporogenes*: its relation to auxin and other growth factors. B. C. J. G. KNIGHT and P. FILDES (Brit. J. Exp. Pathol., 1933, **14**, 112—124).—Pressed baker's yeast and urine contain a substance (I) which enables *B. sporogenes* to grow in a purified medium. (I) resembles auxin. NUTR. ABS. (*m*)

Chemotherapy of pneumococcus infections. Quinine derivatives. M. GUNDEL and L. SEITZ (Arch. exp. Path. Pharm., 1933, **171**, 519—540).—The *in vitro* and *in vivo* activities of aq. 1% quinine phenylquinolinecarboxylate (I) on pneumococci are > those of aq. 0·5% optochin (II). The Na dehydrocholate derivative (III) is stronger *in vitro*, but somewhat weaker *in vivo*, than (I); under both conditions it is stronger than (II). The $SrCl_2$ urea derivative has an activity approx. equal to that of (I) or (III). F. O. H.

Chemical and immunological properties of pneumococci and other heterophile antigens. G. H. BAILEY and M. S. SHORT (Amer. J. Hyg., 1933, **17**, 329—357). CH. ABS.

Properties of pneumocholin, a biochemical antigen. E. E. ZIEGLER (J. Lab. Clin. Med., 1933, **18**, 695—704).—Pneumocholin, produced by lysis of pneumococci in a bile salt, is unchanged in 0·5 hr. at 56°. CH. ABS.

Skin reactions to the specific soluble substances of pneumococcus types I and II. J. R. ALSTON and A. S. R. LOWDON (Brit. J. Exp. Path., 1933, **14**, 1—9). CH. ABS.

Absorption of antitoxins through the skin. R. RICHOU (Ann. Inst. Pasteur, 1933, **51**, 117—145).—In the guinea-pig tetanus antitoxin applied as an ointment to the skin is rapidly absorbed during the first 6 hr., but not to the same extent as by subcutaneous injection. The absorbing power of different areas of the skin varies, that of the stomach being greatest. The difference between various routes of absorption is merely quant.; only 0·1% of the total antitoxin employed is absorbed through the skin. P. G. M.

Skin permeability and anaphylaxis. R. RICHOU (Ann. Inst. Pasteur, 1933, **51**, 146—148).—It is not possible to desensitise the guinea-pig to antitetanus serum by means of skin dressings. Substances penetrating the skin, other than the antitoxin, may give rise to anaphylactic shock. P. G. M.

Red cells and immunity. R. D. DE LA RIVIERE and N. KOSSOVITCH (Ann. Inst. Pasteur, 1933, **51**, 149—159).—Diphtheria toxin is adsorbed on red blood-corpuscles both *in vivo* and *in vitro*, although the affinity varies in different species; rat corpuscles show the least affinity. The toxin is adsorbed on the hæmoglobin in the corpuscles, not on the stroma. Tetanus anatoxin adsorbed on red cells acts as a protective agent against hæmolysis by the toxin. The development of antibodies to purified hæmoglobin is highly sp. P. G. M.

Significance of change in antigenic volume as the result of specific agglutination. F. S. JONES and R. B. LITTLE (J. Exp. Med., 1933, **57**, 729—739). CH. ABS.

Bactericidal substance in urine of patients receiving a ketogenic diet. A. T. FULLER (Biochem. J., 1933, **27**, 976—982).—The urine of patients on a ketogenic diet has a marked bacteriostatic action on *B. coli*. This is mainly due to the presence of *l*-β-hydroxybutyric acid, although the increased acidity of the urine enhances its action. F. O. H.

Urinary antiseptics. Antiseptic power of urine after administration of urotropine and its derivatives. D. BOVET and L. DEMANCHE (Ann. Inst. Pasteur, 1933, **51**, 237—247).—The drugs were administered intravenously and the bactericidal power of the urine was tested at intervals. The most effective was the $C_2H_4I{\cdot}OH$ compound (I) of $(CH_2)_6N_4$ (II); a urine was obtained lethal to *S. aureus* for 7 hr. and to *B. coli* for 5 hr. after injection of 1 g. per kg. of body-wt. (II) is sensitive to changes of p_H, being less active on the alkaline side of p_H 5, but (I) is unaffected. The derivatives were more toxic than (II) itself. P. G. M.

Sterilising action of acids on bacteria. I. Mineral acids. S. TETSUMOTO (J. Agric. Chem. Soc. Japan, 1933, **9**, 67—75).—The action of HNO_3, HCl, H_3PO_4, H_3BO_3, and H_2SO_4 depends only on the p_H; that of dil. aq. $HCrO_4$ and HCNO is due to undissociated mols. CH. ABS.

Relation of some physical properties to bactericidal action of some α-phenyl-substituted acids. L. H. BALDINGER and J. A. NIEUWLAND (J. Amer. Pharm. Assoc., 1933, **22**, 711—716).—The germicidal activity (*B. coli*) of BzOH and α-Ph derivatives of the C_2–C_7 aliphatic acids increases with rise of mol. wt. to C_6 and then is limited by the decreasing solubility. Curves showing adsorption by animal C from aq. solution and the distribution coeffs. between oil and H_2O parallel that of the bactericidal action. E. H. S.

Oligodynamic action of silver, and the rôle of oxygen. A. VAN ACKER (Natuurwetensch. Tijds., 1933, **15**, 93—104).—Various theories are discussed. The oligodynamic action of Ag depends on a chemical action between the Ag and the bacteria, and O_2 plays no part in the process. H. F. G.

Photo-sensitising action of aniline dyes on staphylococci and streptococci. A. SZÜTS (Magyar Orvosi Arch., 1932, **33**, 268—273; Chem. Zentr., 1932, ii, 3903—3904).—The bactericidal action of sunlight and quartz [Hg] light on cultures sensitised by NH_2Ph dyes has been investigated. Me-violet (I), Nile-blue, phenosafranine, and acridine-orange have the strongest photodynamic action. (I) has an inhibiting action even in the dark, but virulent cultures are destroyed only by irradiation. Eosin, resorufin, and phloxin-red have an inhibiting effect only on staphylococci at higher concn. Neutral-red, fluorescein, rose-bengal, and anthracene-yellow are without effect. Sensitisation increases with an increase in concn. and streptococci are more resistant than staphylococci. L. S. T.

Preparation of purified bacteriophage. M. SCHLESINGER (Biochem. Z., 1933, **264**, 6—12).—The prep. of highly purified bacteriophage in quantity is described. The diam. of the particles is about 90 mμ. W. McC.

Chemical mediators of autonomic nerve impulses. W. B. CANNON (Science, 1933, **78**, 43—48).—A review. L. S. T.

Passage of fœtal hormones through the placenta (adrenal and posterior pituitary hormones). L. CATTANEO (Arch. ital. Biol., 1931, **86**, 1—10; Chem. Zentr., 1933, i, 794).—Adrenaline, choline, and pituitary hormone were injected into the fœtal heart and subsequently detected in the maternal blood (rabbit). L. S. T.

A lactation hormone of the adrenal cortex. K. A. BROWNELL, J. E. LOCKWOOD, and F. A. HARTMAN (Proc. Soc. Exp. Biol. Med., 1933, **30**, 783—784).—Adrenal cortical extracts prepared by a process involving chilling to −12° do not support lactation in adrenalectomised rats, although they make possible the successful termination of pregnancy; but the

material separating between 3° and −12° yields an extract, the injection of which enables such animals to suckle their young. The name cortilactin is suggested for this substance. NUTR. ABS. (*b*)

Function of the adrenal cortex. VII. Adrenal cortex and glutathione. K. A. WINTER, M. REISS, and J. VALDECASAS (Endokrinol., 1932, **11**, 171—174; Chem. Zentr., 1933, i, 1465).—Injection of the adrenal cortex hormone (I) into rabbits or dogs considerably increases blood-glutathione. Intravenous injection of (I) or glutathione depresses the R.Q. A. A. E.

Relation between the action of adrenaline on the uterus and the hydrogen-ion concentration of the blood. F. YAGI (Folia Pharmacol. Japon., 1933, **15**, No. 4, 302—308).—Decrease in p_H increases, whilst increase diminishes, the min. dose stimulating the uterus of the non-pregnant rabbit. CH. ABS.

Effect of adrenaline on tissue respiration. B. WALTHARD and H. VON WATTENWYL (Biochem. Z., 1933, **264**, 104—108).—The supposed increase in the respiration of liver (rat, guinea-pig) in Ringer solution produced by adding adrenaline (I) and serum (II) (man, guinea-pig, rat) does not occur, but autoxidation of (I), which may be prolonged by (II), takes place. W. McC.

Mechanism of the antagonistic action of adrenaline and insulin. W. SCHEER (Z. klin. Med., 1933, **123**, 159—167; Chem. Zentr., 1933, i, 1468).—Injection of either or both increases the O_2 requirement. Apparently metabolic changes produced by the two hormones affect different parts of the body. A. A. E.

Hypoglycæmic effect of insulin in dogs under chloralose. E. AUBERTIN and E. TRINQUIER (Compt. rend. Soc. Biol., 1933, **112**, 316—318).—In chloralosed dogs given 0·25 unit insulin per kg. body-wt., intravenously or subcutaneously, the fall in blood-sugar is more rapid and more prolonged than when no chloralose is given. Subcutaneous injection causes greater relative difference in reaction than intravenous. NUTR. ABS. (*m*)

Effect of insulin on blood-sugar after removal of kidneys or ureters. E. AUBERTIN and E. TRINQUIER (Compt. rend. Soc. Biol., 1933, **112**, 318—321).—In dogs insulin, given in doses of 0·25 unit per kg. body-wt., either intravenously or subcutaneously after removal of the kidneys, causes increase in the hypoglycæmic area as compared with normal response. Fall in blood-sugar and prolongation of the hypoglycæmic period increases daily while the animals survive, especially when ligature of the ureters has also been performed. NUTR. ABS. (*m*)

Effect of insulin on blood-sugar of rabbits during infection. L. C. FISHER and H. A. REIMANN (Proc. Soc. Exp. Biol. Med., 1933, **30**, 746—747).—The intracutaneous inoculation of 0·1 c.c. of a 1 : 400 dilution of a culture of Type 1 pneumococci caused healthy rabbits to become more susceptible to the action of insulin. NUTR. ABS. (*b*)

Effect of insulin on optical properties of blood-glucose. J. THOMAS (Compt. rend. Soc. Biol., 1933, **112**, 1258—1260).—Lactic acid, NH_2-acids, glutathione, and glycuronates do not affect the [α] of blood dialysates to an extent > 8—10%, whereas differences from the calc. vals. for αβ-glucose of 25—30% were observed. The blood of untreated diabetics or of depancreatised dogs is considered to contain only αβ-glucose on account of its low [α]; insulin restores the much greater differences usually found in normals. NUTR. ABS. (*b*)

Influence of insulin on muscle-tissue respiration in polyneuritic pigeons. T. INAWASHIRO (Tohoku J. Exp. Med., 1933, **20**, 544—552).—Insulin, when added to the cell prep. or injected subcutaneously into the birds 1 hr. before death, caused a diminution in O_2 uptake in strips of pectoral muscle which varied directly with the amount of insulin used, and was more marked with polyneuritic than with normal pigeons. The blood-sugar of normal pigeons averaged 0·155%, that of polyneuritic birds 0·221%. After insulin injection both normal and, to a greater extent, polyneuritic birds showed diminished vals. NUTR. ABS. (*b*)

Effect of electrical stimulation of the vagus on secretion of insulin. R. GAYET and M. GUILLAUMIE (Compt. rend. Soc. Biol., 1933, **112**, 1197—1201).—Electrical stimulation of the vagal connexions of pancreatic tissue grafted into the neck of the diabetic dog or of transplanted pancreas, transfused by the blood of another animal in which the adrenal veins were ligatured, was without effect on the blood-sugar. Experiments on animals in which precautions were taken to suppress hepatic glycogenolysis by hepatic denervation and extirpation or denervation of the adrenals, and on animals in which, in addition to hepatic denervation, splanchnic section and extirpation of the essential sympathetic ganglia were performed, were negative. The results do not justify the assumption of a nervous control of insulin output. NUTR. ABS. (*b*)

Stimulating action on the pancreatic secretion and hypoglycæmic action of secretin. J. LA BARRE and J. LEDRUT (Bull. Soc. Chim. biol., 1933, **15**, 724—763).—Preps. of secretin (I) which have definite isoelectric points and which give f.-p. curves for their aq. solutions indicative of a pure substance show a hypoglycæmic as well as a stimulating action on the pancreatic secretion. Such preps. treated with Et_2O, dialysed, or pptd. with homopolar substances still retain their hypoglycæmic action. A double pptn. with heteropolar substances such as $CCl_3{\cdot}CO_2H$ or $KClO_3$, however, gives a fraction [excretin (II)] having no hypoglycæmic action. Electrometric titration of (II) indicates that it is a pure substance, and the greater viscosity of aq. solutions of (II) than those of (I) shows that (II) has much larger mols. than (I). A. L.

Use of albino rats for the assay of the male sex hormone. Y. WANG and H. WU (Chinese J. Physiol., 1933, **7**, 135—149).—The seminal vesicles (I) and preputial glands (II) of rats, castrated at the age of 4 weeks, show a marked decrease in wt. during the first 4 weeks. After two daily injections of the male sex hormone, (I) shows an appreciable gain in wt. in 24 hr. and (II) in 48 hr., which is approx.

proportional to the amount of hormone given. The best results are obtained with rats castrated at 4 weeks and given hormone injections 4 weeks after. H. G. R.

Action of the follicular hormone on vegetables. J. PAZLER (Z. Zuckerind. Czechoslov., 1933, **57**, 421—424).—In sand cultures of oats no sp. effect of the hormone on growth was observed. A. G. P.

Stimulation of the reproductive organs of cattle. P. J. KERR (Indian J. Vet. Sci., 1932, **2**, 306—309).—Urine of pregnant cows affords a hormone extract which stimulates the reproductive organs of bulls and cows. CH. ABS.

Sex-physiological studies. X. Conservation of prolan in urine. M. BORST, A. DODERLEIN, and D. GOSTIMIROVIĆ (Munch. med. Woch., 1932, **79**, 1392—1393; Chem. Zentr., 1932, ii, 3904).—Unchanged prolan can be preserved for 356 days and the follicular-ripening hormone for 424 days by the addition of *m*-cresol or Et_2O. L. S. T.

Prolan in the pituitary. I. Prolan in the pituitary lobes and pars tuberalis in man and the ox. II. Production of prolan in basophilic cells. B. ZONDEK (Klin. Woch., 1933, **12**, 22—25; Chem. Zentr., 1933, i, 957).—In the ox the posterior pituitary lobe contains no prolan; in man the test usually gave positive results. It is present only in the parts adjacent to the anterior lobe, and probably originates in basophilic cells. In the pars tuberalis, but not in other parts of the brain, prolan was detected. A. A. E.

Pituitary substance giving increased gonadotropic effects when combined with prolan. H. M. EVANS, M. E. SIMPSON, and P. R. AUSTIN (J. Exp. Med., 1933, **57**, 897—906).—The increased gonadotropic effect obtained by combining prolan with pituitary extracts can be secured equally well by means of preps. which contain large amounts of the growth-promoting or of the gonad-stimulating hormone, neither of which is responsible for the reaction. CH. ABS.

Follicular ripening and luteinising hormone in the anterior pituitary lobe of various animals. H. MAGISTRIS (Pfluger's Archiv, 1932, **220**, 835—841; Chem. Zentr., 1933, i, 1464). A. A. E.

Effect of a fat diet and of anterior pituitary extract on the liver-glycogen of thyroidised rats. H. MAGISTRIS (Compt. rend. Soc. Biol., 1932, **111**, 397—399; Chem. Zentr., 1933, i, 1960).—The power of the liver to form glycogen is retained. A. A. E.

Effect of the anterior pituitary hormone on the blood-sugar. F. BOHM (Z. ges. exp. Med., 1932, **84**, 689—694; Chem. Zentr., 1933, i, 1960—1961).—Intravenous injection of prolan (I) into rabbits raises the blood-sugar; when the val. is > 300 mg. per 100 c.c., glycosuria occurs. Ergotamine suppresses (I) hyperglycæmia; insulin hypoglycæmia is diminished by (I). If the liver is free from glycogen, (I) does not produce hyperglycæmia. A. A. E.

Pituitary and thyroid glands. Effect of anterior pituitary extract on blood-iodine. B. A. HOUSSAY, P. MAZZOCCO, and A. BIASOTTI (Compt. rend. Soc. Biol., 1932, **111**, 401—402; Chem. Zentr., 1933, i, 1960).—Injection of anterior pituitary extract into dogs increased the blood-I. A. A. E.

Influence of anterior pituitary extract on blood-glutathione. H. MAVEROFF (Rev. Soc. Argentina biol., 1932, **8**, 614—615).—Intraperitoneal injection of the extract increases the erythrocyte-glutathione of normal, thyroidectomised, and hypophysectomised dogs. CH. ABS.

Effect of anterior pituitary extract on plasma-protein. I. GOLDBERG (Rev. Soc. Argentina biol., 1932, **8**, 610—613).—In normal dogs daily injection of ox anterior pituitary extract increased the blood-plasma-total protein, -non-protein-N, and -viscosity. In recently thyroidectomised dogs the increase in blood-globulin was proportionally greater. CH. ABS.

Distinction between the anterior pituitary hormone having an excito-secretory action on the thyroid gland, and the ovary-stimulating factor in extracts of the anterior lobe. M. ARON (Compt. rend. Soc. Biol., 1931, **106**, 1044—1046; Chem. Zentr., 1932, ii, 3905).

Adrenotropic hormone of the anterior pituitary lobe. J. B. COLLIP, E. M. ANDERSON, and D. L. THOMSON (Lancet, 1933, **125**, 347—348).—The adrenotropic principle (I) is distinct from the thyrotropic principle. L. S. T.

Are the erythrophore reaction of the minnow and the melanophore reaction of the frog identical? A. JORES and E. W. LENSSEN (Endokrinol., 1933, **12**, 90—101; Chem. Zentr., 1933, i, 1959—1960).—Changes in activity effected by boiling the pigment hormone with NaOH are described. The melanophores of the frog correspond with the alkaline, and the erythrophores with the acid, form of the hormone. Constituents of the anterior pituitary lobe sensitise the latter, but not the former. The two reactions are not identical. A. A. E.

Assaying posterior pituitary extracts for oxytocic activity. J. M. GULLAND (Biochem. J., 1933, **27**, 1216—1217).—Burn's method is simplified. Uterine horns (guinea-pig) can be preserved in Ringer solution. H. B.

Oxytocic hormone of posterior lobe of pituitary gland. II. Action of nitrous and nitric acids. J. M. GULLAND (Biochem. J., 1933, **27**, 1218—1228).—The hormone (I) is rapidly converted by HNO_2 at p_H 3 into a derivative *A*, which has 35% of the oxytocic activity of (I) and is stable at p_H 7·4. This is transformed by HNO_3 (formed by aerial oxidation of HNO_2) or by HNO_2+HNO_3 into a substance *B* (II) (activity 20%), which is gradually converted by high concns. of HNO_2 into a substance *D* (activity 0·1%). HNO_3 converts (I) into a substance *C* (activity about 90%), which is unstable at p_H 7·2°, and is transformed by HNO_2 into a substance probably identical with (II). H. B.

Oxytocic hormone of the posterior lobe of pituitary gland. III. Action of preparations of plant proteolytic enzymes. J. M. GULLAND and T. F. MACRAE (Biochem. J., 1933, **27**, 1237—1247; cf. A., 1932, 655; this vol., 539).—The hormone was

inactivated slowly by two aminopolypeptidase (I) preps. and very rapidly by two dipeptidase (II) preps. and by two proteinase preps., both of which contained some (I), whilst one contained a trace of (II). None of these enzymes (all of which were from yeast), however, is responsible for the inactivation, which is due to a fourth enzyme having a p_H optimum of 7·4 and is present also in papain. Inactivation by the enzyme is never complete, 0·7% of the initial activity remaining; this residual activity is probably due to a derivative of the hormone produced by the action of the enzyme. F. O. H.

Pharmacological standardisation of parathormone. C. L. Rose (J. Lab. Clin. Med., 1932, **18**, 300—304).—The unit is 0·01 of the amount required to produce an increase of 5 mg. of Ca per 100 c.c. in the blood of a 20-kg. dog. Blood-Ca is max. 16—18 hr. after subcutaneous injection. Ch. Abs.

Significance of parathyroid hormone for regulation of calcium metabolism. V. Substances which raise and lower blood-calcium. C. Bomskov and J. Falck (Z. ges. exp. Med., 1933, **87**, 662—667).—Intravenous injection of small amounts of substances which stimulate the secretion of adrenaline (nicotine, strychnine, caffeine) leads to a transitory fall in serum-Ca succeeded by a rise; large amounts produce an immediate sharp rise. These results are similar to those following injections of small and large amounts of parathyroid hormone. This hormone stimulates the production of adrenaline.
Nutr. Abs. (*m*)

Influence of thyroxine, thyreoglobulin, and paroidin on the reduced glutathione content of blood. E. Zunz (Compt. rend. Soc. Biol., 1932, **110**, 1003—1005; Chem. Zentr., 1932, ii, 3907).—Injection of thyroxine into the saphenous vein does not alter the glutathione coeff. (I), but thyreoglobulin (II) raises it. There appears to be no relation between (I) and the accompanying alteration in blood-sugar, nor does the effect of (II) appear to be related to the increased adrenaline secretion. Paroidin (III) increases (I) markedly, and the effect is greatest when the blood-sugar is lowered to the largest extent. (III) has no further effect on (I) when the adrenals are removed. L. S. T.

Non-thyroid substance with thyroid action. I. Abelin and A. Florin (Arch. exp. Path. Pharm., 1933, **171**, 443—456).—Hydrolysis of iodised protein with aq. $Ba(OH)_2$ yields an I-containing substance having physiological properties closely resembling those of thyroxine. Thyroidectomy of the animal to which it is administered has no influence on its activity. The method of Leland and Foster (A., 1932, 432) when applied to various iodised proteins yields small amounts of the thyroxine-like fraction.
F. O. H.

Biological action of vitamins and their sequence. W. Kollath (Naturwiss., 1933, **21**, 537—542).—A discussion. A. C.

Vitamin terminology. J. Kuhnau (Z. Vitaminforsch., 1932, **1**, 184—191; Chem. Zentr., 1933, i, 799). L. S. T.

Synergism amongst vitamins. H. J. Jusatz (Z. ges. exp. Med., 1933, **87**, 529—544).—Vitamin-*B* (I) diminishes the toxic effects produced by feeding excess of irradiated ergosterol (II), but administration of vitamin-*A* (III) does not modify the toxic effects in hypervitaminosis-*D*. Symptoms of *A*- and *D*-hypervitaminosis in the same animal can be produced simultaneously. (I) increases the catalase index of the blood, but (III) does not. Administration of (II) causes an increase in the blood-catalase, although an excess causes a decrease. In advanced stages of hypervitaminosis-*D* ability to produce antibodies is diminished. Nutr. Abs. (*m*)

Deficiency disorder induced in young suckling rats bred on a purified synthetic diet with "Glaxo casein" (caseinogen) as sole source of protein. L. W. Mapson (Biochem. J., 1933, **27**, 1061—1068).—The suckling young of rats receiving "Glaxo casein" as sole source of protein develop a disease characterised by failure of growth, loss of fur, and eventual death. The disease is probably the result of a deficiency and is cured by extracts containing physin (cf. A., 1932, 1174) or the Coward factor (cf. A., 1929, 1496). The possible identity of these two factors is discussed. W. O. K.

Vitamin-*A* in the retina. G. Wald (Nature, 1933, **132**, 316—317).—The unsaponifiable extracts of the visual purple, intact retinas, and the pigment-choroid layers of frogs, sheep, pigs, and cattle show all the characteristics of vitamin-*A*-containing oils. An extract of ox retinas cured rats suffering from avitaminosis. L. S. T.

[Vitamin-*A* in] rice embryo. T. Miki (Arb. med. Univ. Okayama, 1933, **3**, 501—504).—The unsaponifiable fraction of the oil extracted from rice embryo contains vitamin-*A*. Nutr. Abs. (*b*)

Carotene content, vitamin-*A* potency, and anti-oxidants of butter-fat. C. L. Shrewsbury and H. A. Kraybill (J. Biol. Chem., 1933, **101**, 701—709).—The colorimetric determination of carotene (I) by comparison with a dichromate standard is possible with (I) dissolved in light petroleum. When butter-fat is used as solvent the results are consistently high, although the spectrophotometric method is trustworthy. Treatment of butter-fat with charcoal destroys its colour, vitamin-*A* activity, and the natural anti-oxidants which protect (I) from oxidation.
A. L.

Seasonal variation in butter-fat. I. Seasonal variations in carotene, vitamin-*A*, and the antimony trichloride reaction. R. G. Booth, S. K. Kon, W. J. Dann, and T. Moore (Biochem. J., 1933, **27**, 1189—1196).—Blue val. (I) of the untreated butter-fat (II) was valueless as a guide to the vitamin-*A* (III) content, being 0·2—0·1 of the unsaponifiable matter. Variations in (I) between winter and summer butter were due to a higher concn. of inhibitory substance in the latter. When assaying total (III) by colorimetric methods, both (III) and carotene (IV) should be accounted for. Total (III) of (II) in summer is about thrice that in winter, and the activity due to (IV) is also > in winter.
H. G. R.

Threshold of activity of carotene. L. RANDOIN and R. NETTER (Bull. Soc. Chim. biol., 1933, 15, 706—723).—A study of the change in wt. and the preventive and curative effect with respect to xerophthalmia brought about by administration of carotene to young rats deprived of vitamin-*A* indicates that a daily dose of 4×10^{-6} g. is the amount $< 10\times10^{-6}$ g. which has the greatest relative effect. Administration of 10×10^{-6} g. daily does not bring about normal growth as obtained by the daily addition of 1 drop of cod-liver oil, and the effect is not distinctly superior to that of 4×10^{-6} g. daily. A. L.

Method of enhancing the vitamin-*A* value of cod-liver oil. E. R. JANES, H. F. GROVER, and E. J. QUINN (Proc. Soc. Exp. Biol. Med., 1933, 30, 516—519).—The growth of rats depleted of vitamin-*A* is stimulated by giving combined malt extract and cod-liver oil emulsion, but rats given the same dose of the oil alone or of the emulsion and malt extract separately fail to grow and show symptoms of vitamin-*A* deficiency. Vitamin-*A* is therefore best utilised in the malt and oil emulsion. NUTR. ABS. (*m*)

Evaluation of the vitamin-*A* concentrate "Vogan." Avitaminosis-*A*. T. MOLL, F. DOMAGK, and F. LAQUER (Klin. Woch., 1933, 12, 465—467).— Vogan," a vitamin-*A* (I) concentrate derived from fish-liver oils, contains 40,000 rat units (approx. Sherman units) of (I) per c.c. Massive doses of (I) (0·02 c.c. daily of Vogan) were deleterious for mice, causing excessive storage of lipins (II) in epithelial cells. (I) deficiency, on the other hand, caused the epithelial cells to be completely depleted of (II), and it is therefore suggested that (I) is concerned in the metabolism of (II). NUTR. ABS. (*b*)

Comparison between the spectrophotometric and biological assay for the vitamin-*A* content of fish-liver oils. M. A. MAGILL and W. R. BRODE (Ohio J. Sci., 1933, 33, 127—134).—Some agreement was obtained within certain groups of commercial samples. Several closely allied compounds may be responsible for both colour reactions and vitamin properties. Peppermint oil contains a colour-forming compound which has a similar chromogen to that in oils known to contain vitamin-*A*. CH. ABS.

Value of ferrous iodide administered directly and indirectly. H. C. CAMERON (Proc. Soc. Exp. Biol. Med., 1933, 30, 762—765).—No vitamin-*A*-substituting effect is observed on giving FeI_2 alone or combined with linoleic acid. NUTR. ABS. (*m*)

Blood-cholesterol in dogs on a vitamin-*A*-deficient diet. E. P. RALLI and A. WATERHOUSE (Proc. Soc. Exp. Biol. Med., 1933, 30, 519—523).—In dogs fed on a vitamin-*A*- (I) -deficient diet the blood-cholesterol (II) increases when symptoms of (I)-deficiency appear. On giving (I), (II) diminishes. Hence the metabolism of cholesterol appears to be affected by the amount of (I) in the body. NUTR. ABS. (*m*)

Fat-soluble vitamins and nutrition. ANON. (Nature, 1933, 132, 304).—A summary of a lecture on the significance of vitamins-*A* and -*D* in human nutrition and in certain diseases. L. S. T.

***A*- and *D*-Avitaminosis in the guinea-pig. Combined action of the vitamins. Composition of diet and scurvy in the guinea-pig.** P. E. SIMOLA (Acta Soc. med. Fennicæ "Duodecim," 1932, A, 16, No. 1, 16 pp., 12 pp., 8 pp).—A. Carotene prevents the onset of symptoms in guinea-pigs receiving a diet deficient in vitamin-*A*. On a modified McCollum diet, guinea-pigs remain alive for relatively long periods with no marked rachitic changes, but a diet with excess of P is tolerated very badly.

B. The course of *B*-avitaminosis in young rats is not appreciably influenced by varying the amounts of the *A*-, *C*-, and *D*-factors in the diet nor is the course of *C*-avitaminosis in guinea-pigs influenced by varying the *A*- and *D*-factors. The vitamin-*A* content of the livers of half-grown rats with vitamin-*A* deficiency is not influenced by the amount of vitamin-*D* supplied.

C. In guinea-pigs receiving different deficient diets wt. loss is least when a modification of McCollum's rachitogenic diet is used. The shortest life spans are observed with Zilva's scorbutic diet. Scurvy symptoms are most marked with diets containing abundant carbohydrate or fat. Carotene or vigantol exerts no marked effect on the progress of the scurvy. NUTR. ABS. (*m*)

Effect of vitamins on growth, length of life, and fertility. F. GROEBBELS (Klin. Woch., 1933, 12, 215—217).—In rats receiving a diet of caseinogen, rice starch, palmin, salt mixture, and yeast additions of "ossin" (I) (cod-liver oil and egg yolk), cod-liver oil (II), or irradiated ergosterol (III) diminish the fertility of the females (as judged by the no. of young per litter) and the rate of growth and survival of the young. The unfavourable effect on the growth of the young is less with (I) than with (II) or (III). NUTR. ABS. (*m*)

Vitamin-*D*. IV. Ergosterol in soya-bean oil. S. IZUME, Y. YOSHIMARU, and T. HIDAKA (J. Agric. Chem. Soc. Japan, 1933, 9, 246—253).—The sterol, m.p. 136—137° (acetate, m.p. 131—132°), contains 19·8—20·0% (by absorption spectrum) of ergosterol. CH. ABS.

Isomerides of cholesterol and experimental rickets. U. SAMMARTINO (Arch. Farm. sperim., 1933, 56, 343—350).—Rats were fed on a normal diet and on a rachitogenic diet supplemented with either cholesterol (I) or the *iso*cholesterol (II) of De Fazi (this vol., 710), both non-irradiated and irradiated. With irradiated, but not with non-irradiated, (I) and (II), bone-calcification approaches that occurring with the normal diet. F. O. H.

Effect of high doses of irradiated and non-irradiated ergosterol on the albino rat. J. T. HAUCH (Proc. Soc. Exp. Biol. Med., 1933, 30, 475—477).—Toxic effects (I) are observed only with high doses. The (I) recorded by others with comparatively small doses were due to the presence of a toxic substance other than vitamin-*D*. NUTR. ABS. (*m*)

Action and therapeutical importance of the water-soluble derivatives of vitamin-*D*. E. BECCART (Arch. internat. Pharmacodyn. Therap., 1933, 44, 164—172).—Rickets in rats can be cured by H_2O-sol. K vitamin-*D* phthalate. NUTR. ABS. (*m*)

Calcium–phosphorus metabolism in the chicken. IV. Ergosterol requirements of growing chicks. E. J. KING, H. HULL, and G. E. HALL (Poultry Sci., 1933, **12**, 129—132).—Growing chicks consuming a diet with a Ca : P ratio of 1·91 : 1 needed 10 times as many rat-units of vitamin-*D* in the form of irradiated ergosterol (I) as in the form of cod-liver oil (II) to produce leg bones with approx. the same ash content. (I) and (II) were mixed with the diet; the same amount of (I) given separately by mouth produced a higher ash content.

NUTR. ABS. (*b*)

Free fatty acids in cod-liver oils and vitamin-*D*. O. SCHULTZ (Z. Vitaminforsch., 1932, **1**, 287—289; Chem. Zentr., 1932, ii, 3910).—Six oils containing 1—20% of free fatty acid showed agreement in respect of vitamin-*D* content; this deteriorated by about 30% during 2 years. Methods of prep., with the exception of bleaching, had no marked influence on the vitamin content. L. S. T.

Vitamin-*D* activity of butter. I. Chemical differentiation of antirachitic factor of autumn and winter butter from irradiated ergosterol and vitamin-*D* of cod-liver oil. S. K. KON and R. G. BOOTH (Biochem. J., 1933, **27**, 1302—1309).—Autumn and winter butters saponified with aq.-alcoholic KOH lose > 80% of their antirachitic potency. Irradiated ergosterol (I) and cod-liver oil (II) treated in the same way both in the presence and absence of butter are unaffected by the treatment, indicating a chemical difference between the antirachitic factor of butter and those of (I) and (II).

H. D.

Lactic bacteria, lactose, and the international vitamin-*D* standard as calcification factors in rachitic rats. R. LECOQ and H. VILLETTE (Ann. Falsif., 1933, **26**, 409—416).—The Randoin–Lecoq method (A., 1928, 556) produces a rapid development of rickets without greatly affecting the wt. increase of the rats, and this is accompanied by a rise in fæcal p_H which is not necessarily an indication of rickets, although it is corrected by addition to the diet of irradiated ergosterol. The curative dose of international vitamin-*D* standard is 1·4 and the preventive dose 0·7 units per 35—45-g. rat per day. Lactic bacteria oppose the rise in p_H, but do not prevent the incidence of rickets, whilst lactic acid (in place of sucrose) lowers the p_H and frequently produces a change in alimentary equilibrium which results in rickets. In biological analyses the effects of vitamin-*D* and P compounds should be distinguished, although the latter may be expressed in terms of the former if experimental conditions are identical. J. G.

Biological detection of vitamin-*D*. E. BECCARI (Giorn. Biol. appl. Ind. Chim., 1932, **2**, 174—181; Chem. Zentr., 1933, i, 1964).—Intensive growth and change in ash constituents of bones are not exact criteria for vitamin-*D*. A. A. E.

Bone-ash method of determining effectiveness of vitamin-*D* supplements. J. L. ST. JOHN, C. KEMPF, and L. BOND (Poultry Sci., 1933, **12**, 34—36).—Ash of cartilage-free bone is > that of the whole tibia; cartilage ash (I) in rachitic is much < in non-rachitic chicks. (I) may be a better criterion than bone ash of the effectiveness of vitamin-*D* supplements. CH. ABS.

Antineuritic vitamin. II. A. WINDAUS, R. TSCHESCHE, and H. RUHKOPF (Nachr. Ges. Wiss. Gottingen, Math.-Phys. Kl., 1932, 342—346; Chem. Zentr., 1933, i, 1311—1312).—The substance is not $C_{12}H_{17}ON_3S$, but $C_{12}H_{16}ON_4S$ [hydrochloride, m.p. 250° (decomp.); chloroaurate, sinters 190°, decomp. 198°; rufianate (+H_2O), m.p. 291° (decomp.)]. Hot aq. $Ba(OH)_2$ affords NH_3 and H_2S. Hot 2*N*-HCl affords NH_3 only. Cold dil. $KMnO_4$ and hot conc. HNO_3 give H_2SO_4. ·OMe, :NMe, guanidino-, and ·C(SH):NH groups could not be detected.

A. A. E.

Isolation of oryzanin, antineuritic vitamin. II. S. OTAKE (J. Agric. Chem. Soc. Japan, 1933, **9**, 186—196; cf. A., 1932, 657).—Oryzanin hydrochloride, $C_{12}H_{16}O_2N_4S,2HCl$, m.p. 250°, was obtained (1·6 g.) from rice bran (11,500 kg.) by pptg. "oryzanin extract" with $AgNO_3$ and $Ba(OH)_2$ at p_H 4·5—6·8, hydrolysing the ppt. with HCl, repptg. with phosphotungstic acid, preparing the Pt salt, and removing the Pt with H_2S. CH. ABS.

Antineuritic vitamin from rice polishings. VIII. Polyneuritis in experimental animals. A. G. VAN VEEN (Meded. Volksgesond. Ned.-Ind., 1932, **21**, 184—195).—A formula very similar to those put forward by Otake and Windaus is ascribed to "cryst. vitamin-B_1" (I). In rats, a daily dose of $4—6\times10^{-6}$ g. produced a normal rate of growth up to 100—130 g. Increase of dose up to $10—15\times10^{-6}$ g. produced normal growth up to 200 g. It is concluded that the (I) tested also contained vitamin-B_4. (I) stimulated the appetite of polyneuritic animals. 4 mg. of (I) had the same potency as 1 g. (100 international units) of Jansen and Donath's acid clay adsorption product. For the prevention of polyneuritis, "rice-birds required a daily dose of 0·4—0·5 unit, pigeons 2—3, and rats 1—2 units.

NUTR. ABS. (*m*)

Crystalline [picrolonate of] antineuritic vitamin (B_1). A. SEIDELL and M. I. SMITH (J. Amer. Chem. Soc., 1933, **55**, 3380—3383).—Gradual addition of picrolonic acid in MeOH to an aq. solution of the vitamin prep. from brewers' yeast concentrates the vitamin-B_1 into the more sol. portions of the pptd. picrolonate, which after crystallisation from MeOH has m.p. 227° (efferv.) and is curative for polyneuritic rats in doses of 0·015 mg. R. S. C.

Extraction of vitamin-B_1 from fresh yeast. A. SEIDELL (Ann. Brass. Dist., 1933, **31**, 24—26).—Preliminary treatment of yeast with sucrose seemed to permit a more complete extraction of the antineuritic vitamin from the liquefied mass by means of 60—70% EtOH than either Pirie's method or treatment with NaCl. NUTR. ABS. (*b*)

Irradiated adenine sulphate and antineuritic vitamin (B_1). F. SCHULTZ and F. LAQUER (Z. physiol. Chem., 1933, **219**, 158—163).—Neither irradiated nor non-irradiated adenine nor its salts have an antineuritic (B_1) action on pigeons (cf. Guha and Chakravorty, A., 1932, 1294). J. H. B.

Evaluation of food and drugs containing vitamin. II. Vitamin-*B* complex. A. JUNG (Z. Vitaminforsch., 1932, **1**, 192—214; Chem. Zentr., 1933, i, 804).—Vals. for various materials are given. The % vitamin-B_2 requirements of man and rats are approx. identical. A. A. E.

Phosphorylation and phosphatase action in avitiminosis-*B*. J. BODNAR and A. KARELL (Magyar Orvosi Arch., 1932, **33**, 348—350; Chem. Zentr., 1933, i, 1316).—Phosphorylation in the muscle and liver of a pigeon with avitaminosis-*B* is 77—146% > the normal. No difference was observed in phosphatase action. A. A. E.

Apparent effect of thymus-nucleic acid on the incidence of rat polyneuritis. F. F. HEYROTH (Bull. Basic Sci. Res., 1932, **4**, 125—127).—Addition of thymus-nucleic acid to a B_1-free diet restricts the growth of rats and results in an earlier incidence of polyneuritis. CH. ABS.

Gaseous exchange in pigeons in avitaminosis [B_1]. Action of pilocarpine on this exchange in avitaminosis. G. SARZANA (Arch. internat. Physiol., 1933, **36**, 1—12, 13—17).—A. The basal metabolism (I) of pigeons averages 5 g.-cal. per kg./hr. At 29—30° there is no substantial difference in (I) between normal and avitaminous pigeons, but at 12—13° avitaminous birds (II) show a diminished O_2 consumption because (II) cannot adapt themselves to the changed conditions as efficiently as can normal birds.

B. Pilocarpine causes a slight increase in O_2 consumption in pigeons kept for a short time on a diet of polished rice, but when they are in an advanced stage of avitaminosis, there is sometimes a decrease, due to inanition, in this consumption.

NUTR. ABS. (*m*)

Avian polyneuritis. Action of vitamin-B_1 concentrates *in vitro*. A. P. MEIKLEJOHN (Biochem. J., 1933, **27**, 1310—1320).—Addition of vitamin-B_1 (I) concentrate to the minced cerebrum of a (I)-deficient pigeon in the presence of lactate (II) increases the O_2 consumption, but fails to increase the amount of (II) removed. The minced cerebrum of a (I)-deficient pigeon readily removes (II). H. D.

Vitamin-*B*-deficient ration. B. SURE (Proc. Soc. Exp. Biol. Med., 1933, **30**, 779—780).—The diet consisted of caseinogen (purified by washing with acidulated H_2O and with 25% EtOH) 10, salts 4, butter-fat 10, and dextrin 61, together with vitamin-B_2 as beef steak (autoclaved for 6 hr. at 20 lb. pressure, and dried at 100°) 15. Rats fed on this diet were depleted of vitamin-B_1 in 4—6 weeks.

NUTR. ABS. (*b*)

Vitamin-B_2 in fruits. P. L. DAY and W. J. DARBY (J. Home Econ., 1933, **25**, 319—323).—The vitamin-B_2 content of apples and oranges is low and that of avocados and pears somewhat higher.

NUTR. ABS. (*m*)

Vitamin-B_2. P. GYORGY, R. KUHN, and T. WAGNER-JAUREGG (Naturwiss., 1933, **21**, 560—561).—Ovoflavin and lactoflavin (this vol., 298, 522, 847) possess the highest vitamin-B_2 potency recorded, when administered to rats on a diet supplemented by yeast extracts freed from vitamin-B_2 or by cryst. vitamin-B_4 preps. Flavins and associated vitamin-B_2 activity are found both free and bound to material of high mol. wt. Irradiation destroys the vitamin activity. R. K. C.

Vitamin content of mango fruit. M. E. F. CRAWFORD and E. O. V. PERRY (Biochem. J., 1933, **27**, 1290—1293).—The contents of three varieties of mango in vitamins-*A*, -*C*, and -*D* were assayed.

H. D.

Vitamin-*C* in *Citrus* juices. A. H. BENNETT and D. J. TARBERT (Biochem. J., 1933, **27**, 1294—1301).—Ascorbic acid was determined in *Citrus* juices by titration with dichlorophenol-indophenol at p_H 6. Individual variations in reducing power up to 60% were observed in lemons. The presence of preservatives, strong acidification, or boiling causes the reducing power of oranges and lemons to decrease and ultimately to vanish during storage. H. D.

Regeneration of reducing properties of oxidised lemon juice. S. W. JOHNSON (Biochem. J., 1933, **27**, 1287—1289).—Tillmans' observation (A., 1932, 658) that lemon juice oxidised with indophenol, I, or H_2O_2 can regain its reducing capacity when treated with H_2S immediately after oxidation is confirmed.

H. D.

Vitamin studies on pears. I. Vitamins-*A* and -*C* in Winter Nelis and d'Anjou [pears] after prolonged storage. I. A. MANVILLE and F. G. CHUINARD (J. Amer. Dietet. Assoc., 1933, **8**, 504—516).—Vals. for -*A* are 2, 5, and for -*C* 2, 3 Sherman units, respectively. CH. ABS.

Vitamin-*C* content of Baldwin apples and apple products. C. R. FELLERS, M. M. CLEVELAND, and J. A. CLAGUE (J. Agric. Res., 1933, **46**, 1039—1045).—A sufficiency of vitamin-*C* (I) for guinea-pigs was obtained by feeding approx. 4 g. of apples per 300 g. live wt. During storage for 8—10 months the loss of (I) from the apples was approx. 40%. Fresh expressed juice contained nearly as much (I) as did fresh whole fruit. Benzoated or pasteurised cider retained practically no (I) after 48 hr. Canned apple sauce was a poor source of (I). A. G. P.

Vitamin-*C*. VIII. Chemical properties. Isolation from cabbage juice. T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1933, **9**, 197—206).

CH. ABS.

Vitamin-*C*. IX. T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1933, **9**, 311—315).—Vitamin-*C* from cabbage juice (p_H 5) is not extracted from aq. solution by oxide-free Et_2O; after neutralisation with Na_2CO_3 to p_H 7·3 part is extracted by Et_2O. CH. ABS.

Vitamin-*C* in blood and urine? M. VAN EEKELEN, A. EMMERIE, B. JOSEPHY, and L. K. WOLFF (Nature, 1933, **132**, 315—316).—Experiments which indicate that the reducing factor in blood and urine is probably vitamin-*C* are described. Cerebrospinal fluid also yields a substance which reduces 2 : 6-dichlorophenol-indophenol and gives max. absorption at 2650 Å. as does ascorbic acid. L. S. T.

Vitamin-*C* in sea fish and invertebrates. B. VON EULER and H. VON EULER (Svensk Kem. Tidskr., 1933, **45**, 173—180).—Vitamin-*C* (I) was determined

by titration in organs of the following fish: *Salmo salar* (II), *Gadus callarias* (III), *G. virens*, *Raniceps raminus*, *Squalus acanthias*, and *Myxine glutinosa*. The kidneys contained 0·46—0·8 mg. of (I) per g. fresh wt., whilst livers contained < half this amount, and the muscle none. The lens of (II) contained 4·5 mg. and that of (III) 2·3 mg. per g. In 12 species of marine invertebrates the liver, ovaries, or gonads contained on the average 0·26 mg. per g. The algæ *Enteromorpha elaterata* and *Ulva lactuca* contained 0·05 mg. and 0·04 mg., respectively. No parallelism between (I) content and catalase vals. was found. R. K. C.

Ascorbic acid as the antiscorbutic factor. E. L. Hirst and S. S. Zilva (Biochem. J., 1933, **27**, 1271—1278).—Various specimens of ascorbic acid (I) show a marked disparity in antiscorbutic activity when tested on guinea-pigs. Oxidation of (I) with I gave a product only slightly less active than (I) (cf. A., 1927, 702), whilst oxidation with Cl_2 destroyed the activity. The theory that the antiscorbutic activity is a property of (I) *per se* is discussed. F. O. H.

Silver nitrate staining reaction for ascorbic acid in the adrenal, pituitary, and ovary of various species of animals. J. Gough and S. S. Zilva (Biochem. J., 1933, **27**, 1279—1286).—The adrenal cortex (I), anterior (II) and intermediate pituitary lobes, and ovary from various animals [man, ox, dog, cat, guinea-pig (III), rat], whether susceptible to scurvy or not, reduce $AgNO_3$ in the dark. The (I) of (III) on a scorbutic diet supplemented with high doses of decitrated lemon juice does not react with $AgNO_3$ despite complete protection from scurvy. The (II) of oxen when tested on (III) was twice as active as (I), indicating a content of 40—50 international units of vitamin-*C* per g. of fresh tissue. With 42 persons free from clinical scurvy, (I) only occasionally reacted with $AgNO_3$, whilst (II) did so in most cases. F. O. H.

Determination of the vitamin-*C* value of ascorbic acid. K. M. Key and B. G. E. Morgan (Biochem. J., 1933, **27**, 1030—1035).—Guinea-pig tests indicate an equivalence of 7—4 international units of vitamin-*C* per mg. ascorbic acid (I). With graded doses, a response curve is obtained with (I) which is approx. identical with that obtained with orange juice. The trustworthiness of lemon juice as a standard for vitamin-*C* appears to be doubtful; the stability of (I) indicates it to be more suitable. Guinea-pigs vary in their response to (I). F. O. H.

Disappearance of vitamin-*C* from adrenals of scorbutic guinea-pigs. A. E. Siehrs and C. O. Miller (Proc. Soc. Exp. Biol. Med., 1933, **30**, 696—698).—The staining capacity of guinea-pig adrenals with $AgNO_3$ was reduced on the second day on Sherman's scorbutic diet, and had practically disappeared on the sixth. The daily administration of 3 c.c. of orange juice from the eighteenth day restored the max. staining power in four days. Some time elapsed between the disappearance of vitamin-*C* from the adrenals and the appearance of gross scorbutic lesions. Nutr. Abs. (*b*)

In what form is chlorine retained in the organism deprived of the antiscorbutic vitamin? A. Michaux (Bull. Soc. sci. Hyg., 1932, **20**, 345—358; Chem. Zentr., 1933, i, 1314).—On a rachitogenic diet the blood- and tissue-Na, but not -K, of guinea-pigs is increased. A. A. E.

Treatment of scurvy in man with intravenous injection of ascorbic acid. P. Schultzer (Lancet, 1933, **125**, 589—590).—Daily intravenous injections of 40 mg. of ascorbic acid cured scurvy in a man receiving a diet deficient in vitamin-*C*. L. S. T.

Photosynthesis. R. D. Asana (J. Univ. Bombay, 1933, **1**, No. 5, 21—34).—A review. A. L.

Variations in the nightly production of carbon dioxide in higher plants. P. Jaccard (Planta [Z. wiss. Biol.], 1933, **19**, 713—728).—Irregular variations are recorded which are unrelated to the environmental [CO_2], temp., light intensity, or rate of assimilation during the day. A. G. P.

Plant respiration. II. Variations in respiratory quotient during germination of seeds with different food reserves. W. Stiles and W. Leach (Proc. Roy. Soc., 1933, **B**, **113**, 405—428; cf. A., 1932, 1176).—The R.Q. of germinating seeds of *Zea mais*, in which starch is the main reserve, falls from an initial val. of about 1·0 to 0·75 in 2 days, and then rises slowly to 1·0. Other starchy seeds, *Lathyrus odoratus*, *Pisum sativum*, and *Vicia faba*, behave similarly at slightly different levels. In *Fagopyrum esculentum*, however, the R.Q. rises steadily from 0·5 to 1·0. In *Lupinus luteus*, containing much hemicellulose and a little fat, the R.Q. falls after 2 days at 0·92. *Tropæolum majus*, a similar seed with more fat, has the val. 0·75 for 10—11 days. Of seeds with high fat content, *Ricinus communis* shows a fall in R.Q. from 0·85 to 0·5 in 5 days, *Helianthus annuus* an initial increase from 0·75 to 0·85 in 1 day, followed by a continuous fall, and *Cucurbita pepo* similar changes at a higher level. The results are discussed in relation to the nature of the seed reserve. A low or falling R.Q. is ascribed to the utilisation of O_2 for the conversion of fat into carbohydrate. A. C.

Swelling of seeds. III. Respiratory quotient of swelling seeds. E. G. Pringsheim [with Jedlitschka and Gorlich] (Planta [Z. wiss. Biol.], 1933, **19**, 653—712).—Changes in the R.Q. of seeds after swelling under H_2O and in atm. of varying CO_2 and O_2 content are examined and discussed. Modifications of technique are described. A. G. P.

Germination behaviour of *Magnolia grandiflora*. C. R. Evans (Bot. Gaz., 1933, **94**, 729—754).—Pretreatment of seed for germination is examined. Cells of the endosperm contain oil and protein reserves but no starch. Traces of reducing sugars and sol. proteins occur in cells near the embryo. The embryo contains oil and traces of reducing sugars and short-chain proteins, but no protein granules or starch. With the initiation of the germination process, oil decreases and sol. proteins increase in endosperm cells near the embryo. Considerable proportions of starch appear in the cotyledons. No oil disappears from the embryo prior to this stage. Fe is present in all parts of the seed and is abundant in the root tips of the seedling. Epidermal cells of the embryo steadily increase in acidity, and neighbouring cells of the

endosperm change from alkaline to acid. Oxidase is not apparent before the protrusion of the hypocotyl. Glutathione is present in seed during soaking in H_2O, initially in the endosperm, and subsequently throughout the embryo. Peroxidase and catalase occur in the dry seed and increase during germination. A. G. P.

Radial growth of the xylem and the starch reserves of *Pinus sylvestris*: preliminary survey. W. Wright (New Phytol., 1933, **32**, 77—96).—Relationships are traced between growth and the starch content (I) of various organs. In the aerial parts (I) shows a min. in winter (total absence in January) and a max. from April to July with a slight break in May. Fluctuations of (I) in roots are apparently independent. Appearance and disappearance of starch begins first in leaves and branches and is uniform throughout the length of branches and trunk. A. G. P.

Morphological and physico-chemical changes accompanying proliferation of *Bryophyllum* leaves. R. O. Freeland (Amer. J. Bot., 1933, **20**, 467—480).—During the initial formation of foliar shoots the [H·], total acidity, and osmotic pressure of the margins of the proliferating leaves increase. Acidity and [H·] decline later. There is also an accumulation of starch, an increase of reducing sugars and of oxidase, catalase, and diastase around the foliar buds, and, in the entire leaf, an increase in total sugars and sucrose, NH_2-, amide-, and NO_3-N and a decrease in total polysaccharides. A. G. P.

Role of organic acids in plant metabolism. II. T. A. Bennet-Clark (New Phytol., 1933, **32**, 128—161; cf. this vol., 758).—Current theories are reviewed. In the conversion of sugar into malic acid in *Crassulaceæ*, 1 mol. of sugar yields > 1 mol. of acid. The remaining C atoms are probably utilised for the re-formation of polysaccharide. CO_2 is produced from some intermediate product in the conversion of sugar into malic acid and the decreased acidity involved results from the reaction $R{\cdot}CO_2H \longrightarrow RH + CO_2$. A. G. P.

Nitrogen and plant nutrition. N. W. Barritt (Nature, 1933, **132**, 279—280).—A criticism (cf. *ibid.*, 49). L. S. T.

Leguminous bacteria and plants. XIII. Nitrogen economy of oats in mixed culture with peas. U. Wartiovaara (Z. Pflanz. Düng., 1933, **31**, A, 353—359).—In mixed crops on soil poor in N the protein content of oats increased with the proportion of peas in the mixture. Differences were more apparent in the early stages of growth than later (cf. Virtanen, A., 1931, 1100). A. G. P.

Metabolic unity between stock and scion. K. Silberschmidt (Planta [Z. wiss. Biol.], 1933, **19**, 729—780).—Comparison is made of N changes in homoplastic (I) and heteroplastic (II) grafts of tobacco with those in untreated plants. Accumulation of N began in the base of the scion (III) approx. 2 weeks after grafting, vals. for (II) being > for (I). The increase, especially in (II), consisted largely of protein-N. There was a corresponding reduction in the N of the apical portion of the stock (IV). A reverse translocation of N from (III) to (IV) was induced by darkening the leaves of (III) or by cutting (IV) and re-rooting in sand. A. G. P.

Carbohydrate character of the first generation of pea hybrids. C. Bourdouil (Bull. Soc. Chim. biol., 1933, **15**, 790—792).—The crossing of pure strains of peas having smooth and wrinkled seeds gives a first generation of seeds in which the content of free reducing sugar is small, and that of sol. glucosides and starch likewise corresponds with that of the parent having smooth seeds. The pollen of the smooth variety therefore causes an activation of starch synthesis in the ovule of the wrinkled, although the pollen of the wrinkled causes no change in the ovule of the smooth. A. C.

Leaf diagnosis of the potato. II. H. Lagatu and L. Maume (Ann. Agron., 1933, **3**, 1—52; cf. B., 1933, 36).—Experimental data are discussed in relation to the mechanical and mineralogical analysis of soils and their nutrient vals. The development and applications of the authors' method are indicated. A. G. P.

Salazic acid and the constituents of the lichen, *Labaria pulmonaria*. T. J. Nolan and J. Keane (Nature, 1933, **132**, 281).—Methylation of salazic acid (I) with Ag_2O and MeI gives a Me_3 derivative of (I), $C_{18}H_9O_{10}Me_3$, and a Me_5 derivative of hydrated (I), $C_{18}H_9O_{11}Me_5$. Asahina and Asano's constitutional formula for (I) (this vol., 823) is not accepted. *Sticta pulmonaria* (*L. pulmonaria*, Hoffm.) contains no gyrophoric acid, but a pentahydric alcohol, m.p. 102° (acetate, m.p. 74—75°), believed to be arabitol, is present, as well as an acid (stictaic ?), $C_{10}H_{14}O_9$ (acetate, m.p. 239°). L. S. T.

***Globularia alypum*.** J. V. Sanchez (Anal. Fís. Quím., 1933, **21**, 361—363).—The aq. Na_2CO_3 extract yielded cinnamic acid and a little (?) protocatechuic acid. No truxillic acid was found. R. K. C.

Carbohydrates of sunflower seeds. A. Goldovski and A. Bozhenko (Masloboino-Zhir. Delo, 1932, No. 7, 30—34).—58% of the carbohydrates consists of sol. mono-, di-, and tri-saccharides. The kernels do not contain starch or dextrins. Ch. Abs.

Phosphorus-containing compounds in sunflower seeds. A. Goldovski and A. Bozhenko (Masloboino-Zhir. Delo, 1932, No. 10, 21—27).—Of the phosphatides 66·26% is combined with other constituents of the protoplasm. Phytin, combined with inositol, contains 84·61% of the H_3PO_4 present. For the determination of phytin in vegetable materials containing tannins, preliminary oxidation of the latter with $KMnO_4$ is necessary. Ch. Abs.

Tannins of sunflower seeds. A. Goldovski and M. Podolskaya (Masloboino-Zhir. Delo, 1932, No. 12, 20—27).—The tannins (chlorogenic acid) are not present in the hulls. Ch. Abs.

Nucleic acid of rice embryo (oryza-nucleic acid). I. M. Kimura (Bull. Waseda Appl. Chem. Soc., 1933, **19**, 14—21).—*Oryza-nucleic acid* (N 14·42, P 6·81%) gave on hydrolysis pentose, guanine, adenine, and uracil, but not cytosine. Ch. Abs.

Search for alkaloid-free lupins. N. N. Ivanov and M. I. Smirnova (Bull. Appl. Bot., Russia, 1932,

54, 5—24).—Alkaloid-free lupins, suitable as fodder, have the same protein content as lupins rich in alkaloids. Bouchard's (KI_3) and Dragendorff's reagents are employed. CH. ABS.

Search for alkaloid-free lupins. V. S. FEDOTOV (Bull. Appl. Bot., Russia, 1932, **54**, 29—38).—*L. luteus, pilosus,* and *polyphyllus* had a variable, whilst *L. angustifolius, albus,* and *mutabilis* had a const., alkaloid content. CH. ABS.

Use of colour reaction in the search for alkaloid-free lupins. N. N. IVANOV and M. I. SMIRNOVA (Bull. Appl. Bot., Russia, 1932, **54**, 50—51).—The crushed seed is tested with Bouchard's KI_3 reagent. CH. ABS.

Chinese citrus fruit. II. Analysis of the edible portion of Fu Chu (Chinese tangerine). P. P. T. SAH and S. Y. HSIUNG (J. Chinese Chem. Soc., 1933, **1**, 96—99).—Reducing and total sugar, acid val., protein, solids, and volatile matter are determined. J. L. D.

Syringoside from the bark of *Philyrea latifolia*, L., and *P. decora*, L. A. KRAMER (Bull. Soc. Chim. biol., 1933, **15**, 764—780).—Philcoside, the glucoside isolated from *P. latifolia* and *P. decora* (this vol., 544), is identical with syringoside. A. L.

Constituents of Wu Chu Yü (*Evodia rutæcarpa*). A. L. CHEN and K. K. CHEN (J. Amer. Pharm. Assoc., 1933, **22**, 716—719).—Rutæcarpine, $C_{18}H_{13}ON_3$; evodiamine, $C_{19}H_{17}ON_3$; evodin, $C_{26}H_{30}O_8$; and *wuchuyine*, $C_{13}H_{13}O_2N$ (?), m.p. (corr.) 237·5°, $[\alpha]_D^{25}$ —68°, have been isolated from the fruit. E. H. S.

Ether-soluble substances in polished rice and their physiological action. Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 178—219).—Neither the EtOH extract (I) of polished rice nor the Et_2O-sol. portion (II) of (I) when administered to dogs and pigeons *per os* was harmful; both extracts, however, possessed strong hæmolytic power and were toxic when injected. The aq. Na_2CO_3 extract of (II) acidified and extracted with Et_2O gave a mixture of palmitic (III), oleic (IV), and linoleic (V) acids, (V) causing death when injected into rats. The unsaponifiable portion of (II) gave phytosterol and other substances having no toxicity. (III), (IV), (V), hiragonic and clupanodonic acids were all toxic when injected, particularly the two last-named, which do not occur in polished rice. A. L.

Formation of oil in Niger seed (*Guizotia abyssinica*). D. L. SAHASRABUDDHE (Indian. J. Agric. Sci., 1932, **3**, 57—88).—A discussion of theories of fat synthesis. Proteins appear in the seed 15 days after the flower opens, and oil a few days later. Between the 26th and 40th days half the total oil makes its appearance. The % of reducing sugars is greatest about the 27th day, decreases rapidly until the 40th day, and finally disappears at the 45th day when the oil content is at a max. Lower fatty acids are first synthesised and later the higher fatty acids; hexoses and pentoses rather than polysaccharides are the source of the fats. The I val. increases throughout the ripening period (89·5—126·2), whilst the Ac val. decreases (62·4—23·2). An esterase is present which shows max. activity when the oil content is rapidly increasing. P. G. M.

Liquid wax of seeds of *Simmondsia californica*. R. A. GREENE and E. O. FOSTER (Bot. Gaz., 1933, **94**, 826—828).—The consts. of the wax were similar to those of sperm oil and arctic sperm oil. The wax may consist largely of fatty acid esters of decyl alcohol. A. G. P.

Volatile oil and resin of *Cynomarathrum nuttallii*. E. K. NELSON (J. Amer. Chem. Soc., 1933, **55**, 3400—3402).—The ground root contains 6% of volatile oil (of which 95% is β-pinene) and yields to EtOH 15% of a non-volatile resin, containing a neutral *substance*, $C_{16}H_{28}O_2$, m.p. 74—76°, angelic and possibly valeric acid. R. S. C.

Sulphur and phosphorus in various parts of the wheat grain. G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1933, **197**, 285—288).—Wheat grain contains the following ‰ (dry) of S and P, respectively: bran 1·23 and 13·68, flour 1·9 and 1·83, embryo 2·31 and 12·98. The EtOH-sol. part of gluten contains 3·49 and 5·05, and the insol. part 10·02 and 3·04‰ of S and P, respectively. P is, therefore, probably contained in org. combination at least in part. R. S. C.

Silica of the wheat plant. E. BLANCHARD and J. CHAUSSIN (Compt. rend., 1933, **197**, 188—190).—Wheat contains the largest amount of SiO_2 of all cultivated plants, a large % of which is not sol. Oats and maize have also been examined. It is suggested that the SiO_2 diminishes the quantity of org. acid present in the plant. F. R. S.

Constituents of mulberry leaves. II. Reaction of ash. Y. KISHI (J. Agric. Chem. Soc. Japan, 1933, **9**, 160—164).—The ash content and alkalinity increase directly with the degree of maturation. CH. ABS.

Selective absorption of ions not confined to young rootlets. F. J. CRIDER (Science, 1933, **78**, 169).—Selective absorption is not confined to young, elongating rootlets; that of PO_4''' and NO_3' occurs in the woody parts of the roots, but in seedling and in large trees over a wider temp. range than that of root elongation. L. S. T.

Biochemistry of water containing hydrogen isotope. G. N. LEWIS (J. Amer. Chem. Soc., 1933, **55**, 3503—3504).—Tobacco seeds do not germinate in pure H^2H^2O, and growth in 50% H^2H^2O is retarded. J. G. A. G.

Role of peroxidase in the deterioration of frozen fruits and vegetables. M. A. JOSLYN and G. L. MARSH (Science, 1933, **78**, 174—175).—Changes occurring in frozen fruits and vegetables are described. Vegetable peroxidases may not be the chief cause involved in the deterioration. L. S. T.

Effect of yeast extract on the growth of plants. A. I. VIRTANEN and S. HAUSEN (Nature, 1933, **132**, 408—409).—An aq. extract of yeast markedly stimulates the development of blossoms in peas. Follicular hormone has no such effect. L. S. T.

Growth-promoting substances in plants. F. HODER (Med. Klinik, 1932, **28**, 1430—1432; Chem.

Zentr., 1933, i, 1959).—Addition of small quantities of red beet or tomato juice or especially coconut "milk" to nutrient agar markedly promotes bacterial growth thereon. The activity was unaffected after removal of vitamins-*A* and -*D*. The "eubiotic" principle is probably complex. A. A. E.

Growth hormone of plants. III. Inhibiting action on bud development. K. V. THIMANN and F. SKOOG. **IV. Mechanism of the action.** J. BONNER (Proc. Nat. Acad. Sci., 1933, **19**, 714—716, 717—719).—III. The growth hormone, when supplied to plants with the terminal bud removed, inhibits the development of lateral buds.

IV. The hormone (I) acts on the cell-wall through the protoplasm. With low. concn. of (I), respiration (II) of coleoptile sections is stimulated, but is inhibited with high concn. (I) inactivated for growth by H_2O_2 does not stimulate (II). H. G. R.

New eosin-effect on plants. F. BOAS (Ber. Deut. bot. Ges., 1933, **51**, 274—275).—Seedlings of *Lolium perenne*, from seed soaked in eosin solution (1 : 1000) for 48 hr. in darkness, showed modifications of both geotropic and phototropic responses. A. G. P.

Factors affecting the sporulation of *Phyllosticta solitaria* in artificial culture. A. J. MIX (Phytopath., 1933, **23**, 503—524).—Spore production was largely influenced by nutrient conditions and occurs most freely in media of moderate concn. The suitability of N sources for growth and sporulation was in the order, KNO_3>albumin>asparagine> peptone. Glucose, fructose, and sucrose were favourable C sources. Mannose was unfavourable to growth and sporulation, and xylose did not support growth. Fertile pycnidia were formed in media having initial p_H 4·2—5·8. A. G. P.

Pathology of tobacco blackshank. F. T. WOLF (Phytopath., 1933, **23**, 605—612).—The wilting of plants infected with *Phytophthora nicotianæ* is due to the presence of a toxin which is thermostable, non-volatile, and probably a protein. Acids other than $H_2C_2O_4$ are produced by the fungus, but these do not induce wilting. The organism secretes enzymes which enable it to utilise the middle lamella, secondary membranes, starch, sucrose, glucose, and maltose. A. G. P.

Parasitism of *Cuscuta chinensis*. T. SASAKI (Keijo J. Med., 1933, **4**, 261—269).—The high carbohydrate (I) and low chlorophyll contents of *C. chinensis* (II) indicate that (I) is obtained from its host, *Glycine soja*, Benth.; this is confirmed by the high diastase content of (II). The distribution of enzymes, Fe, etc. in (II) is correlated with its parasitic habits. F. O. H.

Micro-determination of water in biological fluids. K. KURODA (Keijo J. Med., 1933, 4, 270—290).—By the use of a capillary container, the H_2O content of 10—30 mg. of fluid can be determined with an accuracy of 0·01—0·03%. Desiccation is by heating at 90° for 3 hr. F. O. H.

Determination of the hydrogen-ion concentration of biological liquids. G. GOLLNOW (Med. Welt, 1932, 6, 1544; Chem. Zentr., 1932, ii, 3923). L. S. T.

Micro-vessel for glass electrode determinations of hydrogen-ion activity of biological fluids. I. R. TAYLOR and J. H. BIRNIE (Science, 1933, **78**, 173—174). L. S. T.

Lipins of mammalian liver. IV. Extraction apparatus for biochemical purposes. E. FRANKEL and A. POLLANZ (Z. physiol. Chem., 1933, **218**, 153—156).—A continuous extraction apparatus of Ni (percolator type) dealing with 12—15 litres of powdered solid is described. J. H. B.

Determination of cholesterol. B. EWERT (Biochem. Z., 1933, **263**, 149—165).—The material (*e.g.*, suprarenal glands) containing 2—20 mg. of cholesterol (free and bound) is ground with sand, extracted with EtOH and Et_2O, and dissolved in $CHCl_3$, which is then removed. Dissolution in EtOH and pptn. with digitonin follow. The error is negligible, but a correction must be applied. W. McC.

Determination of histidine in biological fluids. R. KAPELLER-ADLER (Biochem. Z., 1933, **264**, 131—141; cf. Hunter, A., 1922, ii, 885).—Histidine (I) reacts with Br in dil. AcOH giving a substance which acquires a deep bluish-violet colour when treated with aq. NH_3 and $(NH_4)_2CO_3$ and warmed. A colorimetric method (II) for the determination of (I) based on this sp. reaction (sensitivity 1 : 50,000) is described. The reaction depends on the presence of an intact alanyl group in the side-chain. When (II) is applied to protein hydrolysates interfering substances are removed by oxidation with 0·1*N*-$KMnO_4$ and the (I) is pptd. with Hopkins' reagent. Horse hæmoglobin, casemogen, and fibrin contain, respectively, 7·32—7·45, 4·09—4·14, and 3·33—3·73% of (I). Pregnancy urine contains 6—74 mg. per 100 c.c. of (I), which also occurs, in very small amount, in male urine, but rarely in normal or pathological female urine. W. McC.

Determination of creatinephosphoric acid. O. RIESSER and A. HANSEN (Z. physiol. Chem., 1933, **219**, 57—61).—The method of Fiske and Subbarow gives, in frog muscle, vals. slightly, in rat muscle 50%, < the Lohmann and Jendrassik method, which is more trustworthy. J. H. B.

Ureometer. D. GANASSINI (Arch. Ist. Biochem. Ital., 1933, **5**, 111—118).—The ureometer gives exact micro-determinations of the urea and NH_3 of urine and blood by the NaOBr method. Its use avoids two common causes of error, viz., the error from variable external temp., and the gas error from slow decomp. of NaOBr. R. N. C.

Micro-determination of iodine in blood and other fluid. J. EYCKERMAN (Z. Kinderheilk., 1933, **54**, 435—439).—The method is a modification of Pfeiffer's acid-H_2O_2 method for ashing. NUTR. ABS. (*b*)

Micro-determination of iodine in thyroid gland and other organic compounds. H. J. VAN GIFFEN (Pharm. Weekblad, 1933, **70**, 910—914).—Satisfactory results are obtained by fusing 0·05 g. of thyroid gland with 0·8 g. of nitrate–carbonate fusion mixture, dissolving in H_2O, oxidising the I′ to IO_3' with HOCl, and titrating the liberated I after treatment with KI with 0·0005*N*-$Na_2S_2O_3$. S. C.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1933.

General, Physical, and Inorganic Chemistry.

Intensities of the spectra emitted by high-frequency discharges in helium. J. E. KEYSTON (Phil. Mag., 1933, [vii], **16**, 625—639; cf. A., 1932, 1071).—Measurements on the line, band, and continuous spectra of He have been verified and extended spectrophotometrically. H. J. E.

Excitation probabilities of helium, argon, and neon at zero scattering angle. J. E. TAYLOR and R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1933, **2**, 417—419).—The probability curve for A is linear, but rises more steeply than the He curve; the smooth curve is in accord with the singlet transitions $3'S-4'P$ and $3'S-4'P_0$. In Ne the transitions likely to be involved are $2'S-3'P_1$ and $2'S-3^3P_2$, the triplet transition giving rise to a hump in the curve at about 150 volts. Experimental data are compared with vals. computed from the theory of Massey and Mohr (this vol., 761). W. R. A.

Excited electronic states of Li_2. W. F. FURRY (Physical Rev., 1932, [ii], **39**, 1015—1017; cf. A., 1932, 319). L. S. T.

Zeeman effect of the third positive carbon bands. R. F. SCHMID (Physical Rev., 1932, [ii], **39**, 538—539). L. S. T.

Absorption lines of N V in stellar spectra. C. H. PAYNE (Astrophys. J., 1933, **77**, 299).—These lines have been observed in several Wolf-Rayet stars. L. S. T.

Modification of the intensity in the band spectrum of nitrogen. J. OKUBO and H. HAMADA (Astrophys. J., 1933, **77**, 130—140).—Modifications by changes of pressure, temp., and shape of the discharge tube are discussed. L. S. T.

Equivalent widths in the *A* and *B* bands of oxygen. W. H. J. CHILDS (Astrophys. J., 1933, **77**, 212—220). L. S. T.

Series of alkaline atoms in an electric field. E. AMALDI and E. SEGRE (Nature, 1933, **132**, 444—445).—Details of the absorption spectra (I) of Na and K in an electric field are recorded. (I) polarised parallel and perpendicular to the field have been photographed simultaneously and separated by means of a spar crystal. L. S. T.

Width of the *D* lines in sodium vapour. S. A. KORFF (Physical Rev., 1932, [ii], **39**, 549—560). L. S. T.

Hyperfine structure and nuclear moment of krypton. H. KOPFERMANN and N. WIETH-KNUDSEN (Z. Physik, 1933, **85**, 353—359).—The mechanical moment of Kr^{83} is 7/2. A. B. D. C.

Ratio of oscillator intensities for resonance lines of silver. A. FILIPPOV and I. ISLAMOV (Z. Physik, 1933, **85**, 409—410).—The ratio of f for the doublet components is 2·03. A. B. D. C.

Band spectrum of ionised cadmium hydride. E. SVENSSON and F. TYREN (Z. Physik, 1933, **85**, 257—263).—Dissociation energy of the normal state of Cd^1H is 2·0 volts. A. B. D. C.

Heat of dissociation of the cadmium molecule from thermo-optical observations. A. JABŁONSKI (Z. Physik, 1933, **85**, 268).—A disclaimer of a reference given by Kuhn and Arrhenius (this vol., 759). A. B. D. C.

Hyperfine structure in the spark spectrum of cadmium. E. G. JONES (Proc. Physical Soc., 1933, **45**, 625—626).—The Cd II spectrum has been investigated in the region 4200—8500 Å., three new lines being observed and classified. Of the 13 lines examined only that at 8067 Å. ($6^2S_{1/2}-6^2P_{3/2}$) shows any fine structure. It is calc. that the $g(I)$ factor of the odd isotopes is −1·25 proton magnetons. J. W. S.

Nuclear spin and magnetic moment of tin. S. TOLANSKY (Nature, 1933, **132**, 318).—Structures have been obtained in several lines of the spectrum of Sn II. The nuclear spin is ½. The $g(I)$ factor, calc. by Goudsmit's formula, is −1·81. L. S. T.

Fluorescence of diatomic molecules of antimony. J. GENARD (Physical Rev., 1933, [ii], **44**, 468—469).—Data for the four resonance series of Sb excited by the λλ 2967, 3022, 3126, and 3132 Hg arc lines are given, and lead to the val. 2·21 Å. for the equilibrium interat. separation, and 489×10^{-40} g.-cm.^{2} for the moment of inertia. N. M. B.

Extinction of fluorescence of tellurium vapour by magnetic fields. R. SMOLUCHOWSKI (Z. Physik, 1933, **85**, 191—200; cf. this vol., 759).—The extinction observed does not agree with a diminution of the no. of excited mols., and is explained with the Condon–Lenz theory of intensities. A. B. D. C.

Enhancement of the iodine absorption spectrum by the admixture of oxygen. F. W. LOOMIS and H. Q. FULLER (Physical Rev., 1932, [ii], **39**, 180).—O_2 markedly enhances many of the I absorption bands, and in certain circumstances the I changes colour. L. S. T.

Spectra of halogen molecules. I. Iodine. W. E. CURTIS and S. F. EVANS (Proc. Roy. Soc., 1933, A, 141, 603—625).—The chief problem in the absorption spectrum of I_2 is the nature of the excited states connected with the various systems. Consideration of the potential energy curve for the upper level of Sponer and Watson's ultra-violet system leads to the conclusion that the dissociation products are not excited atoms, but probably ions. Some possible regularities are proposed in the far ultra-violet absorption bands, and new data derived from microphotometer records of the diffuse emission bands are presented. The fluorescence system of diffuse bands due to ultra-violet excitation is considered, and Kuhn's conclusions (A., 1930, 1089) are modified. It is shown that a secondary transition must intervene between those of excitation and fluorescence. L. L. B.

Nuclear moment of xenon. H. KOPFERMANN (Naturwiss., 1933, 21, 704).—The hyperfine structure of a series of Ne lines shows that the mechanical moment of Xe^{129} is 1/2, and of Xe^{131} 3/2. The even isotopes do not give appreciable splitting. The ratio of the magnetic moment (μ) of Xe^{129} to that of Xe^{131} is 1·1; μ_{129} is negative, and μ_{131} positive. A. J. M.

Pressure effects in the spectra Xe I and Xe II. J. F. HEARD (Proc. Physical Soc., 1933, 45, 734—740).—At high pressures the lines of the Xe I spectrum show broadenings which correspond qualitatively with their respective Stark effects, indicating the existence of strong interionic electric fields within the discharge. Many pressure displacements are also found in the Xe II spectrum, and are attributed to interionic fields. J. W. S.

Displacement and asymmetric widening of absorption lines by foreign gases. C. FUCHTBAUER and F. GOSSLER (Naturwiss., 1933, 21, 675—676).—The changes occurring in the Cs absorption lines (4555 and 3786 Å.) by admixture with pure He, Ne, A, and N_2 at 4—5·5 atm., and at 125° (for 4555 Å.) and 180° (for 3786 Å.) were investigated. A. J. M.

Under-water spark spectrum of cerium. J. S. BADAMI (Indian J. Physics, 1933, 17, 19—24).—Wave-lengths and intensities of 128 lines in the region λ 3900—4580, identified with those of the arc spectrum, are tabulated. N. M. B.

Arc spectrum of cerium. P. KARLSON (Z. Physik, 1933, 85, 482—503).—Some 3000 lines and 105 energy levels are tabulated. A. B. D. C.

Temperature classification of the spectrum of neodymium. A. S. KING (Astrophys. J., 1933, 78, 9—45).—2863 Nd lines in the range 2963—7005 Å. are classified on the basis of their relative intensities at three temp. stages of the electric furnace. A comparison of lines apparently common to both Nd and Sm, which might belong to element 61, indicated only chance coincidences of true Nd and Sm lines. L. S. T.

Preliminary list of terms for the arc spectrum of tantalum. C. C. KIESS and H. K. KIESS (Bur. Stand. J. Res., 1933, 11, 277—278).—Terms for Ta I are tabulated. H. J. E.

Radiation of metal surfaces bombarded by positive alkali ions. H. MAYER (Phil. Mag., 1933, [vii], 16, 594—606).—Pt, Cu, and Al bombarded with alkali ions gave a surface luminosity, showing line spectra of the alkali atoms. H. J. E.

Weak lines in the *L*-spectra of 79 Au and 74 W. H. CLAESSON (Z. Physik, 1933, 85, 231—239). A. B. D. C.

Effect of heat on mercury bands. J. G. WINANS (Physical Rev., 1932, [ii], 39, 745—746).—Heating destroys the 4850 band and reduces the intensities of the bands at 2345, 2476, and 2540 Å. and the continuous spectrum between 2536 and 3300 Å. Moderate heating enhances, whilst strong heating destroys, the 3300 band. Only four arc lines are weakened. The weakening of the bands must be due to the destruction of Hg mols. by heat. L. S. T.

Inversion of circular polarisation by thallium fluorescence. W. HANLE (Z. Physik, 1933, 85, 300—303).—Excitation of the λ 5350 Tl line by circularly polarised λ 3776 Tl light gives fluorescence radiation circularly polarised, but in the opposite direction. A. B. D. C.

Absorption spectrum of diatomic bismuth. G. M. ALMY and F. M. SPARKS (Physical Rev., 1933, [ii], 44, 365—375).—Data and analyses for four systems of bands are given: the visible system, 4500—7900 Å., consisting of > 300 bands; the ultra-violet, 2600—2900 Å., system of forty bands; the far ultra-violet system, below 2250 Å., and the violet system, appearing only above 1000°, consisting of fifteen sharp band heads, nine continuous bands, and a series of closely-spaced diffuse bands. There is also an extended continuum around 3100 Å. Potential energy curves for the mol. states are given. The estimated heat of dissociation of the lowest state is 1·71 volts. N. M. B.

Classification of certain lines of radium. W. ALBERTSON (Physical Rev., 1932, [ii], 39, 385—386). L. S. T.

Remarkable optical properties of the alkali metals. R. W. WOOD (Physical Rev., 1933, [ii], 44, 353—360).—Thin films of alkali metals opaque to visible light are highly transparent in the ultra-violet, the commencement of transparency moving towards shorter wave-lengths with decreasing at. no.: Cs 4400; Rb 3600; K 3150; Na 2100; Li 2050 Å. Transparency continues at least as far as 1860 Å., where plane polarisation by reflexion is observed. Reflecting powers of these metals for different wave-lengths have been measured. The refractive index of a K film varies from 0·90 at 2147 to 0·50 at 3100 Å. Total reflexion takes place, the crit. angle not being sharply defined. N. M. B.

Influence of a magnetic field on a glow discharge. T. TAKAMINE, T. SUGA, and A. YANAGIHARA (Nature, 1933, 132, 351—352).—With a He tube, a bright pink-coloured ring (II) suddenly appears around the anode spot (I) when a magnetic field is applied (cf. this vol., 547). (I) gives mainly the at. line spectrum of He, and (II) is rich in the mol. band spectrum. L. S. T.

Hydrocarbon bands in the solar spectrum. R. S. RICHARDSON (Astrophys. J., 1933, **77**, 195—211). L. S. T.

Hyperfine structure in intermediate coupling. G. BREIT and L. A. WILLS (Physical Rev., 1933, [ii], **44**, 470—490).—Mathematical. N. M. B.

Absolute value of transition probabilities in band spectra. R. LADENBURG, S. LEVY, and G. WOLFSOHN (Physical Rev., 1932, [ii], **39**, 180). L. S. T.

Optical properties of the alkali metals. R. DE L. KRONIG (Nature, 1933, **132**, 601).—A discussion. Recent experimental results (this vol., 547, 1096) can be explained by the author's quantum theory of metallic dispersion (A., 1931, 1209). L. S. T.

Electromagnetic fields due to variable electric charges and the intensities of spectrum lines according to the quantum theory. V. FOCK (Proc. Roy. Soc., 1933, **A**, **141**, 550—553).—Polemical against Schott (this vol., 206). The usual methods of calculating the intensities of spectral lines are shown to be correct. L. L. B.

Fine structure in the *K* *X*-ray absorption spectrum of bromine. S. T. STEPHENSON (Physical Rev., 1933, [ii], **44**, 349—352).—An extended Kronig type fine structure, more pronounced for partly polarised than for unpolarised *X*-rays, was found. N. M. B.

Extreme ultra-violet and the very soft *X*-ray region. M. SIEGBAHN (Proc. Physical Soc., 1933, **45**, 689—698).—Using plane and concave ruled gratings at grazing incidence, the Hg arc and Al and Cu spark spectra have been photographed down to 50 Å. The C $K\alpha^{II}$ line has also been investigated and shown to have an extended structure, whilst a no. of new lines have been found in the *X*-ray series. Preliminary experiments on absorption spectra in the *X*-ray region are also reported. J. W. S.

Soft *X*-ray critical potentials of beryllium. R. J. CHRISTENSEN (Physical Rev., 1932, [ii], **39**, 549).—Soft *X*-ray crit. potentials up to 250 volts are recorded for fresh Be surfaces. L. S. T.

Peripheral *X*-ray levels of the heavy elements. J. A. ELDRIDGE (Physical Rev., 1932, [ii], **39**, 177). L. S. T.

***N*- and *O*-series [of tungsten] and *N*-absorption edge of *X*-spectra.** V. DOLEJSEK (Nature, 1933, **132**, 443—444). L. S. T.

Ionisation of light gases by *X*-rays. I. Technique. II. Ionisation of hydrogen by recoil electrons. W. R. HARPER (Proc. Roy. Soc., 1933, **A**, **141**, 669—686, 686—696).—I. A technique is described for determining the ratio of the ionisation in a light gas (H_2 or He) to that in air when ionised by the same *X*-ray beam, homogeneous rays of medium wave-length and soft heterogeneous rays being available for the measurement. The method measures (*a*) the ionisation due to the secondary electrons ejected by the primary beam from the gas, and (*b*) that due to reabsorption by the gas of the fluorescence radiation excited by the primary beam in the gas.

II. The ionisation in H_2 produced by recoil electrons liberated by homogeneous *X*-rays is determined by means of the above technique. The experimental val. agrees with that calc. using Dirac's theory of recoil scattering as a basis. L. L. B.

Ionisation of mercury vapour by positive ions of mercury and potassium. R. M. CHAUDHRI (Proc. Roy. Soc., 1933, **A**, **141**, 386—397).—A method, free from the defects existing in previous methods, is described for the investigation of the ionisation of Hg vapour by Hg^+ and K^+ ions of moderate energies. The Hg^+ ions ionise with greater efficiency than K^+ ions of the same energy. L. L. B.

Evidence on the ionisation potentials of O_2. E. W. PIKE (Physical Rev., 1932, [ii], **39**, 534—535).—The transformation of an oxide surface by means of an intermittent discharge in one of the rare gases may afford evidence in support of Mulliken's val. of 11·7 volts for the ionisation potential of O_2. L. S. T.

Visual observation of interference of slow cathode rays. W. EHRENBERG (Naturwiss., 1933, **21**, 673—674). A. J. M.

Polarisation of electrons by reflexion. T. FÖRSTER (Z. Physik, 1933, **85**, 514—529).—Polarisation cannot be obtained by means of a plane potential barrier. A. B. D. C.

Modified field equations with a finite radius of the electron. M. BORN (Nature, 1933, **132**, 282).—Theoretical. L. S. T.

Nomenclature of the electron. E. A. WILDMAN (Science, 1933, **78**, 191). L. S. T.

Scattering of electrons by metal vapours. I. Cadmium. E. C. CHILDS and H. S. W. MASSEY (Proc. Roy. Soc., 1933, **A**, **141**, 473—483).—The angular distributions of slow electrons scattered from Cd vapour have been examined over the angular range 25—130°. The scattering curves exhibit max. and min. closely resembling those appearing in corresponding curves for Hg vapour. L. L. B.

Anomalous reflexion of high-speed electrons at a single-crystal face. S. KIKUCHI and S. NAKAGAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 256—265).—Results obtained for the reflexion of 100—40-kv. electrons at a ZnS crystal surface are discussed. J. W. S.

Electron diffraction and structure of metallic films. J. A. PRINS (Z. Krist., 1933, **86**, 301—303; cf. A., 1932, 893).—Electron diffraction patterns obtained with fast electrons (30—60 kv.) of films ($< 0{\cdot}1$ μ) of metal supported on collodion show that the cubic metals (*e.g.*, Au, Ag, Al) give perfect powder diagrams indicating completely irregular arrangement of the crystallites. The hexagonal metals (*e.g.*, Sb, Cd, Zn, Bi) give with perpendicular incidence imperfect diagrams, and with oblique incidence fibre diagrams, indicating a tendency of the crystallites towards orientation, most marked in Bi, least in Sb (cf. A., 1930, 1354; this vol., 657). Where there has been allotropic or chemical change subsequent to first deposition the pattern shows traces of that of the first deposit. C. A. S.

Study of crystalline orientation by electron diffraction. J. J. TRILLAT (Trans. Faraday Soc., 1933, 29, 995—1002).—A review of published work. E. S. H.

Emission of electrons from tungsten and molybdenum under the action of soft *X*-rays from copper. J. BELL (Proc. Roy. Soc., 1933, A, 141, 641—651).—The photo-electric emission increases regularly with increase of *X*-ray exciting voltage throughout the range 1—20 kv. Heating may cause either an increase or a decrease in the emission, depending on the previous treatment of the metal, but relative vals. for Mo and W are only slightly affected by heat treatment. The emission from Mo is about 70% of that from W. L. L. B.

Electrostatic deflexion of positive electrons. J. THIBAUD (Nature, 1933, 132, 480—481).—The positive electron has been deflected in an electrostatic field; its sp. charge is of the same order of magnitude as that of the negative electron. L. S. T.

Energy losses of slow electrons in nitrogen. G. W. BRINDLEY (Proc. Leeds Phil. Soc., 1933, 2, 420—426).—By analysing the beam which results from the passage of electrons through N_2 using Whiddington's magnetic spectrum method the energy losses of the electrons are found to occur at 8·6, 12·2-, 12·9, and 14·9 volts. These vals. agree with those of singlet levels calc. from spectroscopic data, but do not agree with Rudberg's vals. (A., 1931, 12) for N_2. W. R. A.

Atomic particles of small range from lithium and boron. F. KIRCHNER (Naturwiss., 1933, 21, 676).—By bombardment with H canal rays particles were obtained from Li with a range of 1—1·5 cm. A considerably weaker group of range 2 cm. was also found, identical with those noted by Cockcroft and Walton at higher potentials. With B, particles with a range of 6 mm. were produced. The proportion of particles with ranges $<$ 2 cm. is, however, much $<$ with Li. A. J. M.

Emission of metallic ions from oxide surfaces. I. Identification of the ions by mobility measurements. L. BRATA. **II. Mechanism of the emission.** C. F. POWELL and L. BRATA (Proc. Roy. Soc., 1933, A, 141, 454—462, 463—472).—I. A method of producing sources of positive ions of Tl, In, and Ga is described. The ions are identified by determining their mobilities in N_2, this giving a measure of their mass. The mobilities of Tl and In ions have also been determined in He, Ne, and A.

II. A method by means of which a known no. of Tl, Ga, or In atoms can be deposited on an Fe oxide surface is described. On heating the oxide a large proportion of the deposited atoms is re-evaporated as ions. An explanation of the characteristics of the positive ion emission from Kunsman sources and of their catalytic action in the synthesis of NH_3 is thus suggested. L. L. B.

Difference in size of ions of zirconium and hafnium. A. HOFFMANN (Naturwiss., 1933, 21, 676).—The lattice consts. (*a*) of $SrZrO_3$ and $SrHfO_3$ are 4·089±0·003 Å., and 4·069±0·003 Å., respectively. The radius of Hf^{++++} is 0·01 Å. $<$ that of Zr^{++++}. A. J. M.

High-speed protons. M. A. TUVE, L. R. HAFSTAD, and O. DAHL (Physical Rev., 1932, [ii], 39, 384—385).—The tracks produced in a Wilson cloud chamber by high-speed protons from a high-voltage tube used with a Tesla coil have been photographed, and preliminary measurements of the range in air of 1000-kv. protons have been made. The results indicate that the law governing the range of protons approximates to the v^3 law which holds for α-particle ranges. L. S. T.

Evaporation of atoms, ions, and electrons from cæsium films on tungsten. J. B. TAYLOR and I. LANGMUIR (Physical Rev., 1933, [ii], 44, 423—458).—Methods of measuring the no. of Cs atoms adsorbed on W, and θ (the fraction of the W surface covered with Cs), are described, giving data for the rates of atom, ion, and electron emission as functions of θ and *T* (the filament temp.). A limiting true monat. layer is found; theory and evidence for a second and polyat. layers are given. The heat of evaporation for Cs from W is 2·83 volts (65,140 g.-cal.). The procedure for obtaining electron and ion emission for zero field, and the large changes in the effect of external field with θ, are described. The calc. contact potential agrees with that calc. from neutral atom evaporation. The condensation coeff. for atoms striking a W filament is unity for θ=0—1. The effect of this and the observed surface migration or diffusion on the mechanism of evaporation and condensation in dil. and conc. films is discussed. A surface phase postulate is developed by which all the properties of the adsorbed film are uniquely determined by θ and *T*. N. M. B.

Nature of gas ions. O. LUHR (Physical Rev., 1933, [ii], 44, 459—462; cf. A., 1932, 4).—The mass of gas ions formed in a glow discharge and aged up to 10^5 impacts was determined by a Dempster type mass-spectrograph. In H_2 the primary ion H_2^- changes within a few thousand collisions to H_3^-, with traces of H^+. The N_2 primary ions N^+ and N_2^+ attach to neutral mols. in about 10^5 impacts to form N_3^+ and N_4^+. In pure O_2 the ions are O_2^+ with traces of O^+. Air ions include all possible N_2 and O_2 ions, the aged air ions consisting mainly of N_3^+, N_4^+, and O_2^+, with oxides of N. Charges are transferred from O_2^+ to NO, NO_2, and N_2O. H_2O vapour readily acquires a charge by transfer. No heavier clusters than N_4^+ and no negative ions were observed. N. M. B.

Emission of positive ions from metals. H. B. WAHLIN (Physical Rev., 1932, [ii], 39, 183).—W wire containing UO_2 emits U^+, W^+, and an ion of mass 254±2, probably UO^+, at approx. 1800°. Ions of Ag and Cu are emitted at temp. near their m.p. L. S. T.

Intensity measurements of molecular rays. L. ESTERMANN and O. STERN (Z. Physik, 1933, 85, 135—143).—Intensity measurements, much more sensitive than those hitherto obtained, were made by observing the increase in electron current due to disturbance of the space charge around a glowing wire by the presence of mol. rays. A. B. D. C.

Test of the classical "momentum transfer" theory of accommodation coefficients of ions at

cathodes. K. T. COMPTON and E. S. LAMAR (Physical Rev., 1933, [ii], **44**, 338—344; cf. *ibid.*, **43**, 169).—The transfer of momentum for A ions striking Mo and Al was measured by the deflexion of a delicate pendulum bob consisting of the metal cathode under investigation. Results support the prediction that the accommodation coeff. should be < 1 only if the mass of the metal atom composing the cathode is $>$ that of the ion (cf. this vol., 109). N. M. B.

Method for determining the thermionic work functions of metals, and its application to nickel. G. W. FOX and R. M. BOWIE (Physical Rev., 1933, [ii], **44**, 345—348).—Experimental. Vals. for Ni are: Φ 5·03±0·05 volts; A 1·38×10³ amp./cm.² deg.² N. M. B.

Collision cross-section of argon atoms for 300- to 2500-volt electrons. R. B. BRODE (Physical Rev., 1932, [ii], **39**, 547). L. S. T.

Molecular scattering in gases. I. Method of crossed molecular beams. R. G. J. FRASER and L. F. BROADWAY. **II. Collision of sodium and potassium atoms with mercury.** L. F. BROADWAY (Proc. Roy. Soc., 1933, **A**, **141**, 626—633, 634—641).—I. The angular distribution of the scattering of mol. beams of Na and K in a stream of *trans*-$C_2H_2I_2$ vapour over an angular range of 2—10° has been determined, using the method of crossed mol. beams.

II. The decay consts. of beams of Na and K in Hg vapour have been measured. The experimental decay curves can be extrapolated to zero angle, if use is made of the collision theory of Massey and Mohr, and thus decay consts. (or mean free paths) may be determined, independent of the geometry of the apparatus. L. L. B.

At. wt. of erbium. Analysis of erbium trichloride. O. HÖNIGSCHMID and W. KAPFENBERGER (Z. anorg. Chem., 1933, **214**, 97—103).—Er_2O_3, examined for purity by its X-ray spectrum, was converted into anhyd. $ErCl_3$. From the ratios $ErCl_3$: 3Ag and $ErCl_3$: 3AgCl the at. wt. 165·204 was found. The previous accepted val. was 167·64. H. J. E.

At. wt. of uranium lead. O. HÖNIGSCHMID, R. SACHTLEBEN, and H. BAUDREXLER (Z. anorg. Chem., 1933, **214**, 104—110).—Nephelometric determinations of the ratio $PbCl_2$: 2Ag : 2AgCl for Pb from a U ore, curit, and Katanga pitchblende, gave vals. of 206·035, 206·032, and 206·022, respectively. These vals. are $>$ those of Baxter and Alter (this vol., 659). H. J. E.

At. wt. of lead from Katanga pitchblende. A. VON GROSSE (J. Amer. Chem. Soc., 1933, **55**, 3893; cf. Baxter and Alter, this vol., 659, 882).—The difference between the at. wts. of Pb from the yellow and the black portions of Katanga pitchblende is due to the greater difficulty with which Pb, as compared with U, is leached from pitchblende. Therefore, the data support the author's theory of the origin of the Ac series. J. G. A. G.

Isotopic constitution of zinc. K. T. BAINBRIDGE (Physical Rev., 1932, [ii], **39**, 847—848).—The mass nos. of the isotopes of Zn, determined by a new method, are 64, 66, 68, 67, and 70 in order of relative abundance. No evidence has been obtained for the existence of Zn^{65} or Zn^{69} (A., 1928, 1069; 1931, 280), and this new analysis indicates that the ions of mass nos. 65 and 69 measured by Aston are hydrides of Zn^{64} and Zn^{68}. The calc. val. for the at. wt. of Zn is 65·32(7)±0·02 on the chemical scale after deducting 2·2 parts in 10^4 to transfer from the physical mass scale. L. S. T.

[Isotopic] constitution of tellurium. K. T. BAINBRIDGE (Physical Rev., 1932, [ii], **39**, 1021).—Aston's analysis (A., 1931, 1208) has been confirmed and extended by the method previously described (preceding abstract). Additional isotopes 124, 123, and 122 with faint indications of 127 have been found. The relative abundances are 130 (33·1), 128 (32·8), 127 (?), 126 (19·0), 125 (4·5), 123 (1·6), 122 (2·9); the "isotopic moment" is 1·74 and the mean mass no. 127·67. Correcting for a packing fraction of —5·0 and changing to the chemical scale gives an at. wt. 127·58±0·15 (cf. Aston's val. 128·03). Te^{124} forms an isobaric triplet with the heaviest isotope of Sn and the lightest of Xe; the remaining isotopes of Te form isobaric pairs. L. S. T.

Relative abundance of the isotopes of lead in uranium-bearing minerals. J. L. ROSE and L. P. GRANATH (Physical Rev., 1932, [ii], **39**, 1017).—The ratio of the contents of the 207 to the 208 isotopes is greater in U-bearing minerals (Belgian Congo) than in ordinary Pb. The association of the Ac-decay product with that of the U series may be universal. Relative abundance of the isotopes can easily be determined by observations of hyperfine structure. L. S. T.

Experiments on isotopes of some of the noble gases and hydrogen by means of J. J. Thomson's mass spectrograph. P. ZEEMAN and J. DE GIER (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 609—611).—Using a new apparatus, some evidence of possible hydrides was found for He, Ne, and A; a H isotope mixture gave evidence of the $(H^1H^2)^+$ and $(H^1H_2^2)^+$ ions. N. M. B.

Nuclear moment of tin. H. SCHÜLER and H. WESTMEYER (Naturwiss., 1933, **21**, 660).—Sn^{117} and Sn^{119} have nuclear moment $I=-0·5$. The at. nuclei can be arranged in two groups according as they have even (a) or odd (b) at. wt. Only those in (b) have magnetic moment. Group (b) can be further subdivided into those with even (b_1), and those with odd (b_2) nuclear charge no. Atoms in (b_1) have nuclear moment either positive or negative, whilst those in (b_2) have positive moment only. In (a), the sum of protons and neutrons is even, whilst in (b) it is odd, so that an unpaired neutron or proton is necessary for the development of magnetic moment. In (b_1) there is an unpaired neutron. A. J. M.

Radiation emitted on disintegration of lithium. A. ECKARDT, R. GEBAUER, and H. R. VON TRAUBENBERG (Naturwiss., 1933, **21**, 694).—The chief component is a soft ray which is reduced to half by passage through 0·3 mm. Pb. The soft components differ slightly in energy from α-rays. When the radiation is passed into several cm. of Pb, an increase in

the no. of particles in the counter tube is observed, perhaps due to neutrons. A. J. M.

β-Disintegration. A. BRAMLEY (Physical Rev., 1932, [ii], **39**, 188).—An integral for the probability of a β-particle emission from the nucleus is derived. The reciprocal of the mean life should vary as the 4·5 power of the energy of the excited α-particle. L. S. T.

Energy relations in the β-ray type of radioactive disintegration. C. D. ELLIS and N. F. MOTT (Proc. Roy. Soc., 1933, **A**, **141**, 502—511).—Experimental evidence is given in support of the hypothesis that the upper limit of the continuous β-ray spectrum corresponds with the difference of binding energies of the initial and final nuclei. L. L. B.

Photo-electric absorption of γ-rays by heavy elements. J. MCDOUGALL and H. R. HULME (Nature, 1933, **132**, 352—353). L. S. T.

Scattering of γ-rays in air and water. W. J. REES and L. H. CLARK (Phil. Mag., 1933, [vii], **16**, 691—703).—The wave-length shift on scattering exceeds the max. predicted by Compton's theory for a single encounter, suggesting that much of the radiation undergoes > one scattering process. H. J. E.

Nuclear excitation by hard γ-rays. T. HEITING (Naturwiss., 1933, **21**, 674).—Al, Fe, Cu, and Pb gave nuclear γ-radiation when excited by Th-*C''* γ-rays, of wave-length 4·7 X. The intensity of the nuclear γ-radiation was proportional to the square of at. no. Secondary radiation without change of wave-length was not observed. A. J. M.

Protons produced in the artificial disintegration of the nitrogen nucleus. E. C. POLLARD (Proc. Roy. Soc., 1933, **A**, **141**, 375—385).—Experiment indicates that entry of the α-particle into the N_2 nucleus is in general over the top of the potential barrier, the height of which is fixed as $4{\cdot}1$—$4{\cdot}4\times10^6$ electron volts. Further study of the absorption curve of the protons confirms the work of Steudel (A., 1932, 980). L. L. B.

Transmutation of lithium by protons and by ions of the heavy isotope of hydrogen. M. L. E. OLIPHANT, B. B. KINSEY, and (LORD) RUTHERFORD (Proc. Roy. Soc., 1933, **A**, **141**, 722—733).—The absorption curve for the disintegration particles produced from Li by protons consists of three parts: a long range of $8{\cdot}4\pm0{\cdot}2$ cm. and two short ranges of $1{\cdot}15\pm0{\cdot}2$ and $0{\cdot}65\pm0{\cdot}2$ cm., respectively. The protons ejected from Li by ions of the heavy isotope of H_2 fall into two groups: one of $13{\cdot}0\pm0{\cdot}2$ cm., corresponding with an energy of $11{\cdot}5\times10^6$ ev., and a shorter-range group which is complex and consists of particles with energies from 1·7 to $8{\cdot}3\times10^6$ ev. The rate of increase in the no. of particles with increase of bombarding energy is much > for protons. The particles are probably He nuclei, the 13·0-cm. group arising from the reaction $_3Li^6+{}_1H^2\longrightarrow{}_0He^4+{}_2He^1$, whilst the complex group is a result of the 3-body nuclear reaction $_3Li^7+{}_1H^2\longrightarrow2{}_2He^4+{}_0n^1$. L. L. B.

Photographic investigation of the transmutation of lithium and boron by protons and of lithium by ions of the heavy isotope of hydrogen. P. I. DEE and E. T. S. WALTON (Proc. Roy. Soc., 1933, **A**, **141**, 733—742).—Using an expansion chamber and double camera, the tracks emitted in the transmutations of Li and B by protons and of Li by ions of the heavy isotope of H_2 have been photographed. The apparatus used for the production of the high voltage and its application to the tubes used for accelerating the bombarding particles was that described by Cockcroft and Walton (A., 1932, 789), and potentials up to 400 kv. were used. The modes of disintegration $_3Li^7+{}_1H^1\longrightarrow{}_2He^4+{}_2He^4$ and $_3Li^6+{}_2H^2\longrightarrow{}_2He^4+{}_2He^4$ have been confirmed (cf. preceding abstract). L. L. B.

Collisions of neutrons with protons. F. N. D. KURIE (Physical Rev., 1933, [ii], **44**, 463—467).—Neutrons from Be containing a Po source eject protons from a surrounding layer of paraffin wax. The Wilson tracks due to the protons are photographed. The bearing on the structure of the neutron of the distribution given by the no. of tracks-angle of projection curve is discussed. N. M. B.

Neutrons and positive electrons. R. FURTH (Z. Physik, 1933, **85**, 294—299).—The hypothesis of elementary indeterminancy gives the mass and radius of the neutron in terms of universal consts., and predicts positive electrons and negative protons. A. B. D. C.

Neutrons and protons in atomic nuclei. H. S. ALLEN (Nature, 1933, **132**, 322).—A brief survey. L. S. T.

Atomic transmutation. ANON. (Nature, 1933, **132**, 432—433).—A brief summary of the British Association (Section A) discussion. L. S. T.

Absorption spectra and atmospheres of the major planets. R. WILDT (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1932, 87—96; Chem. Zentr., 1933, i, 2048).

Solar activity and cosmic rays. V. F. HESS and R. STEINMAURER (Nature, 1933, **132**, 601—602).—The results described support, in part, the corpuscular theory of cosmic radiation. L. S. T.

Cosmic-ray light on nuclear physics. R. A. MILLIKAN (Science, 1933, **78**, 153—158).—A lecture. L. S. T.

Hardest cosmic rays and the electric charge of the earth. W. KOLHORSTER (Nature, 1933, **132**, 407). L. S. T.

Cosmic-ray positive and negative electrons. C. D. ANDERSON (Physical Rev., 1933, [ii], **44**, 406—416; cf. this vol., 441).—Sp. ionisation, as determined by a modified Wilson chamber method, indicates that positrons and electrons occur in nearly equal nos., and have similar energy distribution, curves for which are given. The absorption of Th-*C''* rays, in the light of these results, is discussed. N. M. B.

Atomic disintegration by cosmic rays. J. BARNÓTHY (Z. Physik, 1933, **85**, 201—209).—At. radii are approx. 2½ times less for cosmic rays than those required by artificial disintegration experiments. A. B. D. C.

[Atomic disintegration by cosmic rays.] E. G. STEINKE (Z. Physik, 1933, **85**, 210—211).—The

work noted in the preceding abstract is discussed in the light of more recent empirical data. A. B. D. C.

Absorption of penetrating radiation by water and analysis of the absorption function. W. KRAMER (Z. Physik, 1933, 85, 411—434).—Absorption of penetrating radiation by H_2O of the Alpine lakes is described. An analysis of these together with Regener's results (A., 1932, 440) is possible only if scattered radiation is added to the primary radiation. A. B. D. C.

Penetrating power and absorption coefficient of cosmic rays. E. LENZ (Z. Physik, 1933, 85, 435—438).—Mean range is equal to 3·1 μ, where μ is the absorption coeff. A. B. D. C.

Variation with pressure of residual ionisation in cosmic-ray measurements. P. PFUNDT (Z. Physik, 1933, 85, 439—441).—The dependence of residual ionisation on pressure was studied in a high-pressure ionisation chamber filled with CO_2. A. B. D. C.

Variation with pressure of residual ionisation. E. KORNER (Z. Physik, 1933, 85, 442—447).—Cylindrical ionisation chambers with inner walls contaminated with radioactive substances gave ionisation–pressure curves similar to those observed by Pfundt (cf. preceding abstract). A. B. D. C.

Variation with pressure of residual ionisation. J. A. PRIEBSCH (Z. Physik, 1933, 85, 448—450).—Dependence of residual ionisation on pressure was studied for air and A. A. B. D. C.

Neutrons and magnetic nuclear moments. B. VENKATESACHAR and T. S. SUBBARAYA (Z. Physik, 1933, 85, 264—267).—Assuming neutrons to have orbital moments in nuclei, the magnetic moment of a neutron is 1/2 that of a proton; this gives correctly the magnetic moments of 17 nuclei. A. B. D. C.

Magnetic moments of atomic nuclei. H. SCHULER and H. WESTMEYER (Naturwiss., 1933, 21, 674—675).—If the val. of the magnetic moment of the proton is taken as 2·5/1840 Bohr magneton, the μ/μ_0 vals. (μ_0 being the Bohr magneton) of various elements agree with experimental vals. or are twice these, for elements with odd at. wt. and odd nuclear charge no. For elements of odd at. wt. and even nuclear charge no. it is better to use the val. 1/1840 Bohr magneton for the magnetic moment of the proton. In comparison with the effect on the magnetic moment of the proton, or odd neutrons, that of the nuclear residue is small. No magnetic moment results from the motion and arrangement of charges and masses in the residue. A. J. M.

Nuclear moments and their dependence on atomic number and mass number. N. S. GRACE (Physical Rev., 1933, [ii], 44, 361—364).—Nuclei are grouped into four classes depending on whether the at. no. Z and mass no. are even or odd. Similarities within classes are found, and differences between classes for mechanical and magnetic moments and nuclear g-factors. Results indicate that nearly all nuclei having large magnetic and mechanical moments lie in columns of the periodic table with Z odd, and those having small or zero moments lie in columns with Z even. N. M. B.

Uncertainty principle. H. T. FLINT (Nature, 1933, 132, 282). L. S. T.

Kinetic electron energy and interatomic forces. H. HELLMANN (Z. Physik, 1933, 85, 180—190).—A general relation between kinetic, potential, and total energy is deduced for a system of atoms at rest, and is applied to the interat. forces in crystals and to van der Waals forces of inert gas atoms. A. B. D. C.

Free paths and transport phenomena in gases, and the quantum theory of collisions. I. Rigid sphere model. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1933, A, 141, 434—453).—Using the rigid-sphere model, the range of validity of the classical theory of free paths, viscosity, and diffusion is determined. The use of quantum mechanics improves the applicability of this model to the viscosity of He. L. L. B.

Scattering of light by excited atoms. V. WEISSKOPF (Z. Physik, 1933, 85, 451—482).—The Kramers–Heisenberg formula is extended to include excited at. states of appreciable life period. A. B. D. C.

Coefficients of absorption and opacity of a partly degenerate gas. (MISS) B. SWIRLES (Proc. Roy. Soc., 1933, A, 141, 554—566).—Mathematical. The absorption coeffs. due to both "bound–free" and "free–free" transitions, and the opacity for "free–free" transitions, are evaluated. The results are applied to the two-phase standard model of a star. L. L. B.

Magnetic deviation of oxygen molecules. R. SCHNURMANN (Z. Physik, 1933, 85, 212—230).—Results give O_2 a magnetic moment of 2 Bohr magnetons together with a coupling of this with rotation of the mol. A. B. D. C.

Calculations of atomic wave functions. I. Survey, and self-consistent fields for Cl^- and Cu^+. D. R. HARTREE (Proc. Roy. Soc., 1933, A, 141, 282—301).—The results for Cu^+ are compared with those for the alkali metals, and characteristic differences noted. The relation between the interat. distance in metals and the wave function of the series electron is pointed out. L. L. B.

Intensity distribution in a band system of symmetrical triatomic molecules. Z. W. KU (Physical Rev., 1933, [ii], 44, 383—390).—Mathematical. N. M. B.

Spectrum of hydrogen sulphide. I, II. N. O. STEIN (Astrophys. J., 1933, 77, 270—273; 78, 159—160).—I. No characteristic emission spectrum of H_2S could be observed using a valve oscillator. H_2S gave the Balmer series, the H_2 secondary and continuous spectrum, and a group of diffuse bands, 2470—2860 Å., also given by CS_2, and therefore ascribed to S.

II. The bands, attributed to S, appear to be identical with those of CS. L. S. T.

Intensities of bands in the spectrum of boron monoxide. A. ELLIOTT (Proc. Physical Soc., 1933, 45, 627—634).—The total intensities of the α-bands of BO have been measured. The harmonic wave-function theory shows fair agreement with experiment

for the intensities of the β-bands of BO (A., 1931, 279), but a few bands show divergencies > experimental error. The intensity ratio of the $B^{11}O$ and $B^{10}O$ bands (3·5 : 1) is in good agreement with that determined from the β-bands (3·66 : 1). J. W. S.

Absorption spectrum of chlorine dioxide. Z. W. Ku (Physical Rev., 1933, [ii], 44, 376—382).—Measurements of band heads in the visible and ultra-violet, and a vibrational analysis, are given. Two fundamental bands and one combination band in the region 4—11 μ were recorded. Calc. mol. consts. are consistent with the observed isotope effect. N. M. B.

New band systems in the gadolinium oxide spectrum. G. Piccardi (Nature, 1933, 132, 481).—Formulæ representing two new systems originating at 4615·6 and 4892·1 Å. are given. L. S. T.

Vanadium oxide bands. C. Ghosh (Nature, 1933, 132, 318).—Measurements have been extended to 4500 Å.; band heads are double with a separation of approx. 2·8 ν between them, and the band system is due to a $^2\Sigma \longrightarrow {}^2\Sigma$ transition. L. S. T.

Far ultra-violet eigenfrequencies of the alkali halides. A. Smith (Physical Rev., 1932, [ii], 39, 1013—1014).—Preliminary results for NaCl are recorded. L. S. T.

Absorption spectra of salts with halogenoid complex ions. H. Fesefeldt (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1932, 353—355; Chem. Zentr., 1933, i, 1583—1584).—The absorption spectra of thin layers of cryst. KCN, KCNS, and PbCNS show bands at 169, 183, and 183 mμ, respectively. For KCN the Coulomb fraction of the lattice energy is calc. as 7·62 volts. TlCNS exhibits deformation. A. A. E.

Action of light on rubidium iodide vapour. M. S. Desai (Z. Physik, 1933, 85, 360—365).—Absorption was observed at 3700, 2900, 2548, and 2150 Å., and four corresponding dissociations of the mol. are given. A. B. D. C.

Excitation of the carbon dioxide emission spectrum in a Back box. R. F. Schmid (Physical Rev., 1932, [ii], 39, 539).—The entire CO_2 (or CO_2^+) band spectrum can be obtained from a Back box, with an arc current of approx. 0·5 amp. through streaming CO_2 gas. Most of the band groups appear to be those of a $^1\Sigma \longrightarrow {}^1\Sigma$ transition of a diat. mol. L. S. T.

Doubling and staggering in simple emission bands of the carbon dioxide spectrum. R. Schmid (Z. Physik, 1933, 85, 384—388).—High dispersion shows CO_2 bands near 3670 Å. to consist of doublets 0·3 cm.$^{-1}$ apart. A. B. D. C.

Absorption of amines in the near infra-red. U. Liddel and O. R. Wulf (J. Amer. Chem. Soc., 1933, 55, 3574—3583).—Mol. absorption coeffs., ε, of 34 compounds containing the :NH group have been determined in the neighbourhood of 1·5 μ using, in general, 0·033*M* solutions in CCl_4. Although ε remains of the same order of magnitude, there are definite differences between the vals. of ε for primary and *sec.* aliphatic and aromatic amines as well as variations in the position of the max. of absorption, *M*. The sp. vals. of ε and positions of *M* do not change as the primary and *sec.* aliphatic series are ascended beyond the Et derivatives. An extension of these results for the determination of mol. constitution in certain cases is suggested. J. G. A. G.

Infra-red absorption spectrum of nitrogen tetroxide and the structure of the molecule. G. B. B. M. Sutherland (Proc. Roy. Soc., 1933, A, 141, 342—362).—The absorption bands due to the N_2O_4 mol. have been distinguished from those due to NO_2, and the main bands due to the former have been examined. The data on the infra-red and Raman spectra are in favour of the formula $O_2N{\cdot}NO_2$. Certa in relations between the fundamental frequencies are deduced, and 11 of the 12 frequencies are determined. The binding const. between the two NO_2 groups is calc. to be $1{\cdot}5\times10^5$ dynes per cm., in accord with the ease of dissociation of the mol. and the observed low heat of dissociation (13 kg.-cal. per mol.). L. L. B.

Far infra-red absorption spectra of ammonia and phosphine gases under high resolving power. N. Wright and H. M. Randall (Physical Rev., 1933, [ii], 44, 391—398).—The pure rotation absorption spectra of H_2O vapour, NH_3, and PH_3 were investigated. The NH_3 absorption lines, previously single, were shown as doublets, with separation 1·33 cm.$^{-1}$ The pure rotation lines of PH_3 showed no trace of doubling. Moments of inertia were determined. N. M. B.

Raman effect in water vapour. H. L. Johnston and M. K. Walker (Physical Rev., 1932, [ii], 39, 535).—Raman lines corresponding with shifts of 3654 (±5), 1648 (±5), and 984 (±10) cm.$^{-1}$ have been observed in H_2O vapour at approx. 275° and 2—3 atm. excited by the total radiation of the Hg arc in the visible and near ultra-violet. These are interpreted as pure vibration frequencies and represent the three fundamentals to be expected for the H_2O mol. L. S. T.

Constitution of water in different states. I. R. Rao (Nature, 1933, 132, 480).—The proportions of H_2O, $(H_2O)_2$, and $(H_2O)_3$ mols. present in ice, and in water at 0°, 4°, 38°, and 98°, have been evaluated from Raman data on certain assumptions. The max. no. of the more compact $(H_2O)_2$ mols. found for H_2O at 4° may explain the max. density of H_2O at this temp. L. S. T.

Raman effect of sulphuric acid. L. Medard (Compt. rend., 1933, 197, 582—584).—The fluorescence usually observed in H_2SO_4 is removed by heating at 150° with $KMnO_4$. Pure H_2SO_4 does not show the line 1050 cm.$^{-1}$ appearing first in 98·5% acid; a new line is found at 975, and lines at 391 and 437 in place of that at 415 (cf. A., 1929, 1215; 1931, 997; this vol., 337). Changes on dilution are traced, and lines assigned as follows: 990 to SO_4^{--} 1050 to HSO_4^-, 430 and a line at 565—600 to the heteropolar mol. $[SO_4][H_2]$, and 395, 975, 1150—1180, 1370, and perhaps 920 to the homopolar mol. $SO_2(OH)_2$. C. A. S.

Raman effect in silicic acid esters and silicic acid gels. J. Weiler (Helv. phys. Acta, 1932, 5,

302; Chem. Zentr., 1933, ii, 3839).—Raman spectra for silicic acid esters up to the decameride have been determined. Frequencies for amorphous and cryst. SiO_2 as well as different glasses are compared. The lines 1100 and 1200 cm.$^{-1}$ are independent of the degree of polymerisation, and 850 and 645 cm.$^{-1}$ appear with the monomeric ester, but higher esters show smaller vals. L. S. T.

Ions of the type $M(OH)^{x+}$ in the Raman effect. Z. OLLANO (Nuovo Cim., 1932, [ii], 9, 264—269; Chem. Zentr., 1933, i, 1585).—A discussion of the behaviour of $Bi(NO_3)_3$. A. A. E.

Raman effect at very low temperatures. G. B. B. M. SUTHERLAND (Proc. Roy. Soc., 1933, A, 141, 535—549).—A simple apparatus for the rapid examination of Raman spectra at very low temp. is described. The lines of the Raman spectrum of N_2O_4 are divided into two classes: those due to characteristic vibrations within a mol. of the form $O_2N{:}NO_2$, and those due to oscillations of this mol. about an equilibrium position in the crystal. The failure to obtain any strong Raman spectrum from O_3 indicates that the O_3 mol. is triangular but not equilateral. The Raman spectra of CH_4, NH_4OH, CCl_4, ice, and liquid air have also been examined. The results for CCl_4 at the temp. of liquid air agree with those obtained at room temp., but the results for ice at the temp. of liquid air differ markedly from those obtained at 0°. This can be accounted for by the existence of strong intermol. fields in the crystal. Whilst there is strong evidence in favour of the presence of $(H_2O)_2$ mols. in H_2O and in ice, all the observed phenomena can be better explained without assuming the existence of higher aggregates. L. L. B.

Infra-red and Raman spectra of carbon disulphide. S. BHAGAVANTAM (Physical Rev., 1932, [ii], 39, 1020).—A discussion. L. S. T.

Influence of ultra-violet absorption on the relative intensities of Stokes and anti-Stokes lines in the Raman spectrum. S. C. SIRKAR (Indian J. Physics, 1933, 17, 67—75; cf. A., 1932, 108).—The intensity ratio for the 655 line of CS_2 excited by the 4358 Å. line has been determined, and indicates the influence of the absorption frequency. N. M. B.

Photo-active emanations from irradiated organic substances. C. SERONO and A. CRUTO (Bull. Soc. Chim. biol., 1933, 15, 833—839).—The luminescence produced by lecithin and other lipins and resins when exposed to ultra-violet light is due to oxidation of the unsaturated parts of the mols. The irradiation of lecithin affords the same products as are obtained on treatment with H_2O_2. A. L.

Unidirectional layer photo-effect and Einstein's relation. F. VON KÖROSY and P. SELENYI (Physikal. Z., 1933, 34, 716—718).—The effect of different coloured light on the emission of Se and Cu_2O cells is investigated. A. J. M.

Theory of photo-electric effect on metals. I. TAMM (Physical Rev., 1932, [ii], 39, 170—172).—A reply to criticism (A., 1931, 1106). L. S. T.

Influence of adsorbed gas layer on photo-electric sensitivity. B. ABENDROTH (Z. Physik, 1933, 85, 530—544).—Unimol. layers of H_2O, C_5H_5N, $EtCO_2H$, and C_6H_6 give max. sensitivity for Pt and CdI; zero layer gives zero sensitivity, and this diminishes as the layer increases in thickness beyond the unimol. form. The dipole moment is thus not of primary importance. A. B. D. C.

Photo-electric cells sensitive to red and infra-red light. W. KLUGE (Z. wiss. Phot., 1933, 32, 142—144).—Ag–Cs_2O–Cs cells show max. sensitivities about 400 and 700—800 mμ. J. L.

Conduction in poor electronic conductors. J. FRENKEL (Nature, 1933, 132, 312).—The mechanism of photo-electric conduction is discussed. L. S. T.

Electrical conductivity of inorganic substances with electron conductivity. W. MEYER (Z. Physik, 1933, 85, 278—293).—Variation of the electrical conductivity with temp. is represented by an exponential formula with the index b/T; the variation of the consts. with the substance and metalloid content was investigated for WO_3, ZnO, and UO_2. A. B. D. C.

Dielectric losses of insulating oils at very high frequencies. H. BECK (Physikal. Z., 1933, 34, 721—729).—The dielectric losses of oils at frequencies of 10^7 to 10^8 Hertz was determined by a calorimetric method. No connexion between the losses and the breakdown characteristics at low frequency could be found. Purification of the oil had no effect. The losses are to be ascribed almost entirely to mol. dipoles. A. J. M.

Dipole moment and solvent. H. MÜLLER (Physikal. Z., 1933, 34, 689—710).—An apparatus for the determination of dielectric consts. is described, and used for finding the dependence of mol. polarisation of solutes on the solvent. This is a function of the dielectric const. of the latter, and an empirical relationship can be derived to govern it. The effect can be explained by assuming a saturation effect in the electric field of the dipole, analogous to the theory of the dielectric const. of dil. solutions of electrolytes. A. J. M.

Investigations of the influence of a magnetic field on the dielectric constants of argon and oxygen by means of a new resonance method. H. VOSS (Z. Physik, 1933, 85, 172—179).—Changes of 10^{-8} in the dielectric const. could be measured, but no effect was observed for magnetic fields up to 1080 gauss. A. B. D. C.

Resultant electric moment of complex molecules. H. EYRING (Physical Rev., 1932, [ii], 39, 746—748).—Theoretical. L. S. T.

Relation between apparent atomic volumes and centres of co-ordination of insoluble internal complexes. R. GUTZEIT (Arch. Sci. phys. nat., 1933, [v], 138, 173—176).—Theoretical. C. W. G.

Rotatory dispersion of certain classes of organic molecules. D. BIQUARD (Ann. Chim., 1933, [x], 20, 153—199).—A detailed account of work previously summarised (A., 1932, 679), the vals. of $[\alpha]_{5780}$, $[\alpha]_{5461}$, and $[\alpha]_{4358}$ and dispersions between

5780 and 4358 for *l*-benzyl-lactic acid (I) and its Me_2 ester (II) in various solvents, and for the pure ester at temp. between 21° and 174°, also being given. The existence of an equilibrium mixture of > two forms (two of which are of opposite sign) is assumed with Me phenylsuccinate, *d*-phenyl-lactic acid, its Me_2 ester, (I), and (II). J. W. B.

Optical activity in triphenylmethane derivatives. I. LIFSCHITZ (Z. wiss. Phot., 1933, **32**, 131—141; cf. A., 1931, 349, 840).—Theoretical. Arguments in favour of the existence of optically active halochromic derivatives of CAr_3X are given. F. L. U.

Refractive index. IV. A. M. TAYLOR and A. KING (J. Opt. Soc. Amer., 1933, **23**, 308—312).—The surface layers of molten undecoic, lauric, and myristic acids suddenly become birefringent on cooling to within a few degrees of the m.p., indicating orientation of the mols. D. R. D.

Optical properties of the double salt $(NH_4)_2SO_4,CaSO_4,2H_2O$. A. R. MERZ, J. O. HARDESTY, and S. B. HENDRICKS (J. Amer. Chem. Soc., 1933, **55**, 3571—3573).—The refractive indices of the crystals, *d* 2·07, are recorded. J. G. A. G.

Optical properties of liquid nitrobenzene near its transition point. M. WOLFKE and S. ZIEMECKI (Acta phys. Polon., 1932, **1**, 271—279; Chem. Zentr., 1932, ii, 3828).—The refractive index between 6·4° and 19° has been measured by three different methods; it changes continuously at the transition temp.; on the other hand at 9·5° the mol. refraction showed a discontinuity. The Raman spectrum shows no change at the transition temp. L. S. T.

Two different states of liquid nitrobenzene. M. WOLFKE and J. MAZUR (Acta phys. Polon., 1932, **1**, 71—77; Chem. Zentr., 1932, ii, 3828). L. S. T.

Optical anisotropy of molecular crystals. I. S. B. HENDRICKS and M. E. JEFFERSON (J. Opt. Soc. Amer., 1933, **23**, 299—307).—Densities and refractive indices are given (α, β, γ, from 4861 to 6676 Å.) of BzOH, $(CH_2Ph)_2$, C_6Et_6, $(CH_2)_6N_4$, C_6HMe_5, Ph_2, $C_{10}H_8$, $C_6H_4Br_2$, C_6Me_6, and *o*- and *m*-$C_6H_4(OH)_2$, in the liquid and solid states. Densities only are given for acenaphthene, *p*-$C_6H_4Me{\cdot}NH_2$, *o*-$C_6H_4Me{\cdot}CO_2H$, and C_6H_6. D. R. D.

Dispersion measurements for NaCl in the long-wave infra-red. C. H. CARTWRIGHT and M. CZERNY (Z. Physik, 1933, **85**, 269—277).—Refractive indices and extinction coeffs. were measured between 70 and 125 μ; subsidiary max. observed in the nearer infra-red were absent in this region, in agreement with Born and Blackman's theory (this vol., 661). A. B. D. C.

Dispersion of gases and vapours and its representation by the dispersion theory. V. Interferometer for dispersion measurements in the Schumann region. G. WOLFSOHN (Z. Physik, 1933, **85**, 366—372).—Preliminary measurements were made of anomalous dispersion due to the 1850 Å. Hg line. A. B. D. C.

Dispersion of the Kerr electro-optic effect in the short infra-red spectrum. L. R. INGERSOLL and W. R. WINCH (Physical Rev., 1933, [ii], **44**, 399—405).—Measurements of the Kerr electro-optic effect were made on CS_2, $PhNO_2$, *o*-$C_6H_4Me{\cdot}NO_2$, PhCl, and "halowax" oil in the region 0·589—2 μ. Satisfactory agreement was found with the Havelock formula; the Born and Serber (cf. this vol., 763) formulæ were also satisfactory. N. M. B.

Electrical Kerr effect with gases and vapours at higher temperatures. H. A. STUART and H. VOLKMANN (Ann. Physik, 1933, [v], **18**, 121—149).—An apparatus for the abs. determination of the Kerr const. of vapours up to 230° is described. The dependence of Kerr const. on temp. for EtCl was determined between 15° and 177°. The results confirm the Langevin–Born theory. The Kerr consts. of a no. of org. vapours have been obtained, and for some, *e.g.*, $EtNO_2$ and the lower ketones, the polarisation ellipsoids were calc. and discussed. The const. for $COPr^{\beta}_2$ is negative. A. J. M.

Electric birefringence of camphor. M. SCHWOB (Compt. rend., 1933, **197**, 615—617).—The electric birefringence of camphor has been determined at various temp. from 20° to 183°, in solution in CCl_4 and paraffin oil, and fused, showing that the dispersion is normal. The temp. variation in the oil is in accord with Langevin's law; the sp. birefringence varies with the solvent. These results support the hypothesis of mol. polymorphism in solution (cf. A., 1932, 900). C. A. S.

Cotton–Mouton constant of nitrobenzene at the transition point. H. KÖNIG (Physikal. Z., 1933, **34**, 731—734).—The Cotton–Mouton effect for $PhNO_2$, and the effect of temp. on it, have been investigated. The temp. curve shows no deviation at the supposed transition point of the two liquid forms (9·6°). The val. of the const. at 20° and 546 mμ is $25{\cdot}7\times10^{-13}\pm0{\cdot}4\%$. A. J. M.

Absence of inertia in the diamagnetic Faraday effect. W. HANLE (Z. Physik, 1933, **85**, 304—309).—No inertia was observed for frequencies up to 10^8 Hertz. A. B. D. C.

Magnetic properties of iodine in different solvents. S. S. BHATNAGAR and C. L. LAKRA (Indian J. Physics, 1933, **17**, 43—47).—Vals. of the magnetic susceptibility indicate slight ionisation of I in C_6H_6 and CS_2, but not in *cyclo*hexane. N. M. B.

Influence of temperature on the diamagnetism of certain liquids. M. A. AZIM and S. S. BHATNAGAR (Phil. Mag., 1933, [vii], **16**, 580—593).—The susceptibility of *cyclo*hexane and CCl_4 was independent of temp.; for H_2O, $Pr^{\alpha}OH$, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, and $Bu^{\beta}OH$ it increased with rise of temp. For a no. of aromatic compounds it decreased. For H_2O and alcohols the increase is connected with changing association. The vals. for the aromatic compounds are correlated with the dipole moment and magnetic birefringence. H. J. E.

Diamagnetic susceptibility of the rare gas atoms according to Slater's method. W. R. ANGUS (Physical Rev., 1932, [ii], **39**, 844—845; cf. A., 1932, 795).—Biswas' results (this vol., 449) are incorrect. Vals. for the effective nuclear charge, dia-

magnetic increments, and at. diamagnetic susceptibilities calc. by Slater's method and by a modified method are compared with those calc. by Biswas for Kr, Xe, and Rn. Agreement is not good. L. S. T.

Magnetic properties of mesomorphic substances. Analogies with ferromagnetics. G. FOEX (Trans. Faraday Soc., 1933, **29**, 958—972).—Published data show a close correspondence between the magnetic properties of ferromagnetic and nematic substances, especially in those characteristics which depend on orientation. The changes of magnetic susceptibility with temp. for smectic substances are small and approx. linear while the mesomorphic state persists, becoming very strong and discontinuous on passing into the isotropic state. The effect of a magnetic field on crystallisation and the relation between diamagnetism and mol. structure are discussed. E. S. H.

Molecular configuration of N_2O. C. R. BAILEY and A. B. D. CASSIE (Physical Rev., 1932, [ii], **39**, 534).—Plyler and Barker's data (A., 1932, 108) give a formula N:N·O and not N:N:O. The vals. of the force consts. obtained by the authors for an asymmetrical rectilinear mol. (A., 1932, 444) give a formula N:N:O or :N::N::O:. L. S. T.

Aminoformates of copper and zinc, relatively stable internal complexes involving four linkings. G. GUTZEIT and R. DUCKERT (Arch. Sci. phys. nat., 1933, [v], **15**, 168—173).—The formulæ $(NH_2{\cdot}CO{\cdot}O)M^{II}$ are established. C. W. G.

Surface tension of liquids near the critical temperature. C. A. WINKLER and O. MAASS (Canad. J. Res., 1933, **9**, 65—79).—The surface tension–temp. curves for Me_2O and C_3H_6 have been determined by capillary rise to within 1—2° of the crit. temp. The curves do not appear to be asymptotic to the temp. axis, *i.e.*, the mol. surface energy does not fall to zero when the meniscus disappears. Sugden's equation is valid for the ranges studied, and Katayama's equation is more accurate than that of Ramsay and Shields. The Macleod relation between surface tension and d is valid for Me_2O, but for C_3H_6 the const. increases progressively with rise of temp. The calc. parachor of Me_2O agrees with the theoretical val., but for C_3H_6 it shows an increasing deviation as the crit. temp. is approached. The ring method, with certain modifications, should be applicable to determinations of surface tension in the neighbourhood of the crit. temp.; it yields results confirming that the angle of contact between Me_2O and glass is zero. H. F. G.

Molecular beams of salt vapours. W. H. RODEBUSH and W. F. HENRY (Physical Rev., 1932, [ii], **39**, 386).—No ions could be detected in mol. beams of the alkali halides, but when a beam is passed through an inhomogeneous magnetic field a considerable broadening, due to the magnetic moment of the rotating dipoles, is observed. L. S. T.

***X*-Ray examination of crystals with long-wave radiation.** G. HAGG (Z. Krist., 1933, **86**, 246—252).—Apparatus for use with, *e.g.*, Ca-$K\alpha$ radiation is described. C. A. S.

Deviation from the Bragg equation for the powder method. G. HAGG and G. PHRAGMEN (Z. Krist., 1933, **86**, 306—308; cf. A., 1927, 298).—The effect of refraction of the radiation used on the correctness of the Bragg equation is discussed and shown to be negligible as a rule. It is least when θ is large. If it is necessary to take it into consideration this is best done by calibration, a method for which is outlined. C. A. S.

Heteropolar crystals. H. M. EVJEN (Physical Rev., 1933, [ii], **44**, 501—509; cf. this vol., 1109).—The failure of theories of the solid state to account for the stability of ideal crystals cannot be due to inadequacy of the force postulate. A possible type of departure from the ideal state is considered. The assumption that all crystals have a secondary structure leads to an explanation of the doublet nature of residual rays in cubic crystals and to an improved form of Lindemann's law. N. M. B.

Thermal motions of atoms in crystals. B. D. HOLBROOK (Physical Rev., 1932, [ii], **39**, 177).—An expression, involving only measured quantities, is deduced for the distribution of the atom centres about their mean positions. Atoms possess more translational energy than is predicted by classical theory, indicating the presence of zero-point energy. L. S. T.

Focal conic structures. (SIR) W. BRAGG (Trans. Faraday Soc., 1933, **29**, 1056—1060).—Theoretical. E. S. H.

Theory of recrystallisation. U. DEHLINGER (Metallwirt., 1933, **12**, 48—50; Chem. Zentr., 1933, i, 1569).

Lattice distortion and fibre structure in metals. W. A. WOOD (Nature, 1933, **132**, 352).—As the temp. of a metal is raised, lattice distortion (I) produced by cold-working (A., 1932, 1193) is removed before that of the fibre structure (II), and this intermediate state, in which (II) exists to the exclusion of (I), persists as the metal is slowly cooled. L. S. T.

Relation between the separation processes of single and poly-crystals. P. WIEST (Metallwirt., 1933, **12**, 47—48; Chem. Zentr., 1933, i, 1569).—Experiments concerning the structure and velocity of crystallisation of Cu+10% Ag are described. A. A. E.

Synthetic metal bodies. VII. Crystallisation between surfaces in structural equilibrium. F. SAUERWALD and L. HOLUB (Z. Elektrochem., 1933, **39**, 750—753; cf. B., 1932, 428).—Compression of powdered Fe or Cu above 400° at 3000—5000 kg. per sq. cm. produced blurring of the $K\alpha$ doublet, attributed to inner strain. Powdered Cu, prepared by reduction, showed growth from one crystal to another after heating to 900°, but not at 500°. A powder composed mainly of single crystals, prepared by fusing powdered Cu mixed with MgO and removing the MgO, gave much less growth between crystals at 900° and none at 500°. H. J. E.

Structure of technical zinc dust. G. WASSERMANN (Metallwirt., 1933, **12**, 1—2; Chem. Zentr., 1933, i, 1993).—Debye–Scherrer lines indicate a mean

crystal size of 10 μ; microscopical examination indicates considerable variation in particle size (2—20 μ), the diameter of most of the spherical particles being 5—7 μ. ZnO appears to be present as a film on the Zn particles. A. A. E.

Structure of magnesium, zinc, and aluminium films. G. I. FINCH and A. G. QUARRELL (Proc. Roy. Soc., 1933, **A**, **141**, 398—414).—Electron diffraction examination shows that (i) the structure of a thin Al film deposited on Pt is that of a face-centred tetragonal lattice; (ii) thin layers of Mg and Zn on Pt also show abnormal crystal structure; (iii) heating of the receiver causes the crystals in the films examined to orient themselves in certain preferred directions; (iv) the metal vapours do not diffract, but scatter the electrons. It is concluded that (i) the abnormal crystal structures are due to pseudomorphic strain effects; (ii) such strain effects are not evident at the surface of sufficiently thick films; (iii) in Al the pseudomorphic strain effects are confined to the two dimensions of the basal planes; (iv) Mg, Zn, and Al vapours are monat. L. L. B.

Crystal parameters of four metals when under reduced pressure. E. A. OWEN and E. L. YATES (Phil. Mag., 1933, [vii], **16**, 606—610; cf. this vol., 341).—Measurements on Au, Pt, Pd, and Rh, made without admitting air, after heating to temp. up to 600°, gave the same vals. as after exposure to air. H. J. E.

Rapid method of determining the crystal axes of single-crystal wires of certain metals. R. ROSCOE and P. J. HUTCHINGS (Phil. Mag., 1933, [vii], **16**, 703—707).—A method is given for measuring the direction of the elliptical slip-bands for a stretched single-crystal wire of Cd, and deducing the orientation of the crystal axes. H. J. E.

Cadmium azide. L. BIRCKENBACH (Z. anorg. Chem., 1933, **214**, 94—96).—99·5% pure $Cd(N_3)_2$ is as explosive as $Pb(N_3)_2$. It decomposes in vac. at 100—200° into Cd_3N_2 and N_2. No N_3 or $(N_3)_2$ could be detected in the decomp. products by its effect on a Na film. H. J. E.

Adsorption, oriented overgrowth, and mixed crystal formation. C. W. BUNN (Proc. Roy. Soc., 1933, **A**, **141**, 567—593).—Crystals usually considered as being built up by continual adsorption and inclusion of impurity during growth (" adsorption bodies ") are to be regarded as unstable mixed crystals. The application of knowledge on mixed crystal formation to adsorption leads to the suggestion that the condition for strong adsorption is similarity of lattice structure and interat. distances on sp. planes only. This condition is identical with that necessary for oriented overgrowth of different crystals on each other. Evidence is adduced in support of these conceptions. Thus the 100 plane of NH_4Cl is similar to 001 of $CO(NH_2)_2$; reciprocal modification of habit occurs on these faces, and oriented overgrowths can be obtained with these faces in contact. A simple explanation of habit modification is suggested; on the affected faces a mixed crystal is formed, which, being unstable, tends to redissolve, thus reducing the rate of growth. L. L. B.

Pseudo-crystalline structure of water. R. H. FOWLER and J. D. BERNAL (Trans. Faraday Soc., 1933, **29**, 1049—1056).—Theoretical. E. S. H.

Lattice constants of ferric oxide. S. KATZOFF and E. OTT (Z. Krist., 1933, **86**, 311—312; cf. A., 1932, 1079).—Fe_2O_3 prepared from $Fe(NO_3)_3$ has a $5{\cdot}413_5$, α 55° 17.$_5$′. C. A. S.

Thallous oxide. F. HALLA, H. TOMPA, and L. ZIMMERMANN (Z. Krist., 1933, **86**, 303—305).—TlOH was obtained in white needles by evaporating its aq. solution in vac.; these turn yellow below 100°. Its powder diagram is incompatible with the cubic form, and so lends no support to the existence of Pb_2O (cf. A., 1927, 9). 6 days' heating in vac. failed to remove CO_2 from Tl_2CO_3; if melted in vac. in a SiO_2 vessel a bright yellow solid solution of Tl_2O in Tl silicate is obtained on the walls. Tl_2O is distinctly volatile in vac. at 300°. It is not obtained by heating Tl_2O_3. Decomp. of $Tl_2C_2O_4$ yields Tl. C. A. S.

Potassium and cuprous ferric sulphides. H. O'DANIEL (Z. Krist., 1933, **86**, 192—202; cf. Pogg. Ann., 1869, **136**, 460).—$KFeS_2$ prepared by melting together $1Fe+6S+5K_2CO_3+1Na_2CO_3$ forms small flexible leaflets; if $6K_2CO_3$ replace $5K_2CO_3+1Na_2CO_3$ minute hexagonal crystals are obtained, d 2·66, $a:c=1:0{\cdot}3939$. X-ray: a 13·041, c 5·403 Å., space-group D_{3d}, 8 mols. in hexagonal unit cell. When treated with CuCl–aq. HCl it is slowly and incompletely transformed into $CuFeS_2$ (chalcopyrite) (cf. A., 1932, 682), some $KFeS_2$ apparently remaining in mixed crystals. Probably each crystal of $KFeS_2$ is transformed into a mosaic of minute crystals of $CuFeS_2$. The mechanism of the change is discussed. $CuFeS_2$ is a good, $KFeS_2$ a non-conductor. C. A. S.

Structure of minerals of the stibnite group. W. HOFMANN (Z. Krist., 1933, **86**, 225—245; cf. this vol., 214).—Stibnite has a 11·20, b 11·28, c 3·83 Å., with $4Sb_2S_3$ in the unit cell, space-group V_h^{16}. Sb and S atoms alternate in zigzag chains in the direction of the length of the crystals. Co-ordinates of atoms and detailed structure are given, and the connexion thereof with cleavage and twinning is elucidated (cf. A., 1928, 350). Bismuthite is isomorphous, with a 11·13, b 11·27, c 3·97 Å. C. A. S.

Complex chromium and iron carbides. A. WESTGREN (Nature, 1933, **132**, 480).—The formula of cubic Cr carbide is $Cr_{23}C_6$; space-group O^5. The formula of the Cr W carbide (approx. 7 at.-% W) of this type may be written $Cr_{21}W_2C_6$, whilst the Fe W and Fe Mo carbides (this vol., 896) may be regarded as $Fe_{21}W_2C_6$ and $Fe_{21}Mo_2C_6$, respectively, with W and Mo substituted to some extent by Fe. L. S. T.

Crystal structure of some compounds of the type K_2PtCl_6. G. ENGEL (Naturwiss., 1933, **21**, 704).—The cryst. structure of the salts $A^I{}_2B^{IV}Cl_6$, where A=Rb and Cs, and B=Sn, Te, Pt, Pb, has been investigated. All possess a face-centred cubic lattice. Lattice consts. are given. A. J. M.

Crystal structure of nitropentamminocobaltic perchlorate. L. W. STROCK (Z. Krist., 1933, **86**, 186—191).—$[CoNO_2(NH_3)_5](ClO_4)_2$ (cf. A., 1923, i, 644), d^{22} 2·275, is orthorhombic hemimorphic, C_{2v},

$a : b : c$—1·9135 : 1 : 2·4668. The corresponding nitrate, d^{22} 1·799, is monoclinic hemihedral, C_s, $a : b : c$=0·9995 : 1 : 0·9646, β 90° 11′. Both show strong double diffraction. C. A. S.

Crystal structure of carbonatotetramminocobaltic perchlorate. L. W. STROCK (Z. Krist., 1933, **86**, 270—279; cf. A., 1932, 1116).—$[CoCO_3(NH_3)_4]ClO_4$, d^{22} 1·8474, is orthorhombic hemimorphic, C_{2v}, $a : b : c$=2·2136 : 1 : 0·8548. *X*-Ray : a 18·05, b 8·10, c 6·95 Å., 4 mols. in unit cell, space-group C. A. S.

Crystal structure of magnesium platinocyanide heptahydrate. R. M. BOZORTH and L. PAULING (Physical Rev., 1932, [ii], **39**, 537—538).—A modification of earlier conclusions (A., 1927, 297). The structural unit, 14·6×14·6×6·28 Å.^{3}, contains 4 mols. and has a simple tetragonal lattice. Each Pt is regarded as being surrounded by 4 CN at the corners of a square; the Mg are not between the Pt as previously supposed. L. S. T.

***X*-Ray structure of sodium fluorophosphate.** E. W. NEUMAN (Z. Krist., 1933, **86**, 298—300).—$2Na_3PO_4,NaF,19H_2O$, prepared by dissolving 400 g. Na_2HPO_4, 30 g. NaF, and 13 g. 85% HPO_3 in 450 g. hot H_2O, forms regular octahedra, d 2·2165. *X*-Ray : cubic, a 27·86 Å., 40 mols. in unit cell, space-group (probably) O_h^3 (cf. J.C.S., 1885, **47**, 353). C. A. S.

Structure of the crystals of 12-phosphotungstic acid. J. F. KEGGIN (Nature, 1933, **132**, 351; cf. this vol., 215, 768).—The 12-phosphotungstic acid which crystallises from aq. solutions at room temp. probably contains 30 H_2O to 1 $H_3PW_{12}O_{16}$. The edge of the unit cubic, containing 8 mols. of acid, is 23·281±0·002 Å.; the centres of the acid anions, $(PW_{12}O_{40})'''$ are arranged in positions corresponding with the diamond structure. L. S. T.

Structure of vitreous oxides. W. H. ZACHARIASEN (Physical Rev., 1932, [ii], 39, 185).—An hypothesis which accounts for the limited no. of oxides which have been prepared in a vitreous form is discussed. L. S. T.

Crystal structure of diaspore. M. DEFLANDRE (Bull. Soc. franç. Min., 1932, **55**, 140—165; Chem. Zentr., 1933, i, 2075).—Diaspore has a 4·40, b 9·38, c 2·83 Å.; space-group D_{2h}^{16}. The unit cell contains $2(Al_2O_3,H_2O)$. A. A. E.

Crystal orientation in parallel-fibre aggregates. W. JANSEN (Z. Krist., 1933, **86**, 171—185; cf. this vol., 666).—Laue and rotation photographs of twenty fibrous minerals show structures similar to those of spherulites, save only in fibrous celestite (pseudomorphous after fibrous gypsum) in which there is no orientation. In other cases orientation is accurate to within 1—2°, and usually (in eleven of eighteen cases) along the direction of least identity period. It is due to unidimensional lattice parallelism. C. A. S.

Structure of euclase. J. BISCOE and B. E. WARREN (Z. Krist., 1933, **86**, 292—297; cf. A., 1930, 140).—Euclase, $BeHAlSi_2O_5$, is monoclinic, a 4·62, b 14·24, c 4·75 Å., β 79° 44′, 4 mols. in unit cell, space-group C_{2h}^5. Detailed structure and co-ordinates of all atoms are given. Each Al is surrounded octahedrally by 5 O and 1 OH, each Si tetrahedrally by 4 O, each Be tetrahedrally by 3 O and 1 OH. C. A. S.

Wöhlerite. B. GOSSNER and O. KRAUS (Z. Krist., 1933, **86**, 308—310; cf. A., 1909, ii, 1028).—Wöhlerite is monoclinic, $a : b : c$=1·0523 : 1 : 0·7104, β 109° 3′ : *X*-Ray : a 10·80, b 10·26, c 7·26 Å., 2 mols. in unit cell. The formula $NaCa_2[(ZrF)(NbO)](SiO_4)_2$ is suggested, in which ZrF : NbO is approx. 3 : 2 (mol.). C. A. S.

Inclinations of molecules in some crystalline-fluid substances. K. HERRMANN (Trans. Faraday Soc., 1933, **29**, 972—976).—*X*-Ray examination shows that in Tl stearate and oleate double mols. are arranged at an angle of inclination to the smectic planes, which is greater in the cryst.-fluid phase than in the cryst.-solid phase. E. S. H.

Rotating molecules and the liquid-crystalline state. *X*-Ray examination of long-chain esters. T. MALKIN (Trans. Faraday Soc., 1933, **29**, 977—982).—A study of heating and cooling curves shows that Pr, Bu, and amyl margarates assume the α form more readily than do the corresponding palmitates and stearates. *X*-Ray examination shows that the α forms give only one side spacing of 4·2 Å., whilst the β forms give the two side spacings usually associated with long-chain compounds, thus behaving similarly to the paraffins. The evidence for mol. rotation is discussed, and it is suggested that in the liquid cryst. state the mols. rotate about their long axes, which are perpendicular to the planes formed by the terminal groups. E. S. H.

Arrangement of chain molecules in liquid *n*-paraffins. A. MÜLLER (Trans. Faraday Soc., 1933, **29**, 990—993).—The strong diffraction ring observed appears to be produced by the assembly of the mols. in the liquid, having an average distance of 4·5—5 Å. at temp. near the m.p. E. S. H.

Crystalline phases of some substances studied as liquid crystals. J. D. BERNAL and D. CROWFOOT (Trans. Faraday Soc., 1933, **29**, 1032—1049).—*X*-Ray crystallographic data have been obtained for *p*-azoxyanisole (two forms), *p*-azoxyphenetole, anisylidene-1 : 5-diamunonaphthalene (two forms), cholesteryl chloride and bromide, dibenzylidinebenzidine, and Et *p*-anisylideneaminocinnamate. The results are correlated with optical observations, which were extended to include Et *p*-*p*′-phenylbenzylideneaminocinnamate and Et_2 *p*-*p*′-xylylidenebisaminocinnamate, and lead to the view that mesophases should be considered as definite stages in the progression from ideal liquid to ideal crystal, rather than as anomalies. E. S. H.

***X*-Ray investigation of the crystal structure of *p*-aminoazobenzene.** M. PRASAD and M. R. KAPADIA (Indian J. Physics, 1933, **17**, 77—81).—The unit cell has a 13·69, b 5·604, c 14·18 Å., β 81° 49′; space-group C_{2h}^5, 4 mols. per unit cell, d 1·174. N. M. B.

***X*-Ray investigation of crystals of stilbene and tolane.** M. PRASAD (Phil. Mag., 1933, [vii], **16**, 639—640).—Both compounds show a pseudorhombic symmetry (a 12·20, b 5·72, c 29·0 Å., and a 12·80, b 5·68, c 28·4 Å., respectively). The crystals resemble

those of azobenzene. The ·N:N· and ·C·C· linkings are equiv. in length, within the errors of experiment. The C:C linking is somewhat longer. H. J. E.

Crystal and optical properties of some aromatic fluorine compounds. W. FABER (Z. Krist., 1933, 86, 161—170).—The following data are given: *d*, crystal system, $a:b:c$, β (unless 90°), n_α, n_β, n_γ (Na light): 3-fluoro-4-nitrotoluene, $1{\cdot}43_8$, monoclinic, $0{\cdot}994:1:?$, 123° 25′, 1·42, $<1{\cdot}73$, $>1{\cdot}74$; 2:2′-difluorodiphenyl, $1{\cdot}393_5$, orthorhombic, $0{\cdot}913:1:0{\cdot}870$, 1·623, 1·648, 1·713; 4:4′-difluoro-2-nitrodiphenyl, 1·488, orthorhombic, $0{\cdot}703_7:1:0{\cdot}374_6$, 1·5336, 1·5944, 1·7871; 4:4′-difluoro-3:3′-dimethyldiphenyl, 1·345, orthorhombic, $0{\cdot}955_6:1:0{\cdot}604_4$, 1·5070, $1{\cdot}697_9$, 1·816; 4:4′-dichloro-3:3′-dimethyldiphenyl (m.p. 58—58·5°), 1·330, monoclinic (?), ?:1:?, 1·507, ?, 1·729 (cf. A., 1929, 1051; 1932, 729). C. A. S.

X-Ray analysis of the crystal structure of durene. J. M. ROBERTSON (Proc. Roy. Soc., 1933, A, 141, 594—602).—Durene has a 11·57±0·05, b 5·77 ±0·02, c 7·03±0·05 Å., β 113·3°, space-group C_{2h}^5 ($P2_1/a$), 2 mols. per unit cell. The structure is thus similar to the $C_{10}H_8$–anthracene (I) type, but the cell dimensions give no clue to the orientation of the mols., which is deduced directly from the intensity measurements. The mols. are flat or disc-like, as in (I) and C_6Me_6, but the planes of mols. in neighbouring rows are almost perpendicular, instead of being parallel as in C_6Me_6. The closest distance of approach between atoms in adjacent mols. is 3·71 Å., the corresponding val. for (I) being 3·77 Å. L. L. B.

Direction of growth of the needle-like crystals of glucose penta-acetate and cellobiose octa-acetate. K. HUTINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 270—272).—*X*-Ray patterns are shown for the above crystals prepared by pptn. from $CHCl_3$ solution with MeOH. This form consists of parallel, needle-like unit crystals. J. W. S.

X-Ray interpretation of the molecular structure of gelatin. W. T. ASTBURY and W. R. ATKIN (Nature, 1933, 132, 348). L. S. T.

X-Ray investigations of natural and regenerated silks. I. SAKURADA and K. HUTINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 266—269).—The lattice structure of silk fibres remains unaltered after dispersion and regeneration. The structures of silks from different insects are compared and discussed. J. W. S.

Theory of liquid crystals. C. W. OSEEN (Trans. Faraday Soc., 1933, 29, 883—899).—A mathematical review. E. S. H.

Systems with mixed dimensions. D. VORLANDER (Trans. Faraday Soc., 1933, 29, 899—902).—The formation of liquid crystals is particularly favoured by mols. having mixed dimensions (*e.g.*, consisting of a plane with a straight line attached). E. S. H.

Supercrystallinity of *p*-azoxybenzoic acid. D. VORLANDER (Trans. Faraday Soc., 1933, 29, 902—906).—*X*-Ray examination shows that powdered *p*-azoxybenzoic acid is not liquid-cryst., but solid-cryst. The prep. of *p-azoxybenzoyl chloride*, m.p. 155°, and *Et* *p-azoxybenzoate*, decomp. > 260°, is described. E. S. H.

Liquocrystalline resins and lacquers. D. VORLÄNDER (Trans. Faraday Soc., 1933, 29, 907—910).—A review of published work. E. S. H.

Polymorphism of liquid crystals. A demonstration. D. VORLÄNDER (Trans. Faraday Soc., 1933, 29, 913—914).—Examples of substances having three or four liquid-cryst. phases are given. E. S. H.

Forces causing the orientation of an anisotropic liquid. V. FREEDERICKSZ and V. ZOLINA (Trans. Faraday Soc., 1933, 29, 919—930).—Mainly mathematical. Some observations on the behaviour of liquid crystals in electric and magnetic fields are made. E. S. H.

Swarm theory of liquid crystals. L. S. ORNSTEIN and W. KAST (Trans. Faraday Soc., 1933, 29, 931—944).—Theoretical. E. S. H.

Effect of a magnetic field on the nematic state. H. ZOCHER [with W. EISENSCHIMMEL] (Trans. Faraday Soc., 1933, 29, 945—957).—Mainly mathematical. Nematic conc. solutions of bromo- and chloro-phenanthrenesulphonic acid are exceptions to the rule that optic axes tend to set parallel to the lines of magnetic force. E. S. H.

Alterations in the nature of a fluid from a gaseous to liquid-crystalline conditions as shown by *X*-rays. G. W. STEWART (Trans. Faraday Soc., 1933, 29, 982—990).—*X*-Ray and optical tests agree in showing that the relatively large groups in the liquid crystal do not exist in the liquid, but *X*-ray examination demonstrates the persistence of cybotactic groups in both states. The liquid crystal is regarded as an orderly arrangement of cybotactic groups. E. S. H.

Anisotropic melts: change of state. F. I. G. RAWLINS (Trans. Faraday Soc., 1933, 29, 993—994).—Theoretical. E. S. H.

Lyotropic mesomorphism. A. S. C. LAWRENCE (Trans. Faraday Soc., 1933, 39, 1008—1015).—Observations on both colloidal and crystalloidal solutions (especially of soaps) show that structures can be recognised in the liquids, although they may not be always apparent or highly organised. E. S. H.

Paracrystallinity. F. RINNE (Trans. Faraday Soc., 1933, 29, 1016—1032).—A review of published work on liquid crystals and a discussion of their significance in the study of biological systems. E. S. H.

Physical significance of certain apparent irregularities in the magneto-resistance curves of nickel. M. M. S. GUPTA and M. S. ALAM (Indian J. Physics, 1933, 17, 9—17).—The negative change in resistance of Ni wire (cf. Stierstadt, A., 1931, 898) depends on the max. field used in a cycle, and is not observed if the max. field applied in a resistance–hysteresis cycle exceeds a certain val. The intersections of parts of the hysteresis curves for demagnetisation appear to be due to a process of electrical conduction, no satisfactory theory being available. N. M. B.

Crystal structure and electrical properties. II. Crystal structure and conductivity of Bi single crystals in transverse magnetic fields. O. STIERSTADT (Z. Physik, 1933, 85, 310—331; cf. this vol., 342).—Conductivity in the magnetic field shows the same symmetry as the crystal, and may be used to determine the elementary cell of the crystal system. A. B. D. C.

Magnetic interaction of metal electrons. H. BETHE and H. FRÖHLICH (Z. Physik, 1933, 85, 389—397).—Polemical, against Frenkel's theory of superconductivity (cf. this vol., 769). A. B. D. C.

Theory of the dependence on pressure of the electrical conductivity of metals. W. KROLL (Z. Physik, 1933, 85, 398—402). A. B. D. C.

Pleochroism and birefringence in crystals. K. S. KRISHNAN and B. MUKHOPADHYAY (Nature, 1933, 132, 411). L. S. T.

Pleochroism and the birefringence of the NO_3' ion in crystals. K. S. KRISHNAN and A. C. DASGUPTA (Indian J. Physics, 1933, 17, 49—66).—Data for the pleochroism, birefringence, and principal refractive indices of KNO_3 crystals in the visible and near ultra-violet are given. The 3000 Å. absorption band due to NO_3' is strongly polarised; it has no influence on the principal refractive indices of the ion. N. M. B.

Magneto-optical rotation of nickel. K. H. VON KLITZING (Z. Physik, 1933, 85, 240—252).—Rotation dispersion curves were obtained for the Kerr and Faraday effects up to 3 μ. Zero rotation occurs at 1·5 μ for the Kerr and at 1 μ for the Faraday effect, and this is independent of temp. and field strength. A. B. D. C.

Complex indicatrices of weakly absorbing rhombic minerals. M. BEREK and F. STRIEDER (Z. Krist., 1933, 86, 212—224; cf. A., 1931, 1113).—Using a modification of Berek's microphotometer (cf. A., 1931, 703) the extinction and absorption coeff. along the three principal axes for λλ 6320, 6010, and 5230 of andalusite, cordierite, anhydrite, brookite, and astrophyllite have been determined. From these the positions of the singular optic directions, and the polarisation and absorption axes are deduced for λ 6010. C. A. S.

Allotropism of beryllium. F. M. JAEGER and J. E. ZANSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 636—644; cf. this vol., 15).—*X*-Ray powder spectrograms of the α and β forms gave evidence of a new modification, probably a metastable form of ordinary α-Be. N. M. B.

Supposed allotropy of antimony. A. SCHULZE and L. GRAF (Metallwirt., 1933, 12, 19—21; Chem. Zentr., 1933, i, 1563—1564).—Irregularities between 105° and 110° in the electrical resistance and expansion of polycryst. Sb disappear after tempering at 600°; hence they are due to mechanical deformation. *X*-Ray observations at room temp., 150°, and 210° show the same structure. A. A. E.

Correlation of thermo-electric and thermomagnetic data. L. F. BATES (Phil. Mag., 1933, [vii], 16, 657—672; cf. A., 1932, 324).—Mn_3As_2, unheated after its prep., is ferromagnetic up to approx. 45°. Each subsequent transition from the ferromagnetic to the paramagnetic state progressively increases the intrinsic magnetisation and lowers the Curie point until a steady val. is reached. This is correlated with changes in the thermo-electric power. The changes are due to interaction between the spin moment of one atom and the orbital moment of another. H. J. E.

Dependence of the m.p. of carbon tetrachloride on the previous thermal treatment. W. E. NIEUWENHUIS (Z. Elektrochem., 1933, 39, 727—731).—The m.p., −22·3°, of purified CCl_4 was unaltered by maintaining the liquid at −20°, 17°, or 45° for a time before making the measurement, or by fractionation. The max. variation was 0·04°. Brüll's results (A., 1932, 1194) were not confirmed. H. J. E.

Specific heat of copper from −78° to 0°. S. M. DOCKERTY (Canad. J. Res., 1933, 9, 84—93).—The sp. heat of Cu between −78° and 500° (joules per g. per degree) may be calc. to within 0·05% of the observed vals. by means of the equation $C_p=0{\cdot}3889+5{\cdot}65\times10^{-5}T-2000(1-321^2/28T^2+321^4/910T^4)/T^2$, which contains four terms of the Debye expansion. The agreement between the theoretical and observed vals. of the consts. is discussed. H. F. G.

Isopycnals of liquid helium. W. H. KEESOM and (MISS) A. P. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 612—615; cf. this vol., 894).—Data as previously reported are continued for the range 25—35 atm. Parts of the solidification curve were determined more accurately; the λ point is at 1·753° abs., and 29·91 atm. N. M. B.

Thermal expansion of niobium. P. HIDNERT and H. S. KRIDER (Bur. Stand. J. Res., 1933, 11, 279—284).—Nb (0·93% Sn, 0·26% Fe), annealed at 400°, has a body-centred cubic lattice (a 3·293± 0·002 Å.). The coeff. of expansion, measured between −135° and 305°, increases regularly with rise of temp. H. J. E.

Thermal expansion of electrolytic chromium. P. HIDNERT (Physical Rev., 1932, [ii], 39, 186).—Average coeffs. of expansion per degree are recorded for various temp. intervals from 20° to 500°. L. S. T.

Analysis of Slater's compressibility data. H. M. EVJEN (Physical Rev., 1933, [ii], 44, 491—500).—Slater's data for the alkali halides (cf. A., 1924, ii, 383) are translated into terms of interionic forces and considered in relation to the variation of interat. forces with interat. distances in crystals. N. M. B.

Viscosity of gases and vapours. R. PLANK (Forsch. Ingenieurw., 1933, A, 4, 1—7; Chem. Zentr., 1933, i, 2037).—The dependence of viscosity on temp. and pressure is examined theoretically. A. A. E.

Anomalous viscosity in mesomorphic melts. WO. OSTWALD (Trans. Faraday Soc., 1933, 29, 1002—1005).—Mesomorphic melts of Et *p*-azoxybenzoate, eholesteryl acetate, butyrate, and propionate, in the ranges in which they are anisotropic, show marked structure viscosity, thus indicating a close relation to colloids. E. S. H.

Viscosity of liquid crystals. R. O. Herzog and H. Kudar (Trans. Faraday Soc., 1933, 29, 1006—1008).—Theoretical. E. S. H.

Effect of electrostatic fields on the viscosity of liquids. R. O. Herzog, H. Kudar, and E. Paersch (Naturwiss., 1933, 21, 662).—The effect of an electric field on the viscosity of 17 org. liquids has been investigated and the differences are discussed. A. J. M.

Diffusion coefficients of bromine–argon, bromine–methane, bromine–hydrogen chloride, and bromine–nitrous oxide. J. E. Mackensie and H. W. Melville (Proc. Roy. Soc. Edin., 1932—1933, 53, 255—259).—An extension of previous work (A., 1932, 1081). Visual observations have been checked by photo-electric measurements. H. S. P.

Formation of nuclei from condensed vapours in non-ionised dust-free air. II. System methyl alcohol–water. J. A. Froemke, C. R. Bloomquist, and E. X. Anderson (Z. physikal. Chem., 1933, 166, 305—315; cf. A., 1929, 1234).—The rain point and fog point for H_2O, MeOH, and mixtures of the two have been determined. Condensability is a max. for a mixture of 3 mols. of MeOH with 1 mol. of H_2O. The condensation curves are similar in form to the curves representing the mobility and vol. contraction as a function of the composition. The results support the coalescence theory of drop formation. R. C.

Densities and contraction of binary liquid mixtures. L. A. Alberti (Atti R. Ist. Veneto Sci. Lett., 1932—1933, 92, 1—7; Chem. Zentr., 1933, i, 2064).—Relations between d, vol. contraction, and composition are expressed graphically. A. A. E.

Volume contraction in mixtures of nitrobenzene with benzene and with chloroform. G. Bottecchia (Atti R. Ist. Veneto Sci. Lett., 1932—1933, 92, 9—17; Chem. Zentr., 1933, i, 2064).—With C_6H_6–$PhNO_2$ mixtures at 16—40°, max. contraction occurs at approx. 70 wt.-% $PhNO_2$; with $CHCl_3$–$PhNO_2$ mixtures it occurs at 50% (16°) or 65% (40°) $PhNO_2$. The mean coeff. of expansion between 16° and 40° has been calc.; it is min. in the neighbourhood of max. contraction. A. A. E.

Solvent action. VII. Rotatory power of diethyl tartrate in relation to solvent, concentration, degree of association, and temperature. H. G. Rule, (Miss) M. M. Barnett, and J. P. Cunningham (J.C.S., 1933, 1217—1223).—$M[\alpha]^{20}_{61}$ has been determined in the pure state and in numerous org. solvents. $M[\alpha]$ increases with the polarity of the solvent, and, in the case of non-polar solvents, with the concn. CCl_4, CS_2, and C_6H_{14} give exceptionally high vals., owing to association of the ester. The $M[\alpha]$–T curves for polar and non-polar solvents converge at high temp., the ester itself giving a curve lying between the two extremes. D. R. D.

Diffusion of metals in mercury. F. Weischedel (Z. Physik, 1933, 85, 29—35).—Diffusion coeffs. have been determined for Zn and Cd from electrical conductivity measurements. A. B. D. C.

Diffusion of metals in solid lead. III. Diffusion in gold–lead and silver–lead alloys. W. Seith and A. Keil (Z. physikal. Chem., 1933, B, 22, 350—358; cf. this vol., 669).—Pb is able to form mixed crystals with small amounts of Ag and of Au; solubility data are recorded. Measurements of the rate of self-diffusion of Pb in such mixed crystals show that the rapidity of the diffusion of Au in Pb does not depend on exchange of places of Au atoms and Pb atoms. Self-diffusion is more rapid in mechanically worked than in recryst. Pb; recrystallisation may be delayed by adding 0·03 at.-% of Au or 0·08 at.-% of Ag. R. C.

Dependence of lattice constant on hydrogen concentration in the palladium–hydrogen system. G. Rosenhall (Ann. Physik, 1933, [v], 18, 150—154).—The Pd–H_2 system has been investigated by the X-ray method, and the lattice const. obtained for various Pd/H concns. The results indicate the existence of two phases up to 0·64H/Pd, the lattice const. of one phase remaining const. at 4·02 Å., the other at 3·88 Å. Above this limiting concn. the lattice const. increases with increasing concn. Results of other workers are discussed. A. J. M.

Elastic properties of the mixed crystal series Au–Cu and Au–Pd, and the alloys Cu_3Pt, Cu_3Pd, and CuPd. H. Röhl (Ann. Physik, 1933, [v], 18, 155—168).—Previous investigations on single crystals (A., 1931, 900; this vol., 561) have been continued with mixed crystal series in the polycryst. state. Progressive tempering at 203° produces an initial increase in the extension modulus of polycryst. Cu–Au, but this decreases later. The alloys Cu_3Pt and Cu_3Pd show the same superstructure as Cu_3Au. The resistance–concn. diagram for the Au–Pd system has been derived. Extension and torsion moduli in this system do not agree with the mixture rule. The effect of adsorption of H_2 by these alloys on the elastic consts. is considered. A. J. M.

Spectral analysis by sensitive lines within the range of the glass spectrograph. Spark spectra of high-beryllium- and -nickel-iron alloys. W. Kraemer (Physikal. Z., 1933, 34, 714—715).—Results are given for Be–Fe and Ni–Fe alloys, using the apparatus previously described (A., 1932, 35, 355). A. J. M.

Mixed crystal formation with single and polycrystalline materials. E. Schmid and G. Siebel (Z. Physik, 1933, 85, 36—55).—X-Ray data show the dependence of the grating const. on particle size for the α-cryst. alloys of Al–Mg, Zn–Mg, and Ag–Cu. The saturation limits of Al–Mg and Ag–Cu are also discussed. A. B. D. C.

X-Ray studies on the system (Zn,Cd)–Sb. II. F. Halla, H. Nowotny, and H. Tompa (Z. anorg. Chem., 1933, 214, 196—200; cf. A., 1930, 147).—The unit cell of Cd_3Sb_2 (monoclinic) has a 7·20, b 13·51, c 6·16 Å., β 100° 14′; and that of ZnSb (rhombic) has a 6·17, b 8·27, c 3·94 Å. Each contains 4 mols. At room temp. crystals of Zn_3Sb_2 are decomposed to Zn and ZnSb. F. L. U.

Constitution of the silver-rich aluminium–silver alloys. N. Ageev and D. Shoyket (Inst. Metals, Sept., 1933. Advance copy, 8 pp.).—The Al–Ag system up to 10% Al has been examined by

micrographic and *X*-ray methods. The boundary of the α-phase extends from 5·1% Al at 200° to 6·52% Al at 500° and 6% Al at about 620°, whilst that of the γ-phase extends from 10% Al at 0—200° to about 10·5% Al at 300° and 8·8% Al at 500—600°. Between these two homogeneous fields is a complex region in which α+β, β, and β+γ fields exist above 600°, an α+γ field at 400—600°, and at < 400° α+β′ (with < 7·8% Al) and β′+γ (with > 7·8% Al). The β′-phase is Ag_3Al, and above 400° this is converted into α+γ eutectoid. A. R. P.

Constitution of the aluminium-rich aluminium–copper alloys above 400°. D. Stockdale (Inst. Metals, Sept., 1933. Advance copy, 6 pp.).—The solidus at the Al end of the Cu–Al system is very slightly convex to the Al-rich solid solution (κ) and meets the eutectic horizontal at 5·72% Cu, 548° (*A*). The boundary of κ is a straight line from *A* passing through 3% Cu, 462°. No evidence of the existence of $CuAl_2$ could be obtained; an alloy of this composition always contains two phases at > 400°. A narrow range of solid solutions (θ) exists around 53·5% Cu; this alloy is homogeneous up to 591° and probably melts sharply at this temp. The triple point (θ, θ+liquid, θ+κ) is at 52·47% Cu, 548°. A. R. P.

Solid solutions of lead and tin in bismuth. E. R. Jette and F. Foote (Physical Rev., 1932, [ii], 39, 1018—1020).—The *X*-ray data recorded show that the Bi lattice changes slightly when saturated solutions of Pb or Sn in Bi are formed. L. S. T.

X-Ray investigation of system iron–selenium. G. Hagg and A. L. Kindstrom (Z. physikal. Chem., 1933, B, 22, 453—464).—At 50 at.-% Se two intermediate phases occur. One is stable up to some temp. between 300° and 600°, and has the *B* 10 structure and a simple tetragonal unit cell with *a* 3·765 and *c* 5·518 Å. This is not stable for Se contents > 50 atoms-%. At higher temp. a phase with the *B* 8 structure exists. After dissolving Se, which results in a considerable lattice contraction, it is stable at lower temp. At about 53 atoms-% Se deformation begins and passes through a max. at 55—56 atoms-% of Se; the orthohexagonal unit cell of the *B* 8 structure becomes a monoclinic cell. At 57·5 atoms-% the upper limit of the homogeneity region is reached, and with larger amounts of Se stable intermediate phases seem not to exist. Solutions of Se in FeSe are of the subtractional type. R. C.

Equilibria in alloyed bronzes. I. Cu–Ni–Sn system. II. Lead–tin bronzes. J. Veszelka (Mitt. berg.-huttenm. Abt. Hochschule Sopron, 1932, 4, 162—203; Chem. Zentr., 1933, i, 1674—1675).—I. Alloys up to 15% Ni and 30% Sn have been studied.

II. The solidification and transformation temp. of bronzes are little affected by Pb. A. A. E.

System iron–carbon–silicon. A. Kriza and F. Poboril (Chem. Obzor, 1932, 7, 147—151, 165—171, 192—197; Chem. Zentr., 1933, i, 1342).—The eutectic concns. up to 6% Si have been determined microscopically. At 8% Si there is no homogeneous γ-phase. A. A. E.

Molecular compounds in liquid steel and their influence on deoxidation equilibria. P. Herasymenko and F. Pobořil (Coll. Czech. Chem. Comm., 1933, 5, 331—338).—Thermodynamic considerations afford evidence for the equilibrium $Fe+Si \rightleftharpoons FeSi$. Only the free Si takes part in deoxidation processes. Addition of Mn lowers [Si] owing to the formation of Mn_xSi, where *x* is probably 2 or 3. D. R. D.

Graphical method for converting weight percentage compositions of ternary systems into atomic or molecular percentages. W. Hume-Rothery (Inst. Metals, Sept., 1933. Advance copy, 5 pp.). A. R. P.

Internal friction of liquid mixtures of limited miscibility. I. Ternary system benzene–alcohol–water. II. Binary systems of paraffin oils with water with addition of acids and alkali. M. Pestemer [with M. Birkmann] (Kolloid-Z., 1933, 65, 25—31).—Viscosity data are given for the systems EtOH–H_2O, EtOH–C_6H_6, and EtOH–C_6H_6–H_2O. A ternary max. occurs at EtOH 10, C_6H_6 55, H_2O 35%. The viscosity max. in the miscibility gap of the C_6H_6–H_2O system is relatively weak. No max. is observed in the system paraffin–H_2O. E. S. H.

Ternary azeotropic systems. III. The heteroazeotrope ethyl alcohol–water–carbon disulphide. W. Swientosławski and E. Wardziński (Rocz. Chem., 1933, 13, 379—383).—The heteroazeotrope (I), b.p. 41·345°, contains CS_2 92·36, EtOH 6·55, and H_2O 1·09%. The ratio of the coeff. dp/dt for (I) to that for H_2O is 1·05 at $p=1$ atm. R. T.

Solubility of calcium iodate in water and in aqueous solutions of electrolytes. J. B. Chloupek, V. Z. Daneš, and B. A. Danesova (Coll. Czech. Chem. Comm., 1933, 5, 339—342).—The solubility in H_2O at 25° is 0·303% and is increased by the addition of KNO_3, K_2SO_4, $MgSO_4$, or $MgCl_2$. The solid phase is $Ca(IO_3)_2,6H_2O$. D. R. D.

Solubility of lead chromate. Application to volumetric determination of lead. M. Huybrechts and C. Degard (Bull. Soc. chim. Belg., 1933, 42, 331—346).—The solubility of $PbCrO_4$ in H_2O measured colorimetrically as PbS is 0·00017 g. per litre at 20°. It is greatly decreased by a slight excess of CrO_4''. The solubility in aq. AcOH and aq. NH_4OAc is > in H_2O. H. S. P.

Active oxides. LXVIII. Solubility of active zinc oxide in ammonia. G. F. Huttig and H. Schmeiser (Kolloid-Z., 1933, 65, 77—87; cf. this vol., 774).—The solubility in aq. NH_3 and KOH at 20° of ZnO and its hydrates prepared in different ways has been determined. About 90 min. is generally required for the attainment of equilibrium, although cryst. $Zn(OH)_2$ requires about 1000 min. In general, the solubility is less the higher is the temp. at which the oxide has been heated, and increases with increasing amount of the solid phase to a max. val. ZnO behaves as a mixture of two components having different solubilities. The difference of free energy between these forms is calc. as 700 g.-cal. E. S. H.

Liquid ammonia as a solvent. III. Solubility of inorganic salts at 25°. H. Hunt and L.

BONCYK (J. Amer. Chem. Soc., 1933, **55**, 3528—3530).—The data refer to 26 inorg. compounds. Salts with a common ion decrease, whilst those without a common ion increase, each other's solubility. Some correlations are indicated. J. G. A. G.

Optical properties, densities, and solubilities of the normal formates of some metals of group II of the periodic system. F. W. ASHTON, D. F. HOUSTON, and C. P. SAYLOR (Bur. Stand. J. Res., 1933, **11**, 233—253).—Crystallographic data, densities, and solubilities from 0° to 100° are recorded for the formates of Ca, Sr, Ba, Mg, Zn, and Cd. The system H_2O–$(HCO_2)_2Mg,2H_2O$ has a eutectic at $-5{\cdot}05\pm0{\cdot}03°$ [14·0 g. $(HCO_2)_2Mg$ per 100 g. H_2O]. For the Sr and Cd salts the dihydrate⟶anhyd. salt transition occurs at 72·0—72·5° and 66·0—66·5°, respectively. H. J. E.

Kinetic proof of the law of Berthelot and Jungfleisch concerning the partition of a substance between two immiscible solvents. A. SCONZO (Gazzetta, 1933, **63**, 525—526; cf. this vol., 760).—A correction. O. J. W.

Clean-up of hydrogen by magnesium. A. L. REIMANN (Phil. Mag., 1933, [vii], **16**, 673—686).—1 in every $1{\cdot}5\times10^6$ mols. of H_2 striking a clean Mg surface at room temp. is adsorbed. The adsorbed gas diffuses slowly into the metal. The formation of at. H by the passage of an electric discharge greatly accelerates the adsorption of H_2 by a Mg film. The ratio of adsorbed H atoms to Mg atoms may be as high as 1 : 6. The adsorbed H exerts a v.p., which increases with concn. and rise of temp. The H is also liberated by bombardment with electrons with velocities as low as 4 volts, or by CO^+ ions. H. J. E.

Adsorption. V. Sorption of vapours by activated charcoal. L. J. BURRAGE (Trans. Faraday Soc., 1933, **29**, 665—672; cf. this vol., 898).—The effect of the C_xO_y complex existing at the surface of C on the sorption of H_2O vapour has been studied. The H_2O isothermal at 25° and 23·76—8 mm. consists of a series of steps. When the pressures at which the breaks occur are plotted against their sequence a smooth curve is obtained, especially after flushing out the system (cf. B., 1929, 153). A similar course has been observed in the CCl_4 isothermal at pressures < 4 mm. Little C_xO_y is removed by evacuating at 110°. Evacuation at 800° "cleans up" a large no. of pores, giving rise to an increased adsorptive area; the C_xO_y is then removed as CO, whilst it is removed as CO_2 when the system is flushed out at 100°. E. S. H.

Change in the form of [adsorption] isotherms in the progressive activation of charcoal. B. BRUNS and O. ZARUBINA (Kolloid-Z., 1933, **46**, 279—287).—When C is activated by heating at 850° in a current of CO_2, its adsorptive power for vapours of C_6H_6, Et_2O, and H_2O and for aq. solutions of BuOH, $PrCO_2H$, and PhOH increases progressively with the duration of activation for saturated systems. At lower pressures or concns. the adsorptive power reaches a max. when about 30—50% of C has been lost by combustion. The mechanism of activation is discussed. E. S. H.

Prolongation of life of β-chloro-β-phenylethylamine on charcoal. H. FREUNDLICH and G. SALOMON (Z. physikal. Chem., 1933, **166**, 179—204).—The adsorption of $CHPhCl{\cdot}CH_2{\cdot}NH_2,HCl$ and of $CH_2Br{\cdot}CH_2{\cdot}NH_2,HBr$ from aq. solution on blood charcoal at 0° and 25° follows Freundlich's isotherm and with each the cation is adsorbed more than the anion. The conversion of $CHPhCl{\cdot}CH_2{\cdot}NH_2$ (I) into styreneimine hydrochloride (II) in NaOH solution is strongly retarded by C at 25°. The unimol. velocity coeff., k, decreases as reaction proceeds until the concn. of (I), c, falls to a certain val. which, for a given proportion (m) of C, is independent of the initial concn., a; k subsequently remains const. The initial fall in k is the more pronounced for a given m the higher is a. For a given a the retarding action of the C increases rapidly with m. The retardation is ascribed to the mols. in the unimol. film being oriented so that the reacting groups, Cl and NH_2, rarely come in contact; the only mols. which react are those which reach the interior of the liquid phase. Corresponding with this theory the retardation diminishes rapidly with rise of temp. In the first phase of the reaction, when x is larger, multimol. films are present, and to these and to the non-homogeneous character of the C surface are attributed the peculiarities of this part of the reaction. The formation of (I) from (II) in HCl solution is accelerated by C, and in neutral solution the equilibrium is displaced in favour of (I). The reaction of $CH_2Br{\cdot}CH_2{\cdot}NH_2$ (A., 1930, 551) occurs, not within the liquid phase, but on the C surface. R. C.

Adsorption of gases on palladium oxide. P. V. MCKINNEY (J. Amer. Chem. Soc., 1933, **55**, 3626—3632; cf. this vol., 134, 913).—Between −78° and 218°, O_2 is not adsorbed either by PdO or by PdO partly reduced by CO. CO_2 is adsorbed reversibly, but the adsorption decreases with increased reduction. Adsorption of CO on PdO is physical, but that on Pd is activated at −78°. Chemical adsorption of CO on PdO increases slowly from 0° to a max. at 110° and the gas evaporates only as CO_2, desorption being incomplete below 218°. The rates of adsorption indicate a complex process, and the adsorption of CO by Pd is so strong that reduction of adjacent PdO is not accelerated. J. G. A. G.

[Adsorption of] atomic hydrogen on glass and calcium fluoride. J. H. DE BOER and J. J. LEHR (Z. physikal. Chem., 1933, **B**, **22**, 423—430).—On glass about 3×10^{15} atoms are adsorbed per sq. cm., a monat. film being formed. A vac.-sublimed CaF_2 film takes up more H and retains it more tenaciously, and adsorption is more rapid. The H is released only on heating, presumably due to sintering which reduces the surface area of the CaF_2. R. C.

Relation between van der Waals and activated adsorption on chromium oxide gel. J. HOWARD (Nature, 1933, **132**, 603).—Low-temp. van der Waals isotherms have been determined for Cr oxide gel on which a known amount of high-temp. adsorption of H_2 (I) had taken place. (I) markedly diminishes the van der Waals adsorption. Slow adsorption, often described as chemical, secondary, or activated, is thus a true surface phenomenon. L. S. T.

So-called negative adsorption and vapour-pressure isotherms with permutites and clays. P. SZIGETI (Kolloid-Beih., 1933, **38**, 99—176).—Negative adsorption is observed with permutites and clays only when the substances have been dried at 110°. In a series of chloride solutions the extent of negative adsorption increases with the hydration of the cation (alkali or alkaline earth) of the adsorbent. The phenomenon is also observed in solutions of sucrose or EtOH. In all cases the degree of adsorption increases with dilution. The cause of the phenomenon is attributed to incipient dehydration during drying, resulting in a subsequent transfer of H_2O from the aq. phase. The H_2O v.-p. isotherms show that at equal v.p. the H_2O content of the permutites and clays increases with the degree of hydration of the cation, and is always greater for the permutites; the exponent of the Freundlich isotherm is also greater for permutites. A hysteresis between hydration and dehydration is established only for H-permutite. The modes of binding of the H_2O are discussed. E. S. H.

Sorption of water by asbestos fibre. L. M. PIDGEON and A. VAN WINSEN (Canad. J. Res., 1933, **9**, 153—158).—The relative humidity (R.H.)–% H_2O curve is sigmoid, but no hysteresis is observed between R.H. 30% and 79%; at 90% R.H. the sorption is 2·5%. Below 70% R.H. equilibrium is reached in a few min. and the vals. agree with the adsorption isotherm $x/m=kp^{1/n}$; above 70% R.H. equilibrium is reached more slowly, and sorption increases more rapidly owing to condensation of liquid in the capillaries. A. G.

Sorption of organic vapours by resinous and cellulosic materials. C. H. WINNING and J. W. WILLIAMS (J. Amer. Chem. Soc., 1933, **55**, 3560—3569).—The adsorption of $CHCl_3$ vapour by glyptal, phenophthalein benzoate, benzylcellulose, and cellulose acetate and of Et_2O by natural resins is succeeded by condensation of sorbate in capillary spaces, the capillaries being opened up when the structural units have been completely covered with sorbate mols. Sorption and desorption are not reversible, and although the cellulose derivatives afford closed hysteresis curves, the reduction of the partial pressure of vapour to very low vals. over the resinous materials causes only partial, if any, desorption. Regular arrangement of mols. in the sorbent is believed to favour almost complete removal of sorbed vapours at low partial pressures, whilst random arrangement may lead to conditions resulting in retention. The heats of the several sorption processes have been calc. J. G. A. G.

Behaviour of the barium sulphate micelle towards Congo-red. E. R. RIEGEL and J. RIDSON, jun. (Kolloid-Z., 1933, **64**, 304—307).—The micelle $(BaSO_4)_xBa^{\cdot\cdot}$ adsorbs the anion of Congo-red, forming a red ppt., whilst no adsorption occurs with the micelle $(BaSO_4)_xSO_4^{\prime\prime}$. The micelles may thus be separated. The system should be adjusted to p_H 3·3—3·5. E. S. H.

Exchange of cations by sulphite-cellulose. C. DU RIETZ (Svensk Kem. Tidskr., 1933, **45**, 185—195).—Cellulose (I), although insol. in H_2O, is characterised by an acid group analogous to permutite. Sulphite-(I) has a very strong acidic group (HSO_3) capable of quantitatively accepting cations, a weakly acidic group (probably CO_2H), and a very weak acidic group (probably of a phenolic nature). In agreement with the Donnan membrane equilibrium the partition of equi-valent ions in (I)–H_2O systems is independent of changes in the concn. of the external phase; the absorption of these ions with the greatest valency is, however, favoured. Thus sulphite-(I) partly saturated with $Na^{\cdot}$ readily takes up $Cu^{\cdot\cdot}$ (cf. B., 1931, 670; 1932, 222) and the $Cu^{\cdot\cdot}$ ions are less easily removed by subsequent washing than the $Na^{\cdot}$ ions. The "total lignin acid" can be determined by rapid treatment with $Cu^{\cdot\cdot}$, washing with H_2O, pulping in aq. KCNS in presence of KI, and titrating with 0·01*N*-$Na_2S_2O_3$. F. O. H.

Effect of glycerol on absorption of lactic acid by gels. L. J. WEBER and A. N. RAO (Biochem. Z., 1933, **262**, 119—130).—Absorption of H_2O by gelatin gels (I) is markedly inhibited by glycerol (II), but is increased by lactic acid (III), and the swelling of (I) by (III) in high concns. can be prevented by addition of (II). Diffusion of H_2O or (III) into (I) is inhibited by increasing concns. of (II) in (I), but the absorptive power of (I) for (III) is little affected by the (II) concn. of the solution. Gelatin sols behave like (II) and natural membranes like (I). W. McC.

Capillary systems. XVI (1). Passage of a jet of material particles through a framework. E. MANEGOLD and W. VON ENGELHARDT (Kolloid-Z., 1933, **64**, 307—316; cf. this vol., 774).—Mathematical. E. S. H.

Theory of the phenomenon of liquid drops on the surface of the same liquid. L. D. MAHAJAN (Kolloid-Z., 1933, **65**, 20—23).—The conditions for the formation of a film of air or other medium between a drop and a flat surface of the same liquid are discussed. E. S. H.

Surface solutions. Two-dimensional liquids and unimolecular layers. A. MARCELIN (Kolloid-Beih., 1933, **38**, 177—336).—A comprehensive survey of published work on surface films on H_2O, Hg, and solid surfaces. E. S. H.

Oriented molecules at the solid–liquid interface and the non-specific nature of ordinary adsorption. W. D. HARKINS (Physical Rev., 1932, [ii], **39**, 190).—The heats of immersion (I) of different powdered solids in a series of liquids are approx. equal when no chemical reaction occurs, and the heat evolved may be considered as due, in general, to non-sp. or non-chemical forces. The large increase in (I) produced by addition of polar groups shows that the mols. at the interface are oriented with their polar groups towards the solid and their non-polar groups towards the liquid. L. S. T.

Preparation and properties of thin films of lead sulphide, with special reference to their detector action. I. G. BRUCKMANN (Kolloid-Z., 1933, **65**, 1—11).—Mirrors of PbS are formed by mixing solutions of 4% $Pb(OAc)_2$, 2% $CS(NH_2)_2$, and 2% NaOH. The reaction depends on the catalytic decomp. of a complex salt of $Pb(OAc)_2$ and $CS(NH_2)_2$;

the temp. coeff. is 2·3. Compounds of As, Sb, or Sn, which form sulphides sol. in NaOH, retard the process, whilst particles of dust or of ppt. accelerate it. The amount of PbS pptd. is proportional to the surface; the nature of the surface on which the mirror is deposited has no influence, except with Cu, brass, and bronze, when some Cu_2S is formed. The amount of ppt. is greater when nuclei are already present on the surface. The theory of mirror formation is discussed. E. S. H.

Wetting experiments on hydrophilic and hydrophobic powders in a system of two non-miscible liquids. III. E. Berl and B. Schmitt (Kolloid-Z., 1933, 65, 93—100).—The condition for the separation of two powders by shaking with two immiscible liquids is a difference in wettability of the powders, but this property may be affected in either direction by the presence of a selectively adsorbable substance. A mixture of C and SiO_2 can be separated by shaking with C_6H_6–H_2O mixture, but not when crystal-violet is added; on the other hand, C and $CaCO_3$ can be separated by adding "Tuchrot-*C*." The separation of PbS and ZnS depends on the age of the powder mixture, as the relative wettability is thereby affected; separation of old mixtures may be effected by adding K Et xanthate. A mixture of ZnS and $CaCO_3$ can be separated by K Et xanthate after addition of $CuSO_4$. E. S. H.

Solid–liquid–air angles and their dependence on the surface condition of the solid. F. E. Bartell and A. D. Wooley (J. Amer. Chem. Soc., 1933, 55, 3518—3527).—Corresponding angles of contact are calc. from the heights of columns of 1-$C_{10}H_7Br$ and $C_2H_2Br_4$ advancing and receding in Pyrex and SiO_2 capillaries which have been subject to various pretreatments. Receding angles, *R*, are largely independent of pretreatment and are equilibrium vals. characteristic of the given solid–liquid pair, whereas advancing angles, *A*, are very sensitive criteria of the condition of a solid surface, since a particular pretreatment affords a sp. reproducible val. of *A* for a given liquid. *A* falls rapidly during 1 hr. to a const. val. which decreases, with rise in the temp. of the heat-treatment, to a val. equal to *R* for the particular solid–liquid pair. The contact angle formed by an advancing or a receding liquid is apparently characteristic of the system as it then exists, and thus the contact angle is a very sensitive criterion of the actual energy relations. J. G. A. G.

Surface tension and complex formation in non-aqueous solutions of salts. P. P. Kozakevitsch and N. S. Kozakevitsch (Z. physikal. Chem., 1933, **166**, 113—135).—The surface tension, γ, of solutions of electrolytes and non-electrolytes in various org. solvents has been measured at room temp. For most solutions γ increases linearly with the concn., *c*, at the higher concns., and the departure from linearity in dil. solutions is the more marked the greater is the tendency of the salt to complex formation. Since γ is influenced by several factors, there is rarely any discernible connexion between γ and the surface tension of the pure solute. The degree of dissociation of a salt, so far as it increases the no. of dissolved particles, influences the negative surface activity, *A*, comparatively slightly. Particularly in conc. solutions, *A* runs parallel with the degree of solvation of the undissociated salt mols., *B*. Whilst the cations follow the normal lyotropic series, Li> Na>K, the anion series is reversed, I>Br>Cl, owing to the lyotropic effects being determined by *B*, which is itself decided by the principle of ionic competition (A., 1931, 1231). For solutions in homologous series of alcohols, *A* decreases with increase in the no. of C atoms. The higher alcohols and EtOH have a differentiating action on various salts in so far as *A* is concerned. The γ–*c* curve of C_5H_5N–HCO_2H mixtures has a max. corresponding with the compound $C_5H_5N,4HCO_2H$. R. C.

Osmosis in systems consisting of water and tartaric acid and containing three liquids, separated by two membranes. II. F. A. H. Schreinemakers and H. H. Schreinemachers (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 629—635; cf. this vol., 459).—The influence of the position of the cellophane and pig's bladder membranes, and the use of a compound membrane of the two, were investigated. N. M. B.

Osmotic pressure and viscosity of cellulose nitrate solutions. E. H. Buchner and H. E. Steutel (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 671—677).—The osmotic pressure is not proportional to the concn., even in dil. solutions, and is assumed to consist of two parts, one proportional to the mol. concn., and one representing the interaction with the solvent ($COMe_2$). The viscosity relations are normal. N. M. B.

Calcium oxalate rings. A peculiar case of periodic precipitate formation. H. Doring (Naturwiss., 1933, **21**, 675).—Rings of CaC_2O_4 have been observed under the microscope when a scale leaf of onion (*Allium cepa*) is treated with 0·1*N*-$K_2C_2O_4$. This is an example of non-colloidal periodic pptn., and is a transition between periodic separation of crystals in capillaries and Liesegang rings. A. J. M.

Change of the refractive index of mixtures of ketones and alcohols by small amounts of acid. T. Tomonari (J. Soc. Chem. Ind. Japan, 1933, **36**, 485—487B).—Amounts of mineral acids or of AcOH > about 0·0002% change the n of mixtures of MeOH with $COMe_2$ or *cyclo*hexanone, but not of the pure substances. This is the cause of the change produced by impure cellulose nitrate. A. G.

Properties of quinine dissolved in absolute alcohol. C. Lapp (Arch. phys. biol., 1932, **10**, 42—66; Chem. Zentr., 1933, i, 2254).—Polarimetric and viscosity measurements are reported. The no. of EtOH mols. combined with 1 mol. of quinine increases from 8·1 in a 10·1% solution to 35·4 in a 0·31% solution. Forty EtOH mols. are supposed to form a unimol. layer on the surface of a quinine mol. A. A. E.

Terpenes, sesquiterpenes, and related compounds. III. Molecular depression of the f.p. of camphene. IV. Fusion diagrams of the systems camphene–naphthalene and camphene–diphenyl. S. Uchida and K. Shimoyama (J. Soc. Chem. Ind. Japan, 1933, **36**, 525—527B, 528—529B).

—III. The difference between the limiting vals. for camphene in $C_{10}H_8$ and Ph_2 may be due to the formation of solid solutions.

IV. The diagrams are discussed. J. L. D.

Manganous sulphate. F. Hammel (Compt. rend., 1933, **197**, 684—686).—Cryoscopic determinations with aq. $MnSO_4$ show no differences when different hydrates, or differently prepared sample of anhyd. $MnSO_4$ (cf. A., 1932, 32), are used. C. A. S.

Determination of the size of ultramicroscopic particles by the interference microscope. A. Klimmeck (Z. Physik, 1933, **85**, 68—84). A. B. D. C.

Lower limit of particle size in disperse systems. Gogoberidze (Kolloid-Z., 1933, **65**, 24—25).—The lower limit is expressed by $2\alpha\partial/(p'-p)(1033-\partial)$, where p' and p are respectively the v.p. over curved and plane surfaces, α is the surface tension, and ∂ the v.d. The limit rises with rising temp. E. S. H.

Application of the centrifuge to the classification of suspensoids according to their size. S. A. Kamenetzki (Gorno-Obogat. Delo, 1932, No. 2—3, 77—79). Ch. Abs.

Influence of convection on Brownian movement. III. M. Satô (Z. Physik, 1933, **85**, 403—408).—The effect of convection becomes appreciable only in rarefied gases. A reply is given to Sitte (cf. this vol., 901). A. B. D. C.

Size of electrolytically generated gas bubbles. B. Kabanov and A. Frumkin (Z. physikal. Chem., 1933, **166**, 316—317).—Wark's calculations of the size of gas bubbles (B., 1933, 631) agree with the authors' results (this vol., 1016). R. C.

Rate of settling of a suspension as a function of the concentration of the suspensoid. N. A. Held (Gorno-Obogat. Delo, 1932, No. 9, 3—10).—In suspensions containing $> 10^7$ particles per c.c. the rate of settling follows Stokes' law; in those containing 10^7 to 10^9 partial coagulation occurs, and the rate of settling has no definite val., whilst in those containing 10^9 to 10^{11} coagulation is complete and the rate of settling depends on the concn. In the second and third groups introduction of a stabiliser, *e.g.*, OH′, displaces the regions of partial and complete coagulation towards higher concns. In the first group the rate of settling is independent of the presence of sol. salts, coagulation being accomplished only by raising the temp. Ch. Abs.

Preparation and properties of silver sols by reduction of silver halides with formaldehyde. T. I. Taylor and W. H. Cone (J. Amer. Chem. Soc. 1933, **55**, 3512—3515).—Stable reddish-yellow to ruby-red Ag sols are obtained by adding slowly, with vigorous stirring, 250 c.c. of 0·0004*N*-KBr (or KI) to 250 c.c. of 0·004*N*-$AgNO_3$, followed successively by 10 c.c. of 2% aq. CH_2O and 100 c.c. of 0·03*M*-NaOH. Cataphoretic velocities, conductances, and pptn. vals. are recorded. With the exception of Cl′, anions which normally form a Ag salt of solubility $< 0·002$ g. per 100 g. of H_2O stabilise the colloid. The adsorption of Cl′, Br′, and I′ by colloidal Ag is in the ratio 1 : 2 : 57·7; this is discussed with reference to the structure of the sol particles. J. G. A. G.

Colloidal sulphur solutions [prepared] by the action of iodine on sodium sulphide. A. Janek (Kolloid-Z., 1933, **65**, 87).—S sols may be prepared by adding a 5% solution of I in EtOH to dil. aq. Na_2S, but are stable for only 24—36 hr. E. S. H.

Pupa oil emulsion. I. Properties of dispersed system obtained by boiling dried pupa with water. H. Kaneko and K. Yamamoto (Bull. Sericult., Japan, 1933, **6**, 3—4). E. S. H.

Viscosity of emulsions. E. G. Richardson (Kolloid-Z., 1933, **65**, 32—37).—The viscosity of various conc. C_6H_6-in-H_2O and H_2O-in-C_6H_6 emulsions has been determined by the Couette method. The former show marked structure viscosity. The variation with concn. is given by $\eta-\eta_0e^{k\phi}$, where η_0 and η are the viscosities of the dispersion medium and emulsion, respectively, ϕ is the vol. of the disperse phase, and k varies with the particular system. E. S. H.

Viscosity of ferric phosphate sol at different pressures. S. N. Banerji and S. Ghosh (Kolloid-Z., 1933, **65**, 37—44).—The variation of viscosity of $FePO_4$ sols with pressure is greater the purer is the sol. With progressive dialysis the sol becomes unstable and its viscosity increases. The increase of viscosity with increasing concn. is > a linear function, but becomes more linear at higher pressures. The true viscosity is not measured; the property is defined as the "structure-flow coeff." for a given pressure. The viscosity increases with time and with the presence of electrolytes. The "solid" properties of highly viscous lyophilic sols are attributed to orientation of the micelles. E. S. H.

Viscosimetric investigations on solutions of high-molecular natural substances. I. Rubber in toluene. M. Reiner and R. Schoenfeld-Reiner (Kolloid-Z., 1933, **65**, 44—62).—Solutions of crepe rubber in PhMe of concn. 0·08—1·77% exhibit structure viscosity and deviate from Poiseuille's law. Below the limit specified the solutions behave as Newtonian liquids. The results are shown to be independent of the viscosimeter and are unaffected by temp. The phenomena cannot be explained by streaming orientation, but there is probably a relatively strong cohesive force between the particles of rubber. E. S. H.

Viscosity and elasticity of sols. B. Rabinovitsch (Z. physikal. Chem., 1933, **166**, 257—269).—Solutions of cellite in dioxan, MeOAc, and furfuraldehyde have been examined in capillary viscosimeters. Over a wide range of pressures and capillary radii and lengths the flow is laminary and stationary. The relation between deformation velocity and shearing stress, P, is $\partial v/\partial r=UP+VP^3$, where U and V are consts. of the material and are independent of the solvent (cf. A., 1930, 32). For low vals. of P this becomes Newton's law. From U and V the viscosity, the modulus of elasticity, and the period of relaxation can be calc. The most dil. sols seem to have the properties of a swollen solid rather than a dil. solution. R. C.

Viscosity of colloids in presence of electrolytes. S. GOPALA and K. MURTY (Kolloid-Z., 1933, **64**, 319—320).—Theoretical. The change of vol. and rigidity of the particles of a sol under the influence of additions of electrolytes is held to explain the observed changes of viscosity. E. S. H.

Structure of emulsoid sol particles and their hydration film. N. H. KOLKMEIJER and J. C. L. FAVEJEE (Nature, 1933, **132**, 602—603).—The majority of the *X*-ray lines of powdered cellulose and starch are probably due to the crystal structure of the hydration film surrounding the particles and not to the substance itself. The H_2O film has the structure, more or less deformed, of ordinary ice. L. S. T.

Emulsions. I. J. B. PARKE and H. GRAHAM (J.C.S., 1933, 1214—1217).—The effect of the addition of H_2O on the viscosity of the following emulsions has been examined: C_6H_6–Na oleate (I)–H_2O; tetrahydronaphthalene (II)–(I)–H_2O; C_6H_6–sulphonated fish oil (III)–NaOH–H_2O; (II)–(III)–NaOH–H_2O. In the case of emulsions stabilised by (I) the η–% H_2O curves are smooth, but with (III) there is an abrupt change of η when about 25% of H_2O has been added and a smaller one at approx. 60% H_2O. These changes are correlated with the formation of multiple emulsions preceding a change in the type of emulsion. D. R. D.

Electrical properties of colloids. III. Discrepancies between activity and conductivity in colloid solutions. J. MUKHERJEE (Kolloid-Z., 1933, **65**, 72—77; cf. this vol., 460).—The Cl′ activity of $Al(OH)_3$ sols has been determined by means of the Ag–AgCl and Hg–Hg_2Cl_2 electrodes. Concordant vals. are obtained by these methods. Discrepancies between observed and calc. activities are shown by this system and also by SiO_2 sol containing NaCl. E. S. H.

Physico-chemical investigations on ferric oxide sols. I. Charge of ferric oxide sols on dilution. II. Charge in irregular series. A. LOTTERMOSER and T. Y. CHANG (Kolloid-Z., 1933, **64**, 268—279; **65**, 62—72).—I. Determinations of migration velocity, electrical conductivity, and [Cl′] of $Fe(OH)_3$ sols show that when the sols are diluted with the ultra-filtrate the ζ potential remains unchanged, whilst the dissociation of the colloidal electrolyte increases. When the sols are diluted with H_2O, Cl′ is transferred from the particles to the liquid medium, so that const. [Cl′] is maintained over a wide concn. range, and the ζ potential falls.

II. An electrophoretic investigation of the electrical properties of positively-charged $Fe(OH)_3$ sols shows that as KH_2PO_4 is gradually added the ζ potential is lowered, flocculation beginning at a crit. potential, whilst with excess of KH_2PO_4 peptisation occurs, forming a negatively-charged sol, the charge of which is reduced at still higher concns. of KH_2PO_4. $H^{\cdot}$ and OH′, introduced by the KH_2PO_4, do not influence the course of the phenomena. Up to the discharge point Cl′ is liberated from the particles progressively in exchange for PO_4''', but thereafter PO_4''' is adsorbed without exchange until the sol acquires its max. negative charge, after which the amount of adsorbed PO_4''' remains const. E. S. H.

Variation of the charge of copper ferrocyanide hydrosol in presence of electrolytes and non-electrolytes. S. G. CHAUDHURY (J. Indian Chem. Soc., 1933, **10**, 431—452).—The influence of the method of prep., of centrifuging, and of adding electrolytes, *e.g.*, KCl, with and without EtOH on the cataphoretic velocity of $Cu_2Fe(CN)_6$ sols has been investigated. The results may be qualitatively explained on the basis of Mukherjee's double layer theory. An increase of the velocity is possible without adsorption of similarly charged ions or increase of the dielectric const. Coagulation cannot be regarded as occurring at a crit. potential, and different electrolytes at concns. having the same coagulating effects do not necessarily depress the charge on the colloidal particles to the same extent. H. F. G.

Cataphoretic behaviour of gas-charged particles. A. PILOJAN, N. KRIVORUTSCHKO, and N. BACH (Kolloid-Z., 1933, **64**, 287—293).—Platinised and non-platinised C activated in air at high temp. give positively-charged particles in presence of air in H_2O, dil. HCl, or NaOH. In higher concns. of NaOH a reversal of charge may occur, probably by reason of the formation of a surface layer of acid oxide. After activating in air at 400° for 15 hr. C is negatively charged, but the charge is reversed by $La^{\cdot\cdot\cdot}$ or $Th^{\cdot\cdot\cdot\cdot}$. Platinised C which has been heated in H_2 is negatively charged in H_2O, dil. HCl, or NaOH, and is converted into a positive suspension by adding $Th^{\cdot\cdot\cdot\cdot}$. With sufficient Pt content, the charge of positively-charged particles may be reversed by admitting an atm. of H_2. E. S. H.

Isoelectric point of orange-seed globulin. D. C. CARPENTER and F. E. LOVELACE (J. Amer. Chem. Soc., 1933, **55**, 3738—3740).—The electrophoretic velocity of the globulin (prep. described) is measured in citrate and phosphate buffers at p_H 1·5—7·8, and the electrical charge on the particle calc. The isoelectric point is at p_H 5·23 or c_H $5{\cdot}9\times10^{-6}$. H. B.

Colloidal chemical analysis. II. J. MUKHERJEE, S. ROYCHOUDHURY, S. K. DAS-GUPTA, A. K. SEN, B. MAZUMDAR, and A. CHATTERJEE (J. Indian Chem. Soc., 1933, **10**, 405—430; cf. A., 1931, 1123).—The observed sp. conductivities of $Fe(OH)_3$ sols are much > the vals. calc. from the activity measurements, and it is improbable that the high vals. are entirely attributable to the (unknown) [$H^{\cdot}$], whilst with $Al(OH)_3$ sols the observed vals. are the lower and cannot be explained on the assumption that the current carried by the colloidal particles and associated mobile ions is determined by the cataphoretic speed and free charge. With SiO_2 sols approx. agreement between the two sets of vals. is obtained. In SiO_2 sols containing NaCl the activity of the $H^{\cdot}$ rises more rapidly than the sol concn. as the latter is increased, although the total electrolyte concn. corresponds with that of a dil. solution. The significance of these results is not yet apparent. H. F. G.

Magnetic properties of nickel colloids. C. G. MONTGOMERY (Physical Rev., 1932, [ii], **39**, 163—164).—Magnetic data for sols prepared by dissociating Ni carbonyl dissolved in C_6H_6, PhMe, and *p*-

cymene and by the Bredig method in H_2O and in $Pr^{\beta}OH$ are recorded for fields of 3760 and 3500 gauss, respectively. The uncombined Ni ranges from 0·75 to 14·2%. A possible explanation is advanced. L. S. T.

Study of coagulation by the coagulograph. R. PROCHAZKA (Chim. et Ind., 1933, 29, Spec. no., 281—283).—The separation of O_2 has been examined by means of a dropping Hg electrode. C. W. G.

Nephelometric studies of coagulation processes caused by acceleration of hydrolysis by heating. T. KATSURAI (Kolloid-Z., 1933, 64, 317—319).—The turbidity of aq. $AlCl_3$, $MnCl_2$, and $CoCl_2$ is increased by heating at $> 160°$ and cooling, whilst aq. $NiCl_2$, $CrCl_3$, and $Pb(NO_3)_2$ show no change. The turbidity of aq. $FeCl_3$ is reduced by adding NaCl, $BaCl_2$, or $AlCl_3$, the effect increasing in the order given. E. S. H.

Influence of hydrophilic colloids and adsorbent substances on the solubility of sparingly soluble substances. II. Influence of gum arabic. H. BRINTZINGER and H. G. BEIER (Kolloid-Z., 1933, 64, 300—304; cf. this vol., 902).—Gum arabic increases the solubility in H_2O of BzOH, salicylic acid, cinnamic acid, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, hippuric acid, *o*- and *p*-$C_6H_4Br{\cdot}CO_2H$, camphoric acid, anisic acid, and strychnine, decreases that of anthranilic acid, and has no influence on the solubility of *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. E. S. H.

Continuity of phases during the sol–gel transformation. S. PRAKASH (Kolloid-Z., 1933, 64, 293—300).—The phase rule is applied to colloid systems, assuming an additional degree of freedom due to the electric charge. A two-component gel is in equilibrium at a quintuple point. Experiments on the dehydration, and variation of $[H^{\cdot}]$, viscosity, electrical conductivity, and opalescence during the sol–gel transformation of $Ce(OH)_3$, $Zr(OH)_4$, $Al(OH)_3$, Th arsenate, phosphate, and molybdate afford no evidence of discontinuity. E. S. H.

Changes of surface and structure of gels and minerals at high temperatures. J. SPLICHAL (Chim. et Ind., 1933, 29, Spec. no., 757—781).—SiO_2 gels partly dehydrated at temp. up to 500° were tested for adsorptive power (I) over 10% H_2SO_4 at room temp. For unheated samples (I) varies according to method of prep. and age. It falls but little up to 250°, but is much less at 500°, which reduces the effective surface. Similar tests show that (I) is considerable for a siliceous earth, but very small for crushed rocks consisting of SiO_2. Ignition at 1000° does not affect the structure as shown by *X*-ray analysis, but (I) is destroyed. There is no sign of tridymite rays. At higher temp. cristobalite is formed. Al_2O_3 gel still absorbs 20% H_2O after heating at 500° and (I) is still evident after heating at 1000°. Definite interference rings were not found below 1000°, when those of corundum appeared. The region of stability of γ-Al_2O_3 is thus more limited than is usually believed. Bauxite adsorbs much less H_2O than Al_2O_3 gel, and bohmite, Al_2O_3,H_2O, is the principal product. Fe_2O_3 gels heated at 200° show considerable absorption, but at 250° transformation into hæmatite occurs, with a sharp reduction in the H_2O adsorbed. Samples of natural limonite etc. studied were found to be solid solutions of α-Fe_2O_3,H_2O (goethite) and H_2O. C. I.

Morphology of chemical reactions in colloidal media. IV. Significance of auto-form catalysis and form catalysis in colloidal media in explanation of morphological phenomena. F. M. SCHEMJAKIN (Kolloid-Z., 1933, 64, 324—327; cf. this vol., 780).—The formation of periodic and similar structures in gels is discussed in relation to biological phenomena. E. S. H.

Shaking (thixotropy) effect with cellulose solutions followed by vapour-pressure measurements. M. ULMANN (Z. physikal. Chem., 1933, 166, 147—155).—The v.p. (p) of colloidal dispersions of cryst. cellulose acetate (I) in glacial AcOH is initially $>$ that of the pure solvent, but on keeping falls to that val. This change is reversible, p being raised again by shaking. This effect is absent with mol. dispersion of (I) in AcOH. R. C.

Cinematographic swelling analysis in the dark field by means of the micro-manipulator. I. Mechanism of swelling of cellulose threads, starch grains, and similar structures. K. HESS and B. RABINOVITSCH (Kolloid-Z., 1933, 64, 257—268).—A cinematographic study of the swelling of cellulose, starch, wool, silk, and gelatin indicates that the liquid penetrates the skin of the colloidal substances and reacts with the contents, forming a liquid system which is under considerable internal pressure. The internal liquid is ejected when the skin is punctured by the micro-manipulator. E. S. H.

Mechanism of enzyme action. XI. Cryolysis and charging with gas of lyophilic colloids. I G. WEISS and F. F. NORD (Z. physikal. Chem., 1933, 166, 1—15).—The increase in the surface tension, γ, of 10^{-4} to 10^{-6}% aq. Na oleate (I) caused by absorption of C_2H_4 or C_2H_2 is $>$ otherwise if the solution has previously been frozen. The γ–concn. curves of frozen and unfrozen solutions intersect at about 10^{-3}%. Absorption of N_2O depresses γ. For 10^{-6} to 1% ovalbumin (II) solutions γ is increased by absorption of C_2H_4 and C_2H_2, and, to a smaller extent, by the absorption of N_2O; in each case the increase is greater if the solution has previously been frozen. Gelatin (III) sols behave similarly. The solvent power for C_2H_4 and C_2H_2 of solutions of (I), (II), and (III) is usually increased by a preliminary freezing. The above observations are correlated with changes in the degree of dispersity in accordance with Nord's theory of cryolysis. R. C.

Plant colloids. XXXIV. Particle sizes of oxidised starches, determined by the osmotic and chemical methods. M. SAMEC (Kolloid-Z., 1933, 64, 321—323; cf. this vol., 811).—Fair agreement is reached in the determination of the mol. wt. of six sol. starches by osmometry and by neutralisation of the acid groups formed by oxidation. E. S. H.

Physical chemistry of starch and bread making. XIII. Comparative investigation of peptisation of various native starches with much water. J. R. KATZ and T. B. VAN ITALLIE (Z.

physikal. Chem., 1933, **166**, 27—42; cf. this vol., 903).—In the peptisation the changes in the vol. of decantate, v, in the % of doubly-refracting granules, and in the X-ray diagram in general run parallel. When the end state has approx. been reached at a given temp. the proportion of granules peptised increases with rise of temp. On peptisation the original spectrum is replaced by a V-spectrum. The changes in v, the proportion of sol. starch, and the X-ray diagram indicate that there is a temp. below which no peptisation occurs. The granules in a given specimen of starch differ in their resistance to peptisation. The above parallelism is not, however, always quite perfect, suggesting that peptisation is a complex phenomenon which is the resultant of several inter-related processes. R. C.

Displacement of equilibrium by variation of mass. J. E. VERSCHAFFELT (Compt. rend., 1933, **197**, 683—684).—An error in Étienne's calculation (cf. this vol., 783) is pointed out. C. A. S.

Conditions of equilibria between two phases. G. ANTONOFF (Kolloid-Z., 1933, **64**, 336—337).—Polemical (cf. Taubmann, this vol., 222). E. S. H.

Influence of the methyl, ethyl, and phenyl radicals on the association of salicylic acid derivatives. K. KALINOWSKI (Rocz. Chem., 1933, **13**, 384—398).—The mol. polarisations of Ph, Et, and Me salicylate in C_6H_6 at 40·2° are respectively 256·8, 207·5, and 153·4; the mols. are of the dipole type, and are increasingly associated as the concn. rises and the temp. falls. In solutions containing both Ph and Et salicylate association is $>$ for each ester separately, and occurs between both similar and dissimilar mols. R. T.

Dissociation constant of hypochlorous acid: glass-electrode potential determinations. J. W. INGHAM and J. MORRISON (J.C.S., 1933, 1200—1205).—Potentiometric titration of aq. HOCl with aq. NaOH indicates that the apparent dissociation const., K', $=3{\cdot}47\times10^{-8}$ at 18°. It is calc. that the true const., K, is $2{\cdot}95\times10^{-8}$. D. R. D.

Ionisation constant of monochloroacetic acid, at 25°, from conductance measurements. B. SAXTON and T. W. LANGER (J. Amer. Chem. Soc., 1933, **55**, 3638—3645).—The conductances of 0·00008—0·031N-HCl, $\cdot CH_2Cl\cdot CO_2H$, and their Na salts have been determined. The data are consistent with Shedlovsky's extension of Onsager's equation. The val. $K_a=1{\cdot}396\times10^{-3}$ is derived for the thermodynamic ionisation const. of $CH_2Cl\cdot CO_2H$. At concn. $>0{\cdot}01N$, this val. decreases. From new data for AcOH K_a—$1{\cdot}759\times10^{-5}$. J. G. A. G.

Dissociation of acids in salt solutions. VII. Dissociation constants and activity functions of hydroxy- and ketonic acids in sodium and potassium chloride solutions. E. LARSSON (Z. physikal. Chem., 1933, **166**, 241—253; cf. this vol., 780).—The introduction of OH at the α-C atom of AcOH, $EtCO_2H$, $Pr^{\beta}CO_2H$, or $Bu^{\beta}CO_2H$ or at the β-C atom of a fatty acid, and the introduction of OEt or OPh into AcOH raise $-\log\phi$, at the higher ionic concns. Substitution of OH in the γ or ε position in a fatty acid has no effect. Exchange of two H atoms in the α position in a fatty acid for O markedly increases $-\log\phi$, but exchange in the β position has only a small effect. It is doubtful if ketonic acids are present as such in solution. R. C.

Ionisation constants [at 25°] of methylated quinolines and of saturated bases isolated from petroleum distillates. W. A. FELSING and B. S. BIGGS (J. Amer. Chem. Soc., 1933, **55**, 3624—3625).—The data refer to sixteen mono-, di-, and tri-methylquinolines. In the Me_1 series, location of the Me on the N-ring leads to higher ionisation consts. Max. vals. of K are obtained with Me at position 2 and positions 2 and 6 in the Me_1 and Me_2 series, respectively. J. G. A. G.

Cuprammonium solution. VI. Equilibrium composition. VII. Effect of sucrose on copper concentration. N. ISHII (J. Soc. Chem. Ind., Japan, 1933, **36**, 487—488B, 488—490B).—VI. Cuprammonium solution prepared by the air-bubbling process contains an excess of Cu which ppts. on keeping. The equilibrium [Cu] increases with increasing $[NH_3]$ and with falling temp. At const. temp. $[Cu]=k[NH_3]^{0{\cdot}702}$ in which concns. are in mg.-mol. per 100 c.c.

VII. Recorded data show the increase in the equilibrium [Cu] caused by the addition of sucrose. At const. temp. and $[NH_3]$, $[Cu]=a+b[\text{sucrose}]$. The absorption spectrum is slightly affected. A. G.

Electrochemistry of complex cuprous-halogen anions. S. VON NARAY-SZABÓ and Z. SZABÓ (Z. physikal. Chem., 1933, **166**, 228—240).—Solutions containing the above ions prepared by electrolysis with a Cu anode of 1—6M aq. solutions of KCl, NaCl, HCl, $CaCl_2$, KBr, and KI have been examined. From the relation of the potential of a Cu electrode in the chloride solutions to the $[Cu^{\cdot}]$ and $[Cl']$ the complex ion has been shown to be $CuCl_3''$. The ratio of the activity of $Cu^{\cdot}$ to the $[CuCl_3'']$ is const. for a given total ionic concn., Γ. The variation of the activity coeff. of $CuCl_3''$, γ, with Γ is given by $-\log\gamma=0{\cdot}234\sqrt{\Gamma}$, from which the dissociation const., $(Cu^{\cdot})(Cl')^3/(CuCl_3'')$ is calc. to be $14{\cdot}5\times10^{-7}$. R. C.

Complex compounds in Eder's solution. G. H. CARTLEDGE and S. L. GOLDHEIM (J. Amer. Chem. Soc., 1933, **55**, 3583—3594).—Partition and f.-p. data suggest that complex formation in Eder's solution involves the following: $2HgCl_2+2C_2O_4''$ $Hg_2Cl_2(C_2O_4)_2''+2Cl'$, $HgCl_2+Cl'\rightleftharpoons HgCl_3'$, and $Hg_2Cl_4+Cl'\rightleftharpoons Hg_2Cl_5'$. This scheme harmonises the apparently contradictory reaction velocity data obtained with Eder solutions by various workers using corresponding ranges of concns. Other formulations do not accord with the results. J. G. A. G.

Amphoteric hydrated oxides, their compounds of higher mol. wt., and solutions thereof. XIX. Hetero- and *iso*-polytungstic acids, particularly periodotungstic acids. G. JANDER and H. WITZMANN (Z. anorg. Chem., 1933, **214**, 145—157; cf. this vol., 580).—Diffusion measurements have been undertaken to elucidate the mode of formation of the periodotungstic acids described by Rosenheim (A., 1899, ii, 743), whose preparative and analytical results are confirmed. The diffusion coeff. of the anions in

solutions 0·05*M* with respect to both Na_2WO_4 and $Na_2H_3IO_6$ corresponds with WO_4'' at p_H 9—8, and with HW_6O_{21}''''' in solutions more acid than p_H 6. At p_H 1·5, in presence of excess of H_5IO_6, condensation takes place with formation of the readily hydrolysable $H_5[I(WO_4)_6]$. The constitution of complex tungstic and molybdic acids is discussed. F. L. U.

Activity coefficients of hydroxyl ion in solutions of calcium hydroxide at 30°. E. P. FLINT and L. S. WELLS (Bur. Stand. J. Res., 1933, **11**, 163—171).—The e.m.f. of the cell $H_2|Ca(OH)_2(c)|KCl$ (saturated)$|HgCl+Hg$ has been measured at 30° for vals. of *c* between 0·050 and 1·199 g. CaO per litre. The p_H vals. and activity coeffs. of OH' are recorded. The data lead to $K_w=1·72\times10^{-14}$. H. J. E.

[Free] energy of formation of aluminium oxide from its elements. W. D. TREADWELL and L. TEREBESI (Helv. Chim. Acta, 1933, **16**, 922—939).—From existing thermal data the free energy of formation of Al_2O_3 is calc. for the range 293·1—2600° abs. The val. is 371·1 kg.-cal. per mol. at 298·1° abs. Measurements of the e.m.f. of the $Al–Cl_2$ cell at 380—460° and of the $Al–O_2$ cell at 1118—1378° abs. lead to concordant vals. F. L. U.

Heat capacities of sodium carbonate and hydrogen carbonate and of silver carbonate at low temperatures. C. T. ANDERSON (J. Amer. Chem. Soc., 1933, **55**, 3621—3623).—The entropies calc. from sp.-heat data within the range 53·5—295° abs. by means of the Debye and Einstein functions are Na_2CO_3 32·5, $NaHCO_3$ 24·4, and Ag_2CO_3 40·0 g.-cal. per 1°. J. G. A. G.

Calcium nitrate. IV. Heats of dilution of solutions of calcium nitrate in water. W. W. EWING and A. N. ROGERS (J. Amer. Chem. Soc., 1933, **55**, 3603—3609).—Heats of dilution of 1·39—19·55*M*-$Ca(NO_3)_2$ have been determined and the total and partial heats of dissolution calc. The partial heats of dissolution of H_2O calc. from v.-p. determinations by means of Kirchhoff's equation are consistent with the calorimetric vals. J. G. A. G.

Transformation of solid ammonium chloride near −30°. A. SMITS and C. H. MACGILLAVRY (Z. physikal. Chem., 1933, **166**, 97—112).—Dilatometric investigation has shown that the transformation is practically discontinuous, being almost completed within a few hundredths of a degree (cf. A., 1930, 986). There is, however, hysteresis. It is inferred that the transformation is heterogeneous, but that the way is paved for it by a homogeneous transformation below the transition region. R. C.

Thermal and *X*-ray characterisation of lattice faults in zinc oxide. R. FRICKE and P. ACKERMANN (Z. anorg. Chem., 1933, **214**, 177—188).—The heat of dissolution in aq. HF of ZnO prepared by heating rhombic $Zn(OH)_2$ increases as the temp. and time of its prep. decrease. A difference of 1·3 kg.-cal. per mol. has been observed. *X*-Ray examination shows the higher energy content to be associated with incompleteness of the crystal lattice. F. L. U.

Thermal equilibrium of acetanilide and certain organic compounds. K. HRYNAKOWSKI and F. ADAMANIS (Rocz. Chem., 1933, **13**, 448—453).—The fusion diagrams for NHPhAc with antipyrine, BzOH, quinine, $NHPh_2$, phenacetin, quinol, menthol, $CO(NH_2)_2$, α-$C_{10}H_7·NH_2$, salipyrine, salol, and ethylurethane indicate complete miscibility of the fused constituents and absence of compound formation. R. T.

Thermal analysis of binary systems containing organic nitrates. T. URBANSKI (Rocz. Chem., 1933, **13**, 399—434).—The fusion diagrams for mannitol hexanitrate (I) and *p*-$C_6H_4Me·NO_2$ (II), *p*-$OMe·C_6H_4·NO_2$ (III), *p*-$OEt·C_6H_4·NO_2$ (IV), and 1-$C_{10}H_7·NO_2$ (V) indicate the formation of unstable 1 : 2 compounds with (II), (III), and (IV), and a 1 : 1 compound with (V). Neither compound nor solid solution formation is found in the systems: pentaerythritol tetranitrate (VI) or (I)–*o*-$C_6H_4Cl·NO_2$, *m*-$C_6H_4(NO_2)_2$ (VII), 3 : 5-dinitroanisole, 2 : 4-$C_6H_3Cl(NO_2)_2$, 1 : 3 : 5-$C_6H_3(NO_2)_3$, 2 : 4 : 6-$C_6H_2Me(NO_2)_3$, $C_{10}H_8$, $CO(NPhMe)_2$, and $CO(NPhEt)_2$; erythritol tetranitrate (VIII)–(I), (II), (VI), and (VII); (VI)–(I), (II), (III), and (V). The solubility of the above nitrates in org. solvents increases in the order (VI)<(I)<(VIII). Secondary reactions take place between (I) or (II) and $C_{10}H_8$ or $CO(NPhR)_2$, with the production of NO_2- or NO-compounds. R. T.

Liquidus in the system diphenylamine–centralite [*s*-diphenyldiethylcarbamide]. I. L. MEDARD. **II.** M. GIUA and G. GUASTALLA. **III.** L. MÉDARD (Chim. et Ind., 1933, **30**, 277—280).—I. In agreement with previous results (A., 1932, 376) an equimol. compound, m. p. 37·5°, is indicated by m.-p. observations. The contrary result obtained by Giua and Guastalla (B., 1933, 333) is ascribed to supercooling and the slow rate of formation of the compound. Centralite forms two compounds with H_2SO_4, containing 0·5 mol. and 2 mols. of H_2SO_4, with m.p. 75° and 71°, respectively.

II. Evidence is adduced that m.-p. and f.-p. curves yield concordant results. It is considered that supercooling is immaterial in determining the form of the curve, and that the existence of a compound of the type described by Médard is improbable.

III. The error resulting from supercooling varies and is particularly great in the neighbourhood of a eutectic. H. F. G.

Acetic acid–acetate solutions. A. W. DAVIDSON and W. CHAPPELL (J. Amer. Chem. Soc., 1933, **55**, 3531—3537).—The solubility of $Sr(OAc)_2$ in pure AcOH (14—122°) lies between the vals. for the Ca and Ba salts. $Sr(OAc)_2$,AcOH exists below 113°. The solubility of $Ni(OAc)_2$ at 30° has no definite val. This is attributed to the presence of colloidal constituents which persist until > 15% of NH_4OAc has been added, when const. vals. are obtained and the solid *phase* is $Ni(OAc)_2$,NH_4OAc,2AcOH. In general, NH_4OAc lowers the solubility of $Ni(OAc)_2$. F.-p. depression curves are discussed. J. G. A. G.

Calcium aluminates. III. Crystallisation of calcium aluminate solutions at 90°. G. ASSARSSON (Z. anorg. Chem., 1933, **214**, 158—166).—The equilibrium diagram at 90° is similar to that previously observed at 20° and 40° (A., 1932, 583). The

presence of $4CaO,Al_2O_3,13{\cdot}5H_2O$, $3CaO,Al_2O_3,6H_2O$, $2CaO,Al_2O_3,9H_2O$, and Al hydroxide in the solid phase was established. The last-named occurs partly as gel, and partly as microcryst. aggregates having the average composition $Al_2O_3,3—3{\cdot}5H_2O$.

F. L. U.

Equilibria between water vapour and vanadium and its oxides. M. KOBAYASHI (Bull. Chem. Soc. Japan, 1933, 8, 231—245).—The oxidation–reduction method has been applied to the determination of the equilibria between H_2O and the phases V+VO and VO+V_2O_3 at H_2O v.p. between $1{\cdot}07\times10^{-3}$ and $6{\cdot}65\times10^{-2}$ atm. The reactions involved are $V+H_2O=VO+H+56{\cdot}4$ kg.-cal., and $2VO+H_2O=V_2O_3+H_2+29{\cdot}6$ kg.-cal. The O pressures at various temp., and the free energies and heats of formation of the oxides, have been calc. H. F. G.

System sodium carbonate–calcium carbonate–water. C. R. BURY and R. REDD (J.C.S., 1933, 1160—1162).—From 15° to 37°, the stable double salt is gaylussite, $Na_2CO_3,CaCO_3,5H_2O$; from 40° to 95° it is pirssonite, $Na_2CO_3,CaCO_3,2H_2O$. D. R. D.

Isothermal equilibrium $CaCO_3$ + aq. NH_4NO_3. A. GUYER and H. SCHÜTZE (Helv. Chim. Acta, 1933, 16, 904—913).—Equilibria have been determined at 25°, 40°, 60°, 80°, and 95°, using 0·5—10*M*-NH_4NO_3. The results are in accord with the measured hydrolysis of NH_4NO_3, vals. of which are recorded. F. L. U.

Thermal investigation of calcium silicophosphates. G. BEHRENDT and H. WENTRUP (Arch. Eisenhüttenw., 1933—1934, 7, 95—102).—An optical pyrometric device for observing very small heat effects in taking heating and cooling curves up to 2000° is described and the results obtained for the equilibria in the $CaO–P_2O_5$ (*A*) and $CaO–P_2O_5–SiO_2$ (*B*) systems are described. In *A* max. on the liquidus occur at 1760° ($4CaO,P_2O_5$) and 1775° ($3CaO,P_2O_5$); these compounds form a eutectic with one another at 1568° and 57·4% CaO. The former yields a eutectic with CaO at 1655° and 62·8% CaO, and the latter undergoes a polymorphic transformation at 1460—1480°. In *B* the compound $5CaO,P_2O_5,SiO_2$ shows a well-defined peak in the liquidus surface at about 1900°; it forms a ternary eutectic at 1600° with CaO and $4CaO,P_2O_5$ and a quasi-binary system with $2CaO,P_2O_5$ and with $4CaO,P_2O_5$. A. R. P.

System CaO–FeO–SiO_2. N. L. BOWEN, J. F. SCHAIRER, and E. POSNJAK (Amer. J. Sci., 1933, [v], 26, 193—284).—The system is characterised by three ternary compounds: $CaFeSi_2O_6$ (hedenbergite, stable below 965°), $2CaO,FeO,2SiO_2$ (iron-akermanite, stable below 775°), and $CaFeSiO_4$, the only one stable in contact with liquid. The min. temp. of existence of liquid is 1093°. Of some thirty invariant points, seven are ternary, but there is no ternary eutectic. There are several solid solutions, including wollastonite (I)–$FeSiO_3$, which extends to 76% $FeSiO_3$, and hedenbergite–$FeSiO_3$, which extends to 80% $FeSiO_3$; the latter is stable only at low temp., and at 940—980° is transformed into the (I) series; with a higher $FeSiO_3$ content orthosilicate and tridymite are formed. The principal orthosilicate solid solutions are Ca–Fe olivines (II) extending from Fe_2SiO_4 (fayalite) through $CaFeSiO_4$ to 59% Ca_2SiO_4. (I) solid solutions and (II) co-exist under certain conditions. The inversion temp. of (I) is 1150°. Neither α- nor β-(I) (solid) dissolves appreciable quantities of CaO or SiO_2. The optical and *X*-ray diffraction properties of many of the solid phases have been determined. The results are discussed in reference to the formation and composition of the minerals concerned. H. F. G.

Determination of high-frequency conductivity of uni-univalent electrolytes. E. GLOWATZKI (Ann. Physik, 1933, [v], 18, 217—232).—The method of Rieckhoff and Zahn (A., 1929, 512) has been improved, and used to determine the conductivity change at high frequencies (3×10^8 Hertz) of HCl and NaCl solutions. Deviations are found from theory for uni-univalent electrolytes. A. J. M.

Electrolytic solutions. VI. Conductance of sodium triphenylstannide, sodium triphenylgermanide, and sodium triphenylmethide in liquid ammonia. C. A. KRAUS and W. H. KAHLER. **VII. Conductance of sodium trimethylstannide and of the sodium salts of phenols and thiols in liquid ammonia.** C. A. KRAUS and E. G. JOHNSON. **VIII. Conductance of ternary salts in liquid ammonia.** C. A. KRAUS and P. B. BIEN. **IX. Conductance of salts in benzene.** R. M. FUOSS and C. A. KRAUS (J. Amer. Chem. Soc., 1933, 55, 3537—3542, 3542—3546, 3609—3614, 3614—3620).—VI. The conductances of $NaSnPh_3$, $NaGePh_3$, and $NaCPh_3$ at dilutions between 59 and 59,000 in liquid NH_3 show that although the solutions are unstable at very low concns. these salts are strong electrolytes, the dissociation const. of $NaSnPh_3$ being approx. four times that of $NaBrO_3$. Earlier conclusions (this vol., 907) receive additional support.

VII. The effects of ion size and constitution on the properties of the electrolyte have been investigated. From the dissociation consts., NaOPh $3{\cdot}82\times10^{-4}$, β-$C_{10}H_7{\cdot}ONa$ $6{\cdot}5\times10^{-4}$, α-$C_{10}H_7{\cdot}ONa$ $8{\cdot}08\times10^{-4}$, EtSNa $22{\cdot}5\times10^{-4}$, PhSNa $36{\cdot}0\times10^{-4}$, and $NaSnMe_3$ 36×10^{-4} (approx.), it is inferred that, in general, the most highly ionised electrolytes are those which have the largest ions, the configuration of which is such that the charges are most completely screened by surrounding atoms or groups. The salts are not sufficiently strong electrolytes to conform to the Debye–Hückel relation and the mass-action effect increases as K decreases.

VIII. The data at −33° for concn. $>10^{-4}N$ show that the salts are, in general, weaker electrolytes than those in VII. The conductivity of $CPh_2{\cdot}ONa_2$ almost coincides with that of $CPh_2{\cdot}ONa$ at low concns., but the results cannot be interpreted on the basis of a simple binary or ternary equilibrium. The importance of the constitutional factor is emphasised by the very low conductivity of $CHPh_2{\cdot}ONa$ as compared with that of $CPh_2{\cdot}ONa$. $(NPh)_2K_2$ behaves as a ternary salt, and in accordance with the Debye–Hückel theory, the conductivity is much < for the binary salts. It appears that the anion of the ternary salt $Na_2(SnPh_2)_2$ dissociates partly into $SnPh_2''$.

IX. By means of an improved technique (cf. this vol., 230) conductivity data for 0·03—$10^{-6}N$-tetra*iso*-

amyl ammonium picrate, thiocyanate, fluoride, chloride, bromide, and iodide in C_6H_6 at 25° have been obtained. Conductance min. occur at concn. between 10^{-4} and $10^{-5}N$ and the rise in conductivity with increasing dilution of solutions $< 10^{-5}N$ agrees with the requirements of the law of mass action. Consistent with the absence of solvation, the apparent sizes of ions are: $I' > Br' > Cl' > F'$. The relation between the form of the conductivity curves and the structure of the electrolytes is discussed. J. G. A. G.

Conductivity of tetramethylammonium salts in methyl and ethyl alcohol. T. H. MEAD, O. L. HUGHES, and (SIR) H. HARTLEY (J.C.S., 1933, 1207—1214).—The conductivities of 0·0001—0·0015N-NMe_4 chloride, bromide, picrate, thiocyanate, nitrate, iodide, and perchlorate in MeOH, and of the first five in EtOH, at 25°, have been determined. The mobility of $NMe_4^{\cdot}$ is 70·1 in MeOH and 28·3 in EtOH. Deviations from the Debye–Hückel–Onsager equation are discussed. D. R. D.

Determination and conductance of sulphuric acid in anhydrous acetic acid. W. C. EICHELBERGER and V. K. LA MER (J. Amer. Chem. Soc., 1933, **55**, 3635—3638).—The conductivity curve for H_2O–AcOH mixtures has a sharp max. at 18% AcOH. H_2SO_4 in anhyd. AcOH is determined by conductimetric titration with $Ba(OAc)_2$. Conductivity data for H_2SO_4 in anhyd. AcOH are recorded. J. G. A. G.

Conductivity of ferric chloride in non-aqueous solution. E. WERTYPOROCH and I. KOWALSKI (Z. physikal. Chem., 1933, **166**, 205—218).—The mol. conductivity, λ, of solutions of $FeCl_3$ in the lower alkyl chlorides increases with the dilution when c, the concn., is $<$ about 0·003 mol. per litre, but at moderate concns. varies little with c owing to the formation of such complexes as $[Fe(EtCl)_n][FeCl_6]$. In solutions in higher alkyl chlorides stable complexes are formed and λ remains const. even at the lowest concns. On keeping these solutions λ increases; this is due to the formation of unsaturated hydrocarbons which are incorporated in the cation, this change being less rapid with primary than with *iso*chlorides. Addition of C_6H_6 to $FeCl_3$ solutions in EtCl or EtBr increases λ owing to formation of ethylbenzenes. For solutions in BzCl and AcCl λ is comparatively high, the $FeCl_3$ entering into salt-like complexes in which the cation contains carbonyl compounds. Solutions in CH_2PhCl, $CHPhCl_2$, and $CPhCl_3$ have a very small λ. For solutions of $AlCl_3$ in the higher alkyl chlorides λ increases with c because HCl is readily lost, forming unsaturated hydrocarbons which are added to the cation. $BeCl_2$ and $ZrCl_4$ give conducting solutions in EtBr. R. C.

Potential of the silver–silver iodate electrode at 25°. J. N. PEARCE and V. I. WIRTH (J. Amer. Chem. Soc., 1933, **55**, 3569—3571).—From the e.m.f. of the cell $Hg,Hg_2Cl_2|0·01—0·2M$-$KCl|0·01—0·2M$-$KIO_3|AgIO_3,Ag$, the potential of the Ag, $AgIO_3$, IO_3' electrode is found to be 0·3569 volt. J. G. A. G.

Thallous bromide. F. ISHIKAWA and Y. TERUI (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, **12**, 755—758).—The e.m.f. of the reversible cell $Tl,Hg|TlBr$ (solid), 0·1M-KBr, HgBr (solid)$|Hg$ at 25° is 0·7945 volt. The mol. heat of formation of TlBr (solid) is −41·51 kg.-cal. The solubility product of TlBr is $3·88\times10^{-6}$. H. F. G.

Effect of glass containers on the electromotive force of Weston normal cells. G. W. VINAL and M. L. HOWARD (Bur. Stand. J. Res., 1933, **11**, 255—275).—Solubility of glass containers changes the acidity of the electrolyte, and hence the e.m.f. of the cell. The effect is emphasised by adding powdered glass to the $HgSO_4$ paste. It is greatest for Pb sealing-in glass. The use of fused quartz cells is suggested. Impurities [CdO, PbO, $Al_2(SO_4)_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, and H_3BO_3], added to the $HgSO_4$ paste, altered the hysteresis effect and the temp. coeff. of the cell. H. J. E.

Variation with concentration of Volta potential in systems $Ag|Ag_{aq}^{\cdot}$ and $Cu|Cu_{aq}^{\cdot\cdot}$. M. ANDAUER and E. LANGE (Z. physikal. Chem., 1933, **166**, 219—227).—In the system $Ag|Ag_{aq}^{\cdot}$ the Volta potential, $\Delta\psi$, has been measured for concns. of 0·1 to $10^{-9}N$. The val. of $d\Delta\psi/d\log c$ is about 0·070 volt, showing that the surface potential of the solution does not change by $> 0·01$ volt for a tenfold change in $[Ag^{\cdot}]$. For the system $Cu|Cu^{\cdot\cdot}$ $d\Delta\psi/d\log(Cu^{\cdot\cdot})$ is approx. 0·029 volt. R. C.

Exchange between atoms and ions of a metal. O. ERBACHER (Z. physikal. Chem., 1933, **166**, 23—26).—In the exchange which occurs when Pb or Bi is in contact with a solution of one of its salts, local action is largely or entirely absent if the metal has previously been etched with HNO_3 (cf. this vol., 468); probably the kinetic exchange involves only a monat. surface layer. R. C.

Electrocapillary experiments. I. G. WALTERS (Phil. Mag., 1933, [vii], **16**, 617—625).—Electrocapillary curves for Hg in aq. KCl (0·02N—saturated), 0·5N-KI, 0·5N-KI+0·5N-KCl, and in EtOH saturated with KCl have been determined. In EtOH the max. is much depressed and is flatter. This is accounted for by the very low ion concn. in the EtOH solution. H. J. E.

Measurement of oxidation–reduction potentials in glacial acetic acid solutions. J. B. CONANT and B. F. CHOW (J. Amer. Chem. Soc., 1933, **55**, 3745—3751).—The oxidation–reduction potentials of benzoquinone, tetrachlorobenzoquinone, indo-*o*-cresol, indothymol, and *o*-cresol-indophenol can be measured in AcOH by the method of mixtures or by titration of the oxidant with $Cr(OAc)_2$. The vals. of E^0_h (calc. from results obtained in a series of buffers of const. ionic strength) plotted against $(p_H)^{AcOH}$ give a straight line with the theoretical slope. The relation of the $(p_H)^{AcOH}$ scale to Hammett and Deyrup's acidity function (A., 1932, 921) is discussed briefly. H. B.

Electrolytic reduction potential of organic compounds. XVI. *p*-Aminoazobenzene. M. SHIKATA and I. TACHI (J. Agric. Chem. Soc. Japan, 1933, **9**, 207—213).—The electrolytic reduction potential of *p*-aminoazobenzene (I), which is more negative than that of azobenzene, is more positive in lower than in higher concn. at any p_H. The two vals. obtained refer to a dissociated and an undissoci-

ated form. The reduction potential of the quinonoid form is more positive than that of the azoid form, and that of the dissociated more positive than that of the undissociated form. The calc. solubility of (I) in H_2O at 25° is $2{\cdot}815\times10^{-4}$ g.-mol. per litre. CH. ABS.

Electrolytic reduction potentials of organic compounds. XVII. Dimethylaminoazobenzene. I. TACHI (J. Agric. Chem. Soc. Japan, 1933, 9, 227—234).—Vals. are more negative at higher concns., except at $p_H < 2{\cdot}2$. CH. ABS.

Potential of free radicals of the triphenylmethyl type in glacial acetic acid solutions. J. B. CONANT and B. F. CHOW (J. Amer. Chem. Soc., 1933, **55**, 3752—3758).—Methods previously described (this vol., 1121) are applied to the determination of the oxidation-reduction potentials of CPh_3, benzyl- and phenyl-xanthyl, and their halochromic salts (cf. A., 1925, ii, 874). H. B.

Oxidation-reduction potential of ascorbic acid. R. WURMSER and J. A. DE LOUREIRO (Compt. rend. Soc. Biol., 1933, **113**, 543—544).—The conflicting opinions as to whether ascorbic acid (I) is capable or incapable of forming a thermodynamically reversible oxidation-reduction system arise from the fact that it forms two such systems of different levels of potential. In one of these a stable (II) and in the other an unstable (III) oxidised form is produced. (III) passes slowly into (II). In oxidation-reduction systems of r_H 17 or greater, (I) is readily reduced by the donation of 2 H, and in systems of lower r_H, by very slow donation of 4 H. NUTR. ABS. (*m*)

Theory of cathodic evolution of hydrogen. J. HOEKSTRA (Z. physikal. Chem., 1933, **166**, 76—79).—Volmer's theory (A., 1930, 1376) is criticised. R. C.

Theory of cathodic evolution of hydrogen. M. VOLMER (Z. physikal. Chem., 1933, **166**, 80).—Hoekstra's criticisms (cf. preceding abstract) are refuted. R. C.

Overvoltage. VI. Mechanism of the transfer of electrolytic hydrogen and oxygen through thin sheets of platinum and palladium. A. L. FERGUSON and G. DUBPERNELL (Trans. Electrochem. Soc., 1933, **64**, 253—279; cf. A., 1932, 1208).—$2N$-H_2SO_4 is electrolysed between Pt or Pd foil electrodes which form the end-walls of the cell and the backs of which are in contact with electrolyte in separate external compartments. During electrolysis the relations between the potentials of the front and back of such an electrode are very irregular: the potential of the back may follow closely variations in that of the front or it may remain const. irrespective of such variations for a long period and then perhaps change suddenly towards the potential of the front. Experiments under various conditions indicate that electrolytically liberated H and O do not diffuse through solid metals, but only through definite pores, and that transference of potential to the back of an electrode occurs only if the metal is porous. This view is supported by the observation that whether such transference occurs or not depends on the particular specimen of metal used, irrespective of whether it is acting as cathode or anode. Also such transference of potential is often accompanied by detectable acidification of H_2O in contact with the back of the electrode. Microscopic blisters formed on the front of the electrode (and to a smaller extent on the back) at higher c.d. are attributed to gas liberated from electrolyte in the pores within the metal. The nature of the porosity and the bearing of the results on theories of overvoltage are discussed. H. J. T. E.

Theory of overvoltage. O. ESSIN (Z. physikal. Chem., 1933, **166**, 270—272).—Erdey-Gruz and Volmer's theory of overvoltage is capable of accounting for the connexion between overvoltage and $[H^{\cdot}]$ more satisfactorily than any other theory if the velocity of the opposing reaction is taken into account. R. C.

Polarisation currents due solely to changes in electrode area. K. E. GLIDDEN and W. A. PATRICK (J. Amer. Chem. Soc., 1933, **55**, 3594—3602).—On the assumption that the current between a fixed and an expanding Hg surface in aq. Hg_2SO_4 is due to adsorption of $Hg^{\cdot}$ by sp. rather than electrostatic forces, the data indicate that the adsorption of $Hg^{\cdot}$ rises to a const. val. at concn. $> 0{\cdot}00013M$-Hg_2SO_4. The lowering of interfacial tension between Hg and aq. Hg_2SO_4 suggests the formation of an oriented unimol. layer of charged particles (Hg_2SO_4) at the Hg surface. J. G. A. G.

Electrochemical theory of corrosion. O. P. WATTS (Trans. Electrochem. Soc., 1933, **64**, 219—244).—The fundamental basis and implications of the theory are critically discussed in relation to recent experimental work. Unpublished data of Rummele and Sobota (1932) for single potentials of metals and potentials for liberation of H_2 on them in N-H_2SO_4 and N-Na_2SO_4 are given. Unpublished work of Krombholtz on the effect of dissolved O_2 and H_2 on single potentials of metals in $0{\cdot}1N$-K_2SO_4 and on residual currents is referred to. H. J. T. E.

Electrochemical behaviour of iron in corrosion cells. I. Iron electrode carrying no external current. II. Cathode. III. Current-carrying capacity. H. L. LOCHTE and R. E. PAUL (Trans. Electrochem. Soc., 1933, **64**, 23—40, 41—47, 49—55).—I. Variations of the single potential of Fe wires with time in various electrolyte solutions, and the effects of electrode size, temporary H_2 evolution, rate of stirring, p_H, O_2 concn., and nature of anions present are shown by potential-time curves. The observed single potential is regarded as a mean val. resulting from polarisation of the anodic and cathodic half-elements constituting the metal surface. Half-elements nobler than H_2 can be removed by immersion in $5N$-HCl, and after this or other suitable treatment Fe acts as an indicator electrode towards $H^{\cdot}$ in acid solutions and in deaerated neutral or alkaline solutions. With respect to their influence on the potentials, anions fall into two classes: those which, like Cl', form only sol. $Fe^{\cdot\cdot\cdot}$ corrosion products; and those like PO_4''' which yield insol. products. Anions of the PO_4''' type lead to nobler potentials and inactivity of the electrode in aerated solutions. When both types of ion are present the effect depends on their proportions.

II. The polarisation of Fe wires in $0{\cdot}1N$-NaCl and

-Na_3PO_4 rises notably with increase of c.d., especially in the latter case. During decrease of c.d. in 0·1*N*-NaCl there is a break in the c.d.–potential curve, the polarisation increasing again at low c.d. and local action occurring. The c.d. at this point corresponds with the crit. c.d. required to protect Fe from corrosion.

III. If dissolved O_2 is absent or anions of the Cl′ type are present, the anodic polarisation of Fe at a c.d. likely in corrosion cells is very small, and corrosion is limited by the cathodic polarisation. In the presence of anions of the PO_4''' type in aerated solutions both anodic and cathodic polarisations increase so rapidly with c.d. that little damage can be done. With mixtures of the two types of anion in aerated solutions the effect depends on the ratio of their concns. and on the sp. anions present, but the anode tends to become more active with time, since anions of the Cl′ type accumulate there, whilst those of the PO_4''' type are kept back as insol. corrosion products. In actual corrosion cells the c.d. is probably always very small, but the anodic val. may be as high as 0·1 milliamp. per sq. cm. in special cases. H. J. T. E.

Relations between affinity and reaction velocity. O. Dimroth (Angew. Chem., 1933, **46**, 571—576).—A lecture. E. S. H.

Spark ignition of low inflammable gas mixtures. II. Spectrographic examination of the ignition spark. K. Yumoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 246—255).—For mixtures of air with $< 5\%$ H_2 or $< 10\%$ CO, the igniting power of a short spark (< 4 mm.) which shows a band spectrum is $>$ that of a spark showing a spark spectrum. In long sparks (10—12 mm.) the igniting power is greatest on the portions of the spark where the heads of the N_2 band appear strongly, and especially on the negative side of the spark where the heads of the first negative band are superimposed on the enhanced positive band. With 0·3% N_2 in CO–O_2 mixtures (CO=7%) the N_2 bands are still bright, and coincide with the max. igniting power of the spark, but no conclusion is reached as to whether the excited N_2 and N_2 mols. are directly concerned with the ignition. J. W. S.

Ignition of gases. VIII. Ignition by a heated surface: (*a*) Mixtures of ethane, propane, or butane with air; (*b*) mixtures of ethylene, propylene, or butylene with air. C. A. Naylor and R. V. Wheeler (J.C.S., 1933, 1240—1247; cf. A., 1931, 1240).—The relative ignition temp. and lags in ignition in a quartz bulb at 600—750° were measured for mixtures of air with C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, or C_4H_8. For C_2H_6–air mixtures CH_2O and C_2H_4 are formed during the lag period. Prior addition of these did not shorten the lag, but addition of EtI or EtBr did so. In C_2H_4–air mixtures CH_2O is formed during the lag. For the olefines the ignition temp. falls as the mol. wt. increases. Results are compared with those for CH_4. H. J. E.

Oxidation of triethylphosphine. W. H. Thompson and N. S. Kelland (J.C.S., 1933, 1231—1236; cf. this vol., 917).—The lower crit. explosion pressure of PEt_3, measured from 42° to 100°, was of the order of 12—25 mm. The effect of vessel diam. and added inert gases indicated a chain reaction, with deactivation at the walls. Deactivation can also occur in the gas phase. The slow reaction below the lower limit was probably a wall reaction. The reaction mechanism is discussed. H. J. E.

Polymerisation of gaseous formaldehyde. R. Spence (J.C.S., 1933, 1193—1197).—The reaction at 19—22° on a Pyrex glass surface covered with polymeride was unimol. above approx. 200 mm. pressure. At lower pressures it becomes bimol., and ultimately multimol. Reaction is more rapid on clean glass. At below 50° depolymerisation is very slow. The velocity of this process was measured at 85° (cf. Trautz and Ufer, A., 1926, 821). H. J. E.

Thermal decomposition of trinitrotriazidobenzene and other polynitropolyazidobenzenes. O. Turek (Chim. et Ind., 1933, **29**, Spec. no., 883—887).—The thermal decomp. at different temp. of 1 : 3-dinitro- (improved prep.) and 1 : 3 : 5-trinitro-2 : 4 : 6-triazido- (I) and of 2 : 4 : 6-trinitro-1-azido-benzene (improved prep.) was studied, and the temp. coeffs. and energies of activation are calc., these differing little for the three substances. Interaction of *o*-N_3 and -NO_2 groups produces N_2 and *o*-NO groups. The greater stability of (I) is attributed to its symmetry. A. A. L.

Decomposition of hydrogen peroxide by potassium ferro- and ferri-cyanides. B. S. Srikantan and A. R. Rao (J. Indian Chem. Soc., 1933, **10**, 299—307).—The decomp. of H_2O_2 by $K_4Fe(CN)_6$ is complicated. Reaction of H_2O_2 with $K_3Fe(CN)_6$ is unimol. and is preceded by an induction period, the duration of which is inversely proportional to the concn. of ferricyanide and decreases with rise of temp. The temp. coeff. is about 2·3. Light does not accelerate the reaction, but leads to the formation of Prussian-blue, which acts as centres for the reaction to start, thus eliminating the induction period. An intermediate complex between H_2O_2 and $K_3Fe(CN)_6$ may be formed. E. S. H.

Velocity of alcoholysis of esters of dibasic acids. Z. H. Patel and H. E. Watson (J. Indian Inst. Sci., 1933, **16**, A, 55—67).—The velocity of alcoholysis of the Me and Et esters of oxalic, malonic, succinic, adipic, suberic, azelaic, sebacic, tartaric, and malic acids with EtOH and MeOH in presence of HCl has been studied dilatometrically at 30°. With the symmetrical acids the reaction is unimol., although a slight deviation is observed with $H_2C_2O_4$. The two ester groups in malic acid react at different rates. In the series of unsubstituted acids $H_2C_2O_4$ has the greatest velocity coeff. and malonic acid has the smallest; the vals. for the remaining acids are equal. The reaction velocity is approx. proportional to the concn. of the catalyst (HCl). The equilibrium const. increases slightly from $H_2C_2O_4$ to adipic acid. E. S. H.

Stability of ethylene glycol in acid solution. F. E. Brown and C. E. Headington (Iowa State Coll. J. Sci., 1933, 7, 383—386).—At 107° $C_2H_4(OH)_2$ decomposes very slowly in aq. H_2SO_4 (< 20 wt.-%); the rate increases to 44% in 3 hr. for 35% H_2SO_4. At 107° in presence of HCl in low concn. decomp. occurs;

with 25% HCl at 107°, 54% decomposes in 3 hr. Rise of temp. rapidly increases the rate of decomp. Increase in pressure (H_2) had no effect. CH. ABS.

Velocities of esterification of alcohols in formic acid. II. A. KAILAN and N. H. FRIEDMANN (Monatsh., 1933, 62, 284—316).—The velocity of esterification (v_e) at 15° of EtOH, $Pr^{\alpha}OH$, $Pr^{\beta}OH$ (I), $Bu^{\alpha}OH$ (II), CHMeEt·OH, *sec.*- and *tert.*- (III) -amyl alcohols, $CH_2Pr^{\beta}\cdot CH_2\cdot OH$, and octan-α- and -β-ol (IV) in anhyd. HCO_2H and in presence of "0·104—1·017 mol." H_2O per kg. 100% acid (w_o), both with and without HCl catalysis, has been determined by the f.-p. method (A., 1929, 655). For solutions of C_6H_6, BzOH, $CHCl_3$, and various alkyl formates in HCO_2H the val. of the cryoscopic const. is $< 2·73$, the val. calc. from the heat of fusion (Zanninovitch-Tessarin), and for $w_o = 0·3—2·1$ it is 2·44° and is independent of the H_2O concn. With all the above alcohols esterification is complete. In the uncatalysed reaction as w_o is increased from 0·19 to 1·11, v_e for all the alcohols, except (IV), decreases, by 27% for primary, 19—25% for *sec.*, and 51% for (III). The ratio of v_e for primary, *sec.*-, and *tert.*-alcohols is 1 : 0·27 : 0·25 and 1 : 0·30 : 0·17, respectively, for the two vals. of w_o. No appreciable differentiation is observed between the various primary alcohols, but branching of the chain decreases v_e by about 10%. For $w_o = 0·1$ and 1, for (I) is about 14 and 22% > that for (II), respectively, and that of (III) is approx. twice that of *tert.*-BuOH. In the presence of 0·0007 mol. HCl per kg. of 100% acid and when $w_o = 0·1$, v_e for *sec.*- and *tert.*-alcohols is increased 4·4 and 2·7 times, respectively, and the retarding action of H_2O is now greater, v_e for *sec.*- and *tert.*-alcohols being reduced by 72% and 76%, respectively, as w_o increases from 0·1 to 1·0, and in the catalysed reaction v_e for (IV) is also reduced by 59%. The temp. coeff. for (I) is the same in both acids, v_e being > doubled when t is increased from 15° to 25°. After reduction to the same temp. v_e in HCO_2H, HCO_2H+HCl ($w_o = 0·1$ and 1·0) is, respectively, 15,000—20,000, 8000—10,000, and 2000 times the val. in AcOH under similar conditions (A., 1932, 1210). J. W. B.

Influence of substitution on the velocity of hydrolysis of benzylidene chloride. F. ASINGER and G. LOCK (Monatsh., 1933, 62, 323—343).—The vals. of the ψ-unimol. velocity coeff. k for the irreversible hydrolysis of the following substituted benzylidene chlorides have been determined in H_2O–$COMe_2$ (1 : 1) at 50° or in H_2O–EtOH (1 : 1) at 83·5°. All are prepared by the action of PCl_5 on the appropriate aldehyde: $CHPhCl_2$, *o*- and *p*-chloro-, *m*- and *p*-methyl-, *o*-, *m*-, and *p*-nitro-, m-*chloro*-, b.p. 105°/11 mm., 235—237°/738 mm., o-*methyl*-, b.p. 105—107°/11 mm., 2 : 5- and 2 : 6-dichloro-, 3 : 5-*dichloro*- (this vol., 1162), 2 : 3 : 6-*trichloro*-, m.p. 83°, b.p. 145—150°/12 mm., and 2 : 4 : 6-*trimethyl*- (I), m.p. 37°, b.p. 139—140°/13 mm., -*benzylidene chloride*. In 50% aq. EtOH at 83·5° (determined directly or converted from the vals. in $COMe_2$ at 50°, hydrolysis in dil. EtOH occurring about five times as fast as in $COMe_2$) the vals. of the half-change periods (min.) are, respectively: 2, 97, ɔ, 0·9, 0·027, 10,760, 3207, 7476, 168, 0·3, 2563, 6785, 4925, 123,600, and 0·0025. Thus the retarding action of Cl substitution is in the order $m > o \gg p$, that of NO_2 $o > p > m$, whereas the accelerating action of Me is in the order $p > o > m$. These results, especially the rapid hydrolysis of (I), render untenable the steric hindrance theory previously suggested (A., 1932, 345). Since k is independent of the concn. and of [H·] it is suggested that an unstable intermediate CHPhCl·OH first formed decomposes into PhCHO and HCl. The ratio $k_{\text{unsubstituted}}/k_{\text{substituted}}$ for 4-Cl-, 2 : 6-Br_2- (Cl_2-), 4-NO_2-, and 4-Me substituents in CH_2PhCl is 0·62, 0·12, 0·07, 10·6, and for $CHPhCl_2$ 0·004, 0·00029, 0·00027, and 71·4, respectively. Thus the retarding or accelerating action of substituents is greater in the benzylidene than in the benzyl series. J. W. B.

Pseudo-bases and compounds with reactive groups. Conductivity changes in systems of crystal-violet base and carboxylic acids. R. REBEK and G. MANDRINO (Coll. Czech. Chem. Comm., 1933, 5, 317—330).—The velocity of salt-formation in systems of the type crystal-violet base–org. acid–$COMe_2$ at 25° has been determined conductometrically. In general, the velocity is the higher the stronger is the acid. Discrepancies are attributed to the fact that the vals. taken for the dissociation consts. of the acids refer to aq. solutions. Data, including conductivities of $COMe_2$ solutions, are given for the even fatty acids up to C_{18}, the dicarboxylic acids up to C_5, and for fumaric, maleic, and benzoic acids. D. R. D.

Kinetics of decomposition of trichloroacetic acid. II. Mechanism of decomposition of acid in aniline solutions. H. W. PATWARDHAN and A. N. KAPPANNA (Z. physikal. Chem., 1933, 166, 51—58; cf. A., 1932, 475).—The decomp. at 60—80° in NH_2Ph, and in NH_2Ph–C_6H_6 and NH_2Ph–PhMe mixtures, is unimol. in respect of the acid and bimol. in respect of NH_2Ph, and the temp. coeff., independent of the composition of the solvent, is 3·0. The hydrocarbons merely reduce the NH_2Ph concn. and have no effect on the decomp. The decomp. of the acid occurs either by activation by collision with two NH_2Ph mols., or by slow formation by a triple collision between two NH_2Ph mols. and an acid mol. of an intermediate compound which rapidly decomposes. R. C.

Mode of formation of chlorohydrins. VI. Higher homologues of ethylene chlorohydrin. H. NILSSON and L. SMITH (Z. physikal. Chem., 1933, 166, 136—146; cf. A., 1920, i, 658).—The rates of hydrolysis of the homologues in neutral and alkaline solution at 18° have been determined and used to ascertain the proportions of the isomerides in the mixtures obtained by addition of HCl to C_2H_4 oxides. Substitution of Me for H considerably increases the rate of hydrolysis in alkaline solution, but has little effect on the rate in neutral solution. Michael's rule (A., 1900, i, 321) is confirmed. R. C.

Influence of nuclear substituents on side-chain reactions. I. W. S. NATHAN and H. B. WATSON (J.C.S., 1933, 1248—1252; cf. this vol., 890).—The relation obtained already is shown to apply to the dipole moments of compounds of the type PhX, and the crit. increments of the side-chain reactions of

C_6H_6 derivatives, with X as a nuclear substituent. With X in the *m*-position, halogen derivatives show deviations. With X in the *p*-position, electromeric effects cause complications, but otherwise the relation holds. H. J. E.

Mechanism of bimolecular reactions in solution. Addition of methyl iodide to pyridine in several solvents. W. H. THOMPSON and E. E. BLANDON (J.C.S., 1933, 1237—1240).—The reaction kinetics were studied in $CHCl_3$, $PhNO_2$, CCl_4, and anisole as solvents at 40—60°, and in the gas phase at 215°, and the energies of activation were calc. The reaction rate in solution or in the gas phase was 10^{-4} to 10^{-6} of that for hypothetical gas reactions with the same activation energies. The rate was lowest in CCl_4 and highest in $PhNO_2$, the activation energy being greatest in $PhNO_2$. H. J. E.

Kinetics of the decomposition of the dichlorosuccinic acids. H. V. W. ROBINSON and D. T. LEWIS (J.C.S., 1933, 1260—1262).—The reactions of $C_4H_4O_4Cl_2$ and *iso*-$C_4H_4O_4Cl_2$ with aq. KOH at 25° are bimol. The velocity coeff. for the *iso*-acid falls during the reaction, due to conversion into the normal form. In aq. solution at 70—90° the decomp. is unimol. The velocity is unaltered by added Na_2SO_4. Energies of activation were calc. Holmberg's results (J. pr. Chem., 1892, 46, 394) were confirmed. H. J. E.

Mechanism of substitution in organic compounds. Elimination of bromine from bromoacetic acid and the bromoacetates. H. M. DAWSON and N. B. DYSON (J.C.S., 1933, 1133—1143; cf. this vol., 234).—The replacement of Br by OH in $CH_2Br{\cdot}CO_2H$ or bromoacetates may take place in one or two stages, but the primary stage in all cases involves the liberation of Br as Br′. Measurements of the rate of this process have been made under conditions which eliminate the disturbances due to products of reaction and to variations in the reaction medium. The results obtained with solutions containing (*a*) undissociated mols. of acid, (*b*) ions, (*c*) mols.+ions show that four independent reactions are involved and that the reaction velocity in general may be expressed by $v=v_1+v_2+v_3+v_4=k_1[A']+k_2[A']^2+k_3[HA]+k_4[HA].[A']$. Any one of the four reactions may be made predominant by varying the conditions. In special circumstances the general equation reduces to simple forms which facilitate the determination of the velocity coeffs. The mol–ion mixtures obtained by mixing equiv. solutions of acid and salt show a max. on the velocity–composition curve. The influence of reaction products on the course of the reaction is discussed.

Action of hydrogen chloride on propyl alcohol. Relation between reaction velocity and electrostatic activity. S. KILPI (Z. physikal. Chem., 1933, 166, 285—304).—The rates of reaction of HCl with PrOH and of hydrolysis of PrCl have been measured in PrOH–H_2O mixtures at 96·5° and 110°. The rate of the former reaction varies with [HCl] according to the same equation as represents the variation of the activity of HCl with electrolyte concn. according to the Debye–Hückel theory. With increase in [PrOH] in the solvent the velocity coeff. increases by an amount of the same order as the increase in electrostatic activity of the HCl calc. by Born's equation (Z. Physik, 1920, **1**, 45). The temp. coeff. is independent of the composition of the solvent and is equal to that for the action of HCl on EtOH. The rate of hydrolysis of PrCl is independent of the electrolyte concn., which agrees with Bronsted's theory of complex formation (A., 1925, ii, 681). Referred to the stoichiometric H_2O concn. the rate of hydrolysis in solvent mixtures rich in PrOH is approx. const., independent of the composition of the solvent, and, since the electrostatic activity of a neutral mol. is independent of the dielectric const. of the solvent, agrees with the electrostatic activity of the reactant. Ionic diameters calc. from the velocity data by means of the Debye–Hückel theory are of an acceptable order of magnitude and vary with the composition of the solvent. R. C.

Kinetics of transformation of halogenalkylamines into heterocyclic compounds. V. Effect of phenyl group on ring opening and closing. H. FREUNDLICH and G. SALOMON (Z. physikal. Chem., 1933, 166, 161—178; cf. A., 1926, 1010).—The conversion of $CHPhCl{\cdot}CH_2{\cdot}NH_2$ in alkaline solution into styreneimine hydrochloride, followed by determinations of [Cl′], follows the unimol. law and has the temp. coeff. 3·7 between 0° and 11°. The reverse reaction in HCl solution, which occurs only at $p_H<4$, is bimol., with the temp. coeff. 1·8 between 25° and 35°. $CHPhBr{\cdot}CH_2{\cdot}NH_2,HBr$ rapidly changes into the styreneimine salt in neutral aq. or EtOH solution, which is partly accounted for by the high velocity coeff. of ring closing and the weakness of the base. The introduction of Ph into chloroalkylamines at the C atom to which the Cl is attached greatly increases the rate at which Cl is eliminated and weakens the Ph·CN linking in the styreneimine formed. Measurements with $CH_2Cl{\cdot}CHPh{\cdot}NH_2$ indicate that only a Ph group in the α-position to the Cl increases the mobility of the latter. R. C.

Homogeneous catalysis of gaseous reactions. (A) Influence of iodine on the decomposition of acids, esters, ketones, and halides. (B) Influence of iodine on the decomposition of simple aliphatic amines and of hexane. S. BAIRSTOW and C. N. HINSHELWOOD (J.C.S., 1933, 1147—1155, 1155—1160; cf. A., 1930, 1130).—(A) At 450° I catalyses the homogeneous decomp. of HCO_2Me, forming CH_4+CO_2 (29%) and MeOH+CO (71%). The further decomp. of MeOH is also catalysed, and follows the reactions (1) $MeOH=2H_2+CO$, (2) $H_2+I_2=2HI$, (3) $MeOH+2HI=CH_4+H_2O+I_2$. At 500°, MeOAc decomposes like an ether, forming MeCHO and CH_2O, which decompose further into CH_4+CO and H_2+CO, respectively. The reaction is catalysed by I. The decomp. of HCO_2H, AcOH, Et halides, $COMe_2$, and COMeEt is not catalysed by I. The kinetics are complex.

(B) I catalyses the decomp. of $NHEt_2$, $NHMe_2$, NEt_3, and NMe_3 at 400—550°. For NEt_3 the rate is proportional to the catalyst concn., but in the other cases falls with increasing concn. It is considerably greater for $NHEt_2$ or NEt_3 than for $NHMe_2$ or NMe_3.

The effect of I for NH_2Et or C_6H_{14} at 520—545° is small. The reaction mechanism and the analogy with the catalysed decomp. of ethers, aldehydes, and esters is discussed. H. J. E.

Flame phenomena of carbon monoxide. A. R. J. P. Ubbelohde (J.C.S., 1933, 972—977).—Observations have been made on the influence of H_2O vapour, H_2, and certain metals and salts on a flame of dry CO burning in dry O_2. The CO flame was lit in air and inserted in the O_2 chamber. As self-drying proceeded the flame gradually lengthened and was finally extinguished. With added H_2 the height of the flame increased as the mol. fraction of H_2 decreased. A method of determining H_2 in other gases down to mol. fractions of 10^{-7} is suggested. The formation of O_3, H_2O_2, and N oxides is shown not to be due to photosynthesis or the decomp. of H_2O_2. The effect of the vapours of alkali halides and Pt differs from that of H_2. W. R. A.

Polybasic acids as catalysts for reduction of ammoniacal silver solutions with phosphorous acid. B. Blaser (Z. physikal. Chem., 1933, **166**, 64—75).—If a mixture of a HNO_3 solution of H_3PO_3 and $AgNO_3$ is made ammoniacal, the amount of Ag separating, w, is very small, but if certain acids of high basicity, such as the phosphoric acids or citric acid, are present, w is considerably increased. The effect of the acid passes through a sharp max. with increase in its concn., and at high concns. is negligible. Some acids have no effect. As little as 3×10^{-6} g. of H_3PO_4 has a detectable catalytic action. The ratio H_3PO_3 : added H_3PO_4 for max. w is largely independent of the dilution and temp. For a given H_3PO_4 concn. w passes through a max. with increasing H_3PO_3 concn. R. C.

Ozone as an oxidising catalyst. VI. Action of diluents, of light, and of autoxidation catalysts. VII. Ozonation of hydriodic acid in solution. E. Briner and H. Biedermann (Helv. Chim. Acta, 1933, **16**, 1119—1124, 1125—1130; cf. this vol., 680).—VI. Dilution of ozonised O_2 with N_2 or CO_2 results in diminished catalytic activity of the O_3, but to a smaller extent than when the same degree of dilution is effected by lowering the total pressure. In the oxidation of $NaHSO_3$ or PhCHO the effect of ultra-violet radiation is superposed on that of O_3. The presence of other catalysts, whether positive or negative, diminishes the catalytic effect of O_3 in the oxidation of aq. $NaHSO_3$.

VII. Oxidation of aq. HI by ozonised O_2 is markedly increased in presence of AcOH, as well as by increasing [HI]. In no case does the oxidation yield exceed 100%. F. L. U.

Anti-oxidative action of thyroxine and of substances resembling thyroxine. L. de Caro (Z. physiol. Chem., 1933, **219**, 257—266).—Thyroxine (I), thyronine, di-iodothyronine, di-iodotyrosine, quinol, and toluquinol inhibit oxidation of Na oleate and linoleate (II), and delay decolorisation of carotene (III) in (II). The antagonism (I)–(III) is independent of the thyroid-like action of (I). The anti-oxidative action is probably due to phenolic OH and may be linked with complex formation with heavy metals (Fe, Cu), since KCN has a similar action. J. H. B.

Supposed chain mechanism of the formation of water from detonating gas in presence of platinum-black. B. Foresti (Ateneo Parmense, 1932, **4**, 805—812; Chem. Zentr., 1933, i, 1567).—Reduction of WO_3 to W_2O_5 in presence of Pt observed by Kobosev and Anochin occurs only if the WO_3 and Pt are intimately mixed and the temp. is >50—60°; the presence of a small quantity of H_2O is favourable. Reduction takes place only at the catalytic surface and is due to adsorbed activated H_2. A. A. E.

Chain reactions in heterogeneous catalysis. B. Foresti (Ateneo Parmense, 1932, **4**, 401—407; Chem. Zentr., 1933, i, 1567).—Thermal effects at the catalyst in the hydrogenation of C_2H_4 have been studied by means of a differential microcalorimeter. The reaction is exothermic and of the calc. order; Bennewitz and Neumann's view is therefore incorrect. Reaction in heterogeneous catalysis occurs exclusively at the surface. A. A. E.

Physical state of solid catalysts. E. Audibert and A. Raineau (Compt. rend., 1933, **197**, 596—598).—The d of a catalytic sample of any substance is always $<$ that of the same when non-catalytic; *e.g.*, catalytic Cu had d 7·60 and $7·52\pm0·5$, whilst the d calc. from the X-ray structure of ordinary Cu is 8·9. Also the X-ray pattern of catalytic Cu is always blurred, indicating slight variations in the crystal lattice. Both deviations from normal disappear, with the catalytic activity, on prolonged heating, *e.g.*, for Cu after 6 hr. at 500—700°. It is concluded that for catalytic activity there must be increased distances between the atoms at certain points, which are the "active centres." C. A. S.

Nature of activated carbons. II. E. Berl and L. Reinhardt (Z. physikal. Chem., 1933, **166**, 81—96; cf. A., 1932, 217).—Determinations of the size and shape of the primary particles in various carbons have shown that these properties do not solely determine the activity of a C. Experiments on the change in particle shape on ignition of active C and the treatment of C with K have shown that the activity is a property of unsaturated C atoms at lattice irregularities in the sense of Smekal's "loose places" and Taylor's "active centres." The most active C would therefore consist of free C atoms, *i.e.*, amorphous C; since this is incapable of existence activation must aim at producing unsaturated C atoms on the surface of the primary C particles. The edge C atoms also make a contribution to the activity which varies with the particle shape, and the fall in this contribution, owing to the growth of the primary particles in the direction of the planes of the leaflets, is responsible for the decrease in activity of the C when heated at 1000—1500°. R. C.

Catalytic reduction of magnetic sand.—See B., 1933, 832.

Connexion between centres active in adsorption and catalytic activity. (Measurements with active iron.) R. Klar (Z. physikal. Chem., 1933, **166**, 273—284).—The adsorption of C_2H_4, C_2H_6, and H_2 by samples of Fe of various activities at 0—50° has been measured, the results for C_2H_4 being used to determine the no. of active centres, n; the hydro-

genation of C_2H_4 on the same catalysts has also been studied. The results show that no direct comparison between n and the catalytic activity is admissible; the quality of the active centres must be taken into consideration. The rate of reaction is determined by reduction in the activation energy as a result of the adsorption of the reacting substances. R. C.

Catalysis. P. SABATIER (Chim. et Ind., 1933, 29, Spec. no., 868).—Experiments on the diffraction of electrons at the surface of Ni in the presence of H_2 at low pressures (A., 1931, 12) are considered to support the intermediate compound theory of catalysis. A. A. L.

Synthesis of benzine.—See B., 1933, 773.

Anodic behaviour of nickel. III. K. GEORGI (Z. Elektrochem., 1933, 39, 736—743; cf. A., 1932, 1093).—The rate of dissolution of Ni in N-HCl increases proportionately to the amount of 30% H_2O_2 added. In N-H_2SO_4 the rate first increases linearly, but falls very rapidly between 0·3 and 0·6% H_2O_2. $FeCl_3$ added to N-HCl resembles H_2O_2, but in N-H_2SO_4 containing $Fe_2(SO_4)_3$, Ni behaves as a noble metal. CrO_3 in N-HCl resembles H_2O_2; in N-H_2SO_4 it resembles $Fe_2(SO_4)_3$. Simultaneous potential measurements are recorded. Results are correlated with and support the author's theory of active centres on the electrode. H. J. E.

***KZ*, KG_I, and KG_{II} during the formation of the cathode deposit.** A. GLAZUNOV and J. JANOUSEK (Chim. et Ind., 1933, 29, Spec. no., 739—742).—In the electrolysis of $AgNO_3$ with flat electrodes the no. of centres of crystallisation increases with increasing c.d. and with diminishing concn. of the electrolyte. The latter is considered to be due to the action of the combined forces KG_I, normal to the cathode and along the lines of force, and KG_{II} parallel to the cathode surface, since the crystals are shown to grow in both these directions. A. A. L.

Relation between the direction of growth of the cathode deposit and the form of the lines of electric force. A. GLAZUNOV and O. RADA (Chem. et Ind., 1933, 29, Spec. no., 736—738).—When $AgNO_3$ is electrolysed in shallow vessels with obstacles between the cathode and anode Ag is deposited along the direction of the theoretical lines of force. A. A. L.

Electrolytic reduction of ketones in glacial acetic acid. I. Reduction of aromatic ketones. S. SWANN, jun. (Trans. Electrochem. Soc., 1933, 64, 245—252).—In H_2SO_4–AcOH solution $COPh_2$ was electrolytically reduced at all cathode materials tried at 60—90°, the main identifiable product being benzpinacolin, but no reduction occurred at room temp. The best yields of purest product were obtained at an Fe cathode at 0·3 amp. per sq. cm. in a solution containing 30% H_2SO_4. H. J. T. E.

Amino-acids and related compounds. VII. Oxidation of amino-acids. Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, 8, 213—230).—The ease of oxidation at a PbO_2 anode of a no. of NH_2-acids in 0·33M solution in 2N-H_2SO_4, as indicated by the rate of evolution of NH_3, falls in the order (*a*) glycine, valine, glutamic acid, alanine; (*b*) leucine, aspartic acid; (*c*) tyrosine (I), phenylalanine (II), the members in each group differing but little from one another. In the case of (I), (II), tryptophan, and histidine humin is formed after a time and the solution darkens; with lysine and proline darkening but no humin formation takes place. Carbonyl derivatives could not in general be isolated. H. F. G.

Photographic reciprocity law failure for radiations of different wave-length. J. H. WEBB (J. Opt. Soc. Amer., 1933, 23, 316—323).—The relation between intensity, time of exposure, and density of image has been investigated for rapid blue-sensitive and panchromatic plates, using various Hg lines from 3650 to 6910 Å. The simple reciprocity law does not apply, but the form of the curves is in all cases identical when the points of equal time of exposure are made to coincide. Curves are given for intermittent light of various frequencies. D. R. D.

Silver chromate [in photographic emulsions]. LÜPPO-CRAMER (Z. wiss. Phot., 1933, 32, 129—130). —Ag_2CrO_4 emulsion in gelatin gives on exposure a latent image which can be physically developed. Development is greatly hastened if the exposed plate is treated with 0·1% aq. KI. More conc. solutions, KBr, or KCl cause fogging. The emulsion has a max. sensitivity to yellow light. J. L.

Photographic effect of *X*-rays. G. W. BRINDLEY and F. W. SPIERS (Phil. Mag., 1933, [vii], 16, 686—691).—The density of blackening, D, was proportional to the intensity of monochromatic X-radiation, I, for vals. of $D < 1{\cdot}4$. The variation of D with I was measured by an absorption method, the films providing the absorbing medium. H. J. E.

Chemical action of Röntgen rays. P. GÜNTHER (Angew. Chem., 1933, 46, 627—631).—A lecture.

Relative effects produced by 200-kv. Röntgen rays, 700-kv. Röntgen rays, and γ-rays. II. Effects on iodides, Eder's solution, and photographic film. H. Q. WOODARD, E. H. QUIMBY, and H. R. DOWNES (Amer. J. Roentgenol., 1933, 29, 308—326).—When the radiation output is standardised by ionisation measurements the effect produced (liberation of I, pptn. of HgCl, or darkening of film) varies with the quality of the radiation. The variation is different for different substances. CH. ABS.

Decomposition of ethyl chlorothioncarbonate in darkness and by the action of light. A. BERTHOUD and D. PORRET (Helv. Chim. Acta, 1933, 16, 939—942).—Freshly prepared ClCS·OEt undergoes very little decomp. at room temp., but more on heating. The action is not influenced by light. In the prep. by Delepine's method ($CSCl_2$+EtOH in Et_2O) a catalyst appears gradually to be formed which accelerates the decomp. F. L. U.

Response of a photographic emulsion to α-rays. T. R. WILKINS and R. N. WOLFE (J. Opt. Soc. Amer., 1933, 23, 324—332).—The equation $D = D_{max.}(1-e^{-c_1 N})$ holds for commercial emulsions of any thickness. The data indicate that an α-particle must actually hit a grain in order to affect it, a fact which may be utilised for the determination of grain-size. Plates may be temporarily desensitised to the lumines-

cence produced by α-rays in air by means of an aq. solution containing 10 g. of $K_2Cr_2O_7$ and 4 c.c. of conc. H_2SO_4 per litre. D. R. D.

Attempt to prepare a chloride or fluoride of xenon. D. M. Yost and A. L. Kaye (J. Amer. Chem. Soc., 1933, **55**, 3890—3892).—Experiments affording negative results are described. J. G. A. G.

Double nitrate of copper and ammonium. J. Milbauer and J. Doskař (Chim. et Ind., 1933, 29, Spec. no., 787).—No true Cu NH_4 nitrate exists. If solutions are mixed in the ratio 1 mol. $Cu(NO_3)_2,6H_2O$ to 12 mols. NH_4NO_3 and evaporated with agitation a blue cryst. product is obtained. This, however, contains only entrained Cu, which is readily removed by recrystallisation. C. I.

Existence of ammoniates of double salts. G. Spacu and P. Spacu (Z. anorg. Chem., 1933, **214**, 113—142).—Tensimetric experiments have established the existence of *compounds* of NH_3 with double chlorides as follows (figures denote no. of mols. of NH_3 combined with 1 mol. of the respective double salts): Rb_2CuCl_4 10, 5, 3, 2, 1; $CsCuCl_3$ 10, 5, 1; Cs_2CuCl_4 10 6, 3, 2; $Cs_3Cu_2Cl_7$ 13, 10; Cs_2CoCl_4 9, 5, 2, 1; $CsNiCl_3$ 1; K_2FeCl_5 11, 6, 5, 2; $KAuCl_4$ 10, 3, 2; $RbAuCl_4$ 13, 12, 5, 4, 3; $CsAuCl_4$ 11, 10, 6, 5, 4, 3; K_2ZnCl_4 12, 5, 3, 1; $(NH_4)_2ZnCl_4$ 11, 10, 5, 4, 2; $(NH_4)_3ZnCl_5$ 12, 6; $(NH_4)_4CdCl_6$ 13, 12, 4. The above are distinguished from the NH_3 compounds with the simple heavy metal chlorides by their composition, colour, heat of formation, and NH_3 pressures. Ephraim's statement (A., 1917, ii, 319; 1919, ii, 291) that combination of NH_3 with double salts requires a preliminary decomp. of the latter is incorrect. F. L. U.

Hydrazinates of silver halides. H. Gall and H. Roth (Z. anorg. Chem., 1933, **214**, 201—208; cf. A., 1932, 919).—By the action of a dry EtOH solution of the appropriate base on a dry C_5H_5N (or 2-C_5H_4NMe) solution of AgX, the following *compounds* have been obtained: $3AgCl,N_2H_4$; $3AgBr,N_2H_4$; $AgBr,N_2H_4$; $2AgI,N_2H_4$; $AgCl,NHPh\cdot NH_2$; $AgBr,NHPh\cdot NH_2$. F. L. U.

Change in constitution of tricalcium phosphate on fusion. A. Travers and Bauer (Helv. Chim. Acta, 1933, **16**, 918—922).—An account of work previously published (this vol., 794). F. L. U.

Zinc phosphate cement. F. Halla and A. Kutzelnigg (Z. Stomatol., 1933, **31**, 177—181; Chem. Zentr., 1933, i, 2524).—ZnO and 89% H_3PO_4 afford a product giving *X*-ray lines of $Zn_3(PO_4)_2,4H_2O$ (hopeite); free ZnO is also present. A. A. E.

Reactions in the solid state at higher temperatures. X. Course of the reaction. W. Jander and W. Scheele (Z. anorg. Chem., 1933, **214**, 55—64; cf. A., 1932, 128).—The theory is advanced that, in the reaction between two solid particles, an amorphous or pseudomorphic reaction skin is first formed; from this crystals of the product form. Mixtures of $BaCO_3+MoO_3$, $BaCO_3+WO_3$, $ZnO+Cr_2O_3$, and $ZnO+Al_2O_3$ were heated at 250—550°, and the adsorption of Me-violet and fuchsin on the product was examined. At the temp. of incipient reaction adsorption increased (amorphous skin formation). At higher temp. it fell (cryst. product). Reaction zones are illustrated by photomicrographs of Mg_2TiO_4, formed from MgO and TiO_2 at 1500°. H. J. E.

Electrometric studies of the precipitation of hydroxides. X. Action of ammonia on solutions of potassium mercuri-iodide, and mercuric bromide, nitrate, sulphate, and perchlorate. XI. Constitution of ammoniacal solutions of (*a*) silver nitrate, (*b*) silver oxide. H. T. S. Britton and (Miss) B. M. Wilson (J.C.S., 1933, 1045—1049, 1050—1053).—X. In the action between NH_3 and $HgBr_2$ the NH_3 caused pptn. at a lower p_H than with NaOH. The composition of the ammoniated ppt. varied somewhat and did not correspond with either "fusible" or "infusible" white ppt., or with the bromide of Millon's base. K_2HgI_4 did not react unless sufficient NaOH was added to raise the p_H by 1; then the Nessler colour is produced followed by a ppt. $Hg(NO_3)_2$, in dil. HNO_3, gave a white ppt. with 2 mols. of NH_3. $Hg(ClO_4)_2$ and 2 mols. of NH_3 reacted to give a pale yellow ppt. With $HgSO_4$ in the presence of H_2SO_4, the p_H vals. are comparable with those prevailing with NaOH. In all cases the ppt. is an ammoniacal basic salt of variable composition. Control of the composition by variation of conditions is discussed.

XI. The variation in p_H during the addition of NH_3 and of NaOH to $AgNO_3$ has been investigated by means of a glass electrode. The p_H curves are given for both hydroxides in various concns. The formation of $Ag(NH_3)_2NO_3$ in solution is indicated and the mobility of $Ag(NH_3)_2^+$ is 62·0. By a glass electrode titration of an NH_3 solution of Ag_2O with HNO_3 a p_H curve is obtained; the base $Ag(NH_3)_2OH$, stronger than NH_4OH, is formed. W. R. A.

Reactions in the solid state. M. Paic (Arh. Hemiju, 1933, **7**, 114—119).—The *X*-ray spectra of the products indicate the following reactions between solid substances: $HgSO_4+2HgO\longrightarrow 3HgO,SO_3$; $3HgO,2SO_3,2H_2O$ (I)$+3HgO\longrightarrow 2(3HgO,SO_3)+2H_2O$; $HgSO_4+HgS\longrightarrow\beta$-$HgSO_4,HgS$; $HgSO_4+HgI_2\longrightarrow HgSO_4,HgI_2$; (I)$+HgI_2\longrightarrow 3HgO,HgI_2,2SO_3+2H_2O$. (I) also reacts with HgS, yielding unidentified products. R. T.

Borates and boron. L. Hackspill (Helv. Chim. Acta, 1933, **16**, 1099—1118; cf. this vol., 894).—A lecture reviewing recent work. F. L. U.

Production of large artificial graphite crystals. A. Goetz, A. B. Focke, and A. Faessler (Physical Rev., 1932, [ii], **39**, 168—170).—Unicryst. flakes of Ceylon graphite, treated with HF and HCl to remove SiO_2 and Fe, are suspended in a 3% solution of gum dammar in C_6H_6 and allowed to settle in an inhomogeneous electromagnetic field. Evaporation of the C_6H_6 leaves an artificial crystal of considerable rigidity. L. S. T.

Transformation of diamond into graphite. E. Szarvasy and B. Lanyi (Math. Nat. Anz. ung. Akad. Wiss., 1932, **48**, 137—146; Chem. Zentr., 1933, i, 1564).—Diamond powder heated for 7 hr. at 1370° gives non-transparent black crystals, but no Debye–Scherrer graphite lines appear; these lines appear after

heating at 1600°, but diamond lines are still present after heating at 1750°, although not at 2000°. A. A. E.

Fission of carbon monoxide on iron oxide and iron. H. A. Bahr and V. Jessen (Ber., 1933, 66, [*B*], 1238—1247; cf. Gluud *et al.*, A., 1929, 1409).—Fe_2C (9·7% C) can very probably be prepared pure from Fe and CO at as low a temp. as possible ($\ll$ 225°); at 230—400°, a mixture of Fe_2C and Fe_3C with free C probably results, whereas at $>$ 400° only Fe_3C (6·68% C) is produced. Carbonised products obtained by means of Fe oxide always contain O; detection of combined C by hydrogenation with H_2 is not quite trustworthy in this case and must be performed at 255—260°. Products obtained with Fe at $\ll$ 330° are free from O; at higher temp. the oxidising action of the liberated CO_2 is observed. Hydrogenation of combined C with H_2 can take place at 280—290°. Carbide formation from CO and Fe occurs relatively rapidly; subsequently, the main reaction is the separation of free C. H. W.

Iodine and aqueous solutions of ammonia. E. Chirnoaga and E. Chirnoaga (Z. anorg. Chem., 1933, 214, 167—176).—When boiling aq. NH_3 is added to powdered I and the mixture shaken, no $N_2H_3I_3$ is formed, but a solution of I in aq. NH_4I. If $[NH_3]$ $\gg$ 2% NH_4IO_3 is also present. The ratio (free I/I′) is about 1 and is independent of the concn. Part of the I is present as ultramicrons and can be pptd. by $Al^{\cdots}$ or $Th^{\cdots\cdot}$. F. L. U.

[Preparation and properties of] ammonium azide. W. S. Frost, J. C. Cothran, and A. W. Browne (J. Amer. Chem. Soc., 1933, **55**, 3516—3518).—The solubility in H_2O, C_6H_6, Et_2O, EtOH, and MeOH at 0—40° and the d of the saturated solutions have been determined. Solid NH_4N_3 has d^0 1·3459 and the v.p. between 15° and 134° is given by $\log p_{mm.} = -3428{\cdot}6/T + 11{\cdot}325$. Dissociation of the vapour is indicated. J. G. A. G.

Constitution of azoimide and azides. A. Hantzsch (Ber., 1933, 66, [*B*], 1349—1354).—Alkyl azides show discontinuous or selective absorption and are non-electrolytes. Since aryl azides have the structure $\overset{N}{\overset{\|}{N}}\!>\!NAr$, and N^V exists only in O compounds or NH_4 salts, alkyl esters are $\overset{N}{\overset{\|}{N}}\!>\!NAlk$. To N_3H the cyclic structure is also assigned by reason of its analogy with N_3Alk and its existence in H_2SO_4 as the trisulphate, incompatible with the possession of N^V. Since the liquid acid is associated, the structure is expanded to $HN\!<\!\overset{N}{\overset{\|}{N}}\cdots\overset{N}{\overset{\|}{N}}\!>\!NH$. The alkali and NH_4 salts are electrolytes with continuous or general absorption in which the positive metals, as cations, are equally bound to all the negative atoms as anions. Only feebly positive metals are united in their salts to a single atom, and then, as ψ-salts, differ markedly in absorption from true salts. Since all true azides correspond with the *sym.* type and, in general, *sym.* are more stable than *asym.* complexes, it is assumed that N_3' is *sym.* and is thus distinct from nearly all other anions in the absence of a central atom. Cyanoazide is more strongly absorbent than any other azide, is hydrolysed normally to $N_3CO{\cdot}NH_2$ and N_3CO_2H, and therefore contains 2CN; it is $NC{\cdot}N\!<\!\overset{N}{\overset{\|}{N}}\cdots\overset{N}{\overset{\|}{N}}\!>\!N{\cdot}CN$. H. W.

Oxidation of phosphorus by water at high temperatures and under pressure. I. Red phosphorus. II. Yellow phosphorus. I. N. Buschmakin, M. V. Risakov, and A. V. Frost. **III. Phosphine. IV. Phosphorous acid.** I. N. Buschmakin and A. V. Frost (J. Appl. Chem. Russ., 1933, 6, 577—587, 588—606, 607—612, 613—620).—I. The reaction of oxidation of red P by H_2O takes place in two stages, liquefaction and oxidation of the products. The former stage consists of the reactions: $P_4+6H_2O=2H_3PO_3+2PH_3$; $P_4+8H_2O=2H_3PO_4+2PH_3+2H_2$; $P_4+12H_2O=4H_3PO_3+6H_2$; $P_4+16H_2O=4H_3PO_4+10H_2$; its duration falls from 2 hr. at 280° to 4 min. at 400°, and in presence of NiO catalyst to 4 min. at 280°. The second stage, which is practically completed in 3 hr., consists of the reactions: $H_3PO_3+H_2O=H_3PO_4+H_2$; $4H_3PO_3=3H_3PO_4+PH_3$; $PH_3+3H_2O=H_3PO_3+3H_2$; $PH_3+4H_2O=H_3PO_4+4H_2$; the velocity of these reactions is unaffected by NiO. The relative concns. of H_2O and P depend on the dimensions of the apparatus used, a certain optimum val. existing in each case. Under optimum conditions complete dissolution of P is obtained, to yield H_2 containing traces of PH_3 and P, and 20—25% solutions of H_3PO_4 with only traces of PH_3 and H_3PO_3. The process is unaffected by varying the partial H_2 pressure from 100 to 350 atm.

II. Yellow P is converted into H_3PO_4 as above, at 325°, and in presence of 1% of NiO. Apparatus is described for prep. on a technical scale.

III. PH_3 undergoes oxidation to H_3PO_3 and H_3PO_4 according to the equations given above. The reactions are catalysed by Ag and Cu_3P_2.

IV. Anhyd. H_3PO_3 decomposes at 280° as follows: $4H_3PO_3=3H_3PO_4+PH_3$. At higher temp. the reaction $PH_3+3H_2O=H_3PO_3+3H_2$ takes place, the necessary H_2O being obtained by dehydration of H_3PO_4. In presence of small quantities of H_2O the reaction commences at 330°, and proceeds as above, whilst with excess of H_2O the extremely slow reaction $H_3PO_3+H_2O=H_3PO_4+H_2$ takes place. A no. of oxides have no catalytic action on this reaction, but rapid and quant. conversion is attained in 30 min. at 350° by adding excess of aq. NH_3, when pure NH_4 phosphate crystallises on cooling. R. T.

Metaphosphoric acid. A. Travers and Chu (Helv. Chim. Acta, 1933, **16**, 913—917).—In a mixture of aq. phosphoric acids containing excess of 10% NH_4Cl, $ZnSO_4$ ppts. only $H_4P_2O_7$ when the p_H is adjusted to 3·7—4·7, whilst H_3PO_4 is quantitatively pptd. as $ZnNH_4PO_4$ at p_H 7·0. Pptn. of HPO_3 is prevented by the NH_4Cl. Using this method of separation it is shown that no $H_4P_2O_7$ is formed either by the action of P_2O_5 on H_2O at 0° or by dissolving the product obtained by heating $(NH_4)_2HPO_4$ to dull redness. "Glacial metaphosphoric acid" of commerce consists of a mixture of H_3PO_4 with a (probably tri-)metaphosphate of Na. F. L. U.

The two forms of phosphorous acid. R. Dolique and A. Grangiens (Compt. rend., 1933,

197, 618—620).—Results obtained by Dubrisay's method (cf. A., 1918, ii, 368), with a solution of stearic acid in vaseline oil as dropping fluid, show that the acid produced by adding $\frac{1}{n}PCl_3$ to H_2O is at first preponderantly $P(OH)_3$ or $PHO(OH)_2$ according as n is $>$ or $<$ 50—75; more conc. or more dil. solutions tend to the same equilibrium mixture on keeping (cf. A., 1925, ii, 316). C. A. S.

Phosphorous fluorochlorides. H. S. Booth and A. R. Bozarth (J. Amer. Chem. Soc., 1933, **55**, 3890).—Fluorination of PCl_3 by SbF_3 in the presence of $SbCl_5$ yields PF_3 together with smaller quantities of the colourless *gases* PF_2Cl, b.p. −48°, m.p. −166°, and $PFCl_2$. 50% of a mixture of PCl_3 and PF_3 is converted into PF_2Cl and $PFCl_2$ by passage over porcelain at 200°. J. G. A. G.

Interaction of phosphorus bromide and chloride. I. A. Renc (Rocz. Chem., 1933, **13**, 454—463).—Mixtures of PCl_5 and PBr_5 in the proportions 1 : 5 to 1 : 1 yield red crystals, of composition $PCl_{0\cdot06}Br_{5\cdot63}$—$PCl_{2\cdot55}Br_{5\cdot97}$, and a light red liquid. When the ratio is 5·5 : 4·5 to 3 : 2 the mixture consists of two liquid phases, one light red, and the other deep red, composition $PCl_{2\cdot47}Br_{5\cdot80}$—$PCl_{3\cdot15}Br_{5\cdot71}$. Mixtures in the ratios 7 : 3 to 9 : 1 yield three phases: yellow crystals, $PCl_{4\cdot22}Br_{0\cdot80}$—$PCl_{4\cdot65}Br_{0\cdot35}$, a deep red liquid, $PCl_{...}Br_{3\cdot94}$—$PCl_{3\cdot4}Br_{3\cdot3}$, and a light red liquid. R. T.

Action of nitric acid on hypophosphoric acid. B. Blaser (Z. physikal. Chem., 1933, **166**, 59—63).—Pure HNO_3 does not oxidise $H_4P_2O_6$ at the b.p., but catalyses its hydrolysis: $H_4P_2O_6+H_2O=H_3PO_3+H_3PO_4$. The H_3PO_3 formed is not attacked even by boiling 86% HNO_3. The hydrolysis of H_3PO_2 in aq. HNO_3 and HCl at 40° is unimol.; conc. HNO_3 is a weak acid. R. C.

Sulphur monoxide. II. Preparation and properties of pure sulphur monoxide. H. Cordes and P. W. Schenk (Z. anorg. Chem., 1933, **214**, 33—43; cf. this vol., 475).—SO was prepared at a SO_2 pressure of 10 mm. by using a more powerful discharge. The formula was proved by analysis ($2SO\rightarrow S+SO_2$). SO is inert towards O_2 at room temp. It reacts when sparked, but not explosively at the low pressures used. SO attacks Hg, Fe, Cu, and brass rapidly, but not rubber. With H_2O, S and polythionic acids, and with aq. KOH a strongly reducing solution, are formed. By inflating a rubber bladder in a glass vessel containing SO at a low pressure it could be compressed to 40 mm. pressure. The odour of SO resembles that of S heated just below its ignition point. H. J. E.

Complex and internally complex compounds of quinquivalent molybdenum. A. Rosenheim and C. Nernst (Z. anorg. Chem., 1933, **214**, 209—224; cf. A., 1932, 484).—The following *compounds*, prepared from $MoCl_5$, are described: with pyrocatechol ($C_6H_4O_2=P$),

$(NH_4)_2H[MoOP_3],0\cdot5PH_2,3H_2O$;
$KH_2[MoOP_3],0\cdot5PH_2,4H_2O$;
$(CN_3H_6)_2[Mo(OH)_3P_2],3H_2O$;
$(CN_3H_6)_2H[MoOP_3],5H_2O$;
$(C_5H_6N)_2H[MoOP_3],2H_2O$;
$(C_5H_6N)H[Mo(OH)_3P_2]$; $Tl_2[Mo(OH)_3P_2]$; with salicyclic acid or its Me ester,

$(C_5H_6N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_4\cdot CO_2]$,
$(C_9H_8N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_4\cdot CO_2]$,
$Mo(OH)_2Cl_2(O\cdot C_6H_4\cdot CO_2Me)$; with 2-hydroxy-*m*-toluic acid, $(C_5H_6N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_3Me\cdot CO_2]$,
$(C_9H_8N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_3Me\cdot CO_2]$; with phenols, $MoCl_2(OPh)_3$, $MoCl_2(O\cdot C_6H_4Me)_3$ *m*- and *p*-, $Mo(OH)Cl_2(SPh)$, $Mo(OH)Cl_2(O\cdot C_{10}H_7)_2$ (β);
also $[(CH_2)_6N_4H]_3[Mo_2O_3Cl_7],6H_2O$,
$(C_5H_6N)_2[Mo_2O_3Cl_4(C_2O_4)],2H_2O$,
$(C_9H_8N)_2[Mo_2O_3Cl_4(C_2O_4)],H_2O$,
$(NH_4)_3[(MoO_2)_2(HCO_2)_5],0\cdot5HCO_2NH_4,0\cdot5H_2O$, and
$K_3[(MoO_2)_2(HCO_2)_5],0\cdot5HCO_2H,0\cdot5H_2O$. Complex and internally complex Mo^V compounds present a close analogy with those of Nb and Ta, not with those of As and Sb. F. L. U.

Polonium. E. Rona (Pharm. Presse, 1932, **37**, Wiss.-prakt. Heft, 168—170; Chem. Zentr., 1933, i, 1599).—A review of properties and application to biological problems. A. A. E.

Interaction of saturated solutions of potassium chromate and manganous chloride. H. Wunschendorff and (Mme.) P. Valier (Compt. rend., 1933, **197**, 584—585).—On adding a boiling saturated solution of K_2CrO_4 to one of $MnCl_2$ as long as a ppt. is formed the red ppt. first formed turns black. The latter is well washed and boiled out with H_2O, giving a red solution which on evaporation to a syrup and finally over CaCl, gives ruby crystals of $MnCr_2O_7$, whilst the black ppt. is $Cr_2(MnO_4)_3$ (cf. A., 1907, i, 961; 1910, ii, 299) C. A. S.

Bromine fluoride, BrF. O. Ruff and A. Braida (Z. anorg. Chem., 1933, **214**, 81—90).—BrF was prepared by the interaction of Br and F at 10°, and was purified from Br, BrF_3, and BrF_5 by fractional condensation. It is also formed in the interaction of Br with BrF_3 or BrF_5 (cf. A., 1932, 133). It forms a reddish-brown gas and a dark red liquid, b.p. approx. 20°, f.p. −33°. At 50° it decomposes rapidly into BrF_3, BrF_5, and Br. The formula was established from the gas density and analysis. The liquid Br fluorides are partly miscible. Only traces dissolve in liquid Br. H. J. E.

BrF_3. O. Ruff and A. Braida (Z. anorg. Chem., 1933, **214**, 91—93; cf. A., 1932, 707).—The v.p. was measured between −5° and 80°. The b.p. (extrapolated) is 127±1°, and the heat of vaporisation approx. 10 kg.-cal. per mol. The high val. for the Trouton const. (25·3) indicates association of liquid BrF_3. H. J. E.

Extraction of rhenium from molybdenite. E. Kronmann, V. Bibikova, and M. Askenova (Z. anorg. Chem., 1933, **214**, 143—144; cf. A., 1932, 1224).—Experimental details are given. F. L. U.

Rhenium. M. Prettre (Bull. Soc. chim., 1933, [iv], **53**, 669—681).—A lecture on the extraction, properties, determination, and compounds of Re.

Rhenium trichloride. W. Geilmann, F. W. Wrigge, and W. Biltz (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1932, 579—587; Chem. Zentr., 1933,

i, 1598—1599).—$ReCl_4$, when heated in an indifferent gas, affords $ReCl_3$, which is purified by sublimation in vac. at 500—550°. It forms reddish-black lustrous crystals, apparently trigonal; the magnetic susceptibility at 20° is $-0{\cdot}13\times10^{-6}$. $ReCl_3$ is only slightly ionised in aq. solution. Characteristic reactions are described. Heating with KCl in vac. at 600° affords K_2ReCl_6 and Re. A. A. E.

Magnetic and *X*-ray investigations of the ageing of hydrated ferrous oxide. O. Baudisch and L. A. Welo (Naturwiss., 1933, **21**, 659—660).—Freshly prepared FeO,H_2O will reduce alkali nitrates only in the presence of O_2, and at the same time any oxidisable compound present may be oxidised. In the absence of O_2 the FeO,H_2O remains unchanged, and will not effect these reactions. This power is also lost with keeping under anaerobic conditions. FeO,H_2O kept for some days and oxidised by the air gives a ferromagnetic red Fe_2O_3,H_2O, the space lattice of which corresponds with α-Fe_2O_3. Since it is ferromagnetic, γ-Fe_2O_3 must be present. FeO,H_2O changes into compounds with less H_2O on keeping, the H_2O previously combined chemically being now held by adsorption. In presence of O_2, H_2O is eliminated even at room temp., and breaks up according to the equation $H_2O\longrightarrow H+O(H_2O_2)$, a reaction which is not possible with the aged compound, which will not therefore react as above. A. J. M.

Iron chloride and other metallic chlorides in the Friedel–Crafts reaction. E. Wertyporoch [with I. Kowalski and A. Roeske] (Ber., 1933, **66**, [*B*], 1232—1238).—Measurements of electrical conductivity and transport nos. of $FeCl_3$ in EtCl, EtBr, Pr$^{\alpha}$Cl, Pr$^{\beta}$Cl, Bu$^{\alpha}$Cl, Bu$^{\beta}$Cl, *n*- and *iso*-amyl chloride, *n*-$C_6H_{13}Cl$, BzCl, and AcCl, supported by the behaviour in individual cases after addition of C_6H_6, C_6Et_6, COPhMe, or $COPh_2$, lead to the conclusion that the production of alkyl- or acyl-benzenes from hydrocarbons and alkyl or acyl chloride in presence of $FeCl_3$, as in the case of $AlCl_3$ or $AlBr_3$, is due to the production of a conducting, ternary complex in which a loosening of the halogen linking in the alkyl (acyl) chloride and of the H linking in the hydrocarbon occurs; stabilisation occurs by elimination of HCl and production of alkyl-(acyl-)benzene. The complex formation is much less complete than with the freely sol. $AlCl_3$ or $AlBr_3$ and the yields of alkylbenzenes are very poor. The amounts of CH_2Ph_2, $CHPh_3$, CPh_3Cl, COPhMe, and $COPh_2$ obtained by use of $FeCl_3$ are about half those obtained in presence of $AlCl_3$. The high conductivity of HCl in MeCN is increased by dissolution of $ZnCl_2$, apparently owing to complex formation. $ZrCl_4$ is slightly sol. in EtBr and causes conversion of C_6H_6 into C_6Et_6. $BeCl_2$ in EtBr does not react with C_6H_6, but, at higher temp., behaves towards $CPhCl_3$ in the same manner as $AlCl_3$. Even under increased pressure and temp., the chlorides of Hg, Tl, Th, Ti, and Sn do not cause reaction between C_6H_6 and EtBr or C_6H_6 and $CHCl_3$ in the sense of the Friedel–Crafts change. H. W.

Hexacyanocobaltic acid and *n*-propyl alcohol. F. Holzl, W. Brell, and G. Schinko (Monatsh., 1933, **62**, 349—358; cf. A., 1931, 944, 1382).—By passing HCl gas into a solution of $H_3[Co(CN)_6]$ (I) in Pr$^{\alpha}$OH (II) is obtained the *oxonium* salt $[Co(CN)_6](H_2OPr^{\alpha})_3$ (of type $[A]R_3$), and tensimetric measurements with the efflorescent product also indicate the existence of the salts $[A]H_2R$ and $[A]HR_2$. The continuous rate of fall of acid titre observed when (I) is heated in (II) at 98° is increased and becomes irregular in the presence of increasing amounts (0—10%) of H_2O, indicating the sequence of reactions (1) esterification of (I) to a carbylamine complex (which occurs in H_2O-free media); (2) fission of free HCN (accelerated by H_2O); (3) and (4) a two-stage hydrolysis of the carbylamine; (5) introduction of aquo-groups in place of NC; and (6) the formation of highest complexes. In 98% Pr$^{\alpha}$OH after 42 hr. a violet *compound* $[(H_2O)_2(NC)_3Co{\cdot}CN{\cdot}Co{\cdot}CNPr^{\alpha}(CN)_3(OH_2)]H\rightleftharpoons[(HO)(NC)_3H_2OCo{\cdot}CN{\cdot}Co{\cdot}CNPr^{\alpha}(CN)_3(OH_2)]H_2$ is isolated, and from the 90% Pr$^{\alpha}$OH solution the dark red *compound* $[(H_2O)(NC)_4Co{\cdot}CN{\cdot}Co(CN)_4(OH_2)]H_3\rightleftharpoons[(HO)(NC)_4Co{\cdot}CN{\cdot}Co(CN)_4(OH)]H_5$ is obtained, which gives no carbylamine, a NH_2Pr^{α} odour with alkali, and loses 9·17% H_2O in a vac. to give the compound $[(CN)_3{:}Co{:}(CN)_3{:}Co{:}(CN)_3]H_3$. J. W. B.

Constitution of nitro-aquo-cobaltic salts. J. Meyer and O. Rampoldt (Z. anorg. Chem., 1933, **214**, 1—15; cf. A., 1926, 925).—From *cis*- and *trans*-[Co en$_2$ClNO$_2$] salts (I) (Werner, A., 1901, i, 512) the *cis*- and *trans*-forms of the *compounds* [Co en$_2$(H$_2$O)(NO$_2$)](SO$_3$·C$_{10}$H$_6$·NH$_2$)$_2$ (II) and its trihydrate were prepared. Action of H_2SO_4, H_2SeO_4, HNO_3, and $H_2C_2O_4$ on (II) gave the corresponding *cis*- and *trans*-salts of these acids. All were anhyd. The *d*- and *l*-*cis* forms of (II) were isolated by hydration of the corresponding forms of (I). The two optically active forms gave identical crystals, differing from the inactive form. The *compounds*, *trans*-[Co(NH$_3$)$_4$(H$_2$O)(NO$_2$)](SO$_3$·C$_{10}$H$_6$·NH$_2$)$_2$ and *trans*-[Co(NH$_3$)$_4$(NO$_2$)I]I were prepared. The constitution is discussed. H. J. E.

Nickel nitrites of bivalent metals. A. Ferrari and R. Curti (Gazzetta, 1933, **63**, 499—506; cf. A., 1932, 483).—The *compounds* $Ba_2[Ni(NO_2)_6]$, $Sr_2[Ni(NO_2)_6]$, and $Pb_2[Ni(NO_2)_6]$, the prep. of which is described, have a cubic structure very similar to that of K_2PtCl_6, with 4 mols. per unit cell and *a* 10·67, 10·54, and 10·55 Å., respectively. The corresponding Ca_2, Ba Sr, Ba Ca, and Sr Ca compounds could not be obtained. O. J. W.

Bivalent rhodium. H. Reihlen and W. Huhn (Z. anorg. Chem., 1933, **214**, 189—195).—Na_2 or Na H *salts* of the acids $H_2[Rh(SO_3)_2]$, $H_4[Rh(SO_3)_2SO_4]$, and $H_6[Rh_2(SO_3)_4SO_4]$, in which Rh is bivalent, have been obtained by the action of aq. Na_2SO_3 or $NaHSO_3$ on $RhCl_3$. F. L. U.

Complex compounds. A. A. Grinberg (Ann. Inst. Platine, 1933, No. 10, 47—64).—The results of physico-chemical research on the co-ordination compounds of the Pt group are discussed. R. T.

Complex platinum compounds. I. I. Tschernaev (Ann. Inst. Platine, 1933, No. 10, 33—46).—The work of the Institute since 1918 is reviewed. R. T.

Spectroscopic analysis of minerals with the acetylene–air burner. A. K. RUSSANOV (Z. anorg. Chem., 1933, **214**, 77—80).—A method of introducing finely-powdered minerals into a C_2H_2–air stream, which then burns at a jet, is described. Reproducible flame conditions, suitable for quant. spectrum analysis, are obtained. 0·005 Rb or 0·004% Cs was detectable. H. J. E.

Determination of rock constituents by semi-micro-methods. (MISS) W. C. A. GUTHRIE and (MISS) C. C. MILLER (Min. Mag., 1933, **23**, 405—415).—Details are given of the method of working on separate portions of 0·1 g. Analyses are given of crinanite, olivine-dolerite, olivine-basalt, and a plastic clay; compared with standard analyses made on the same materials they show no loss in accuracy. L. J. S.

Indirect chemical determination of minerals in a polished surface by "spotting." G. GUTZEIT, M. GYSIN, and R. GALOPIN (Arch. Sci. phys. nat., 1933, [v], **15**, 192—196).—The application of org. reagents is described. C. W. G.

Fluorescence indicators. K A. JENSEN (Z. anal. Chem., 1933, **94**, 177—179).—14 new fluorescent indicators for acidimetry, covering the p_H range 0·0—11, are described. The use of an ultra-violet lamp (cf. this vol., 242) is recommended. J. S. A.

Titration with fluorescence indicators. S. MALOWAN (Chem.-Ztg., 1933, **57**, 755).—Acid–alkali titrations of coloured or turbid liquids can be carried out in ultra-violet light, using methylumbelliferone as indicator. E. H. S.

Application of the thermionic valve in potentiometric titration. K. MASAKI and O. HIRABAYASHI (Bull. Chem. Soc. Japan, 1933, **8**, 245—254).—The grid of the valve is rendered positive with respect to the filament, and the resulting grid current is employed to polarise the Pt electrodes. Part of the grid current is shunted in order to maintain a const. p.d. between the electrodes up to the equivalence point. The approach to the end-point is clearly indicated, and it is therefore unnecessary to plot the readings. Typical results for a variety of titrations are given. H. F. G.

Electrometric determination of halogens. J. L. TREMBLAY (Arch. phys. biol., 1932, **10**, 67—73; Chem. Zentr., 1933, i, 2282—2283).—The potentiometric determination of Br′ and I′ in presence of much Cl′ has been studied. Cl′ in serum can be determined without previous destruction of protein if the p_H is sufficiently far removed from the isoelectric point (4·7). A. A. E.

Determination of iodine liberated from iodides by nitrous acid. A. GUERBET (J. Pharm. Chim., 1933, [viii], **18**, 258—262).—Following the liberation of I by HNO_2 and extraction of the I by $CHCl_3$, the addition of $NaHCO_3$ to the $CHCl_3$ extract renders the subsequent titration with $Na_2S_2O_3$ inaccurate owing to the small but significant formation of NaOI which reacts with $Na_2S_2O_3$ to form $NaHSO_4$. Substitution of Na_2SO_3 for $Na_2S_2O_3$, however, enables an accuracy of ±0·5% to be attained. F. O. H.

Use of glycerol in iodometry. A. T. BAWDEN and S. K. DYCHE (Ind. Eng. Chem. [Anal.], 1933, **5**, 347).—I may be weighed, without loss by volatilisation, by adding a quantity to a solution of glycerol (2 vols.) and saturated aq. KI (1 vol.) and noting the increase of wt. An open vessel may be used. E. S. H.

Colorimetric determination of fluorine. W. D. ARMSTRONG (Ind. Eng. Chem. [Anal.], 1933, **5**, 300—302).—F′ is determined by comparing its fading action on the colour of Fe^{III} acetylacetone with that of a similar solution to which has been added a known amount of F′, thus eliminating differences due to acidity. E. S. H.

Acidimetric determination of sulphide and hydrosulphide in presence of one another. K. A. JENSEN and O. V. RASMUSSEN (Z. anal. Chem., 1933, **94**, 180—183).—The accuracy of Podreschetnikov's method (cf. B., 1926, 154) is enhanced by titrating the Na_2S to an end-point at p_H 9·6—10, using thymolphthalein (I) as indicator. The sample is dissolved in H_2O, treated with $BaCl_2$ or $SrCl_2$, and an aliquot part titrated with 0·1*N*-HCl, using (I); 10 c.c. of CH_2O solution are added and titration is continued with phenolphthalein. J. S. A.

Photometric investigation of Nessler reaction and Witting method for determination of ammonia in sea-water. H. E. WIRTH and R. J. ROBINSON (Ind. Eng. Chem. [Anal.], 1933, **5**, 293—296).—Photometric investigation of the colours developed by four Nessler reagents at low NH_3 concns. in H_2O and sea-H_2O shows that, whilst all the reagents have a non-sensitive region in H_2O, Treadwell's reagent has no non-sensitive region in sea-H_2O. It is possible to determine 0·003 mg. N as NH_3 without the device of adding known amounts of NH_3. The sensitivity of the Treadwell reagent increases with increasing [Cl′]. There is no error due to adsorption in determining NH_3 in sea-H_2O by Witting's method. E. S. H.

Determination of nitrogen in calcium cyanamide in presence of nitrate.—See B., 1933, 827.

Determination of phosphorus in copper and copper–zinc alloys.—See B., 1933, 792.

Electrolytic determination of arsenic. F. N. MOERK (Trans. Electrochem. Soc., 1933, **64**, 173—186).—An improved form of the electrolytic modification of the Gutzeit method for the determination of small amounts of As has been developed, and the influence of varying the operating conditions has been examined. Under the standardised conditions recommended for the highest accuracy the time required for the test is notably shortened. H. J. T. E.

Determination of silver and copper in alloys.—See B., 1933, 792.

Qualitative analysis with small quantities. IV. Detection of alkaline-earth metals. A. J. SCHEINKMANN and A. B. POLITZSCHUCK (Z. anal. Chem., 1933, **94**, 192—193).—Ca, Sr, and Ba carbonates are dissolved by warming with NH_4OAc. Ca may then be pptd. by $K_4Fe(CN)_6$, Ba by cold Na_2SO_4, and Sr by boiling the filtrate from the Ba pptn.

Detection of barium, strontium, and calcium in the course of systematic analysis. J. Brintzinger and H. Brintzinger (Z. anal. Chem., 1933, **94**, 166—170).—Ba, Sr, and Ca are pptd. by addition of conc. H_2SO_4 to the (conc.) filtrate from group II. $CaSO_4$ is extracted with hot dil. HCl and yields characteristic crystals of $CaSO_4,2H_2O$ when evaporated on a micro-slide. $SrSO_4$ and $BaSO_4$ are reduced to sulphides on a Pt wire in the reducing flame, dissolved in HCl, and Ba is pptd. with H_2SiF_6. The solution is evaporated to dryness, K_2CrO_4 added, and Sr pptd. with KIO_3. J. S. A.

Indirect colorimetric determination of calcium. E. M. Emmert (Plant Physiol., 1933, **8**, 469—473).—The method is based on the fact that in NH_3-free solutions of $Fe^{\cdot\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, and PO_4''', addition of NaOH ppts. Fe and Mg as hydroxides and Ca as $Ca_3(PO_4)_2$. The reduction in PO_4''' content of the solution is thus a measure of the $Ca^{\cdot\cdot}$ present, and is determined by the Mo-blue method. Org. matter may be removed by ignition. Al, if present, reacts similarly to Fe. If the $[PO_4'''']$ is high relative to $[Ca^{\cdot\cdot}]$ the accuracy of the method is lessened. This is obviated by preliminary addition of known amounts of Ca. A. G. P.

Quantitative spectrographic studies of co-precipitation. II. Group II elements with barium sulphate. L. Waldbauer and E. St. C. Gantz (Ind. Eng. Chem. [Anal.], 1933, **5**, 311—313).—When solutions of sulphates are added to aq. $BaCl_2$, the sulphates of Ca, Sr, and Cd, but not those of Be, Mg, or Zn, are co-pptd. with $BaSO_4$. When CdI_2 is used there is evidence of preferential adsorption of I' or CdI_4''. E. S. H.

Determination of magnesium. C Brioux (Rapport, Inst. Recherches Agron. Paris, 1932, 177; Proc. Internat. Soc. Soil Sci., 1933, **8**, 119).—To avoid co-pptn. of Mg during the removal of Fe and Al by aq. NH_3 in the presence of much NH_4 salts, double pptn. or the use of a very slightly alkaline solution is recommended. If Ca is present in Mg solutions during pptn. of the latter as $MgNH_4PO_4$ the Ca phosphate also pptd. is insol. in NH_4 citrate. Vals. for Mg obtained by a single pptn. as $MgNH_4PO_4$ are unduly high. The ppt. is redissolved in HCl and repptd. by addition of a min. of aq. NH_3 No further addition of NH_4 phosphate is made. A. G. P.

Reagent for magnesium: 5-*p*-acetamidophenylazo-8-hydroxyquinoline. G Gutzeit, R. Monier, and R. Bachoulkova-Brun (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 203—206).—An alkaline solution of this substance (prep. described) gives a violet colour with $Mg^{\cdot\cdot}$ in dilutions $< 1 : 10{,}000$. $Sn^{\cdot\cdot}$ and metals giving coloured ppts. with alkali hydroxides must be absent. $Ca^{\cdot\cdot}$ decreases the sensitivity of the test, but other metals do not interfere. Solid carbonates containing Mg give the colour with the reagent in EtOH. R. S. C.

Ignition of magnesium ammonium phosphate. VIII. S. J. Kiehl and H. B. Hardt (J. Amer. Chem. Soc., 1933, **55**, 3555—3560; cf. this vol., 352).—During the process of losing H_2O in the early stages of ignition, $MgNH_4PO_4,6H_2O$ has the property of attaching firmly within its structure certain volatile org. compounds which, if present, later decompose with the deposition of graphitic C. The luminescence or flash during the ignition of $MgNH_4PO_4,6H_2O$ and $MgNH_4PO_4,H_2O$ is due to the large evolution of heat which accompanies the rapid crystallisation of $Mg_2P_2O_7$ at 550—600°. The transformation is slower and occurs without the flash at 500°. J. G. A. G.

Quantitative analysis of the hydrogen sulphide group. J. Kunz (Helv. Chim. Acta, 1933, **16**, 1044—1049).—A scheme of separation based on pptn. by H_2S in presence of graded concns. of HCl is described. F. L. U.

Accuracy of lead analyses. L. T. Fairhall (J. Ind. Hyg., 1933, **15**, 289).—A reply to the criticisms of the author's methods by Kehoe and co-workers (cf. this vol., 1200). F. O. H.

Detection and determination of small amounts of inorganic substances by colorimetric methods. N. Strafford (Inst. Chem., 20 Feb., 1933, 36 pp.).—A review, with outlines of the procedures recommended for a no. of metals. The depth of colour produced in the Kastle–Meyer method of determining Cu is independent of the Cu content of the solution, as the reaction is purely catalytic, and the method is therefore of little val. H. F. G.

Detection and determination of small quantities of mercury. F. Cucuel (Mikrochem., 1933, **13**, 321—364).—A review.

Asbestos in permanganate titrations. R. W. Curtis and J. Finkelstein (Ind. Eng. Chem. [Anal.], 1933, **5**, 318—319).—Filter-paper reacts with 0·1*N*-$KMnO_4$, but asbestos does not. E. S. H.

Bunsen's method [of analysis of oxides]. New apparatus. K. Braddock-Rogers and K. A. Krieger (Ind. Eng. Chem. [Anal.], 1933, **5**, 342—344).—The accuracy of Bunsen's method for the decomp. and analysis of $KMnO_4$, Pb_3O_4, PbO_2, and MnO_2 is confirmed. HBr and HCl are of equal val. in this reaction. The use of $Na_2S_2O_3$ is preferred to H_3AsO_3 in the determination. A modified apparatus is described. E. S. H.

Organic reagents in qualitative analysis. I. Separation of iron, chromium, and aluminium. L. Lehrman, E. A. Kabat, and H. Weisberg (J. Amer. Chem. Soc., 1933, **55**, 3509—3511).—Excess of 10% aq. $(CH_2)_6N_4$ completely ppts. $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $Cr^{\cdot\cdot\cdot}$ from boiling aq. solutions of $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, and $Zn^{\cdot\cdot}$ containing excess of NH_4NO_3. The degree of separation is such that 1 mg. of one metal is detected in the presence of 100 mg. of another. J. G. A. G.

Precipitation of iron as basic acetate. P. Wegner, C. Cimerman, and M. Gorni (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 157—158).—$FeOAc(OH)_2$ is pptd. at $p_H < 6$, the optimum val. of the latter being 4·2. C. W. G.

Application of sodium salt of *p*-toluenesulphonchloroamide ("chloramine") in volumetric analysis. A. S. Komarovski, V. F. Filonova, and I. M. Korenman (J. Appl. Chem. Russ., 1933, **6**, 742—748).—*p*-$C_6H_4Me{\cdot}SO_2NClNa$ (I) can be applied in place of I for titrating $Fe(CN_6)''''$,

CNS′, N_2H_4, H_3PO_2, and CS_2. The titre of 0·1004*N*-(I) remained const. during 40 days, and fell to 0·0991*N* after 90 days. R. T.

Adaptation of the dimethylglyoxime–benzidine test for cobalt to the usual scheme of qualitative analysis. A. W. Scott (J. Amer. Chem. Soc., 1933, **55**, 3647—3648).—The mixture of NiS and CoS is dissolved in HCl containing HNO_3. The liquid is evaporated. There are then added successively dil. AcOH, 1 g. NaOAc, 0·5 c.c. of 0·5% benzidine in EtOH, and excess of dimethylglyoxime in EtOH. Ni is removed by filtration. A red filtrate indicates Co. The method is satisfactory with concn. of Ni times ≯ 50-fold that of Co. J. G. A. G.

Determination of antimony in copper alloys. —See B., 1933, 792.

Colorimetric determination of bismuth. C. Mahr (Z. anal. Chem. 1933, **94**, 161—166; cf. this vol., 1025).—A dil. HNO_3 solution of the sample is treated with excess of solid $CS(NH_2)_2$ (I). $Fe^{\cdots}$ if present is first reduced by N_2H_4. Pptd. compounds of (I) with heavy-metal salts are filtered off, washed with a saturated solution of (I) in dil. HNO_3, and the filtrate is diluted to a definite vol. The yellow colour is compared with that produced in a solution of known Bi content. 0·01% Bi in Pb or Cu may be determined. Addition of KF destroys the yellow coloration produced by Sb if present. J. S. A.

Potentiometric determination of gold in alkaline solutions with vanadyl sulphate. C. del Fresno and E. Mairlot (Z. anorg. Chem., 1933, **214**, 73—76; cf. this vol., 800).—$NaAuO_2$ may be determined with 0·1*N*-$VOSO_4$ at 30—70° in presence of 7·5—30% alkali. The reaction is $AuO_2' + 3VO'' + 8OH' \rightarrow Au + 3VO_3' + 4H_2O$. H. J. E.

Spot method for the approximate determination of platinum. N. A. Tananaev and G. T. Michaltschischin (Z. anal. Chem., 1933, **94**, 188—192).—0·002 c.c. of a 0·01% Pt solution is added to a drop of saturated aq. $TlNO_3$ absorbed on filter-paper, and treated with a drop of acid $SnCl_2$. The deep orange coloration produced is compared with that given by the solution under examination. One or other solution is so diluted that the intensities are matched. Au and Pd interfere; the stain produced is sol. in aq. NH_3. J. S. A.

Delayed relay for thermostats. J. Korpiun and A. Geldbach (Z. Elektrochem., 1933, **39**, 755—756).—In the valve circuit described a controlled time lag from a fraction of a sec. to several min. occurs in breaking the heating current circuit. Fouling of the Hg contact of the thermoregulator is thereby avoided. H. J. E.

Adjustable temperature regulator. W. G. Parks (Ind. Eng. Chem. [Anal.], 1933, **5**, 357).—The height of the Hg can be varied by adjusting a plunger fitted to a side tube, thus avoiding the necessity of removing Hg when the temp. is to be changed. E. S. H.

Camera for Laue spectrograms. R. Stratta (L'Ind. Chimica, 1933, **8**, 986—987).—A simple form of camera with centering device is described. H. F. G.

Sodium lamp. W. A. N. Markwell (Perf. Ess. Oil Rec., 1933, **24**, 294—295).—Two glow electrodes (W), surrounding an electron-emitting material, are contained in an atm. of inert gas together with some Na. The electrodes provide the necessary heat during the starting period (20 sec.), and are then switched off. The discharge then takes place through the Na. The emitting surface is about 10×15 mm. and of the total intensity, about 99% is due to Na-*D* line. Little heat is generated and radiation is const. in intensity. E. H. S.

Origin and development of absolute colorimetry by means of grey solutions. A. Thiel (Z. anal. Chem., 1933, **94**, 170—177).—A review. Polemical. Procedure to avoid possible deterioration of the grey solutions is discussed. J. S. A.

Interferometry. II. Construction, testing, and use of reflexion echelons for the visible and ultra-violet regions. W. E. Williams (Proc. Physical Soc., 1933, **45**, 699—726).—Details of the construction and method of testing reflexion echelons are considered, different methods of mounting being compared. A method for using the instrument for wave-length measurements is described. The echelon provides an alternative method of standardising length units in terms of light wave-lengths. J. W. S.

Rotating chamber for interferometric determination of refractive indices of solutions. A. Kruis and W. Geffcken (Z. physikal. Chem., 1933, **166**, 16—22).—The construction and manipulation are described. R. C.

***X*-Ray method for quantitative comparison of crystallite orientation in cellulose fibres.** W. A. Sisson and G. L. Clark (Ind. Eng. Chem. [Anal.], 1933, **5**, 296—300).—The method described is based on the assumption that the distribution of the crystallites around the pencil of *X*-rays is proportional to the distribution of intensity around the 002 diffraction ring. A microdensitometer with rotating stage is used for the intensity measurements. Results for three grades of cotton are given. E. S. H.

Tyndallmetric examination of filtered liquors. A. B. Cummins and M. S. Badollet (Ind. Eng. Chem. [Anal.], 1933, **5**, 328—332).—The turbidity of the filtrate is determined photometrically from the intensity of the Tyndall beam produced in it under standard conditions. The application of the method to refining of sugar is discussed and results are given. E. S. H.

Micro-absorption spectra. C. R. Naeser and B. S. Hopkins (Ind. Eng. Chem. [Anal.], 1933, **5**, 358).—A simple procedure is described. E. S. H.

Silver filter for ultra-violet light. G. C. Brock (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 563—566).—The filter is prepared from a lantern slide, which is exposed, developed to a brown colour, and then the emulsion stripped and supported between two plates of "Uviol" glass or "Vita-glass." The filtering action, attributed to the presence of colloidal Ag, is superior to that of sputtered or chemically deposited films. Max. transmission occurs at about 3000 Å. J. W. S.

Conditions for securing accuracy in spectrophotometry. F. Twyman and G. F. Lothian (Proc. Physical Soc., 1933, 45, 643—662).—Basic principles in the design and use of spectrophotometers are discussed. The applications of absorption photometry to chemistry are considered and the photographic, visual, and photo-electric methods compared. The uses of spectrophotometry as a means of describing a radiation, especially in connexion with colorimetry, the comparison of light sources, and quant. spectrum analysis, are also discussed. J. W. S.

Device for measuring intensity of illumination [in plant work]. H. R. Rosen and W. M. Roberds (Science, 1933, 78, 241—242). L. S. T.

Measurement of critical potentials with a screened grid valve. F. L. Arnot (J. Sci. Instr., 1933, 10, 294—295).—A 4-electrode wireless valve containing a trace of Hg may be used. C. W. G.

Calibration and salt error of the antimony electrode. Its application in soil reaction measurements. N. J. King (Ind. Eng. Chem. [Anal.], 1933, 5, 323—327).—Calibration of the Sb electrode in many series of buffer solutions shows a linear relation between e.m.f. and p_H between p_H 3·0 and 12·0. Contrary results of previous investigators have been due to the presence of KCl. The use of the Sb electrode in N-KCl is recommended in soil studies, the salt error having been determined. E. S. H.

Standard-cell comparator. A specialised potentiometer. H. B. Brooks (Bur. Stand. J. Res., 1933, 11, 211—231).—The difference between the e.m.f. of the cell under test and that of the reference cell is added automatically (algebraically) to the e.m.f. of the latter. The e.m.f. is thus indicated directly. H. J. E.

Suitability of some rectifier photo-cells for the measurement of daylight. H. H. Poole and W. R. G. Atkins (Sci. Proc. Roy. Dublin Soc., 1933, 20, 537—546).—Under conditions specified the cells appear to be suitable for approx. comparative measurements. H. G. R.

Selenium rectifier photo-electric cell. V. N. Lepeshinskaya (J. Exp. Theor. Phys., U.S.S.R., 1932, 2, 388—392). Ch. Abs.

Use of gas-filled photo-electric cells in photometric measurements. T. D. Gheorghiu (Ann. Physique, 1933, [x], 20, 133—242).—A detailed description is given of a spectrophotometer in which two photo-cells of known characteristics are used, one being employed for control purposes to permit the use of an unstable light source. The accuracy of the arrangement is discussed in detail. Beer's law holds for solutions of $CuSO_4$, but not for $CuCl_2$ or for alkaline solutions of Cu tartrates and Cu racemate. The deviations are attributed to the presence of complex ions. At equal concn., Cu d- and l-tartrates absorb the Hg green line equally, but the racemate is more transparent and a mixture of equal parts of d- and l-tartrate solutions much more opaque. The absorption min. is the same for d- and l-tartrates and racemate, but that of the mixture is at a lower wavelength. The significance of these results is discussed. J. W. S.

Improved form of mercury distiller. P. G. N. Nayar, V. V. Rao, and B. Dasannacharya (Indian J. Physics, 1933, 17, 91—93).—An apparatus dispensing with the auxiliary vac. pump is described. N. M. B.

Improved chain-packed distilling column. S. T. Schicktanz (Bur. Stand. J. Res., 1933, 11, 89—92).—The column is 250 cm. long and is packed with jeweller's brass locket chain, size nos. 13—18. From 1500 c.c. of a 50 mol.-% mixture of C_6H_6 and $C_2H_4Cl_2$ (b.p. 3·42° apart), a distillate of 450 c.c. of pure C_6H_6 and a residue of 350 c.c. of pure $C_2H_4Cl_2$ were obtained. D. R. D.

Automatic water still. H. B. Gordon (Ind. Eng. Chem. [Anal.], 1933, 5, 357).—The still, designed for a small laboratory, can be made from simple apparatus. E. S. H.

Variable-control still head for laboratory columns. S. C. Rothmann (Ind. Eng. Chem. [Anal.], 1933, 5, 338—339). E. S. H.

Modified Soxhlet [extractor]. T. R. Liston and W. M. Dehn (Ind. Eng. Chem. [Anal.], 1933, 5, 306). E. S. H.

Mechanically operated burette. C. H. Whitnah (Ind. Eng. Chem. [Anal.], 1933, 5, 352—354).—The apparatus is designed to add aq. NaOH to a reaction mixture as required to maintain a const. e.m.f. over periods up to several days. E. S. H.

Microburette for potentiometric micro-analysis. H. L. Lochte and A. Hoover (Ind. Eng. Chem. [Anal.], 1933, 5, 335).—The apparatus can be used for potentiometric titrations with 1 c.c. or less of 0·1—0·01N solutions. E. S. H.

Continuous air-lift extractor. Application to determination of benzoic acid. R. P. Chapman and L. P. Hammett (Ind. Eng. Chem. [Anal.], 1933, 5, 346—347).—Continuous circulation of the solvent (CCl_4) through the solution to be extracted and through 0·1N-NaOH is caused by a current of air. E. S. H.

Ground-glass junctions. H. L. Baumbach (Ind. Eng. Chem. [Anal.], 1933, 5, 349).—A hollow cone of sheet Cu is used. The inside of the cone is used for grinding the taper and the outside for grinding the socket. E. S. H.

Measurement of viscosity by oscillating columns. S. Venkataraman (Indian J. Physics, 1933, 17, 25—42).—A new method for liquids, by measuring photographically the damping of their oscillations in a tube, is described. Data are obtained for CCl_4, CS_2, $CHCl_3$, EtOAc, C_6H_6, PhMe, AcOH, C_5H_5N, xylene, and H_2O. N. M. B.

Microvolumetric procedure. A. Romwalter (Mitt. berg.-hüttenmänn. Abt. Hochsch. Sopron, 1932, 4, 67—76; Chem. Zentr., 1933, i, 1482).—A simple apparatus for the determination of the vol. of gas evolved in reactions involving a few mg. of substances is described. A. A. E.

Copper to glass seals. H. de Laszlo (J. Sci. Instr., 1933, 10, 296—297).—Cu tubing is turned down to a feather edge, coated with $Na_2B_4O_7$, and sealed to the inside of a glass tube. C. W. G.

Silicon tetrafluoride volatilisation. W. D. ARMSTRONG (Ind. Eng. Chem. [Anal.], 1933, 5, 315—317).—A simplified apparatus for the evolution and collection of SiF. in quant. analysis is described. E. S. H.

Preparation of permeable extraction thimbles for laboratory filtration. F. J. WILLIAMS (Ind. Eng. Chem. [Anal.], 1933, 5, 322). E. S. H.

Multiple steam-bath. W. L. BEUSCHLEIN and W. M. DEHN (Ind. Eng. Chem. [Anal.], 1933, 5, 327). E. S. H.

Circulator for ice water. L. L. ENGLISH (Ind. Eng. Chem. [Anal.], 1933, 5, 351). E. S. H.

Use of pump as gas sampler. R. C. LEE (Ind. Eng. Chem. [Anal.], 1933, 5, 354—356).—The advantages of a metal plunger pump are discussed. E. S. H.

Air trap for water lines. L. LEHRMAN and E. A. KABAT (Ind. Eng. Chem. [Anal.], 1933, 5, 358). E. S. H.

Simple automatic pressure regulator. C. C. COFFIN (J. Amer. Chem. Soc., 1933, 55, 3646—3647).—The device described has been used for obtaining const. temp. between 210° and 280° with the vapour of boiling Hg. J. G. A. G.

Automatic pressure regulators for vacuum distillation. II. Sulphuric acid as a manostat fluid. E. B. HERSHBERG and E. H. HUNTRESS (Ind. Eng. Chem. [Anal.], 1933, 5, 344—346; cf. this vol., 480).—A modified apparatus is described, in which H_2SO_4 replaces Hg as a manostat liquid. In view of the increased viscosity of H_2SO_4, the diam. of the column should be about four times that used with Hg. Evolution of gas is negligible when H_2SO_4 (d 1·71) is used. E. S. H.

Micropyknometer for determination of displacements of isotopic ratio in water. E. S. GILFILLAN and M. POLANYI (Z. physikal. Chem., 1933, **166**, 254—256).—A pyknometer by means of which 10^{-5} to 10^{-2} mg. may be weighed is described. R. C.

Apparatus for taking samples of gas at the moment of explosion. A. G. SUVOROV (J. Appl. Chem. Russ., 1933, 6, 753—754).—Apparatus is described. R. T.

Influence of surface tension on hydrometer readings. B. SCHEDA (Chem. Fabr., 1933, 6, 413—414).—An example of the error introduced by surface tension variation in hydrometer readings is in the apparent alteration of d for distilled H_2O as determined by the hydrometer, if a trace of oil is floating on the surface. Determinations of d for aq. solutions are on this account uncertain in the third or fourth decimal point. By the construction of pairs of hydrometers of which the capillarity consts. are in a fixed ratio the error can be corr. An example of the use of such pairs is in the determination of d for dil. EtOH solutions, when results obtained in this way closely approach those given by the pyknometer. C. I.

Geochemistry.

Presence of formaldehyde in rain and dew and its formation by photo-oxidation of organic compounds and the problem of carbon assimilation. N. R. DHAR and A. RAM (J. Indian Chem. Soc., 1933, **10**, 287—298).—CH_2O does not appear to be formed in atm. electrical discharges. Dew contains more CH_2O than rain-H_2O (about 0·0015 g. per litre). Numerous org. substances yield CH_2O when exposed to sunlight and air; in some cases CH_2O is believed to be a direct product of photo-oxidation, whilst in others it may be obtained from the photosynthesis of the energy-rich CO_2 and H_2O produced by photo-oxidation. The relation between respiration and photosynthesis in plants is considered, and a theory of C assimilation is advanced. E. S. H.

Characteristics of bore-hole waters in the Karachukhur district. I. TOLBIN (Azerbaid. Neft. Choz., 1933, No. 3, 56—62).—The primary salt content (Palmer) increases from 72 to 97% in the fourth horizon of the Apsheron peninsula. d decreases with stratigraphic depth from 1·143 to 1·042. The alkalinity of some horizons increases from roof to wings. The secondary Palmer alkalinity content is $< 0·1\%$. The waters are hard. The primary alkalinity begins in the wings of the fifth and sixth horizons. CH. ABS.

Meteoric iron and silica-glass from the meteorite craters of Henbury (Central Australia) and Wabar (Arabia). L. J. SPENCER [with M. H. HEY] (Min. Mag., 1933, 23, 387—404).—Meteorite craters are not merely percussion indentations; they are explosion craters due to the sudden vaporisation of part of the material, both of the meteorite and of the earth's crust, at the high temp. developed by the impact. The meteoric irons from both localities are of exactly the same type, namely, a medium octahedrite containing Ni 7·3%, with little Co, Cu, and S; d 7·69. They are found scattered outside the craters, the larger masses showing the normal octahedral lamellar structure of a single crystal, whilst in the smaller twisted masses there is a partial obliteration of this structure with granulation of the kamacite (transformation of α-Fe into γ-Fe at 850°). These are only weathered remnants of larger masses torn asunder by the explosions. The associated iron-shale, representing the weathered product, contains Fe_2O_3 78·45, FeO 8·32, NiO 5·28, CoO 0·32, etc., and consists of a mixture of limonite, hæmatite, magnetite, and trevorite ($NiFe_2O_4$).

SiO_2-glass, of rare occurrence in nature, shows a remarkable development at Wabar, building the rims of the meteorite craters. A snow-white highly vesicular glass, formed by the fusion and boiling of the clean desert sand, contains SiO_2 92·88% with small amounts of Ti, Al, Fe, Mn, Mg, Ca, Sr, Na, K, H_2O; d 2·10, n 1·468. Bombs of this material shot out from the craters are coated with a thin skin of black SiO_2-glass free from bubbles and containing Fe_2O_3 0·28, FeO 5·77, NiO 0·35 (Fe : Ni as in the meteorite); d

2·24, n 1·500. Embedded in some of the vesicular SiO_2-glass are numerous ($>2\times10^6$ per c.c.) polished spheres (0·003—0·14 mm. diam.) of Ni–Fe containing Ni 8·8%. These represent a rain of molten metal into a pool of boiling SiO_2. The vaporisation of Fe, Ni, and SiO_2 indicates temp. up to about 3500°. At Henbury the SiO_2-glass is less abundant, and being formed from a ferruginous sandstone it is less pure; SiO_2 68·88%, d 2·31, n 1·545. L. J. S.

Biological detection of radioactivity of rocks. O. Muck (Strahlenther., 1933, **46**, 378—383; Chem. Zentr., 1933, i, 2429).—The reaction depends on the vasoconstriction of probed nasal mucous membrane after contact of the human body with radioactive material. A. A. E.

Geochemistry of boron. II. V. M. Goldschmidt and C. Peters (Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl., 1932, 528—545; Chem. Zentr., 1933, i, 2074—2075; cf. this vol., 928).—Numerous determinations of B in eruptive rocks and minerals, sedimentary rocks, sea-H_2O, weathering products, and soils have been carried out. Magmatic rocks usually contain $>$ 0·0005—0·001% B_2O_3. High vals. are obtained for sea salts and sediments. B is also contained in siliceous skeletons of sea organisms and in coral. The origin of B and Cl in the sea is discussed. A. A. E.

Crystal chemistry of the silicates. F. Machatschki (Geol. For. Stockholm Forh., 1932, **54**, 447—470; Chem. Zentr., 1933, i, 1575).—The chief structural types of silicates are discussed. A. A. E.

Bismuthite. M. A. Peacock (Z. Krist., 1933, **86**, 203—211).—Well-developed crystals of bismuthite occur at Tasna (Bolivia) associated with pyrite, mispickel, jamesonite (?), and metavauxite. The bismuthite is orthorhombic holohedral, $a:b:c$—0·9862 : 1 : 1·0493, and contains Bi 76·51, Sb 3·58, S 20·07%. C. A. S.

Minerals from the gorge of the Lieser near Spittal (Carinthia). H. Heritsch (Z. Krist., 1933, **86**, 253—269; cf. this vol., 892).—The following minerals occur near the junction of pegmatite with garnet-gneiss, amphibolite, and eclogite: (I) dark green hornblende, d 3·15, $a:b:c$=0·5406 : 1 : 0·2829, β 73° 52′, n_α 1·651, n_β 1·659, $n_\gamma-n_\alpha$ 0·022; (II) pistacio-green epidote, $a:b:c$=1·589 : 1 : 1·791, and 1·636 : 1 : 1·868, β 63° 48′ and 63° 57′, n_β 1·731; (III) greyish-green clinozoisite, d 3·28, n_α 1·715, n_β 1·722, $n_\gamma-n_\alpha$ 0·014; (IV) bluish-green zoisite, n_β 1·703; (V) plagioclase (albite-oligoclase), d 2·63, n_α 1·535, n_β 1·540, $n_\gamma-n_\alpha$ 0·009; (VI) pyrrhotite, d 4·63, Fe 60·50, Ni 0·74, S 38·06%; (VII) clove-brown axinite, d 3·280, $a:b:c$=1·170 : 1 : 0·778 and 1·204 : 1 : 0·897, α 96° 18′ and 97° 59′, β 99° 14′ and 99° 54′, γ 104° 13′ and 103° 51′, n_α 1·686, n_β 1·693, $n_\gamma-n_\alpha$ 0·010. Analyses of (I), (III), (V), and (VII) are (in that order): SiO_2 44·25, 37·57, 63·61, 41·39; TiO_2 0·55, 0·18, 0, 0; Al_2O_3 10·09, 28·20, 21·56, 18·31; Fe_2O_3 4·09, 6·61, 1·07, 0·65; FeO 14·54, 1·87, 0·15, 8·12; MnO 0·19, 0·12, trace, 2·70; MgO 9·76, 0, 0·12, 1·64; CaO 11·34, 23·56, 2·30, 20·13; Na_2O 0·63, 0·08, 9·42, 0·22; K_2O 1·41, 0·01, 1·29, 0·05; B_2O_3 0, 0, 0, 5·37; H_2O 3·44, 1·93, 0·63, 1·80. There also occur in small quantities blue asbestiform hornblende, graphite (in the pegmatite), chalcopyrite, specular iron, analcite, and perhaps natrolite. The paragenesis indicates deposition from gradually cooling H_2O. C. A. S.

Anapaite, ainigmatite, and eudidymite. C. Palache (Z. Krist., 1933, **86**, 280—291).—Anapaite, $Ca_2Fe(PO_4)_2,H_2O$ (cf. A., 1902, ii, 268; 1903, ii, 303), is triclinic, $a:b:c$=0·8575 : 1 : 0·9401, α 108° 56′ 40″, β 104° 5′ 40″, γ 78° 25′ 24″. Ainigmatite (or cossyrite) (cf. A., 1929, 1223) is triclinic, $a:b:c$=1·0014 : 1 : 0·5853, α 97° 2·5′, β 96° 49·5′, γ 112° 26·5′. Eudidymite is monoclinic, $a:b:c$=1·7103 : 1 : 1·8951, β 76° 42′. Previous results are discussed. C. A. S.

Frequent presence of pyrite crystals in the diatoms of lacustrine chalk: their probable bacterial origin. E. Joukowsky (Arch. Sci. phys. nat., 1933, [v], **15**, 182—185).—Descriptions are given. C. W. G.

Indium and scandium in pegmatite. H. Romeyn, jun. (J. Amer. Chem. Soc., 1933, **55**, 3899—3900).—Preliminary. The samples contain 1·0—2·8% In and 0·5—1·2% Sc. J. G. A. G.

Recent limestones. J. Pia (Tsch. Min. Petr. Mitt., 1933, Erganz.-Bd., 1—420).—A comprehensive treatise with review of the extensive literature on the deposition of $CaCO_3$ from solution. This takes place under a variety of conditions (abiogenic, physiological, and org.) and with many kinds of resulting products. L. J. S.

Petrography and petrology of the Mount Devon diabase porphryry. G. A. Muilenburg and S. S. Goldich (Amer. J. Sci., 1933, [v], **26**, 355—367).—The dike was extruded as a porphyritic magma, large crystals of basic plagioclase having been formed prior to intrusion. Secondary products were formed by the action of hydrothermal solutions derived probably from the main reservoir from which the magma was extruded. The secondary change is regarded as an end phase of the primary intrusion. H. F. G.

Portlandite, a new mineral from Scawt Hill, Co. Antrim. C. E. Tilley (Min. Mag., 1933, **23**, 419—420).—The larnite–spurrite rock occurring at the contact of dolerite and chalk contains in cavities colourless hexagonal plates with d 2·23, n_ω 1·575, n_ϵ 1·547, and the spacings a 3·64, c 4·85 Å. These characters together with microchemical tests identify the mineral with $Ca(OH)_2$, which has been previously found in Portland cement briquettes (Ashton and Wilson, A., 1927, 402). The mineral is associated with afwillite, and both have evidently been derived by the hydration of larnite and spurrite. L. J. S.

Piedmontite in quartz-muscovite-schist from New Zealand. F. J. Turner (Min. Mag., 1933, **23**, 416—418).—A reddish schist from Shotover valley, western Otago, thought to be coloured with hæmatite, when examined in micro-sections was found to contain piedmontite. Details are given of the optical characters. L. J. S.

Forms under which platinum and allied metals occur in nature. O. E. Zvjagintzev (Ann. Inst. Platine, 1932, No. 10, 14—33).—A discussion. R. T.

Malayan soils. I. Introduction. H. A. TEMPANY. **II. Classification and properties.** J. H. DENNETT (Malay. Agric. J., 1933, **21**, 345—361).—The composition and conditions of formation of these soils are discussed. A. G. P.

Lithology and palæobotany of certain British coals. R. CROOKALL (Fuel, 1933, **12**, 276—279).—The conditions under which the original plant débris was deposited are discussed in relation to the formation of the different lithological types (fusain, durain, clarain, and vitrain) in British coals. The important factors in this process were (*a*) the level at which the waters stood in relation to the accumulating plant débris, and (*b*) the plant parts present. Numerous lenticles of fusain indicate that, during the accumulation of the plant débris, the general level of the peat-like matter approximated to that of the swamp waters, so that masses of débris were frequently exposed to sub-aërial decay. In some cases the rarity of durain is to be correlated with the scarcity of Lycopods in the flora of the immediate roofs of the co-extensive seams. The fragile nature of some coals may be due to the high proportion of clarain and fusain (*e.g.*, Kent coals), or to the exceptional development of cleat. A. B. M.

Organic Chemistry.

Nature of valencies in organic chemistry. G. URBAIN (Bull. Soc. chim., 1933, [iv], **53**, 637—652).—A lecture.

Theory of free radicals of organic chemistry. E. HUCKEL (Faraday Soc., Sept., 1933, Advance proof; cf. this vol., 890). R. S. C.

Chemistry of radicals with tervalent carbon. K. ZIEGLER (Faraday Soc., Sept., 1933, Advance proof).—The tendency to dissociation of substituted ethanes is influenced by both the unsaturation and the size of the substituents. The latter factor operates by increasing the distance separating the ethane C atoms. Published work is reviewed and it is stressed that quant. data are essential for further progress. R. S. C.

Free radicals and ions as factors in chemical change. T. M. LOWRY (Faraday Soc., Sept., 1933, Advance proof).—A summary is given of the ways in which C·C linkings may rupture and of the methods used for investigation of the problem. R. S. C.

Use of free methyl and ethyl in chemical synthesis. F. A. PANETH [with H. LOLEIT and W. LAUTSCH] (Faraday Soc., Sept., 1933, Advance proof).—By decomp. of the Pb compounds Me, Et, and CH_2Ph (but not Pr, Bu, CH_2, or Ph) radicals are obtained in low concn. Me or Et radicals with cold As, Sb, or Bi mirrors give $AsMe_3$, $(AsMe_2)_2$, $(AsMe)_5$, $AsEt_3$, $(AsEt_2)_2$, $(AsEt)_5$, $SbMe_3$, $(SbMe_2)_2$, m.p. 17·5°, $SbEt_3$, $BiMe_3$, and $BiEt_3$. With hot mirrors an increased proportion of the less volatile mono- and di-alkyl compounds is formed, together with $(SbEt_2)_2$ and $(BiMe_2)_2$. $SbEt_2O_2H$ is prepared. R. S. C

Preparation of tetramethylmethane (neopentane) and determination of its physical constants. F. C. WHITMORE and G. H. FLEMING (J. Amer. Chem. Soc., 1933, **55**, 3803—3806).—CMe_4, b.p. 9·4°/760 mm., f.p. −19·5° (corr.), is conveniently prepared in 42—50% yield from MgMeCl and Bu$^\gamma$Cl in PhMe at 45—50°. Numerous physical data are given. H. B.

Hexamethylethane. F. C. WHITMORE, C. J. STEHMAN, and J. M. HERNDON (J. Amer. Chem. Soc., 1933, **55**, 3807—3809).—C_2Me_6, m.p. 101°, is obtained in 10% yield from MgMeCl and CMe_3·CMe_2Br (I) in xylene at 60°, in 18—19% yield from MgBu$^\gamma$Cl and AgBr in Et_2O, and in 50% yield from $ZnMe_2$ and (I) in xylene. Other methods tried are summarised. H. B.

Antimony trichloride as reagent for the ethylenic linking. S. SABETAY (Compt. rend., 1933, **197**, 557—559).—30% $SbCl_3$–$CHCl_3$ solution with ethylenic compounds or certain aldehydes gives yellow, brown, red, or blue (much less intense than with carotenoids) colours and usually a pink, yellow, or brown ppt. The reaction is negative for saturated or aromatic (otherwise saturated) compounds, and for styrene, cinnamic and crotonic acids, allyl alcohol, and C_2HCl_3. Bases give white ppts. Et octinenoate gives a pink ppt. R. S. C.

Preparation of Δ^α- and *iso*-butene. H. PINES (J. Amer. Chem. Soc., 1933, **55**, 3892—3893).—Pure Δ^α-butene is obtained when Bu$^\alpha$OH is passed at the rate of 75 g. per hr. through a glass tube filled with Al_2O_3 at 375—425°. The discrepancy between this result and that of Matignon *et al.* (this vol., 693) is probably due to the method of analysis used by the last-named. Pure *iso*butene is prepared by Ipatiev's method (A., 1903, i, 594). H. B.

Polymerisation of diolefines with olefines. II. Function of Δ^β-pentene in the polymerisation of isoprene. C. A. THOMAS and W. H. CARMODY (J. Amer. Chem. Soc., 1933, **55**, 3854—3856).—Polymerisation of pure isoprene (I) by solid $AlCl_3$ occurs slowly and gives an insol. polymeride (II). When dry HCl is passed into a mixture of (I), $AlCl_3$, and naphtha, (II) and sol. polymeride (III) result; the amount of (III) produced is related to the quantity of the hydrochloride of (I) formed [when sufficient of this is used to dissolve all the $AlCl_3$, (III) is the sole product]. The yield of (III) is also increased with other mutual solvents ($PhNO_2$, EtOAc) for (I) and $AlCl_3$. The function of Δ^β-pentene in the polymerisation previously studied (A., 1932, 830) is to act as a "solubiliser" for the $AlCl_3$. The mechanism of polymerisation of (I) is discussed (cf. Houtz and Adkins, this vol., 600). H. B.

Ozonisation of lycopene. Formation of lævulic acid and lævulaldehyde. H. H. STRAIN (J. Biol. Chem., 1933, **102**, 151—155).—Ozonisation of lycopene (I) yields, according to the conditions, lævulaldehyde [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p.

235·5—236·5° (corr.)] or lævulic acid [2 : 4-dinitrophenylhydrazone, m.p. 203—205·5° (corr.); β-*naphthylhydrazone*, m.p. 136·5° (corr.)], the max. yield of the latter being 1·32 mols., thus confirming Karrer's formula for (I). Citral, but not xanthophyll, forms the same products under similar conditions. R. S. C.

Fluorination of organic compounds. III. Action of fluorine on organic compounds. W. Bockemuller (Annalen, 1933, **506**, 20—59; cf. A., 1931, 611).—*n*-Hexadecane (1 mol.) and F (1 mol.) (prep. by electrolysis of fused KHF_2 described in detail) in CCl_4 at 15° give a *fluorohexadecane*, b.p. 104—112°/0·2 mm., m.p. 7° (previous softening). $PrCO_2H$ (or PrCOCl) similarly affords (at 0°) a mixture of β- and γ-fluorobutyric acids, b.p. 80—98°/13 mm. [from which a p-*phenylphenacyl* ester (I), m.p. 92°, is prepared], since hydrolysis (aq. NaOH) gives $CHMe{:}CH{\cdot}CO_2H$ and γ-butyrolactone; some γγγ-trifluorobutyric acid is also produced, since treatment of the original product with aq. $NaHCO_3$ and subsequent distillation gives a residue containing $(\cdot CH_2{\cdot}CO_2H)_2$. *α-Fluorobutyric acid*, b.p. 90°/13 mm. [p-*phenylphenacyl* ester, m.p. 91·5°, not identical with (I)], is obtained by hydrolysis (dil. HCl) of its *Et* ester, b.p. 138—141° (prepared from $CHBrEt{\cdot}CO_2Et$ and AgF–CaF_2 at 150°). (I) is also prepared from the hydrolysis product of the similar fluorination of Pr·CO·OAc. $Pr^{\beta}CO_2H$ is fluorinated to (mainly) β-*fluoroisobutyric acid*, b.p. 80—82°/13 mm. *cyclo*Hexane and F in CCl_2F_2 at −80° give cyclo*hexyl fluoride*, b.p. 100°, and higher F-compounds. C_2Cl_4 and F similarly afford (mainly) $C_2Cl_4F_2$, b.p. 91°, m.p. 26·5° (cf. Booth *et al.*, A., 1932, 496), some C_2Cl_5F, m.p. about 100°, a trace of CCl_3F, and some *octachlorodifluorobutane*, b.p. 139—142°/13 mm. [which may be formed thus: $C_2Cl_4+F_2 \longrightarrow \cdots\cdots CCl_2{:}CCl_2\cdots\cdots F_2 \longrightarrow \cdots\cdots CCl_2{\cdot}CCl_2{\cdot}CCl_2{\cdot}CCl_2\cdots\cdots F_2 \longrightarrow (\cdot CCl_2{\cdot}CCl_2F)_2$]. *n*-$\Delta^{\alpha}$-Hexadecene and F in CCl_4 at 15° give *difluorohexadecane*, b.p. 103—106°/0·2 mm.; oleic acid (II) affords a *difluorostearic acid* (III), m.p. 81° (softens at 80°) [in one case, using (II) from a different source, an *isomeride*, m.p. 95°, was also produced], whilst elaidic acid furnishes a *difluorostearic acid*, m.p. 84—85°, which differs from (III). In all these cases, substitution occurs also. $CHMe{:}CH{\cdot}CO_2H$ and F in CCl_4 at 0° afford two αβ-*difluorobutyric acids*, m.p. 81° (IV), and b.p. 100—102°/13 mm. (V), and an *acid*, $C_8H_{12}O_4F_2$ [Me_2 ester (VI), b.p. 105—115°/0·5 mm.]. (IV) and (V) are hydrolysed (aq. NaOH) to *α-fluorocrotonic*, m.p. 112°, and impure α-fluoro*iso*crotonic acid, respectively, whilst (VI) and MeOH–KOH give an unsaturated *acid*, $C_8H_{10}O_4$, m.p. 240—244° (decomp.).

Fluorination of C_6H_6 in CCl_4 does not give simple substitution products, but yields a F-containing tar; PhBr, *p*-$C_6H_4Br_2$, *m*-$C_6H_4(NO_2)_2$, and benzoquinone behave similarly. BzOH and F in CCl_4 at 15° afford an amorphous product (the F content of which increases with time of fluorination); in presence of Br at 0°, CO_2H is eliminated and fractions, b.p. 110—120°/13 mm., and 150—160°/13 mm., of the composition $C_6H_6Br_2F_4$ and $C_6H_6Br_3F_3$, respectively, are isolated. These are partly converted by Zn-Cu into aromatic compounds which yield non-homogeneous bromofluoronitro-compounds. In the above fluorinations, the F is diluted with about an equal vol. of CO_2. H. B.

Preparation of *iso*propyl bromide from *iso*propyl alcohol. E. A. Werner (J.S.C.I., 1933, **52**, 285—286T).—Experiments on the prep. of $Pr^{\beta}Br$ (I): $Pr^{\beta}OH+KBr+H_2SO_4=Pr^{\beta}Br+KHSO_4+H_2O$, have shown that if the anhyd. alcohol is used, or $<10\%$ of H_2O is present, the yield of alkyl bromide is poor (about 38%) on account of the simultaneous production of much propylene (II). With greater dilution the formation of (II) can be completely suppressed, and although this tends to suppress esterification of the alcohol, the yield of (I) is considerably increased at the expense of formation of (II). Thus a yield of pure (I), b.p. 60—61°, equal to 73·5% was obtained by heating at 90—115° a mixture of $3Pr^{\beta}OH,H_2O$ 100 g., H_2SO_4 150 g., and $NaBr,2H_2O$ 210 g. No (II) was formed.

Sorbyl chloride [α-chloro $\Delta^{\beta\delta}$-hexadiene]. II. T. Reichstein and G. Trivelli (Helv. Chim. Acta, 1933, **16**, 968—975; cf. A., 1932, 498).—Sorbyl chloride [α-chloro-$\Delta^{\beta\delta}$-hexadiene] (I), b.p. 45·5°/12 mm. (improved prep.), and NaOPh in Et_2O yield o-$\Delta^{\beta\delta}$-*hexadienylphenol*, b.p. 100°/0·2 mm., hydrogenated (PtO_2–Et_2O) to *o-n*-hexylphenol and a neutral substance, b.p. 72°/0·2 mm., which is not Ph hexadienyl ether. (I), Mg, and CO_2 in Et_2O afford an unsaturated acid hydrogenated to immediately homogeneous α-ethyl-*n*-valeric acid and a hydrocarbon $C_{12}H_{18}$ (II), b.p. 90—95°/11 mm., which is the main product when Mg–Cu is used in absence of CO_2. Hydrogenation of (II) does not lead to *n*-dodecane. Ozonisation of (II) and subsequent oxidation with $KMnO_4$ yields $(\cdot CH_2{\cdot}CO_2H)_2$. (II) is probably a mixture of δε-divinyl-$\Delta^{\beta\zeta}$-octadiene and δ-vinyl-$\Delta^{\beta\zeta\theta}$-decatriene. H. W.

Analysis of liquid organic substances by the conductometric method. K. Šandera (Chim. et Ind., 1933, **29**, Spec. no., 231—234).—The mixture of org. liquids is saturated with a suitable electrolyte, and the conductivity of the solution determined. The method is standardised by measurements with mixtures of known concn., and has been applied to mixtures of H_2O and EtOH (using $CaSO_4$, K_2SO_4 or KCl), H_2O and MeOH (using $CaSO_4$) and pentane and MeOH (using KCl as electrolyte). J. W. S.

Tschugaev reaction for dehydrating alcohols. F. C. Whitmore and C. T. Simpson (J. Amer. Chem. Soc., 1933, **55**, 3809—3812).—The Tschugaev method (A., 1900, i, 129) applied to *n*- and *iso*-amyl alcohols gives Δ^{α}-pentene and $CH_2{:}CHPr^{\beta}$, respectively; octyl alcohol furnishes almost equal amounts of Δ^{α}- and Δ^{β}-octene. No rearrangement occurs. The Na (K) xanthate is best prepared from an excess of the alcohol and equimol. quantities of NaOH (KOH) and CS_2 or equimol. amounts of the reactants in Et_2O–CCl_4. *n*-AlkO·CS_2Me are relatively stable to heat; they can be distilled in vac. H. B.

Hexacyanocobaltic acid and *n*-propyl alcohol. —See this vol., 1131.

Configuration-specific esterification of *sec.*-alcohols in presence of brucine or strychnine.

R. WEGLER (Annalen, 1933, 506, 77—83; cf. A., 1932, 1094).—Treatment of *dl*-CHPhMe·OH, CHPhPr$^{\beta}$·OH, and CHPhEt·OH with Ac_2O in presence of brucine and CCl_4 gives (−)-acetates; the (−)-antipode is esterified more readily in each case. CHMeBu·OH affords a (+)-acetate and is thus configuratively related to the above series; the opposite antipode is esterified more readily with CHMeEt·OH, OH·CHMe·CH_2Ph, and *cyclo*hexylmethylcarbinol (I). Except for (I), the residual alcohol is dextrorotatory. (+)-Benzoates are obtained (using BzCl) from the above and CHMePr$^{\beta}$·OH (II), CHPhBu·OH, *cyclo*hexylpropylcarbinol, *cyclo*hexylethylcarbinol, OH·CHPr$^{\beta}$·CH_2Ph, and CHBuPr$^{\beta}$·OH; some of the residual alcohols are dextro- and some lævo-rotatory. All the above alcohols [except (II)] and CHEtPr·OH, CHEtBu·OH, and OH·CHEt·CH_2Ph give (+)-benzoates in presence of strychnine; (II) affords a (−)-benzoate. H. B.

Rearrangement of *tert.*-butylmethylcarbinol (pinacolyl alcohol). II. Dehydration. F. C. WHITMORE and P. L. MEUNIER (J. Amer. Chem. Soc., 1933, 55, 3721—3722; cf. this vol., 486).—Dehydration of CHMeBu$^{\gamma}$·OH over H_3PO_4 on SiO_2 gel at 300°/2500 lb. pressure gives CMe_2:CMe_2 and CH_2:$CMePr^{\beta}$ in the ratio 2 : 1, together with 3% of the normal dehydration product, CH_2:$CHBu^{\gamma}$. H. B.

Dehydration of *tert.*-alcohols containing a neopentyl system. II. Methyl*iso*propyl*tert.*-butyl-, methyldi*tert.*-butyl-, and methylethylneopentylcarbinols. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1933, 55, 3732—3738).—Dehydration of CMeEtBu$^{\gamma}$·OH with 2-$C_{10}H_7$·SO_3H gives the same mixture of olefines as is obtained using I (A., 1932, 1232). Dimethyl*tert.*-amylcarbinol, b.p. 86·5°/60 mm., obtained in 78% yield from MgMeCl and CMe_2Et·CO_2Et, is similarly dehydrated to (mainly) $\beta\gamma\gamma$-trimethyl-Δ^{α}-pentene, b.p. 107·5—108·7°, and < 6% of $\beta\gamma\gamma$-trimethyl-Δ^{γ}-pentene (formed by rearrangement of a Me group). MgMeCl and COPr$^{\beta}$Bu$^{\gamma}$ [prepared (*a*) by oxidation (CrO_3) of CHPr$^{\beta}$Bu$^{\gamma}$·OH, (*b*) from COMeBu$^{\gamma}$, MeI, and $NaNH_2$ in Et_2O–C_6H_6, and (*c*) $COPr^{\beta}_2$, $NaNH_2$, and Me_2SO_4 in PhMe] give CMePr$^{\beta}$Bu$^{\gamma}$·OH, b.p. 62°/12 mm., which is dehydrated (2-$C_{10}H_7$·SO_3H) to $\gamma\gamma$-dimethyl-β-*iso*propyl-Δ^{α}-butene and $\beta\gamma\gamma\delta$-tetramethyl-Δ^{α}-pentene (rearrangement product) in the ratio 3 : 1, and a trace of $\beta\gamma\delta\delta$-tetramethyl-Δ^{β}-pentene (by normal dehydration involving the Pr$^{\beta}$ group). CMeBu$^{\gamma}_2$·OH, b.p. 122·5—123°/100 mm., m.p. 42°, from MgMeCl and $COBu^{\gamma}_2$, is dehydrated to > 90% of $\gamma\gamma$-dimethyl-β-*tert.*-butyl-Δ^{α}-butene and some unidentified material of low b.p. Methylethylneopentylcarbinol, b.p. 62—62·5°/14 mm., from MgEtBr and Me neopentyl ketone, is dehydrated without rearrangement to (mainly) $\gamma\varepsilon\varepsilon$-trimethyl-$\Delta^{\beta}$-hexene, < 5% of $\beta\beta\delta$-trimethyl-Δ^{γ}-hexene, and a trace of $\delta\delta$-dimethyl-β-ethyl-Δ^{α}-pentene. The structures of the olefines are proved by ozonolysis. The results show the great tendency of *tert.*-alcohols to dehydrate without rearrangement; this is in marked contrast to the related primary and *sec.*-alcohols containing the neopentyl group, which dehydrate mainly with rearrangement (cf. *loc. cit.*). H. B.

Trialkylethinylcarbinols. D. D. COFFMAN, J. C. Y. TSAO, L. E. SCHNIEPP, and C. S. MARVEL (J. Amer. Chem. Soc., 1933, 55, 3792—3796).—Mg cetyl bromide and CH_2:CBr·CH_2Br in Et_2O and N_2 give 14·8% of β-*bromo*-Δ^{α}-*nonadecene*, b.p. 168—172°/0·5 mm., m.p. 10—10·5°, converted by $NaNH_2$ in xylene into Δ^{α}-*nonadecinene*, b.p. 144°/1·5 mm., m.p. 37—38° (*Hg* derivative, m.p. 96—97°). This is converted as described previously (A., 1928, 988) into *tri*-Δ^{α}-*nonadecinylcarbinol* (I), m.p. 71—72° (the *Me ether*, m.p. 44—45°, prepared from the ·OMgBr derivative and Me_2SO_4, could not be cleaved by liquid Na–K alloy), which with AcOH–conc. H_2SO_4 gives *di*(*tri*-β-*ketononadecylmethyl*) *ether* (?), m.p. 56—58°. (I) and 40% HBr or AcBr in Et_2O or C_6H_6 give a *compound*, m.p. 37—38°, which is not the expected bromide; (I), $SOCl_2$, and C_5H_5N afford a *compound*, m.p. 40—42°. Mg Δ^{α}-propinyl bromide (II) and Et_2CO_3 yield *tri*-Δ^{α}-*propinylcarbinol*, m.p. 134—135°, which is reduced (H_2, PtO_2, EtOH) to CPr^{α}_3·OH, and is converted by PCl_5 in C_6H_6 into a *compound*, $(C_{10}H_9Cl)_2$, m.p. 153—154° (violent decomp.), the Cl of which is not removed by "mol." Ag. $COPr_2$ and (II) give *di*-n-*propyl*-Δ^{α}-*propinylcarbinol* (III), b.p. 196—197°, also reduced to CPr^{α}_3·OH, which with PCl_5 or $SOCl_2$ affords liquid products which decompose on distillation. Me ethers could not be prepared from (I) or (III) and MeOH–conc. H_2SO_4. H. B.

Determination of the configuration of polyhydroxy-compounds. B. ENGLUND (Svensk Kem. Tidskr., 1933, 45, 196—202).—A crit. review of methods of determining structure from complex formation with H_3BO_3 and As compounds. R. P. B.

Stability of ethylene glycol in acid solution.—See this vol., 1123.

Oxidation of αβ-glycols by lead tetra-acetate and periodic acid. P. KARRER and R. HIROHATA (Helv. Chim. Acta, 1933, 16, 959—962).—Comparative examination of the oxidation of βε-dimethyl-*n*-hexane-βγ-diol and α-phenyl-β-methylpropane-αβ-diol shows HIO_4 to be the more suitable reagent for operation in H_2O; otherwise $Pb(OAc)_4$ is probably to be preferred by reason of the subsequent ready removal of Pb salts. H. W.

Partial acetonisation of sugars and sugar alcohols. III. αβ-*iso*Propylidene-*d*-mannitol and partly acylated derivatives of *d*-mannitol. L. VON VARGHA (Ber., 1933, 66, [*B*], 1394—1399; cf. this vol., 490).—*d*-Mannitol is converted by $COMe_2$, H_3BO_3, and conc. H_2SO_4 into αβ-iso*propylidenemannitol* δε-*borate* (I), m.p. (indef.) 75—90°, converted by evaporation with MeOH into αβ-iso*propylidene*-d-*mannitol* (II), m.p. 167°, $[\alpha]_D^{20}$ +3·48° in H_2O. The position of the alkyl group in (II) follows from the non-identity of (II) with γδ-*iso*propylidene-*d*-mannitol, the conversion of (II) by CPh_3Cl in C_5H_5N into ζ-*triphenylmethyl*-αβ-iso*propylidene*-d-*mannitol*, m.p. (indef.) 45—55°, $[\alpha]_D^{20}$ +3·29° in $CHCl_3$ [also obtained from (I)], by $COMe_2$ and anhyd. $CuSO_4$ into αβεζ-di*iso*propylidene-*d*-mannitol, m.p. 122°, $[\alpha]_D^{25}$ +1·2° in H_2O, and by $COMe_2$–conc. H_2SO_4 into tri*iso*propylidene-*d*-mannitol. The δε position of $B(OH)_2$ is preferred, since any other eventuality

involves the possibility of introducing a further :CMe_2 or :$B(OH)_2$. (II) and Ac_2O in C_5H_5N afford αβ-iso*propylidene*-d-*mannitol* γδεζ-*tetra-acetate* (III), m.p. 107°, $[\alpha]_D^{20}$ +28·04° in $CHCl_3$, whilst (II), BzCl, and C_5H_5N give αβ-iso*propylidene*-d-*mannitol* γδεζ-*tetrabenzoate* (IV), m.p. 114°, $[\alpha]_D^{23}$ +47·84° in $CHCl_3$. αβεζ-*Di*iso*propylidene*-d-*mannitol* γδ-*diacetate* (V) has m.p. 123°, $[\alpha]_D^{20}$ +26·72° in $CHCl_3$. Hydrolysis of (III) by 70% AcOH at 50° leads to d-*mannitol* γδεζ-*tetra-acetate*, m.p. 92°, $[\alpha]_D^{20}$ +31·61° in $CHCl_3$, +26·0° in H_2O. Similar hydrolysis of (IV) and (V) leads, respectively, to d-*mannitol* γδεζ-*tetrabenzoate*, $[\alpha]_D^{15}$ +52·56° in $CHCl_3$, and d-*mannitol* γδ-*diacetate*, m.p. 139°, $[\alpha]_D^{15}$ +45·32° in H_2O. H. W.

Formation of cyclic acetals from aldehydes or ketones and alkylene oxides. M. T. Bogert and R. O. Roblin, jun. (J. Amer. Chem. Soc., 1933, **55**, 3741—3745).—Ethylene oxides (0·25 mol.) react with COR_2 or RCHO (0·2 mol.) in presence of anhyd. $SnCl_4$ (0·01 mol.) at 40—45° to give 25—35% yields of the :CR_2 and :CHR ethers of the ethylene glycols; increases in the amount of $SnCl_4$ or rise of temp. cause the formation of "polymeric" material. Traces of ethers are formed using $ZnCl_2$, $FeCl_3$, $SbCl_3$, $AlCl_3$, or $SnCl_4,4H_2O$, but no appreciable reaction occurs with $CaCl_2$, NH_4Cl, HCl, H_2SO_4, or $POCl_3$. The benzylidene, heptylidene, *methylhexylmethylene*, b.p. 97° (all b.p. are corr.)/23 mm., and *phenylmethylmethylene*, b.p. 103·5—104·5°/23 mm., m.p. 62° (corr.), *ethers* of $(\cdot CH_2\cdot OH)_2$ and the *benzylidene*, b.p. 118°/23 mm., *heptylidene*, b.p. 102·5—103·5°/23 mm., *methylhexylmethylene*, b.p. 102°/23 mm., and *phenylmethylmethylene*, b.p. 105°/23 mm., *ethers* of $OH\cdot CHMe\cdot CH_2\cdot OH$ are described. H. B.

Formation of alkyl nitrites in dilute solutions. Butyl and amyl nitrites. W. A. Noyes (J. Amer. Chem. Soc., 1933, **55**, 3888—3889).—A convenient method of prep. of Bu$^\alpha$ and amyl nitrites is given. In the production of $EtO\cdot NO$, the EtOH functions as an acid and the HNO_2 as a base. H. B.

Phosphoric esters of xylose and of 5-methyl-*iso*propylidenexylose. Their bearing on the nature of the pentose of yeast nucleic acid. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1933, **102**, 347—355).—*iso*Propylidenexylose and $POCl_3$ in cold C_5H_5N give a product, which with hot 2*N*-H_2SO_4 affords *xylose-5-phosphoric acid* [*Ba* salt (I), $[\alpha]_D^{22}$ about +5·0° in H_2O; *Na* salt, $[\alpha]^{22}$ about +3·2° in H_2O and about +4·8° in half-saturated borax solution]. *iso*Propylidenexylose 5-benzoate and 5-acetate afford (probably 5-)*phosphoric acids* (*Ba* salts), which, when hydrolysed, give probably (I). 5-Methyl-1 : 2-*iso*propylidenexylose (II) gives a 3-*phosphoric acid* [*Ba* salt (impure), $[\alpha]_D^{22}$ +4·0° in H_2O], which with BaO in MeOH gives only (II), no migration having occurred. (I) is shown by reduction to give a γ-glucoside. R. S. C.

Preparation of aliphatic mercaptans and sulphonic acids of high mol. wt. G. Collin, T. P. Hilditch, P. Marsh, and A. F. McLeod (J.S.C.I., 1933, **52**, 272—275T).—Improved methods of prep. are given for higher alkyl mercaptans (I) from the corresponding halides, and for oxidation of (I) to the corresponding sulphonic acids (II), which are isolated as Na salts. Nearly theoretical yields of (I) are obtained when the halides are heated in an autoclave at 130—160° with dry EtOH–NaSH saturated with H_2S. The simple (I) oxidise extremely readily to disulphides (III), even by exposure to air. The (I) or (III) are best oxidised to (II) by $KMnO_4$ in $COMe_2$ or AcOH, or by CrO_3 in AcOH; the soft soap-like, hygroscopic (II) may be "salted out" from the aq. solutions of the oxidation products by means of aq. HCl, and are then best converted into the cryst. Na salts for analysis. The following are described: n-*octadecyl*, m.p. 56°, and n-*dodecyl mercaptan*, m.p. 18—20°; α-*thiolpalmitic acid*, m.p. 82°, 9(or 10)-*thiolstearic acid*, liquid; *di*-n-*octadecyl*, m.p. 62·5°, *di*-n-*hexadecyl*, m.p. 54°, and *di*-n-*dodecyl disulphide*, m.p. 32°. By oxidation of (I) or (III) the following products were obtained: from *n*-octadecyl mercaptan or disulphide, *Na* n-*octadecylsulphonate* and a neutral *compound*, m.p. 112°; from *n*-hexadecyl, *Na* n-*hexadecylsulphonate* and a neutral *compound*, m.p. 95°; from *n*-dodecyl, *Na* n-*dodecylsulphonate* and traces of a neutral *compound*, m.p. 71°; from α-thiolpalmitic acid, a Na_1 salt, probably $C_{14}H_{29}\cdot CH(SO_3Na)\cdot CO_2H$.

Preparation and properties of anhydrous acetic acid. W. C. Eichelberger and V. K. La Mer (J. Amer. Chem. Soc., 1933, **55**, 3633—3634).—Large quantities of AcOH are best purified by refluxing with CrO_3 in amount slightly > required to react with H_2O present, distilling, and dehydrating with $B(OAc)_3$. AcOH, m.p. 16·60°±0·01, has sp. conductivity $1\cdot4\times10^{-8}$ reciprocal ohm at 25°. J. G. A. G.

Elimination of bromine from bromoacetic acid and bromoacetates.—See this vol., 1125.

Preparation of nonoic acid and its catalytic reduction to nonaldehyde. H. Paillard and A. Demolis (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 131—137).—The yield of nonoic acid (I) obtained by alkali fusion of undecenoic acid varies from 20 to 77% being greatest with KOH (3 parts) at 350° (time of fusion, 35 min.). (I) is best reduced to nonaldehyde (70% yield) by passage with HCO_2H over $MnCO_3$ on pumice at 330—350° and atm. pressure. $MnCO_3$ on SiO_2 gel and $Mn(OH)_2$ are ineffective, and CO–H_2O mixtures (1 : 1) cannot replace HCO_2H. R. S. C.

Isomeric [fatty acid] esters. J. R. Ruhoff and E. E. Reid (J. Amer. Chem. Soc., 1933, **55**, 3825—3828).—Numerous physical data are determined for fifteen esters, $R\cdot CO_2R'$, where R=H—*n*-$C_{14}H_{29}$ and R′=*n*-$C_{15}H_{31}$—Me. The following are new: *Pr*$^\alpha$ *tridecoate*, b.p. 194°/30 mm., m.p. —5·74°; n-*amyl undecoate*, b.p. 193°/30 mm., m.p. —21·17°; n-*hexyl decoate*, b.p. 193°/30 mm., m.p. —17·67°; n-*nonyl heptoate*, b.p. 193°/30 mm., m.p. —11·14°; n-*decyl hexoate*, b.p. 193°/30 mm., m.p. —19·29°; n-*undecyl valerate*, b.p. 193·5°/30 mm., m.p. —23·14°; n-*tridecyl propionate*, b.p. 195°/30 mm., m.p. —0·42°; n-*pentadecyl formate*, b.p. 201·5°/30 mm., m.p. 13·69°. H. B.

Addition of hydrogen bromide to olefines. Undecenoic acid. J. C. Smith (Nature, 1933, **132**,

447; cf. this vol., 805).—HBr passed into 10% solution of undecenoic acid in light petroleum gave 70—80% yields of practically pure κ-bromoundecoic acid: when O_2 is removed by H_2 or by addition of $NHPh_2$, a mixed product in which the ι-Br-acid predominates is obtained. L. S. T.

Capillary fractionation of fatty acids. R. Dubrisay (Chim. et Ind., 1933, **29**, Spec. no., 1045—1047; cf. A., 1932, 1198).—Considerable fractionation of mixtures of two acids, *e.g.*, oleic, arachidic, or stearic and lauric acids, or a purification of crude oleic acid, can be effected by producing a lather in an aq. 0·1% solution of the mixed soaps and separating the froth, which is richer in the more surface-active constituent, from the remainder. E. L.

Radical interchange of alkyl orthoformates. H. W. Post and E. R. Erickson (J. Amer. Chem. Soc., 1933, **55**, 3851—3854).—$CHCl_3$ (1 equiv.), NaOR (R=Et or Pr) (1·5 equivs.), and NaOR′ (R′=Pr, Bu, *n*- and *iso*-amyl) (1·5 equivs.) give mixtures of $CH(OR)_3$, $OR'\cdot CH(OR)_2$, $OR\cdot CH(OR')_2$, and $CH(OR')_3$. Equilibrium mixtures of the four esters are obtained also when mixtures of $CH(OR)_3$ and $CH(OR')_3$ are kept at room temp. for 1 month. $OPr\cdot CH(OEt)_2$ in presence of P_2O_5 gives all four possible esters, whilst $CH(OPr)_3$ and EtOH afford $CH(OEt)_3$ (2·1%), $OPr\cdot CH(OEt)_2$ (42%), $OEt\cdot CH(OPr)_2$ (40%), $CH(OPr)_3$ (15·9%), EtOH, and PrOH. The reaction $CH(OEt)_3+EtSH \rightleftharpoons EtOH+SEt\cdot CH(OEt)_2$ occurs at room temp. H. B.

Fixation of Sb_2O_3 by monohydroxy-monoacids. Volmar and Duquénois (Compt. rend., 1933, **197**, 599—600; cf. this vol., 376).—Only α-OH-acids react with Sb_2O_3, the reaction velocity being greatest with *tert.*-OH. The following are described: *Na antimonyl glycollate* ($+H_2O$), and *α-hydroxybutyrate*, and *Na* ($+2H_2O$), and *K antimonyl α-hydroxy*iso*butyrate*. A. A. L.

Benzyl compounds of α-hydroxy-acids and their application to syntheses. I. Derivatives of glycollic acid. H. O. L. Fischer and B. Gohlke (Helv. Chim. Acta, 1933, **16**, 1130—1142).—The chlorides of benzyloxy-acids are condensed with OH-acid, alcohols, etc. in the presence of *tert.* bases and the CH_2Ph group is removed from the product by hydrogenation in presence of Pd. $CH_2Cl\cdot CO_2H$ is converted by a large excess of $CH_2Ph\cdot ONa$ in $CH_2Ph\cdot OH$ at 150° into *benzyloxyacetic acid*, b.p. 136°/0·2 mm., which with PCl_5 in $CHCl_3$ affords *benzyloxyacetyl chloride* (I), b.p. 81°/0·2 mm. (*benzyloxyacetanilide*, m.p. 49°). (I), $OH\cdot CH_2\cdot CO_2H$ and $NPhMe_2$ in $CHCl_3$ give *benzylglycollylglycollic acid*, b.p. 151°/0·05 mm., m.p. 59° after softening at 55—56°, whence (Pd–H_2–AcOH) glycollylglycollic acid, m.p. 97—99°. (I) and *iso*propylideneglycerol yield iso*propylideneglyceryl benzyloxyacetate*, b.p. 152—153°/0·04 mm., whence iso*propylideneglyceryl hydroxyacetate*, b.p. 91°/0·05 mm., hydrolysed by 12·5% AcOH to *glyceryl α-hydroxyacetate* (*Ac*$_2$ derivative, b.p. 118°/0·05 mm.). Glycerol yields non-cryst. *glyceryl tribenzyloxyacetate* and non-cryst. *glyceryl trihydroxyacetate* (*Ac*$_3$, b.p. 177—180°/0·05 mm., and *Bz*$_3$, m.p. 83—85° after softening at about 78°, derivatives). β-Di*iso*propylidenefructose is converted into the 6-*benzyloxyacetate*, m.p. 84°, and 6-*hydroxyacetate*, m.p. 128°, $[\alpha]_D^{21}$ −30·65° in $CHCl_3$. *iso*-Propylideneglucose gives the 3 : 5 : 6-*tribenzyloxyacetate*, m.p. 73°, whence the non-cryst. 3 : 5 : 6-*trihydroxyacetate* and *glucose* 3 : 5 : 6-*trihydroxyacetate*. Glucose gives the *pentabenzyloxyacetate*, hydrogenated to the non-cryst. *pentahydroxyacetate*. H. W.

Optical rotations of configuratively related methoxypropiono- and β-methoxybutyro-nitriles. P. A. Levene and R. E. Marker (J. Biol. Chem., 1933, **102**, 297—302).—Et lactate, $[M]_D^{25}$ −7·55°, with MeI–Ag_2O gives *Et* l-α-*methoxypropionate*, b.p. 142°, $[M]_D^{0}$ −119·6°, hydrolysed to the corresponding *acid*, b.p. 92°/15 mm., −80·7°, whence, by way of the chloride and amide, the *nitrile*, b.p. 115°/735 mm., $[M]_D^{20}$ −117·5°, was obtained. *Et* l-β-*hydroxybutyrate*, b.p. 74°/12 mm., $[M]_D^{25}$ −33·0° (from the acid, $[M]_D$ −25·0° in H_2O), gives similarly l-β-*methoxybutyric acid*, b.p. 115°/15 mm., $[M]_D$ −13·7° (*Et* ester, b.p. 165°, −10·6°), and the *nitrile*, b.p. 129°/740 mm., $[M]_D^{25}$ +13·9°. The rotation contributions of the CO_2H, CO_2Et, and (probably) CN groups are of opposite order in the two series. R. S. C.

Titanium potassium oxalate. L. Stuckert (Chem.-Ztg., 1933, **57**, 754—755).—Ti K oxalate (I) may be prepared on the technical scale by treating TiO_2 with highly-conc. aq. NaOH at 300—400° and finally at 600—650°, and converting the K_2TiO_3 formed into (I) by dissolving in the theoretical amount of aq. $H_2C_2O_4$. The yield is 90—96%. E. S. H.

Carbon syntheses with malonic and related acids. I. A. Michael and J. Ross (J. Amer. Chem. Soc., 1933, **55**, 3684—3695).—Paracetaldehyde (I), $CHMe(CO_2H)_2$, Ac_2O, and AcOH at 100° (bath) followed by gentle ebullition give tiglic (II) and β-*acetoxy-α-methylbutyric acid* (III), b.p. 147—150°/10 mm.; possible reaction mechanisms are discussed. Distillation of (III) at atm. pressure affords (II). The above reagents with a little conc. H_2SO_4 give *γ-hydroxybutane-ββ-dicarboxylic acid* (IV), m.p. 135° (decomp.), and its β-lactone (V). (IV) decomposes when heated at the m.p. (vac. or atm. pressure) to MeCHO and $CHMe(CO_2H)_2$, whilst (V) at >100°/vac. passes into α-methyl-β-butyrolactone, b.p. 80°/15 mm. (lit. 67°/21 mm.) [distillation of the free acid in a vac. gives (II)]. (I), $CHEt(CO_2H)_2$, Ac_2O, and AcOH afford α-ethylcrotonic and a little β-acetoxy-α-ethylbutyric acid (?), b.p. 156—160°/10 mm. Prolonged interaction of paraformaldehyde (VI), ethane-ααβ-tricarboxylic acid (VII), Ac_2O, and AcOH at room temp. and subsequent heating gives paraconic and a little itaconic acid; (I) and (VII) similarly yield β-*carboxy-γ-methylparaconic acid*, m.p. 165°. (VI), *s*-$C_2H_2(CO_2H)_4$, Ac_2O, and AcOH afford the *γ-dilactone* (VIII), m.p. 178° (decomp.), of αδ-dihydroxybutane-βγγ-tricarboxylic acid, which when heated gives the *γ-dilactone* (IX), m.p. 138°, of αδ-dihydroxybutane-βγ-dicarboxylic acid (X). When (IX) is boiled with 2 equivs. of NaOH, approx. equal amounts of two stereoisomeric Na_2 salts are formed; the more sol. salt gives (IX) on acidification, whilst the less sol. Na_2 salt

($+8H_2O$) affords (after drying and decomp. with Et_2O–HCl) the *γ-monolactone*, m.p. 122°, of the *meso*-form of (X). Distillation of the syrupy residue from the prep. of (VIII) at 20 mm. gives a mixture of (IX) and an unsaturated *isomeride*, m.p. 165°, which may be $O<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CO-C:CH_2\end{matrix}$ or $O<\begin{matrix}CH_2\cdot C\cdot CO_2H\\ CO-CMe\end{matrix}$. α-Carboxy-α-methyl-β-butyrolactone (XI), prepared from MeCHO, $CHMe(CO_2H)_2$, and Ac_2O–conc. H_2SO_4 (cf. Meldrum, J.C.S., 1908, **93**, 605), decomposes when heated to the relatively stable α-methyl-β-butyrolactone. The thermal decomp. and properties of (XI) and related β-lactonic acids (lit.) are discussed: the results show that an intramol. strain in β-lactone rings can be only one of the energy factors which determine physical and chemical stability of such rings. Deductions made solely from Baeyer's strain theory are, therefore, erroneous. H. B.

Oxytetronic acid, the simplest substance of the ascorbic acid type. F. Micheel and F. Jung (Ber., 1933, **66**, [*B*], 1291—1292).—Treatment of Et benzoyloxyacetate with K (Na is without action, whilst $NaNH_2$ affords $OH\cdot CH_2\cdot CO\cdot NH_2$, and EtOBz) leads with loss of EtOBz to β-*keto*-α*γ*-*dihydroxy*-n-*butyrolactone* (I), $\begin{matrix}CH_2\cdot CO\\ O-CO\end{matrix}>CH\cdot OH$ or $\begin{matrix}CH_2\cdot C(OH)\\ O-CO\end{matrix}>C\cdot OH$, m.p. 153°, which closely resembles ascorbic acid, but has no antiscorbutic action. With NaOH and phenolphthalein 1 OH is immediately determinable. (I) powerfully reduces $AgNO_3$ in acid solution and reacts with I (2 atoms per mol.). H. W.

C_4-Saccharic acids. VII. Preparation and resolution of *dl-threo*-αβ-dihydroxybutyric acid. J. W. E. Glattfeld and J. W. Chittum (J. Amer. Chem. Soc., 1933, **55**, 3663—3668).—*dl-threo*-αβ-Dihydroxybutyric acid (I), best prepared by oxidation of crotonic acid (II) with $AgClO_3$ and OsO_4 at room temp. (cf. Braun, A., 1929, 293), is resolved by brucine into forms of $[\alpha]_D$ +15·1° and −15° and by quinidine (cf. Morrell and Hanson, J.C.S., 1904, **85**, 197) into forms of $[\alpha]_D$ +15·45° and −15·5° (mean vals.). During the prep. of (I) by oxidation of (II) with $KClO_3$ and OsO_4 (A., 1927, 1054), a compound $C_4H_8O_4$,$C_4H_7O_4K$ [m.p. 104—107°, when prepared from (I) and its K salt], is produced. H. B.

Substances produced by action of moulds. II. Constitution of glauconic acids. H. Sutter and N. Wijkman (Annalen, 1933, **505**, 248—254; cf. A., 1931, 523).—Glauconic acid I (I), $C_{19}H_{22}O_4$, contains 1 active H (Zerevitinov); glauconic acid II and the thermal fission product $C_{11}H_8O_6$ have none. The NO_2-derivative of (I) is an ester and regenerates (I) on hydrolysis. The aldehyde $C_7H_{12}O$ (II), obtained by thermal decomp. of (I), readily gives a H_2-derivative, b.p. 63—64°/50 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 123°), oxidised by CrO_3–H_2SO_4 to a hexoic acid [? (III); p-*phenylphenacyl* ester, m.p. 65° (diffuse)] and by Ag_2O to hexane-γ-carboxylic acid (III), b.p. 103°/11 mm. (*amide*, m.p. 104—105°). Oxidation of (II) with O_3 gives EtCHO and COEt·CHO; it is therefore CHEt:CEt·CHO. H. A. P.

Syntheses of *d*- and *l*-ascorbic acid (vitamin-*C*). T. Reichstein, A. Grussner, and R. Oppenauer (Helv. Chim. Acta, 1933, **16**, 1019—1033; cf. this vol., 1035).—*d*-Xylose (I) is converted into its phenylosazone and thence by means of PhCHO into *d*-xylosone (II) [more readily prepared from (I) and H_2O_2 and purification through the Pb salt]. (II) is transformed by HCN–H_2O in presence of KCN and N_2 followed by hydrolysis with HCl into d-*ascorbic acid* (III), m.p. 187—189° (decomp.), $[\alpha]_D$ −48·3° in MeOH [conveniently purified through the *brucine* salt, m.p. 209° (corr., decomp.)]. *l*-Ascorbic acid (IV), m.p. 187—189° (corr., decomp.), $[\alpha]_D^{23}$ +48° in MeOH, is obtained similarly from *l*-xylose. Admixture of equal amounts of (III) and (IV) leads to dl-*ascorbic acid*, m.p. 168—169° (corr.). (III) does not show marked antiscorbutic action. d-*Saccharomonolactone monohydrate*, m.p. (indef.) 85—90° according to the rate of heating, l-*gulonolactone*, m.p. 185—187° (corr., slight decomp.), l-*gulonamide*, m.p. 124·5—125·5°, which is not successfully degraded to *l*-xylose by OCl′, and *d*-galacturonic acid are incidentally described. H. W.

Constitution of ascorbic acid. R. W. Herbert, E. L. Hirst, E. G. V. Percival, R. J. W. Reynolds, and F. Smith (J.C.S., 1933, 1270—1290).—A detailed account of work summaries of which have already appeared [A., 1932, 548, 982, 987 (Cox); this vol., 100, 489, 490 (Cox), and 594]. Ascorbic acid, $\begin{matrix}C(OR)-CO-O\\ C(OR)\cdot CH(OH)\end{matrix}>CH\cdot CH_2\cdot OH$ (I; R=H), m.p. 192° [*Ca*, $[\alpha]_i^{19}$ +91° in H_2O, and *brucine*, m.p. 216—217° (decomp.), salts], is proved to be the enolic form of 3-keto-*l*-gulofuranolactone. The main evidence is as follows: oxidised by 2I in acid solution (I) gives $\begin{matrix}CO-O\\ C(OH)_2\cdot C(OH)_2\end{matrix}>CH\cdot CH(OH)\cdot CH_2\cdot OH$, $[\alpha]_{5780}$ +56°→ 0° in 28 hr. [loss of absorption band similar to that of $(HO\cdot C\cdot CO_2H)_2$], further oxidised by NaOI to $H_2C_2O_4$ and *l*-threonic acid [also by $KMnO_4$ oxidation of (I)], methylated to *Me trimethyl*-l-*threonate*, b.p. 120°/13 mm., $[\alpha]_{5780}^{18}$ +49° in MeOH (*amide*, m.p. 78°, $[\alpha]_{5780}^{20}$ +68° in MeOH), and oxidised by HNO_3 (*d* 1·2) to *d*-tartaric acid. With CH_2N_2 at −5° (I) gives dimethylascorbic acid (*Ba* salt) [(I) R—Me], which with saturated NH_3 in MeOH at 35° gives the *amide* $C_8H_{15}O_6N$+MeOH, m.p. 124°, $[\alpha]_{5780}$ −24° in 50% H_2O–MeOH, formed (contrary to Micheel and Kraft, this vol., 489) by addition of NH_3 at the ·O· linking; and converted into tetramethylascorbic acid (II) by Ag_2O–MeI. Ozonolysis of (II) gives the neutral ester $CO_2Me\cdot CO\cdot O\cdot CH(CO_2Me)\cdot CH(OMe)\cdot CH_2\cdot OMe$, which with NH_3–MeOH gives $(\cdot CO\cdot NH_2)_2$, 3 : 4-dimethyl-*l*-threonamide, and the epimeric 3 : 4-dimethyl-*l*-erythronamide, whereas hydrolysis with 0·27*N*-$Ba(OH)_2$ gives the Ba salts of the corresponding acids. Structures for the various $NHPh\cdot NH_2$ derivatives are given. Only (I) is consistent with *X*-ray and absorption spectra data. *Me dimethoxymaleate*, b.p. 85°/0·03 mm. (absorption band at 255 mμ, ε 6000), is prepared from the $(OH)_2$-acid by CH_2N_2 followed by Ag_2O–MeI. J. W. B.

Synthesis of *d*-glycuronic acid. L. Zervas and P. Sessler (Ber., 1933, **66**, [*B*], 1326—1329).—Condensation of 1 : 2-*iso*propylidene-*d*-glucofuranose with PhCHO and P_2O_5 affords 3 : 5-benzylidene-1 : 2-

*iso*propylidene-α-*d*-glucofuranose (I), m.p. 149—150° (corr.), $[\alpha]_D^{20}$ +23·1° in $CHCl_3$, probably identical with the compound of Brigl *et al.* (A., 1932, 1115). Oxidation of (I) with $KMnO_4$ in slightly alkaline solution leads to 3 : 5-*benzylidene*-1 : 2-iso*propylidene*-α-d-*glycuronic acid* (II), m.p. 170° (corr.), $[\alpha]_D^{20}$ +30·3° in $COMe_2$, catalytically converted (H_2–Pd black–EtOH) into 1 : 2-iso*propylidene*-α-d-*glycuronic acid* (III), m.p. 147° (corr.), $[\alpha]_D^{20}$ −9·2° in H_2O (initial val.). (II) or (III) is readily hydrolysed by dil. acid to *d*-glycurone, m.p. 177° (corr.), $[\alpha]^{20}$ +19·4° in H_2O. H. W.

Oxidation of δ-ketogluconic acid with nitric acid in presence of vanadium. W. E. Barch (J. Amer. Chem. Soc., 1933, **55**, 3653—3658).—Oxidation of Ca δ-ketogluconate with HNO_3 (2—4 mols.) in presence of a little Na_3VO_4 at 100° (bath) gives (after gas evolution ceases) *d*- (I) (14·2—27·8%) and *dl*- (II) (0—8·5%) -tartaric acids, trihydroxyxyloglutaric acid (III) (0—5·9%), and $H_2C_2O_4$ (IV) (11·4—17·3%). Fission of the chain occurs on both sides of the CO group, and 50% of the original mol. is converted into (I)+(IV). (II) arises from (III). It is suggested that the oxidation involves the formation of unstable nitrates which then lose HNO_2. H. B.

Fats and thiolacetic acid. G. Axberg and B. Holmberg (Ber., 1933, **66**, [*B*], 1193—1198).—$SH{\cdot}CH_2{\cdot}CO_2H$ (I) combines readily with unsaturated fats and fatty acids to preparatively uninviting products. The reaction can be used in determining the I val. by treating the fat with excess of (I) in air or CO_2 at room temp., dissolving the product in AcOH, adding I solution until a yellow colour persists, and titrating excess of I by $Na_2S_2O_3$ in presence of starch. Under the stated conditions, well-defined limiting vals. are invariably obtained after 12 hr. These vals. agree closely with, but are usually slightly >, the Hübl I vals. Rise of temp. leads to less trustworthy results and should be used only in the case of solid fats to ensure only liquid phases. The choice of CO_2 or air appears immaterial. Technical (I) may replace the pure material, but the use of specimens with high acid equiv. appears inadvisable. H. W.

Raman effect and problems of constitution. IV. Carbonyl frequencies and molecular constitution. K. W. F. Kohlrausch and A. Pongratz (Ber., 1933, **66**, [*B*], 1355—1369; cf. this vol., 144).—Measurements are recorded of the ·CO· frequencies for the compounds R·CHO, R·COMe, $R{\cdot}CO_2H$, $R{\cdot}CO_2Me$, $R{\cdot}CO_2Et$, R·COCl, HCO_2R, $ClCO_2R$ (R= H, Me, Et, Pr$^\alpha$, Bu$^\alpha$, Bu$^\beta$, *n*-amyl, *n*-hexyl, *n*-heptyl, Pr$^\beta$, CHMeEt, CMe_3, CMe_2Et). The frequencies are const. and independent of the length of the side-chain and may therefore be regarded as characteristic of X in R·CO·X. The frequency heights have no direct connexion with the wt. of X, but depend on the nature of the atom or group of atoms directly united to CO; they are due therefore to a typical constitutive effect exerted by the vicinal atom on the strength of the C:O linking. In the compounds $Me{\cdot}CO{\cdot}X$, $CH_2R{\cdot}CO{\cdot}X$, $CHR_2{\cdot}CO{\cdot}X$, and $CR_3{\cdot}CO{\cdot}X$ (X=OH, OMe, OEt, Me, Cl, H) a slight effect is attributable to branching of the chain in the α-position, but the change is negligible in comparison with that exercised by the vicinal atom. With unsaturated materials, such as $CH_2R{\cdot}CO{\cdot}X$, $>C{:}CH{\cdot}CO{\cdot}X$, Ph·CO·X (X=OH, OEt, OMe, Me, H) a more marked effect is observed when conjugation is possible. In the compounds $(CO_2Me)_2$, $(CO_2Et)_2$, $CH_2(CO_2Me)_2$, $CH_2(CO_2Et)_2$, $CH(CO_2Me)_3$, $CH(CO_2Et)_3$, $C(CO_2Et)_4$, $(\cdot CH_2{\cdot}CO_2Me)_2$, $(\cdot CH_2{\cdot}CO_2Et)_2$, and $CO_2Me{\cdot}CH(CH_2{\cdot}CO_2Me)_2$, the conjugation of 2 CO leads to marked exaltation, which diminishes when CH_2 separates 2 CO and disappears when 2 CH_2 are interposed. Accumulation of CO groups at the same C atom causes a further feeble exaltation. Possibly the supposed symmetry is not quite complete in certain cases. Observations with $COMe{\cdot}CO_2H$, $COMe{\cdot}[CH_2]_2{\cdot}CO_2H(Me)(Et)$, $COMe{\cdot}CMe_2{\cdot}CO_2Me$, and $CO_2Et{\cdot}CH_2{\cdot}C(CO_2Et){:}CH{\cdot}CO_2Et$ are recorded. The work of Hayashi (this vol., 764) on Ac_2, CH_2Ac_2, $[CH_2]_2Ac_2$, and *m*-$C_6H_4(OH)_2$ is not confirmed.

β-Hydroxymethyl-Δ$^\alpha$-buten-γ-one. H. Gault and L. A. Germann (Compt. rend., 1933, **197**, 620—621).—In the prep. of $CH_2Ac{\cdot}CH_2{\cdot}OH$ (cf. G.P. 223,207), there is also formed β-*hydroxymethyl*-Δ$^\alpha$-*buten*-γ-*one*, b.p. 92—95°/15 mm. (dibromide), identified by hydrogenation (Ni) to $CHAcMe{\cdot}CH_2{\cdot}OH$. H. . P.

Preparation of diacetyl. A. K. Plisov (J. Appl. Chem. Russ., 1933, **6**, 739—741).—In the prep. of Ac_2 from COMeEt and $EtNO_3$ higher yields are obtained by treating the CAcMe:N·OH (I) with HNO_3 without isolation of (I). R. T.

Determination of the mol. wt. of carbohydrates. A. Beiser and H. Pringsheim (Ber., 1933, **66**, [*B*], 1296—1298; cf. this vol., 149).—Contrary to Berner, it is maintained that the principle of additivity is not applicable to cryoscopic determinations of mol. wt. when EtOH is present in dil. solution. In very dil. solution, α-methylglucoside and sucrose appear colloidal in boiling H_2O, whereas they yield normal vals. at higher concn. (cf. Hess *et al.*, this vol., 47). In consequence of lack of knowledge of the state of solution at different concn. and temp., such measurements should not form the basis of theoretical conclusions in carbohydrate chemistry. Application of the osmometric method to the determination of the mol. wt. of di- (I) and tetra- (II) -amylose is not admissible, since the stabilising EtOH distils during the experiments (*loc. cit.*). The transformation of (II) into (I) by displacement of p_H towards the alkaline side could not be confirmed in cryoscopic measurements. H. W.

3- and 5-Methylxylose. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1933, **102**, 331—346).—*iso*Propylidenexylose 5-benzoate, m.p. 83·5—84·5°, is probably homogeneous, but with MeI–Ag_2O gives, probably by partial migration, 3-*methyl*iso*propylidenexylose* 5- (I) (about 70%), m.p. 64—65·5°, $[\alpha]^{20}$ −50·2° in $CHCl_3$, and 5-*methyl*iso*propylidenexylose* 3-*benzoate* (II) (about 20%), b.p. 164—167°/0·1 mm., $[\alpha]_D$ −33·0° in $CHCl_3$, and 3 : 5-dimethylxylose, a syrup. (II) with BaO in MeOH gives 5-*methyl*iso*propylidenexylose* (III), m.p. 80·5—81·5° (lit. 78°), $[\alpha]_D$ −20·2° in H_2O, hydrolysed by 0·1*N*-H_2SO_4 to 5-*methylxylose* (IV), a syrup, $[\alpha]_D^{20}$ +32·8°—→+36·4°

in 4 hr. in H_2O [p-*bromophenylosazone*, m.p. 170—171° (decomp.), $[\alpha]_D^{20}$ −50°⟶−30° in 24 hr. in C_5H_5N–EtOH (2 : 3)], which reduces cold Fehling's solution. (I) gives similarly 3-*methyl*iso*propylidene-xylose*, a syrup, $[\alpha]_D^{27}$ −54·1° in H_2O, and 3-*methyl-xylose* (V), m.p. 103—104°, $[\alpha]_D^{20}$ +55·2°⟶+14·8° in 4 hr. in H_2O [p-*bromophenylosazone*, m.p. 153—155° after sintering and decomp. at 142—143°, $[\alpha]_D$ +6·0⟶−14·0° in 24 hr. in C_5H_5N–EtOH (2 : 3)], which reduces slightly warm Fehling's solution. *iso*-Propylidenexylose affords 5-*triphenylmethyl*iso*propyl-idenexylose*, m.p. 118—119°, $[\alpha]_D^{25}$ +10·5° in $CHCl_3$, which with MeI–Ag_2O gives 5-*triphenylmethyl*-3-*methyl*iso*propylidenexylose*, a syrup, $[\alpha]^{22}$ −40·9° in $CHCl_3$, hydrolysed by cold HBr–AcOH to (V). 5-*p*-Toluenesulphonyl*iso*propylidenexylose (VI) and NaOMe at 20—25° give 1 : 2-iso*propylidene*-3 : 5-*anhydroxylose*, b.p. 63—65°/0·1 mm., m.p. 16·9—17·3°, $[\alpha]_D^{20}$ +11·7° in $CHCl_3$ and +14·7° in H_2O. This, or (VI), with hot NaOMe gives (III). *iso*Propylidenexylose or (IV) affords 3 : 5-dimethyl*iso*propylidenexylose, $[\alpha]_D^{22}$ −46·9° in H_2O [p-*bromophenylosazone*, m.p. 107—108·5°, $[\alpha]_D^{22}$ −46°⟶−30° in C_5H_5N–EtOH (2 : 3)], whence by hydrolysis and oxidation 2 : 3-dimethylxylolactone (*p*-bromophenylhydrazide, m.p. 95—96°, $[\alpha]_D$ +6·0° in EtOH) was obtained. The glucoside formation of (IV) and (V) consists of a single and double reaction, respectively.

R. S. C.

Derivatives of *iso*propylidenexylose. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1933, **102**, 317—330).—*iso*Propylidenexylose (modified prep.) gives the following derivatives: 5-*benzoate* (possibly impure), m.p. 83·5—84·5°, $[\alpha]_D^{20}$ +5·5°; 5-p-*C e·SO₂*, m.p. 133—134°, $[\alpha]_D^{20}$ −13·0°; 3 : 5-*diacetate*, a syrup, $[\alpha]_D^{20}$ −6·1°; 3-*acetate* 5-*benzoate*, m.p. 84·5—85·5°, $[\alpha]_D^{22}$ −26·5°; 3-p-$C_6H_4Me{\cdot}SO_2$ 5-*acetate*, m.p. 84·5—85°, $[\alpha]_D^{20}$ −33·0°, and 5-*benzoate*, m.p. 94·5—95·5°, $[\alpha]^{20}$ −64·0°; 5-p-$C_6H_4Me{\cdot}SO_2$ 3-*acetate*, a syrup, $[\alpha]_D^{20}$ −17·9°, and 3-*benzoate*, m.p. 86—87°, $[\alpha]_D^{20}$ −37·0°; 5-*iodide*, m.p. 108—109°, $[\alpha]_D^{22}$ −40°; 5-*nitrate*, m.p. 115·5—116·5°, $[\alpha]_D^{20}$ −24·8°; 5-*carbobenzyloxy*-, m.p. 90—91°, $[\alpha]_D^{20}$ +7·5°, hydrolysed by dil. alkali, but not by dil. acids. The structures are proved by reaction of the 5-*p*-$C_6H_4Me{\cdot}SO_2$ derivatives with NaI. All [α] are in $CHCl_3$.

R. S. C.

Acetone [*iso*propylidene] derivatives of *d*-ribose. P. A. Levene and E. T. Stiller (J. Biol. Chem., 1933, **102**, 187—201).—Owing to steric causes, ribose, pure $COMe_2$, and H_2SO_4 (0·2%) give abnormally 2 : 3-iso*propylideneribofuranose* (I), b.p. 110—117°/0·05 mm. (*acetate*, b.p. 119—121°/0·1 mm.), and (probably) 2 : 3-iso*propylidene*-1 : 5-*anhydroribofuranose* (II), b.p. 55—60°/0·05 mm., m.p. 61—62°, $[\alpha]_D$ −64·35° in MeOH. With HCl there is formed also a *substance*, $C_8H_{12}O_4$, m.p. 93—94°, b.p. 105—115°/0·07 mm. The structure of (I), and thus of (II), is proved by the following reactions. By Purdie's method (I) gives *methyl*-2 : 3-iso*propylidene*-5-*methyl-riboside*, b.p. 62—65°/0·03 mm., hydrolysed by HCl–MeOH at 70° to *methyl*-5-*methylriboside* (III), b.p. 70—77°/0·12 mm., and by 0·04*N*-HCl at 100° to 5-*methyl-ribofuranose* (IV) [p-*bromophenylosazone*, m.p. 161—162° (decomp.), $[\alpha]_D^{25}$ −48° in EtOH–C_5H_5N (3 : 2)]. The rate of glucoside formation by (III) proves its furanose structure. (III) gives by Purdie's method *methyltrimethylribofuranoside*, b.p. 68°/0·05 mm., hydrolysed to the known 2 : 3 : 5-trimethylribose, whence the corresponding γ-lactone was obtained by Br–H_2O. (I) and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at 37° give abnormally the 1 : 5-$(C_6H_4Me{\cdot}SO_2)_2$ derivative, m.p. 122—123°, whence 1-p-*toluenesulphonyl*-2 : 3-iso*propylideneribose* 5-*iodide*, m.p. 120°, $[\alpha]^{23}$ +84·6° in $CHCl_3$, and 5-*nitrate*, m.p. 156°, were obtained. (II) is stable to NaOI, Fehling's solution (until hydrolysed by acid), and NaOMe at 125°.

R. S. C.

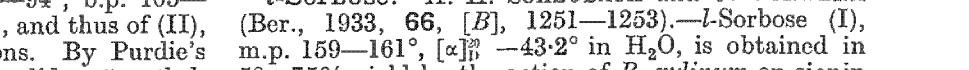
Distinction of keto- from aldo-hexoses. A. Castiglioni (Z. anal. Chem., 1933, **94**, 96—101).—An improved form of Tollens' test. A 0·1—0·8% solution of the sugar is heated with 5 vols. of HCl (*d* 1·09—1·18), best to 70°. A reddish-brown coloration develops rapidly with ketoses, slowly with aldoses. Fructose and sucrose may be detected in presence of a large excess of glucose, lactose, or galactose.

J. S. A.

Behaviour of hexoses in presence of animal charcoal and iron phosphate complexes. K. Wunderly (Helv. Chim. Acta, 1933, **16**, 1013—1018).—*d*-Fructose (I) and *d*-glucose do not suffer decomp. in the presence of animal C and absence of O_2; $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, $MgHPO_4$, or alkali phosphate buffering in the region p_H 4·5—7·5 is without influence. (I) in presence of alanine (II) suffers more decomp. in presence of C than in the system (I)–(II). Admixture of $KFe(C_2O_4)_2$ and $Na_4P_2O_7$ gives a complex which expedites the O-free decomp. of the system (I)–*dl*-alanine.

H. W.

Action of acetic anhydride and sulphuric acid on *iso*propylideneglucose. H. H. Schlubach, W. Rauchenberger, and A. Schultze (Ber., 1933, **66**, [*B*], 1248—1251; cf. Schultze, Diss., Hamburg, 1930).—The action of Ac_2O–H_2SO_4 at 0° on *iso*propylideneglucose triacetate leads to *iso*propylideneglucose penta-acetate (I), m.p. 140°, $[\alpha]_D^{18}$ +60·4° in $CHCl_3$, identical with the product obtained by Brigl *et al.* (this vol., 810) by means of $ZnCl_2$. The $:CMe_2$ is eliminated by alkali with unusual ease. NH_3–EtOH converts (I) into *iso*propylideneglucose in poor yield. NH_3–Et_2O gives small amounts of an *isomeride*, m.p. 140°, $[\alpha]_D^{18}$ +3·0° in $CHCl_3$ (? α- and β-forms). Dil. HCl in AcOH hydrolyses (II) to non-cryst. glucose tetra-acetate (II), $[\alpha]_D^{18}$ +32° in $CHCl_3$, converted by the successive action of MeI and Ag_2O, Me_2SO_4, and 7% HCl into 2 : 3 : 5 : 6-tetramethylglucose, $[\alpha]_D^{19}$ −30° in $CHCl_3$. Liquid HCl transforms (I) into acetochloro-γ-glucose, converted by Ag_2CO_3 and $COMe_2$–H_2O into (II). (I) is therefore



H. W.

***l*-Sorbose.** H. H. Schlubach and J. Vorwerk (Ber., 1933, **66**, [*B*], 1251—1253).—*l*-Sorbose (I), m.p. 159—161°, $[\alpha]_D^{20}$ −43·2° in H_2O, is obtained in 50—75% yield by the action of *B. xylinum* on sionin (technical sorbitol) if the concn. of AcOH in the solution is increased to 0·5% to prevent infection. (I) is transformed by Ac_2O–H_2SO_4 into an unstable, brown syrup, whereas use of $ZnCl_2$ under defined

conditions leads to a Ac_5 derivative (II) (probably *keto*-l-*sorbose* 1 : 3 : 4 : 5 : 6-*penta-acetate*), m.p. 96·5—97·5°, $[\alpha]_D^1$ +2·9° in $CHCl_3$. Attempts to transform (II) into an acetohalogenosorbose led to non-cryst. material. H. W.

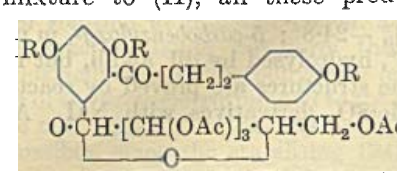
Microscopical detection of fructose. M. Wagenaar (Pharm. Weekblad, 1933, **70**, 1029—1034).—The solid sugar, suspended in a 2% solution of α-$C_{10}H_7$·OH in glycerol, is treated with conc. H_2SO_4, whereby the crystals of a ketose are coloured bluish-violet. It is possible to detect 1% of sucrose in glucose, arabinose, maltose, or galactose and 0·1% in lactose. It is not possible to differentiate fructose, sucrose, and raffinose. S. C.

β-4-Glucosido-β-glucosan and 4-galactosido-β-glucosan. P. Karrer and J. C. Harloff (Helv. Chim. Acta, 1933, **16**, 962—968; cf. A., 1932, 46).—Acetobromocellobiose and $NHMe_2$ in $CHCl_3$ at room temp. afford *dimethylaminocellobiose hepta-acetate*, m.p. 210—211°, $[\alpha]_D^{18}$ −10·1° in $CHCl_3$; the corresponding *methiodide* is transformed by $Ba(OH)_2$ into *cellobiose anhydride* [β-4-*glucosido*-β-*glucosan*] (I) (*hexa-acetate*, m.p. 144°, $[\alpha]_D^{17}$ −46·24° in $CHCl_3$). (I) is not affected by emulsin, but is transformed by the enzyme from *Helix pomatia* into glucose and β-glucosan (II) (triacetate, m.p. 110°). Similarly, acetobromolactose yields *dimethylaminolactose hepta-acetate*, m.p. 154°, $[\alpha]_D^{18}$ −21·37° in C_6H_6, converted successively into the *methiodide* and 4-*galactosido*-β-*glucosan* (*hexa-acetate*, m.p. 206°, $[\alpha]_D^{18}$ −38·89° in $CHCl_3$), hydrolysed to galactose and (II). H. W.

Heart glucosides. II. Genuine glucosides of *Digitalis lanata*, digilanias *A*, *B*, and *C*. A. Stoll and W. Kreis (Helv. Chim. Acta, 1933, **16**, 1049—1098; cf. this vol., 877).—Fresh *lanata* leaves are ground with $(NH_4)_2SO_4$ to a uniform paste; the press-cake is extracted with EtOAc and the extract conc. to a viscous mass at ≯ 35°/vac. The residue is triturated with Et_2O until it is mainly solid and then digested with boiling Et_2O. Tannins are removed from the residue by treatment with $Pb(OH)_2$ in MeOH–H_2O. The filtrate is greatly conc. at a low temp., thereby yielding a ppt. of "total digilanids" (I), which, after repeated crystallisation from MeOH, has m.p. 245—248° (decomp.) when rapidly heated. (I) consists of an isomorphous mixture of three glucosides separable into its components by fractional distribution between MeOH–H_2O and $CHCl_3$–MeOH; full details are given for operation with homogeneous mixtures and also in presence of an intermediate solid phase. Thus are obtained: *digilanid* A, $C_{49}H_{76}O_{19}$, m.p. 245—248° (decomp.), $[\alpha]_D^{20}$ +31·9° in 95% EtOH, +23·2° in dioxan, hydrolysed by H_2SO_4 in EtOH–H_2O to digitoxigenin, m.p. 250° (corr.), $[\alpha]_D^{20}$ +18·1° in MeOH, digitoxose (II), and *digilanidobiose*, $C_{12}H_{22}O_9$, decomp. 227° (corr.) after softening at 215—220°, $[\alpha]^{20}$ +29·8° in H_2O and AcOH; *digilanid* B, $C_{49}H_{76}O_{20}$, m.p. 245—248° (corr., decomp.), $[\alpha]^{20}$ +36·7° in 95% EtOH, +31·8° in dioxan, hydrolysed to gitoxigenin, m.p. 232° (corr.), $[\alpha]_D^{20}$ +36·1°±2° in MeOH (II), glucose (III), and AcOH; *digilanid* C, $C_{49}H_{76}O_{20}$, m.p. 245—248° (decomp.), $[\alpha]_D^{20}$ +33·4° in 95% EtOH, +22·6° in dioxan, hydrolysed to digoxigenin, m.p. 220° (corr.), $[\alpha]_D^{20}$ +23·2° in MeOH, (II), (III), and AcOH. H. W.

Natural glycosides. V. Ruberythric acid. E. T. Jones and A. Robertson. VI. Hexose residue of phloridzin. A. Müller and A. Robertson (J.C.S., 1933, 1167—1169, 1170—1172).—V. With MeI–Ag_2O in $COMe_2$ the Ac_7 derivative (I), m.p. 260°, of alizarin-β-gentiobioside (II) +6H_2O, m.p. 96—98°, and anhyd., m.p. 178—180° (prep. by modification of Zemplen and Müller's method, A., 1929, 1281), gives its *Me ether*, m.p. 240°, hydrolysed by HCl in MeOH–AcOH to 1-*O*-methylalizarin. When treated with 5% aq. NaOH a suspension of (I) in MeOH affords (II). Alizarin-β-cellobioside (III), m.p. 260° (Ac_8 derivative, m.p. 143—145°, becoming solid at 170—180°, and remelting at 224—225°), is similarly prepared. Ruberythric acid (IV) is not identical with (II), (III), or alizarin-2-β-maltoside, but is hydrolysed by emulsin to alizarin (V) and a pentose (phloroglucinol and orcinol reactions) and is probably a pentosido-β-glucoside. Hepta-acetylprimeverose (by a modification of Helferich and Rauch's method, A., 1927, 859) with Ac_2O and saturated HBr in AcOH gives *hexa-acetylprimeverosidyl bromide* (amorphous), converted by (V), quinoline, and Ag_2O into the Ac_7 derivative, m.p. 241°, of alizarin-β-primeveroside, not identical with the Ac derivative of (IV).

VI. Hydrolysis of phloridzin (I) with 0·2*N*-H_2SO_4 affords phloretin and glucose. With MeI and K_2CO_3 in boiling $COMe_2$ (I) gives its Me_3 ether +H_2O (II), sintering at 73°, m.p. 75—76° (lit. 63—65°), further methylated (MeI–Ag_2O) to the *Me_7 ether*, which is hydrolysed in $COMe_2$ by 10% H_2SO_4 to *O*-trimethylphloretin (III) and 2 : 3 : 4 : 6-tetramethylglucose, thus indicating the pyranose structure. With *O*-tetra-acetyl-α-glucosidyl bromide, Ag_2O, and quinoline at 30—35° (III) gives *O-tetra-acetyltrimethylphloridzin* (IV, R=Me), m.p. 94—95°, $[\alpha]_{5461}^{21}$ −44·64° in $CHCl_3$, hydrolysed by 0·5*N*-NaOMe in MeOH in a freezing mixture to (II), all these products being



(IV.) (I, R=H, Ac=H; II, R=Me, Ac=H)

identical with specimens similarly prepared from the natural product (I). Either synthetic or natural (II) is hydrolysed by emulsin in aq. EtOH at 37° to (III) and glucose. (I) is therefore a β-glucopyranose. J. W. B.

Alcoholytic degradation of starch. E. Berner and F. Melhus (Ber., 1933, **66**, [*B*], 1333—1338; cf. this vol., 937, 938).—Trihexosan, obtained by the action of glycerol (I) on starch at 205° (cf. Pictet *et al.*, A., 1922, i, 987), contains about 4% of combined (I); assuming the reaction to be alcoholysis, the mean mol. wt. of the degraded product is 2000—2500. Treatment of starch with (I) at 180° during 40 hr. yields a mixture of α- and β-glycerylglucoside (II). $[\alpha]_D$ about +60°, transformed into the *hexa-acetate*, $[\alpha]_D$ +56·9° in C_6H_6, and thence by NaOH and

Me_2SO_4 into the *Me*$_6$ *ether*, b.p. 127°/0·1 mm., $[\alpha]^{20}$ +59·9° in $CHCl_3$, hydrolysed by 2*N*-HCl to 2 : 3 : 4 : 6-tetramethyl-α-glucose, m.p. 83°, $[\alpha]^{20}$ +83·2° in H_2O (final val.); at 210°, degradation is accompanied by loss of H_2O. Reaction occurs at 130° in presence of H_3PO_4. $C_2H_4(OH)_2$ and starch at 180° during 24 hr. yield a mixture of glycylglucosides, $[\alpha]_D$ +77·8°, converted into their penta-acetates (α-*form*, m.p. 66°, $[\alpha]_D^{20}$ +143·0° in C_6H_6, +123·3° in EtOH). In absence of catalyst, starch is little acted on by MeOH, whereas methylated starch (OMe=39%; $[\alpha]$ +186° in $CHCl_3$) is readily converted into a mixture of 2 : 3 : 6-trimethyl-α- and -β-glucoside, b.p. 115°/0·04—0·05 mm., $[\alpha]_D^{20}$ +60·8° in H_2O. Starch is readily degraded by PhOH and $CH_2Ph\cdot OH$. H. W.

Solubility of inulin. E. Yanovsky and R. M. Kingsbury (J. Amer. Chem. Soc., 1933, **55**, 3658—3663).—The solubility of dahlia inulin (I) in H_2O and 50% EtOH at various temp. is considerably < that of chicory inulin (II) (cf. Wolff and Geslin, A., 1920, i, 424). (I) and (II) both exist in two modifications having differing solubilities. The more sol. form of (II) (obtained by crystallisation from aq. EtOH) gradually changes into the less sol. stable form. The presence of fructose increases the solubility of (I), but has no effect with (II), whilst "sol." inulin (A., 1931, 776) does not affect either solubility. Inulin is slowly deposited from supersaturated solutions until normal solubility is reached. H. B.

Inulin and inulinases. XIII. P. Ohlmeyer and H. Pringsheim (Ber., 1933, **66**, [*B*], 1292—1295; cf. A., 1932, 934).—Schlubach's method of purifying inulin (I) (A., 1932, 1021) can be shortened by keeping the 5% solution for some days at room temp. instead of freezing it. The final product (55% yield) has $[\alpha]_D^{20}$ −40·2° in H_2O, 0·035% ash, and does not reduce Fehling's solution. Quant. hydrolysis of (I) with *Aspergillus* inulinase yields 90—92% of cryst. fructose (II). The mother-liquors contain 1·5% of glucose (III) (as determined *loc. cit.*) and this val. is confirmed by separation of residual (II) as the phenylmethylosazone. The hypothesis that the production of (III) arises from isomerisation of γ-fructose in an acid medium is not supported by the observation that the same proportion of (III) results from hydrolysis with 0·05*N*-H_2SO_4 or by enzyme action at p_H 3·8 or 6·0. Further, the theoretical ratio of (II) to (III) is observed when sucrose is subjected to enzymic hydrolysis under the same conditions as (I). Although it appears improbable that (III) arises from impurities in (I) the question is not regarded as settled. H. W.

Influence of iodine on the decomposition of simple aliphatic amines and of hexane.—See this vol., 1125.

Reaction of nitrogen trichloride with Grignard reagents. G. H. Coleman, M. A. Buchanan, and W. L. Paxson (J. Amer. Chem. Soc., 1933, **55**, 3669—3672).—NCl_3 reacts with RMgX (R=Et, Pr$^\beta$, Bu$^\alpha$, *sec.*-Bu, Bu$^\gamma$, *n*-amyl, Ph, $\cdot CH_2Ph$, $\cdot CH_2\cdot CH_2Ph$; X=Cl, Br, I) in Et_2O to give N_2, NH_3, NH_2R, and NHR_2 (small yield); with $CH_2Ph\cdot MgCl$, a trace of $N(CH_2Ph)_3$ is also formed. The yield of NH_2R decreases in the order X=Cl, Br, I. The yields of amines are generally considerably smaller than with NH_2Cl (A., 1928, 622; 1929, 431). Methods of analysis (lit. and modifications) of solutions of NCl_3 are compared. H. B.

Alkylation of secondary amines with aldehydes and ketones. A. Skita, F. Keil, and H. Haveman (Ber., 1933, **66**, [*B*], 1400—1411; cf. A., 1928, 1120, 1228; 1930, 327).—Hydrogenation of *sec.* amines (I) in presence of aldehydes is a general method for the prep. of *tert.* amines (II), but the yields are greatly reduced if (I) contains a branching of the C chain in the α-position to N. With aromatic aldehydes the production of (II) depends on the mol. wt. of (I). In general, the proximity of Ph to N diminishes the capacity of alkylation. Reaction between (I) and ketones (III) depends on the mol. wt. and constitution of both reactants. (I) of medium mol. wt. with >NMe react with (III) containing ·COMe. Replacement of Me by Et or higher radical greatly reduces the reactivity, as does a branch in the C chain in α-position to N. In *o*-methyl*cyclo*hexanone the CO is greatly protected by Me, but the influence is not so obvious in the *m*- and *p*-isomerides. The following compounds are described: ethyl*iso*amylamine, b.p. 124—128°, from MeCHO and *iso*amylamine or NH_2Et and *iso*valeraldehyde (IV), whence *ethyliso*amyl-*heptylamine*, b.p. 112—113°/11 mm. (*H oxalate*, m.p. 75—76°), and -γη-*dimethyloctylamine*, b.p. 136—137°/11 mm. (*H oxalate*, m.p. 81—82°); di*iso*amylamine, from (IV) and NH_3 in presence of Ni, whence *ethyl*-, b.p. 75—78°/11 mm. (*picrate*, m.p. 95—96°; *picrolonate*, m.p. 114—115°; *methiodide*, m.p. 148·5—149·5°), and *butyl*-di*iso*amylamine (V), b.p. 100—103°/11 mm. (*picrate*, m.p. 117—118°) [(V) is also prepared by use of crotonaldehyde and is formed from MeCHO through $OH\cdot CHMe\cdot CH_2\cdot CHO$]; *di*-*iso*amyl-γη-*dimethyloctylamine*, b.p. 161—162°/12 mm. (*H oxalate*, m.p. 112—113°); *ethyl*-, b.p. 186—188°/10 mm. (*H oxalate*, m.p. 94—95°), and iso*amyl*-, b.p. 208°/13 mm. (*H oxalate*, m.p. 100—101°), -*di*-γη-*dimethyloctylamine*; *tri*-γη-*dimethyloctylamine*, b.p. 237—239°/12 mm. (*H oxalate*, m.p. 105—106°); n-*propyldi*iso*propylamine*, b.p. 145—147° (*picrate*, m.p. 120—121°); *di*-α-*methylpropylheptylamine*, b.p. 249—252° (*picrolonate*, m.p. 105—106°); diphenyl-methylamine; -ethylamine (Br_2-compound, m.p. 107—108°); -n-*propylamine*, b.p. 154°/12 mm. (Br_3-compound, m.p. 76—77°); -n-*butylamine*, b.p. 164°/11 mm. (Br_2-compound, m.p. 56—57°); -iso*butylamine*, b.p. 156—157°/11 mm.; *methyl*-iso*propyl*-α-*methylpropylamine*, b.p. 132—133° (*picrate*, m.p. 142—143°); -*di*-α-*methylpropylamine*, b.p. 155—157° (*picrate*, m.p. 92—93°); -α-*methylpropyl*-α′-*methylbutylamine*, b.p. 170—172° (*picrolonate*, m.p. 130—131°; *picrate*, m.p. 87—88°); -α-*methylpropyl*-α′-*methylamylamine*, b.p. 192—193° (*picrolonate*, m.p. 98—99°); -α-*methylpropyl*-α′-*methylhexylamine*, b.p. 211—213° (*picrolonate*, m.p. 99—100°); -α-*methylpropyl*-α′-*methylheptylamine*, b.p. 224—225°; -α-*methylpropyl*cyclo*hexylamine*, b.p. 208—209° (*picrate*, m.p. 110—111°); -α-*methylpropyl*-p-*methyl*cyclo*hexylamine*, b.p. 221—222° (*picrolonate*, m.p. 138—139°); -α-*methylpropyl*-m-*methyl*cyclo*hexylamine*, b.p. 218—219° (*picrate*, m.p. 92—93°); *ethyl*iso*propyl*-α-*methylpropylamine* (*picrate*, m.p. 118°); *ethyl*iso*propyl*iso*amylamine* b.p.

163—164°/762 mm. (*picrate*, m.p. 60—61°); iso-*propyldi*iso*amylamine*, b.p. 206—208° (*picrate*, m.p. 80—81°). *Methyl-α-methylpropyl-α'-ethylpropylamine*, b.p. 168—171°/744 mm. (*picrolonate*, m.p. 115—116°), is obtained from $COEt_2$ and NHMe·$CHMeEt$, from COMeEt and NHMe·$CHEt_2$ and from CH_2O and NH($CHMeEt$)·$CHEt_2$. *Methyl-α-ethylpropylamine*, b.p. 106—107° (*H oxalate*, m.p. 142—143°), and *α-methylpropyl-α'-ethylpropylamine*, b.p. 150—152° (*picrolonate*, m.p. 187—188°), are incidentally described. H. W.

Diaminobutanes. I. *dl*-αβ-Diaminobutane; αβ-diamino-β-methylpropane (*dl*-αβ-diaminopropane). E. Strack and H. Schwaneberg (Ber., 1933, **66**, [*B*], 1330—1333; cf. A., 1932, 727).—The best yields of diamines from aminonitriles are obtained when reduction (H_2–Pd or Na–abs. EtOH) is effected in very dil. solution. The following salts of *dl*-αβ-diaminobutane are described: hydrochloride, m.p. 189—190°; *sulphate*, m.p. > 300°; chloroplatinate, decomp. > 250°; *chloroaurates*, $R,2HAuCl_4,H_2O$ [$R=C_4H_{12}N_2$], m.p. 199—200° after softening at 190°, $R,2AuCl_3$, decomp. 217° after softening at 212°, R,HAu_2Cl_5, decomp. 195—200°; picrate, decomp. 256° after softening at 200°; *picrolonate*, decomp. 267—269°; *salts*, $R,HgCl_2$, m.p. 190°, and $R,3HgCl_2$, m.p. 147°; *Bz*$_2$, m.p. 186°, and *di*-m-*nitrobenzoyl*, m.p. 198°, derivatives. αβ-Diamino-β-methylpropane gives a hydrochloride, m.p. 303°, picrolonate, decomp. 260—262° after softening at 256°; *mercurichloride*, m.p. 151—152°; chloroplatinate, m.p. 270°; chloroaurates, $R',2HAuCl_4,2{\cdot}5H_2O$ ($R'=NH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2$), m.p. 135° (sealed tube) or m.p. (anhyd.) 233°, and $R,2AuCl_3$, m.p. 228°; picrate, m.p. (anhyd.) 241° (+H_2O), decomp. 235° after softening at 230°; *sulphate*, m.p. > 300°; *Bz*$_2$, m.p. 182·5° after softening at 180°, and *di*-m-*nitrobenzoyl*-, m.p. 174° after softening at 171°, derivatives. H. W.

Autoxidation of amino-acid derivatives and their degradation by ozone. II. F. Bergel and K. Bolz (Z. physiol. Chem., 1933, **220**, 20—26; cf. this vol., 494).—α-Dimethylamino*iso*butyric acid (from α-bromobutyric acid and $NHMe_2$) on autoxidation in presence of animal C undergoes 100% decomp. into CO_2, $NHMe_2$, and $COMe_2$, under conditions in which α-amino*iso*butyric acid is completely resistant. All types of NH_2-acids in H_2O are attacked by O_3 with the formation of products similar to those obtained by autoxidation. J. H. B.

Behaviour of carbamide derivatives, amino-acids, and peptides towards animal charcoal. K. Wunderly (Helv. Chim. Acta, 1933, **16**, 1009—1013).—$CO(NH_2)_2$, biuret, barbituric acid, urethane, phenylurethane, hydantoic acid, and diketopiperazine are unaffected when heated in dil. aq. solution with animal or sugar C. In 24 hr. at 80° serine, sarcosine, *dl*-glycylglycine, and *dl*-leucylglycylglycine are deaminated to the extent of 20%, 5%, 40%, and 8%, respectively. H. W.

Deamination of glycine by pyrocatechol derivatives and identification of glyoxylic acid as intermediate product. H. K. Barrenscheen and W. Danzer (Z. physiol. Chem., 1933, **220**, 57—60).—Methylamino- (I), amino- (II), and ethylamino-acetopyrocatechol (III) are inferior to adrenaline in catalysing the deamination of glycine in presence of O_2. (II) and (III) are better than (I) at p_H 6·8 and equal to pyrocatechol (IV); at 7·7 they are less active than (IV) owing to their low solubility. $CHO{\cdot}CO_2H$ was isolated as the 2:4-dinitrophenylhydrazone from the deamination products, indicating $NH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow NH{:}CH{\cdot}CO_2H \longrightarrow CHO{\cdot}CO_2H + NH_3$. J. H. B.

Lead compounds of glycine, cysteine, and β-thiolpropionic acid. R. Klement (Ber., 1933, **66**, [*B*], 1312—1315).—Na cysteine and $Pb(OH)_2$ afford the compound $NH_2{\cdot}CH<^{CO-O}_{S-CH_2}>Pb$, identical with that of Bauer *et al.* (this vol., 940). $SH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ (I) and $Pb(OAc)_2$ or $SH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Na$ and $Pb(OH)_2$ afford the *salt* $Pb[S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2]_2$, converted by boiling 2*N*-Na_2CO_3 into $PbCO_3$, (I), and the *compound* $CH_2<^{CO-O}_{CH_2{\cdot}S}>Pb$. Pb in Pb glycine (II) is in complex union with NH_2, since (II) is unaffected by liquid NH_3, whereas anhyd. $Pb(OAc)_2$ yields the unstable *substance* $Pb(OAc)_2,NH_3$. H. W.

Preparation of glycyltaurine and glycylcysteic acid. J. White (J. Biol. Chem., 1933, **102**, 249—251).—$CH_2Br{\cdot}COBr$ (I) and taurine in *N*-NaOH at 0° give *glycyltaurine*, cryst. (50% yield). (I) does not condense with cysteic acid. Diglycylcysteine and Br–H_2O at 0° give a 91% yield of *glycylcysteic acid*, cryst. R. S. C.

Oxidation of *d*-glutamic acid by chromic acid and by acid permanganate. E. J. H. Chu and C. L. Tseng (J. Chinese Chem. Soc., 1933, **1**, 46—50).—*d*-Glutamic acid with hot $Na_2Cr_2O_7$–H_2SO_4 or $KMnO_4$–H_2SO_4 during 6—7 hr. affords $(\cdot CH_2{\cdot}CO_2H)_2$, CO_2, and NH_3. J. L. D.

Protein problem: methylation of arginine. W. Zimmermann and A. Canzanelli (Z. physiol. Chem., 1933, **219**, 207—214).—Arginine salts with Me_2SO_4 and an excess of MgO give *arginine-α-betaine* (I), $NH{:}C(NH_2){\cdot}NH{\cdot}[CH_2]_3{\cdot}CH<^{CO}_{NMe_3}>O$ [*diflavianate*, m.p. 190° (decomp.); *dipicrate*, m.p. 168—169°; *sesquichloroaurate*, m.p. 195—197°]. Hydrolysis of (I) with aq. $Ba(OH)_2$ yields $CO(NH_2)_2$ and ornithine-α-betaine (II) [*diflavianate*, m.p. 240—242° (decomp.); *dipicrate*, decomp. 118—120°, or (+H_2O) m.p. 91°]. δ-Benzoylornithine with Me_2SO_4 and MgO and subsequent hydrolysis with 50% H_2SO_4 gave (II) in poor yield. Arginine carbonate with Me_2SO_4 and $BaCO_3$–$Ba(OH)_2$ (cf. Engeland and Kutscher, A., 1913, i, 194) affords trimethylarginine (III) [*diflavianate* (IV), decomp. 225—228°; *dichloroaurate*, m.p. 174°]. Hydrolysis of (IV) with aq. $Ba(OH)_2$ for 5 hr. eliminates 2 Me with the $CO(NH_2)_2$ radical and gives (?) α-methylornithine [*flavianate*, m.p. 222—223° (decomp.); *picrate*, m.p. 205—206°], not identical with δ-methylornithine or its piperidone (*flavianate*, m.p. 260—262°; *picrate*). Hydrolysis of (IV) with aq. $Ba(OH)_2$ for 2 hr. yields, without loss of Me, a trimethylcitrulline [*flavianate*, m.p. 235°

(decomp.); *picrate*, decomp. 214—216°]. (III) is always formed in methylation if the mixture becomes acid, probably owing to transformation of (I) primarily formed. J. H. B.

Racemisation and oxidation of cystine in acid solution. J. C. ANDREWS (J. Biol. Chem., 1933, **102**, 263—268).—$Cu^{\cdot\cdot}$ (but no other substance) catalyses the aerial oxidation of cystine (I) to cysteic acid in HCl, but not in H_2SO_4 or H_3PO_4. H_3PO_4 racemises (I) faster than does HCl or H_2SO_4. R. S. C.

Mesocystine. H. S. LORING and V. DU VIGNEAUD (J. Biol. Chem., 1933, **102**, 287—295).—Details are given for the prep. of *dl*- [*phenylcarbamido*-derivative, m.p. 195—196° (corr.); *diformyl* derivative, m.p. 196—198°, resolved by the strychnine salt] and *meso-cystine*, decomp. 200—218° [*diformyl* derivative, m.p. 192—193° (corr.) (*strychnine* salt, $+4H_2O$, m.p. 133—135°, anhyd., decomp. 175—176°, $[\alpha]_D^{25}$ −21·5° in H_2O, irresolvable)]. R. S. C.

Decomposition of the phenylhydantoin of cystine. J. C. ANDREWS and (MISS) K. C. ANDREWS (J. Biol. Chem., 1933, **102**, 253—262).—The phenylhydantoin of cystine [*l*- (I), m.p. 114·5°, $[\alpha]_D^{25}$ −155° in $COMe_2$; *dl*-, m.p. 177°] (modified prep.) is slowly racemised by hot, dil. acid, and is decomposed by hot H_2O and rapidly by dil. NaOH to 3-phenyl-5-methylenehydantoin, Na_2S, and S, the reaction being catalysed by Pb or glass. (I) and Br–H_2O at 0° give the *phenylhydantoin hydrobromide* of cysteic acid, m.p. 138°, $[\alpha]_D$ −41·4° in $COMe_2$, decomposing very readily to give, amongst other products, SO_4''. R. S. C.

Condensation of bromal hydrate with aliphatic amides. B. H. YELBURGI (J. Indian Chem. Soc., 1933, **10**, 383—390).—Condensation of bromal hydrate with the appropriate aliphatic amides gives the bromalamide, converted by Ac_2O–NaOH into the anhydrodi-derivative and by reduction (Zn–AcOH) into the bromoethylene compound. The following have been prepared: *bromalformamide*, m.p. 139—140° (*Ac*, m.p. 107—108°, *Bz*, m.p. 139°, and *anhydrodi*-derivatives, m.p. 170°); *Me*, m.p. 106°, *Bz*, m.p. 122°, and *anhydrodi*-derivatives of bromalacetamide, m.p. 183—185°; *bromalpropionamide*, m.p. 174° (*Ac*, m.p. 96—98°, *Bz*, m.p. 113—115°, *Me*, m.p. 85—87°, and *anhydrodi*-derivatives, m.p. 192°); *Ac*, m.p. 96—98°, *Bz*, m.p. 122°, *Me*, m.p. 101°, and *anhydrodi*-derivatives of bromoalbutyramide, m.p. 155°; *bromal*-iso*butyr*-, m.p. 156° (*Ac*, m.p. 141—143°, *Bz*, m.p. 131—132°, *Me*, m.p. 135°, and *anhydrodi*-derivatives, m.p. 155°); -iso*valer*-, m.p. 149° (*Ac*, m.p. 140—142°, *Bz*, m.p. 98—100°, *Me*, m.p. 115—117°, and *anhydrodi*-derivatives, m.p. 130—132°); *-hexo-*, m.p. 146° (*Ac*, m.p. 120—122°, *Bz*, m.p. 132—134°, *Me*, m.p. 105—107°, and *anhydrodi*-derivatives, m.p. 153°); *-hepto-*, m.p. 142° (*Ac*, m.p. 135—136°, *Bz*, m.p. 126°, and *Me* derivatives, m.p. 93—95°); *-octo-*, m.p. 139° (*Ac*, m.p. 129°, *Bz*, m.p. 108—110°, *Me*, m.p. 85°, and *anhydrodi*-derivatives, m.p. 166°); and *-nono-*, m.p. 139° (*Ac*, m.p. 121°, *Bz*, m.p. 123—126°, and *Me* derivatives, m.p. 72—74°), *-amide*; β-*tribromo*-α-*chloroethyl-formamide*, b.p. 80°/15 mm., *-acetamide*, b.p. 76°/8 mm., *-acetchloroimide*, b.p. 138°/25 mm., *-propionamide*, b.p. 120°/19 mm., and *-butyramide*, b.p. 126°/15 mm.; β-*dibromoethylene-acet-*, m.p. 82°, *-propion-*, m.p. 84—86°, *-butyr-*, m.p. 78—80°, iso*butyr*-, m.p. 80—82°, -iso*valer*-, m.p. 68—70°, *-hexo-*, m.p. 74—75°, *-octo-*, m.p. 115°, and *-nono-*, m.p. 63—64°, *-amide*; and β-*bromoethylene*-iso*valer*-, m.p. 71—74°, *-hexo-*, m.p. 61—63°, *-octo-*, m.p. 67—71°, and *-nono-*, b.p. 148°/10 mm., *-amide*. F. R. S.

Synthesis of *l*-asparagine from *l*-glutamine. M. BERGMANN, L. ZERVAS, and L. SALZMANN (Ber., 1933, **66**, [*B*], 1288—1290; cf. A., 1932, 935).—Benzylcarbonato-*l*-aspartic anhydride is converted by $CH_2Ph{\cdot}OH$ at 100° mainly into the CH_2Ph *H* ester $CO_2H{\cdot}CH_2{\cdot}CH(NH{\cdot}CO_2{\cdot}CH_2Ph){\cdot}CO_2{\cdot}CH_2Ph$, m.p. 84—85°, transformed successively into the corresponding *chloride*, m.p. 81—82°, and *amide*, m.p. 132° (corr.), which, when treated with Pd-black and H_2 in MeOH, gives PhMe, CO_2, and *l*-asparagine, $[\alpha]_D$ +20·6° in 0·1*N*-HCl. Similarly benzylcarbonato-*d*-glutamic anhydride is transformed successively into the non-cryst. α-CH_2Ph ester, its *chloride*, *amide*, m.p. 123° (corr.), and *d*-glutamine, m.p. 184—185°, $[\alpha]_D^{19}$ +8·0° in H_2O. H. W.

Thiocarbamyl chloride. Thiocyanic acid. M. BATTEGAY and E. HÉGAZI (Helv. Chim. Acta, 1933, **16**, 999—1008).—Treatment of a saturated solution of NH_4CNS in H_2O at −5° with 50—60% H_2SO_4 in amount not quite sufficient to liberate HCNS completely, followed by extraction with ether so as to produce a > 20% solution and treatment of the dried extract with HCl, leads to *thiocarbamyl chloride* (I), $NH_2{\cdot}CSCl$, decomp. 75—80°, which with H_2O and bases suffers the change $NH_2{\cdot}CSCl \longrightarrow HCl + HSCN$. With alcohols (I) affords alkoxythioformamides, $OR{\cdot}CS{\cdot}NH_2$, of which the following are described: Me, m.p. 42—43°; Et, m.p. 40—41°; Pr^{β}, m.p. 79—80°; Bu^{α}, m.p. 20—21°; Bu^{β}, m.p. 51—53°; $OH{\cdot}CH_2{\cdot}CH_2$, m.p. 68—69°. With excess of (I) dithioallophanates are obtained. With MeOH methylthiolformamide is also produced, indicating the equilibrium $NH_2{\cdot}CSCl \rightleftharpoons HCl + S{:}C{\cdot}NH$. With PhOH (I) gives phenylxanthamide and *p-hydroxythiobenzamide*, m.p. 175° (decomp. with production of *p*-$CN{\cdot}C_6H_4{\cdot}OH$), mixed with a small proportion of the *o*-isomeride, m.p. 117—118°. H. W.

Action of sodium on aliphatic diazo-compounds. E. MÜLLER and H. DISSELHOFF (Naturwiss., 1933, **21**, 661).—CPh_3Na with EtOH- and H_2O-free CH_2N_2 (A., 1930, 1027) yields an explosive Na compound which with BzCl gives a *substance*, $C_8H_6ON_2$, not identical with diazoacetophenone. Similarly diphenyldiazomethane affords an Et_2O-sol. compound which on decomp. with H_2O yields a *substance*, $C_{32}H_{26}N_2$, not identical with diphenylketazine. CPh_2Na also reacts with PhN_2 (cf. A., 1901, i, 678). F. O. H.

Formation of free radicals from aliphatic azo-compounds. F. O. RICE and B. L. EVERING (J. Amer. Chem. Soc., 1933, **55**, 3898—3899; cf. Leermakers, this vol., 1039).—Measurements of the rate of disappearance (method: A., 1932, 1108) of the active fragments obtained from β-azopropane (in $COMe_2$) indicate the formation of a fragment of relatively long life. H. B

Preparation and application of organomagnesium compounds without use of ether. II. Action of magnesium on alkyl and aryl chlorides. P. SCHORIGIN, V. ISSAGULIANZ, and A. GUSSEVA (Ber., 1933, **66**, [*B*], 1426—1431).—Mg and 1-$C_{10}H_7Cl$ react vigorously at 200—220° with copious sublimation of $C_{10}H_8$ and production of 10—13% of $C_{10}H_7$·MgCl. Boiling CH_2PhCl and Mg react very energetically with evolution of HCl and formation of a glassy mass probably due to a condensing action of $MgCl_2$, similar to that of $AlCl_3$, $FeCl_3$, or $SnCl_4$. Bu^{a}Cl, *iso*-$C_5H_{11}Cl$, and *n*-$C_8H_{17}Cl$ react moderately violently near their b.p.; the intermediate organomagnesium compounds are completely decomposed, with the formation of R·R, RH, and R—H, leaving a residue probably of $MgCl_2$ and Mg. The formation of organo-Mg derivatives is placed beyond doubt by the production of nonoic acid from *n*-$C_8H_{17}Cl$ and Mg in CO_2, although $(CH_2)_2O$ is without action. Treatment of RCl with Mg activated by I and PhCHO affords CHPhBz·OH. Moderation of the reaction between *iso*-$C_5H_{11}Cl$ or Bu^{a}Cl and Mg by addition of PhMe gives the corresponding *p*-alkyltoluenes characterised by oxidation to terephthalic acid; this change is not caused by $MgCl_2$. The compound, m.p. 209—211° (A., 1931, 1411), is *p*-phenyldiphenyl. H. W.

Action of sodium on gallium trimethyl and gallium dimethyl chloride in liquid ammonia. C. A. KRAUS and F. E. TOONDER (J. Amer. Chem. Soc., 1933, **55**, 3547—3554; cf. this vol., 599).—In liquid NH_3 at −33°, the reaction $2GaMe_3,NH_3+Na=[GaMe_3]_2NH_2Na+0{\cdot}5H_2+NH_3$ (I) is accompanied by $2GaMe_3,NH_3+2Na=[GaMe_3]_2Na_2+2NH_3$ (II) to the extent of 0—30%, depending on the conditions. With Li and liquid NH_2Et at −33°, the reactions are $GaMe_3,NH_2Et+Li=GaMe_3,NHEtLi+0{\cdot}5H_2$ and the analogue of (II). $Na_2[GaMe_3]_2$ reacts with NH_4Br: $Na_2[GaMe_3]_2+2NH_4Br=2GaMe_3,NH_3+2NaBr+H_2$, whereas $Li_2[GaMe_3]_2$ decomposes during the evaporation of the NH_2Et as follows: $Li_2[GaMe_3]_2+2NH_2Et\longrightarrow 2GaMe_3,NHEtLi+H_2$. With one equiv. of Na the reaction $GaMe_2Cl+Na=GaMe_2+NaCl$ (III) is followed by the formation of $GaMe_2,NH_3$, which decomposes after the evaporation of the solvent: $GaMe_2,NH_3=GaMe_2{\cdot}NH_2+0{\cdot}5H_2$. With two equivs. of Na, (III) is followed by the slow reaction $GaMe_2,NH_3+Na=GaMe_2,NaNH_2+0{\cdot}5H_2$ and $GaMe_2,NH_3$ is regenerated on the addition of NH_4Br. J. G. A. G.

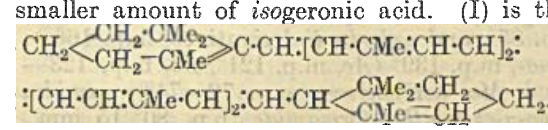
New hydrocarbons of the *cyclo*pentane series and their passivity towards catalytic dehydrogenation. N. D. ZELINSKI, S. E. MICHLINA, and M. S. EVENTOVA (Ber., 1933, **66**, [*B*], 1422—1426).—*cyclo*Pentanone (I) and *n*-C_6H_{13}·MgBr yield 1-n-*hexyl*cyclo*pentan*-1-*ol*, b.p. 120—121°/15 mm., converted by heating with cryst. $H_2C_2O_4$ into n-*hexyl*cyclo*pentene*, b.p. 204—205°/740 mm., which is reduced (Pt–C at 200°) to n-*hexyl*cyclo*pentane* (II), b.p. 204—206°/748 mm. *n*-C_8H_{17}·MgCl and (I) yield 1-n-*octyl*cyclo*hexan*-1-*ol*, converted successively into n-*octyl*cyclo*pentene* and n-*octyl*cyclo*pentane* (III), b.p. 133—134°/26 mm. Mg *cyclo*pentyl chloride and powdered trioxymethylene give cyclo*pentylmethyl alcohol*, b.p. 162—163°/753 mm., converted by red P and I into an iodide (IV), b.p. 75°/19 mm., which with Na in Et_2O affords *dicyclo*-[0 : 1 : 3]-hexane and a non-homogeneous mixture converted by Pd–C at 300° into Ph_2 and α^3-*di*cyclo*pentylethane*, b.p. 206—207°/748 mm. (IV) is therefore a mixture of *cyclo*pentylmethyl and hexyl iodide. (II) and (III) are stable in presence of Pt–C at 300°. H. W.

Kinetics of a diene synthesis. A. WASSERMANN (Ber., 1933, **66**, [*B*], 1392—1394).—By periodic measurement of the intensity of colour, the reaction between *p*-benzoquinone and *cyclo*pentadiene (I) is shown to be bimol. in *n*-C_6H_{14}, CCl_4, C_6H_6, EtOH, and AcOH. That between (I) and *cyclo*pentadienequinone is also bimol. H. W.

Kinetics of the irreversible catalysis of *cyclo*hexene and the *cyclo*hexadienes. N. D. ZELINSKI and G. S. PAULOV (Ber., 1933, **66**, [*B*], 1420—1422; cf. A., 1925, i, 122).—In presence of Pd sponge at 35°, *cyclo*hexene, b.p. 83·5° (corr.), is converted into C_6H_6 and *cyclo*hexane; the reaction, measured by periodic titration with Br in $CHCl_3$, is sesquimol. $\Delta^{1:3}$- and $\Delta^{1:4}$-*cyclo*Hexadiene react vigorously in contact with Pd (Pt) sponge; the first violent action $2C_6H_8=C_6H_{10}+C_6H_6$ is followed by the slower change, $3C_6H_{10}=C_6H_6+2C_6H_{12}$. H. W.

1-Methyl*dicyclo*-[1 : 2 : 2]-heptane and its behaviour during catalytic dehydrogenation and hydrogenation. Fission of the *cyclo*pentane ring by catalytic hydrogenation. N. D. ZELINSKI, B. A. KAZANSKI, and A. F. PLATE (Ber., 1933, **66**, [*B*], 1415—1419).—*endo*Methylenetetrahydrobenzaldehyde (I), b.p. 71—72°/9 mm., is transformed through the hydrazone into 2-*methyl*dicyclo-[1 : 2 : 2]-Δ^5-*heptene* (II), b.p. 115·5—117°/750 mm. Hydrogenation of (I) (Pt sponge or, preferably, Pd sponge) leads to *endomethylenehexahydrobenzaldehyde*, b.p. 62—64°/12 mm., similarly converted into 2-*methyl*dicyclo-[1 : 2 : 2]-*heptane* (III), b.p. 125—126·5°/761 mm., which is stable towards $KMnO_4$. Hydrogenation of (II) as gas at 130° (Pt–C) gives a product, b.p. 120—124°/727 mm., not completely identical with (III), whereas at room temp. (EtOH–Pd sponge) the product is homogeneous and identical with (III). Passage of (III) over Pt–C at 300 in H_2 leads to addition of 2H and formation of the saturated system C_nH_{2n}. One of the pentamethylene rings suffers fission in contact with Pt giving a monocyclic *cyclo*pentane hydrocarbon which may undergo further rupture of the ring. *cyclo*Pentane is almost quantitatively transformed into *n*-pentane by passage over Pt–C at 300° in H_2.

Vegetable colouring matters. LII. Constitution of α-carotene. P. KARRER, R. MORF, and O. WALKER. **LIII. Xanthophyll and violaxanthin.** P. KARRER, A. ZUBRYS, and R. MORF (Helv. Chim. Acta, 1933, **16**, 975—977, 977—979).—LII. Ozonisation of α-carotene (I), separated from β-carotene by $Ca(OH)_2$, leads to geronic acid and a somewhat smaller amount of *iso*geronic acid. (I) is therefore



By reason of its acidity, fuller's earth is unsuitable for the purification of (I).

LIII. Elucidation of the structure of (I) (see above) leads to the constitution (OH·CH<$\begin{smallmatrix}CH_2\cdot CMe_2\\ CH_2\cdot\!-\!CMe\end{smallmatrix}$>C·)·[CH:CH·CMe:CH]$_2$·[CH:CH·CH:CMe]$_2$·CH:CH·CH<$\begin{smallmatrix}CMe_2\cdot CH_2\\ CMe{=}CH\end{smallmatrix}$>CH·OH for xanthophyll (II). The *sec.* OH groups in (II) are characterised by reduction of (II) from grass or stinging nettles to perhydroxanthophyll, which is oxidised by CrO_3 in AcOH to perhydroxanthophyll diketone (*disemicarbazone*, m.p. 158°). H. W.

Carotene. V. Formation of geronic acid by ozonisation of carotene, dihydrocarotene, and related compounds. H. H. Strain. **VI. Hydrogenation of α- and β-carotene.** J. H. C. Smith (J. Biol. Chem., 1933, **102**, 137—150, 157—160; cf. A., 1932, 619).—V. The yield of geronic acid (I) obtained by ozonisation of (*a*) carotene or dihydrocarotene, or (*b*) β-ionone, β-*cyclo*citral, or β-*cyclo*geranic acid, varies widely according to the conditions, the max. being (*a*) 0·67 and (*b*) 0·78 mol. (I) is best determined as 2 : 4-*dinitrophenylhydrazone*, m.p. 133—134° (corr., decomp.), decomposed by alkalis and rapidly hydrolysed by the $NaHSO_3$ compound of glyoxal in AcOH. α-Ionone similarly gives *iso*geronic acid (5—8% only) [2 : 4-*dinitrophenylhydrazone*, m.p. 140—141° (corr.)]. Citralcyanoacetic acid and H_3PO_4 give chiefly α-*cyclo*citral.

VI. α- and β-Carotene in AcOH or AcOH–*p*-menthane absorb 11 mols. of H_2 (PtO_2), if the solvent has not come into contact with rubber or tap-grease. R. S. C.

Significance of tautomerism and of reactions of aromatic compounds in the electronic theory of organic reactions. C. K. Ingold (J.C.S., 1933, 1120—1127).—The internal polar properties of atoms or groups are classified according to (1) time-dependence or (2) mechanism. The characteristics distinguished in (1), viz., polarisation (dipole moment μ) and polarisability (deformation coeff. α), differ in dimensions by an amount corresponding with the dimensions of an electric force The effects categorised in (2) differ in the source of their energy. The zero moment of alkyl groups in hydrocarbons (polarisation) coupled with the reactivity of the latter towards electrophilic (electron-seeking) reagents (polarisability) necessitates the recognition of an "inductomeric" in addition to an inductive effect, the two being distinguished by their time-dependence. Similarly the tautomeric mode of electron displacement is split up into electromeric (*E*, polarisability, time-variable) and mesomeric (*M*, permanent polarisation, originally designated electronic strain) effects. Anomalous orientation (*op*-substitution coupled with nuclear deactivation) in aromatic substitution by electrophilic reagents, and the decrease in strength of BzOH by a *p*-OMe substituent, despite the electron-attracting dipole of their latter, are considered from this point of view. The driving power of the inductive effect (octet stability) is quantum mechanical, but the energy of the mesomeric effect is regarded as arising from a form of wave-mechanical degeneracy, evidence being adduced in support of this view. J. W. B.

Influence of nuclear halogens on aromatic side-chain reactivity. G. M. Bennett (J.C.S., 1933, 1112—1114).—On the basis of results previously summarised (this vol., 499), various side-chain velocity data, and the strengths of halogeno-substituted anilines and benzoic acids, it is suggested that, contrary to hitherto accepted ideas, the electromeric effect (*E*) of the halogens decreases in the order F> Cl>Br>I. *E* is regarded as an ethenoid or butadienoid polarisation in the Ph nucleus promoted by the electron-repelling outer field of the halogen atom (*loc. cit.*). J. W. B.

Effect of nuclear halogen substituents on triad prototropic systems in relation to aromatic side-chain reactions. C. W. Shoppee (J.C.S., 1933, 1117—1120).—Results previously summarised (A., 1930, 912; 1931, 834; 1932, 384) and side-chain velocity data (lit.) show that the effect of halogen substituents anticipated on the basis of the order of their $-I$-effects, F>Cl>Br>I, is inverted in all cases except for the mobility of prototropic systems activated by aryl groups. The last type of reaction is unique in that both the postulated reaction phases, (*a*) the approach of the negative (catalytic) ion, and (*b*) the cationisation of the mobile H, are facilitated by electron-recession. It is suggested that other aromatic side-chain reactions involve two rate-affecting phases of opposite polar types (cf. Baker, *infra*) and hence for type *B* reactions (electron-recession) the velocity coeffs. for ambipolar ($-I$, $+T$) substituents should pass through a max. In the curves connecting relative velocities and the series I, Br, Cl, F (increasing $-I$, diminishing $+T$) the position of the max. may vary according to the way in which mol. circumstances weight the opposing polar phases, and data illustrating each type of curve are cited. Similar curves for type *A* reactions (electron accession) exhibit min., indicating the probable existence of two or more reaction mechanisms, each possibly complex. J. W. B.

Anomalies in the reactivities of side-chain halogens with special reference to reaction mechanism. J. W. Baker (J.C.S., 1933, 1128—1133).—The ψ-unimol. velocity coeffs. (10^3k, min.$^{-1}$) for the reaction (I) $CH_2RX+C_5H_5N\longrightarrow CH_2R\cdot NC_5H_5\}X^{\ominus}$, and (II) $+NH_2Ph\longrightarrow CH_2R\cdot NHPh+HX$, previously determined (A., 1932, 744, 1241), indicate that the reaction requires electron-accession to (*A*), or recession from (*B*), the side-chain when R=*p*-Y·C_6H_4· and *p*-Y·C_6H_4·CO·, respectively, the nature of R thus predisposing the mol. to react mainly by one or the other type of mechanism. The observed velocity of side-chain reactions is probably determined by two (or more) rate-affecting factors of opposite polar types (cf. Shoppee, preceding abstract) and (for X=Br) evidence for this view is adduced from (*a*) the influence of ambipolar substituents on 10^3k for I*A* (I, 3·3; Br, 3·0, Cl, 3·2; H, 4·4) and II*A* (45, 41, 44, and 35, respectively); (*b*) the effect of *m*- (10^3k 1·36) and *p*- (1·56) -NO_2 substituents on I*A*; (*c*) the relative facilitating and retarding effects of unipolar substituents (accelerating influence of group > its retarding influence on a reaction of

opposite polar type; (*d*) the results of Dawson and Dyson (this vol., 1125); and (*e*) the effect of base concn. on the reaction velocity of I*A* (10 mols., 10^3k 4·4; 20 mols. 8·2) and I*B* (10 mols. 6·5; 20 mols. 11). The effect of varying X (Cl, Br, or I) on *k* is discussed and possible mechanisms for the reactions are suggested. J. W. B.

Hydrogenation of aromatic compounds at temperatures close to their decomposition [points] in presence of catalysts. V. Ipatiev (J. Amer. Chem. Soc., 1933, **55**, 3696—3701).—C_6H_6 and $C_6H_4Me_2$ are not hydrogenated at 400—450°/65—100 atm. using MoO_3 catalysts; $C_6H_4Me_2$ decomposes to C_6H_6 and PhMe. Hydrogenation of $C_{10}H_8$ at > 450°/65—80 atm. (initial pressure) using NiO, Fe_2O_3, and MoO_3 catalysts gives 1 : 2 : 3 : 4-tetrahydronaphthalene (I) almost exclusively; reaction proceeds (probably) 9 : 10-H_2- ⟶ 1 : 4-H_2- ⟶ (I). Above 450°, the (I) formed decomposes into C_6H_6 hydrocarbons; with Ni catalysts naphthens are formed, showing that some mols. of the monocyclic aromatic compounds are hydrogenated during this decomp. Similar hydrogenation of PhOH in presence of MoO_3, Fe_2O_3, or CuO gives 10—30% of *cyclo*hexane. Thiophen has no effect on the rate of destructive hydrogenation of $C_{10}H_8$, but decreases the yield of hydrocarbons during the reduction of PhOH. H. B.

Catalytic oxidation of benzene to maleic acid. J. S. Salkind and S. Zolotarev (J. Appl. Chem. Russ., 1933, **6**, 681—684).—Air is passed through C_6H_6 at 15°, the vapour is heated to 360°, and passed over V_2O_5 catalyst at 410—430°, when 14—17% yields of $(CH{\cdot}CO_2H)_2$ (I) are obtained. The issuing gas contains in addition $(CH{\cdot}CO)_2O$, CO_2, benzoquinone, and unchanged C_6H_6, which is recovered by adsorption on cooled SiO_2 gel. The process consists probably of the reactions: C_6H_6 ⟶ PhOH ⟶ *p*-$C_6H_4(OH)_2$ ⟶ benzoquinone ⟶ (I). R. T.

Action of aluminium bromide on benzene. E. Wertyporoch and H. Sagel (Ber., 1933, **66**, [*B*], 1306—1312).—Protracted action of $AlBr_3$ on C_6H_6 at 18° gives a liquid (I) and an oily (II) layer. Fractional distillation of (I) affords no evidence of PhMe or PhEt, but yields a liquid $C_7H_6O_5$ with a phenolic odour which contains 2 OH (Zerevitinov), is stable towards $KMnO_4$, and is hydrogenated to a mixture of phenols; phenyl*cyclo*hexane, Ph_2, and *o*-diphenyl-*cyclo*hexane are identified. (II) yields PhOH but not $C_{10}H_8$, a *phenylcyclohexanediol*, m.p. 178—179°, and a phenyl*cyclo*hexanol, *cyclo*hexane, and a mixture of phenylated methyl*cyclo*pentanes and *cyclo*hexanes. H. W.

ψ-Halogens. XXII. Reaction of metallic salts with iodine and bromine in presence of benzene. L. Birckenbach and J. Goubeau (Ber., 1933, **66**, [*B*], 1280—1287; cf. A., 1932, 1120).—The salt is covered with C_6H_6 and treated with small, successive quantities of I or Br at room temp. until the colour persists. Substitution in the C_6H_6 is observed in the presence of salts of Ag, Hg^{II}, and Au^{I} and to a smaller extent in that of Cu^{I} or Cu^{II}, but not of Zn, Cd, Tl^{I}, or Pb^{II} even after addition of $AlCl_3$. Reasons are advanced for attributing the success of the reaction to the comparatively non-polar type of the active salts. The change consists in a primary, equilibrated formation of a mixed halogen the action of which on C_6H_6 is facilitated by $AlCl_3$. A direct substitution is excluded, since I or Br does not react with C_6H_6 in presence of Na_2CO_3 or CaO and the rate of the observed reaction depends greatly on the anion. Reaction between $AgNO_3$ and I is accelerated by HNO_3. Conc. H_2SO_4 is helpful in the cases of I and Ag_2SO_4, Hg_2SO_4, and $HgSO_4$, but not of $PbSO_4$. The main product of the change is invariably PhBr or PhI, the other component of the mixed halogen seldom appearing in the final product. Small amounts of $PhNO_2$ and PhOAc, respectively, are observed in the actions with $AgNO_2$ and I or Br and AgOAc with Br. H. W.

Electrochemical experiments with *p*-fluorotoluene and *p*-fluorobenzoic acid; di-*p*-fluorobenzoyl peroxide and its decomposition. F. Fichter and J. Rosenzweig (Helv. Chim. Acta, 1933, **16**, 1154—1158).—*p*-C_6H_4FMe is immediately converted by electrolytic oxidation into *p*-$C_6H_4F{\cdot}CO_2H$ (I), degradation with formation of CO_2 also occurring; the formation of *p*-$C_6H_4F{\cdot}CHO$ cannot be detected. *p*-$C_6H_4F{\cdot}CO_2Na$ in MeOH, like other aromatic acids with CO_2H attached directly to the nucleus, does not undergo Kolbe's electrosynthesis, the F being incapable of protecting the nucleus from oxidation. *Di-p-fluorobenzoyl peroxide*, m.p. 97°, slow decomp. 99—100°, from *p*-$C_6H_4F{\cdot}COCl$ in Et_2O and BaO_2,H_2O, is converted at 250° into 4 : 4′-difluorodiphenyl mixed with more complex condensation products and regenerated (I). H. W.

Monochlorination of *m*-nitrotoluene. W. E. Evison (J.S.C.I., 1933, **52**, 275—276T).—*m*-$C_6H_4Me{\cdot}NO_2$ is smoothly chlorinated (Fe catalyst) to a mixture of Cl_1- and Cl_2-derivatives which cannot be separated by distillation. On reduction it gives an oil which contains 30% of 6-chloro-*m*-toluidine; a part of this base crystallises, whilst the remainder is isolated as oxalate, picrate, or sulphate. The dichloroamino-compounds are easily removed, as their hydrochlorides are almost completely hydrolysed by H_2O; 2 : 5-dichloro-*m*-toluidine appears to preponderate in the basic mixture which is thus separated. About 21% of the 2-Cl- and small quantities of the 4-Cl-isomerides can then be isolated as their Ac derivatives, by acetylating and fractionating the residual oil. From the oxidation product of the mixed chloronitrotoluenes, 4-chloro-3-nitrobenzoic acid is most easily isolated, and is present to the extent of 10—15%.

Absorption spectra of 2 : 4 : 6-trinitrotoluene. M. M. Pavlik (Chim. et Ind., 1933, **29**, Spec. no., 245—259).—The photochemical decomp. of 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ (I) has been followed by investigation of the absorption spectra and extinction coeffs. of the fused compound and of its solutions in org. solvents before and after exposure to light. The absorption spectra of its decomp. products, *o*- and *p*-quinoxime, have also been investigated. The quantities of these compounds produced in (I) can be determined by spectrum analysis. Ther-

mal decomp. and the action of alkalis lead to products similar to those of the photochemical decomp.
J. W. S.

Volume effects of alkyl groups in aromatic compounds. I. Influence of 2 : 6-dinitration on a group ·CR_1R_2Alk. II. Influence of a group ·CR_1R_2Alk on vicinal substitution. R. J. W. Le Fevre (J.C.S., 1933, 977—980, 980—984).—I. The expectation, based on scale drawings (cf. this vol., 557), that spatial interference of the Pr^β with the adjacent NO_2 groups in 1 : 4 : 6 : 3 : 5-$C_6HMePr^\beta R(NO_2)_2$ would lead to geometrical isomerism has not been realised where R is OH, OAc, OBz, Cl, or Br, all attempts at fractionation of 4 : 6-dnitrocarvacrol, m.p. 121—122°, its acetate, m.p. 74—75°, and benzoate, m.p. 100—101°, proving unsuccessful. The reported existence of isomeric 3 : 5-dinitro-2-chloro- or -bromo-*p*-cymenes (cf. A., 1889, 493) is disproved, the sole nitration product being in each case the cryst. form, which was obtained in almost quant. yield and gave 3 : 5-*dinitro*-2-*piperidino*-p-*cymene*, m.p. 123—124°, with $C_5H_{11}N$. Attempts to realise a similar interference with the ·CMe_3 group in the artificial musks were frustrated by their lack of reactivity. "Musk xylol" [1 : 3 : 5 : 2 : 4 6-$C_6Me_2Pr^\beta(NO_2)_3$] could not be oxidised to a carboxylic acid and did not react with aromatic aldehydes, although 2 : 4 : 6-trinitro-*m*-xylene readily gives 2 : 4 : 6-*trinitro*-1 : 3-*distyrylbenzene*, m.p. 145—146°. "Musk ambrette" [1 : 3 : 2 : 4 : 6 : 5-$C_6MePr^\beta(NO_2)_3$·OMe] could not be demethylated and reacts only very slowly with $C_5H_{11}N$ to give the *piperidino*-derivative, $C_{16}H_{22}O_6N_4$, m.p. 184°.

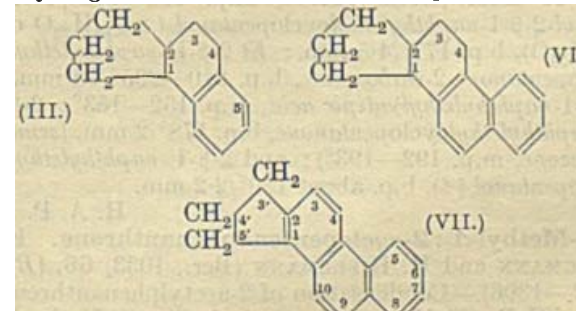
II. Preferential substitution of *p*-cymene in the 2-position is confirmed, 70%, 59%, and 54% of homogeneous 2-substituted derivatives being isolated on nitration, chlorination, and bromination, respectively. Current electronic theories require preferential 3-substitution, and it is suggested that the steric effect of the Pr^β group is the disturbing factor. p-*Cymene*-3-*carboxylic acid*, m.p. 82—83° (from 3-bromocymene, Mg, and CO_2), and 2-p-*cymeneazo*-β-*naphthol*, m.p. 131—132°, are described. H. A. P.

Nitration of 4-nitro-*o*-tolyl *p*-toluenesulphonate. F. H. Curd and A. Robertson (J.C.S., 1933, 1166—1167).—With HNO_3 (*d* 1·5) at room temp. 4-*nitro*-o-*tolyl* p-*toluenesulphonate*, m.p. 123—124° (from 4-nitro-*o*-cresol, *p*-C_6H_4Me·SO_2Cl, and anhyd. Na_2CO_3), gives the corresponding 2-*nitro*-p-*toluenesulphonate*, m.p. 120—121°, but with conc. H_2SO_4–HNO_3 (*d* 1·5) at < 40° or 0°, 4 : 6-*dinitro*-o-*tolyl* 2-*nitro*-p-*toluenesulphonate* (I), m.p. 125—126°, is obtained. With piperidine at 100° or 10% KOH in aq. EtOH, (I) gives 4 : 6-*dinitro*-p-*cresol*, m.p. 115° (and 2-nitro-*p*-toluenesulphonic acid), the *Me ether*, m.p. 80—81°, of which is converted by H_2SO_4–HNO_3 into 3 : 4 : 5-trinitro-2-methoxytoluene, identical with a specimen prepared from 4-nitro-2-methoxytoluene (A., 1901, i, 590), and is reduced by $SnCl_2$–HCl–MeOH to 5-*nitro*-2-*methoxy*-p-*toluidine*, m.p. 152°, from which 5-nitro-2-methoxytoluene is obtained by elimination of the NH_2 group by diazotisation. J. W. B.

Catalytic oxidation of acenaphthene in solution. R. Duckert (Arch. Sci. phys. nat., 1933, [v], **15**, 244—263, 343—371).—The % oxidation of acenaphthene (I) to naphthalic acid (II) and acenaphthenequinone (III) (9 : < 1) is (*a*) at atm. pressure, 0 without and < 2 with a catalyst in absence of a solvent, (*b*) at 200° and 8 kg. per sq. cm. initial pressure, in absence of a solvent, < 5, (*c*) at 175—300° and 2—8 kg. per sq. cm. with various catalysts in H_2O, AcOH, PhCl, or $C_6H_4Cl_2$, 2—24 [best with $Mn(NO_3)_2$ in $C_6H_4Cl_2$ at 300° and 3—5 kg. per sq. cm.]. Decomp., always considerable, is very great in case (*b*). The method of separation of (II) and (III) from much (I) and resin is modified. R. S. C.

Rearrangements of polyinenes. V. Reactions of 1 : 1′-bis-(1 : 3-diphenylindenyl). M. T. Goebel and C. S. Marvel (J. Amer. Chem. Soc., 1933, **55**, 3712—3715).—1 : 1′-Bis-(1 : 3-diphenylindenyl) (I) (this vol., 57), also prepared by the action of *s*-$C_2Me_4Br_2$ on the Na alkyl (II) from 1 : 3-diphenylindene and 40% Na–Hg, is oxidised ($K_2Cr_2O_7$–AcOH or O_2 in boiling xylene) to *o*-$C_6H_4Bz_2$ and is cleaved slowly by 1% Na–Hg and readily with 40% Na–Hg or liquid Na–K alloy to (II). (II) and $ClCO_2Me$ give *Me* 1 : 3-*diphenylindene*-1-*carboxylate*, m.p. 99—100°; the free acid could not be obtained by hydrolysis or from (II) and CO_2. Reduction (HI, P, AcOH) of (I) affords 1 : 3-diphenylhydrindene. (I) dissolves in xylene to a faint yellow solution which deepens in colour when heated in absence of air and then fades on cooling; continued heating and cooling changes (I) into a gummy solid. The above reactions show that (I) dissociates into an unstable free radical and is a new type of hydrocarbon containing an active C·C linking.

Polycyclic compounds related to sterols. I. G. A. R. Kon (J.C.S., 1933, 1081—1087).—12-*Methyl*- (I), b.p. 157°/16 mm., and 11-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (II), b.p. 133°/2·8 mm., 1 : 2-cyclo*pentano*- (III), b.p. 138°/19 mm., and 1 : 2-cyclo*pentano*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (IV), b.p. 128°/12 mm., 1 : 2-(5′-*methyl*cyclo*pentano*)-, (?) (V), b.p. 141—145°/2 mm., and 1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (?) (VI), b.p. 142°/2 mm., are prepared. On dehydrogenation with Se (I) and (II) give phenanthrene



with ease, (III) and (IV) give 4 : 5-*benzohydrindene*, b.p. 118°/0·5 mm. (*picrate*, m.p. 108°), the latter with some difficulty, (V) gives 5′-*methyl*-1 : 2-$\Delta^{1',3}$ (or $\Delta^{1',4}$)-cyclo*pentadienophenanthrene* (cf. VII), m.p. 182° [*picrate*, m.p. 199—200° (decomp.)] (reduction of this with Na and 95% EtOH did not give pure products), and (IV) gives 1 : 2-$\Delta^{1',3'}$(or $^{:4'}$)-cyclo*pentadienophenanthrene*, b.p. 182—183° (*picrate*, m.p. about 124°), and 1 : 2-*cyclo*pentenophenanthrene (VII) ("1 : 2-*cyclo*-

pentanophenanthrene " of Ruzicka, this vol., 820; cf. *ibid.*, 710), m.p. 135—136° [*picrate*, m.p. 133—134°; $C_6H_3(NO_2)_3$ *compound*, m.p. 165·5°], apparently identical with the " Diels hydrocarbon." In synthesising the compounds (I)—(VI) modifications of Bardhan and Sen-Gupta's phenanthrene synthesis (A., 1932, 1241) were used, the yield of the 2-β-arylethyl*cyclo*-pentanones or -hexanones being much improved by hydrolysis of the 2-carboxylic esters with $Ba(OH)_2$ or KOH and re-cyclisation of the resulting dicarboxylic acid :

$$(CH_2)_n\!<\!\begin{matrix}C(CH_2\cdot CH_2Ar)\cdot CO_2Et\\ CO\end{matrix} \longrightarrow (CH_2)_n\!<\!\begin{matrix}CH(CH_2\cdot CH_2Ar)\cdot CO_2H\\ CO_2H\end{matrix} \rightarrow (CH_2)_n\!<\!\begin{matrix}CH\cdot CH_2\cdot CH_2Ar\\ CO\end{matrix}$$

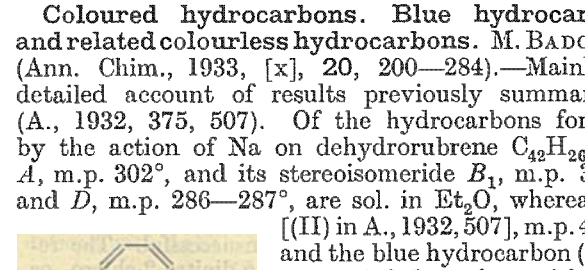
Introduction of the Me group is effected with MgMeI or, if on a C atom common to two rings, by alkylation of the 2-alkyl*cyclo*ketones by the $NaNH_2$ method (cf. A., 1927, 666). The following are described : α-(β-*phenylethyl*)*pimelic acid*, m.p. 64—65°; 1-*methyl*-2-β-*phenylethyl*cyclo*hexanol*, b.p. 140°/3 mm.; 2-*methyl*-2-β-*phenylethyl*cyclo*hexanone*, b.p. 152°/4 mm. (*semicarbazone*, m.p. 178°) (from 2-methyl*cyclo*hexanone, $NaNH_2$, and $CH_2Ph\cdot CH_2Br$); 2-*methyl*-2-β-*phenylethyl*cyclo*hexanol*, b.p. 159°/3 mm.; *Et* 2-β-*phenylethyl*cyclo*pentanone*-2-*carboxylate*, b.p. 192°/6 mm. (*semicarbazone*, m.p. 163°); α-(β-*phenylethyl*)*adipic acid*, m.p. 97—98°; 2-β-*phenylethyl*cyclo*pentanone*, b.p. 163°/13 mm. [*semicarbazone*, m.p. 213° (decomp.)]; 1-*methyl*-2-β-*phenylethyl*cyclo*pentanol*, b.p. 134—135°/5 mm. (dehydrated by heat to an unsaturated *hydrocarbon*, $C_{14}H_{18}$, b.p. 120°/7 mm.); 2-β-*phenylethyl*cyclo*pentanol*, b.p. 131°/1·5 mm.; β-1-*naphthylethyl bromide* (VIII) (from the alcohol and 30% HBr–AcOH), b.p. 172°/20 mm.; *Et* 5-*methyl*-2-β-1-*naphthylethyl*cyclo*pentanone*-2-*carboxylate*, b.p. 227°/4 mm. [from K derivative of Et 5-methyl*cyclo*pentanone-2-carboxylate and (VIII) in $C_6H_4Me_2$]; α-*methyl*-α-(β-1-*naphthylethyl*)*adipic acid*, m.p. 155—156°; 5-*methyl*-2-β-1-*naphthylethyl*cyclo*pentanone*, b.p. 222—225°/10 mm. (*semicarbazone*, m.p. 171—172°); 5-*methyl*-2-β-1-*naphthylethyl*cyclo*pentanol* (? $C_{18}H_{22}O$ or $C_{18}H_{24}O$), b.p. 177°/4·5 mm.; *Et* 2-β-1′-*naphthylethyl*-cyclo*pentanone*-2-*carboxylate*, b.p. 210—235°/10 mm.; α-(β-1-*naphthylethyl*)*adipic acid*, m.p. 152—153°; 2-β-1′-*naphthylethyl*cyclo*pentanone*, b.p. 178°/2 mm. (*semicarbazone*, m.p. 192—193°); and 2-β-1′-*naphthylethyl*-cyclo*pentanol* (?), b.p. about 180°/2·2 mm.

H. A. P.

3′-Methyl-1 : 2-*cyclo*pentenophenanthrene. E. Bergmann and H. Hillemann (Ber., 1933, **66**, [*B*], 1302—1306).—Condensation of 2-acetylphenanthrene with $CH_2Br\cdot CO_2Me$ and Zn–Cu in boiling C_6H_6 leads to *Me* β-*hydroxy*-β-2-*phenanthrylbutyrate*, m.p. 107—109°, dehydrated by 85% HCO_2H to *Me* β-2-*phenanthrylcrotonate*, m.p. 147—148°, which is reduced (Pd–$BaSO_4$–H_2) to *Me* β-2-*phenanthrylbutyrate*, m.p. 76—78° [corresponding *acid* (I), m.p. 125—127°]. (I) is transformed by the successive action of $SOCl_2$ and $AlCl_3$ in $PhNO_2$ into 6 : 7-(1′ : 2′-*naphtha*)-3-*methylhydrind*-1-*one*, m.p. 135—136°, reduced (Zn-Hg, conc. HCl) to 3′-*methyl*-1 : 2-cyclo*pentenophenanthrene* (II), m.p. 126—127° (*picrate*, m.p. 130—131°). Although identity is not at present claimed, (II) is closely similar to the hydrocarbon obtained by Diels by dehydrogenation of cholesteryl chloride by Se (this vol., 1047). Analyses of the picrate, m.p. 120—122° after darkening at 117°, appear to indicate $C_{18}H_{16}$.

H. W.

Coloured hydrocarbons. Blue hydrocarbon and related colourless hydrocarbons. M. Badoche (Ann. Chim., 1933, [x], **20**, 200—284).—Mainly a detailed account of results previously summarised (A., 1932, 375, 507). Of the hydrocarbons formed by the action of Na on dehydrorubrene $C_{42}H_{26}$ (I), *A*, m.p. 302°, and its stereoisomeride B_1, m.p. 338°, and *D*, m.p. 286—287°, are sol. in Et_2O, whereas *C*, [(II) in A., 1932, 507], m.p. 400°, and the blue hydrocarbon (III), m.p. 465° [together with unchanged (I)], are insol., and are separated by long fractional crystallisation from CS_2. For short reaction periods (10 days) *A* and *B* are the main products, but on prolonged action (3 months) these are replaced by (III), *C*, and *D*. Spectrophotometric data (visible and ultra-violet) for these hydrocarbons and for dihydro-, tetraphenyl-, and ψ-rubrene indicate their close relationship, all being characterised by a group of three bands. On the basis of these data and known types of reaction of Na with benzenoid hydrocarbons the structures here given are provisionally assigned :



D forming an intermediate between the two groups of hydrocarbons into which *A* and *B*, and (III) and *C*, respectively, fall.

J. W. B.

Steric hindrance. VIII. J. von Braun and E. Anton [with C. Kemeny] (Ber., 1933, **66**, [*B*], 1373—1378; cf. A., 1932, 1242).—*cyclo*Pentylmethylamine, prepared in > 90% yield from the acid and N_3H in $CHCl_3$, is converted into the *Bz* (I) derivative, b.p. 185°/0·7 mm., m.p. 75°, transformed by PCl_5 at 100° into cyclo*pentylmethyl chloride* (II), b.p. 60°/50 mm. The homogeneity of (II) follows from its successive conversion by way of the iodide, *cyanide*, b.p. 110—115°/80 mm., acid, and its chloride into *cyclo*pentylacetamide, m.p. 144°. (II) reacts very slowly with $NHEt_2$, piperidine, or NaOPh. *cyclo*Pentylacetonitrile is reduced by Na–EtOH to β-cyclo*pentylethylamine*, b.p. 158—159° [non-hygroscopic *hydrochloride*, m.p. 195°; *picrate*, m.p. 142°; *Bz* (III) derivative, b.p. 184°/0·2 mm., m.p. 62°], whence β-cyclo*pentylethyl chloride*, b.p. 84—86°/60 mm., which is little reactive. 2 : 3 : 3-Trimethyl-*cyclo*pentylamine (dihydro-β-campholenamine; dihydro*iso*lauronamine) yields a *Bz* derivative (IV), b.p. 184°/0·4 mm., m.p. 50°, converted by PCl_5 into

2 : 3 : 3-*trimethylcyclopentylmethyl chloride*, b.p. 73°/14 mm., which reacts with difficulty with piperidine. Interaction of N_3H with *iso*campholic or α-campholenic acid affords 2 : 2 : 3-*trimethylcyclopentylmethylamine*, b.p. 71—73°/12 mm. (*picrate*, decomp. 222° after darkening at 205°; *chloroaurate*; *chloroplatinate*, decomp. 245°); the *Bz* derivative (V), b.p. 185°/0·3 mm., m.p. 92°, and PCl_5 yield an *imidochloride*, b.p. 150—152°/14 mm., converted by distillation under atm. pressure into 2 : 2 : 3-*trimethylcyclopentylmethyl chloride*, b.p. 60°/12 mm. (corresponding *bromide*, b.p. 73°/13 mm.). 1 : 4 : 5 : 5-Tetramethyl*cyclo*pentylmethylamine (VI) (from campholonitrile, Na, and EtOH) gives a Bz derivative (VII), transformed by PCl_5 into a mixture of 1 : 4 : 5 : 5-tetramethyl*cyclo*pentylmethyl chloride and a hydrocarbon $C_{10}H_{18}$ (VIII), b.p. 54—55°/14 mm., 175°/756 mm. (VI) does not smoothly lose NH_3 when distilled with H_3PO_4. Successive treatment of (VI) with Me_2SO_4–NaOH and then with KI affords 1 : 4 : 5 : 5-*tetramethylcyclopentylmethyltrimethylammonium iodide*, decomp. 310—312°; the corresponding hydroxide when distilled with or without alkali yields almost exclusively 1 : 4 : 5 : 5-*tetramethylcyclopentylmethyldimethylamine*, b.p. 91°/12 mm., $[\alpha]_D$ +72·8° (*picrate*, m.p. 176°), transformed by syrupy H_3PO_4 in CO_2 into the *hydrocarbon* $C_{10}H_{18}$, b.p. 154—157°/760 mm., not identical with (VIII). Comparative hydrolyses of the Bz derivatives with 38% HCl at 120° during 4 hr. indicate the possibility of the separation of types (II) and (I) from (IV), but not of (IV) from (V). There seems little possibility in this direction of utilising the varying reactivity of Cl in the chlorides. H. W.

Nitration of disulphonanilides. F. Bell and R. Cohen (J.C.S., 1933, 1290).—Mononitration of *di*-m-*nitrobenzenesulphonanilide*, m.p. 189°, is accomplished with fuming HNO_3 (conc. HNO_3 has no action); treatment of the resultant product with conc. H_2SO_4 gives di-*m*-nitrobenzenesulphon-*m*-nitroanilide and *m*-nitrobenzenesulphon-*p*-nitroanilide. *Di*-m-*nitrobenzenesulphon*-p-*toluidide*, m.p. 199°, is similarly nitrated to the 2-*nitro*-p-*toluidide*, m.p. 208°, which with conc. H_2SO_4 gives m-*nitrobenzenesulphon*-2-*nitro*-p-*toluidide*, m.p. 136°. *Di*-m-*nitrobenzenesulphon*-o-*toluidide*, m.p. 226°, affords the 4-, m.p. 221°, and 6- (I), m.p. 185°, -*nitro*-o-*toluidides*; (I) is converted by piperidine into m-*nitrobenzenesulphon*-6-*nitro*-o-*toluidide*, m.p. 148°. H. B.

Polyhalogenodinitrobenzenes. S. S. Joshi and S. M. Sane (J. Indian Chem. Soc., 1933, **10**, 459—463).—With the appropriate amine, 1-chloro-4-bromo-2 : 6-dinitrobenzene gives 4-bromo-2 : 6-dinitro-aniline, m.p. 159°, -diphenylamine, m.p. 122°, -*dimethylamine*, m.p. 119°, and -*phenylpiperidine*, m.p. 110°, 4 : 4′-*dibromo*-2 : 6 : 2′ : 6′-*tetranitrodiphenyl*-p-*phenylenediamine*, m.p. > 300°, 3-*bromo*-o-*nitrophenoxazine* (from *o*-aminophenol), m.p. 179°, and o-*bromo*-7-*nitro*-2-*phenyl*-ψ-*aziminobenzene* (from NH_2NHPh), m.p. 199°; the 4-I-compound gives 4-*iodo*-2 : 6-*dinitro-aniline*, m.p. 175°, -*dimethylaniline*, m.p. 100°, -*diphenylaniline*, m.p. 135°, and -*phenylpiperidine*, m.p. 99°, 3-*iodo*-5-*nitrophenoxazine*, m.p. 210°, and 5-*iodo*-7-*nitro*-2-*phenyl*-ψ-*aziminobenzene*, m.p. 209°. 1-Chloro-2-bromo-4 : 6-dinitrobenzene yields 2-*bromo*-4 : 6-*dinitrophenylpiperidine*, m.p. 127°, and 7-*bromo*-5-*nitro*-2-*phenyl*-ψ-*aziminobenzene*, m.p. 174°, whilst the 2-I-compound forms 2-*iodo*-4 : 6-*dinitro-aniline*, m.p. 158°, -*diphenylamine*, m.p. 144°, and -*dimethylaniline*, m.p. 112°, 2 : 2′-*di-iodo*-4 : 6 : 4′ : 6′ - *tetranitrodiphenyl* - p - *phenylenediamine*, m.p. > 300°, 7-*iodo*-5-*nitro*-2-*phenyl*-ψ-*aziminobenzene*, m.p. 192°, and 3 : 5-dinitrophenoxazine, m.p. 214—215°. F. R. S.

Reaction of formaldehyde with diphenylamine. D. Craig (J. Amer. Chem. Soc., 1933, **55**, 3723—3727).—$NHPh_2$ (1·5 mols.), 36% CH_2O (0·19 mol.), and conc. HCl (1 c.c.) in EtOH (250 c.c.) at 40—100° (bath) give (mainly) 4 : 4′-dianilinodiphenylmethane (I), m.p. 122—123° [synthesised (Ullmann method) from 4 : 4′-diaminodiphenylmethane and *o*-$C_6H_4Cl{\cdot}CO_2H$]; resins are produced with equiv. amounts or excess of CH_2O. Equimol. quantities of CH_2O and $NHPh_2$ in C_6H_6 give tetraphenyldiaminomethane (II), m.p. 104—105° [the specimen prepared by Houben and Arnold (A., 1908, i, 533) is probably contaminated with (I)], which is hydrolysed (dil. acid) to CH_2O and $NHPh_2$, but with $NHPh_2$ and a little conc. HCl in EtOH passes into (I); with dry HCl alone, resinification occurs. Hydrogenolysis of (II) using a Cu chromite catalyst gives $NHPh_2$ (main product), NPh_2Me, and (I). The *compound* $(NPh_2Me,HCl)_2,ZnCl_2$ has m.p. 186—188° (decomp.). H. B.

Condensation of ethyl propylacetoacetate with aromatic amines. II. G. V. Jadhav (J. Indian Chem. Soc., 1933, **10**, 391—394).—Et *n*-propylacetoacetate has been heated with further aromatic amines (cf. A., 1931, 1407). Except with *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$, *s*-diarylcarbamides were obtained together with the acetoacetarylamide, but α-$C_{10}H_7{\cdot}NH_2$ gave only $CO(NH{\cdot}C_{10}H_7)_2$, m.p. 296°. The following appear to be new : n-*propylacetoacet*-β-*naphthylamide*, m.p. 115—116°, -o-*phenetidide*, m.p. 90—91°, -p-, m.p. 95—96°, and -m-*hydroxyanilide*, m.p. 223—224° (*Ac* derivative, m.p. 165°), -o-, m.p. 83—84°, -m-, m.p. 88—89°, and -p-*chloroanilide*, m.p. 123—124°, and -m-, m.p. 95—96°, and -p-*nitroanilide*, m.p. 118—119°. F. R. S.

Nitration of aceto-α-naphthalide and preparation of 2- and 4-nitro-α-naphthylamines. H. H. Hodgson and J. Walker (J.C.S., 1933, 1205—1207).—Various methods of mononitration of α-$C_{10}H_7{\cdot}NHAc$ are investigated (cf. A., 1924, i, 637); the use of HNO_3 (*d* 1·42) at 5—10° affords the best yield (87%) and purest product. Hydrolysis (50% H_2SO_4–EtOH) of the nitration mixture, dissolution of the 2- (I) and 4- (II) -nitro-α-naphthylamines in $PhNO_2$, and passage of dry HCl through the solution give the hydrochloride of (II); addition of conc. H_2SO_4 to the filtrate ppts. the sulphate of (I). The free bases are obtained by trituration of the salts with H_2O. Superheated steam removes the slowly volatile (I) from its mixture with (II). The f.-p. diagram of 2-nitroaceto-α-naphthalide [best prepared by partial hydrolysis (EtOH–NaOH) of (III) (below)] and the 4-NO_2-isomeride (IV) [prepared readily from (II) and Ac_2O in AcOH] indicates the existence of the 1 : 1-compound (III), m.p. 171°, described by Lellmann and Remy (A., 1886, 754), and of a metastable eutectic con-

taining about 60 mols.-% of (IV). 2-Nitro-α-naphthol and (I) readily crystallise together in equimol. proportion; the f.-p. diagram does not indicate 1 : 1-compound formation. H. B.

Manufacture of *p*-aminodiphenyl and derivatives thereof.—See B., 1933, 857.

Formation of azides from the *N*-nitroso-derivatives of hydrazo-compounds. G. Longo (Gazzetta, 1933, **63**, 463—471).—Arylhydrazinecarboxylates, $NHAr{\cdot}NH{\cdot}CO_2R$ (I) are prepared from $NHAr{\cdot}NH_2$ and $ClCO_2Me$(or Et) in presence of C_5H_5N; with $NaNO_2$ and AcOH they yield *N*-NO-derivatives, $NAr(:NO){\cdot}NH{\cdot}CO_2R$ (II), and with CrO_3 substituted benzeneazocarboxylates,, $NAr{:}N{\cdot}CO_2R$ (III). When heated with 10% NaOH, (II) give the azides ArN_3 in very small yield, with N_2 and decomp. products. The following are described: *Me*, m.p. 180°, and *Et*, m.p. 198—199°, p-*nitrophenylhydrazinecarboxylates* [*NO*-derivatives, m.p. 125—126° and 110—111° (decomp.)]; *Me*, m.p. 84—85°, and *Et*, m.p. 74—75°, p-*nitrobenzeneazocarboxylates*; *Me* 2 : 4-*dinitrophenylhydrazinecarboxylate*, m.p. 138°; *Me*, m.p. 110—111°, and *Et*, m.p. 105°, p-*bromophenylhydrazinecarboxylate* [*NO*-derivatives, m.p. 92° and 104—105° (decomp.)]; *Me* p-*bromobenzeneazocarboxylate*, m.p. 75—76°; *Me* p-*tolylhydrazinecarboxylate*, m.p. 112° [*NO*-derivative, m.p. 55—56° (decomp.); *Et* ester, m.p. 88°, no NO-derivative]; *Me* p-*toleneazocarboxylate*, m.p. 29—30°. Formyl-*p*-nitrophenylhydrazine forms with amyl nitrite and HCl the N-*NO*-derivative, m.p. 109—110° (decomp.). For *p*-bromo- and *p*-nitro-phenylsemicarbazide the new m.p. 223° and 220° are found. Attempts to prepare compounds of type $NAr{:}N{\cdot}C(OH){:}NOH$ and $NHAr{\cdot}NH{\cdot}C(OH){:}NOH$ from (III) and (I), respectively, or from the corresponding amides, failed. E. W. W.

Reaction between diazonium salts and trinitromethane. G. Ponzio (Gazzetta, 1933, **63**, 471—478).—The formula $R{\cdot}N_2{\cdot}NO{:}C(NO_2)_2$ (A., 1915, i, 1012) is preferred to that proposed by Quilico (this vol., 59) for the products from diazonium salts and nitroformates; their decomp. products cannot be formulated $R{\cdot}N(NO){\cdot}N{:}CO$ (Quilico, *loc. cit.*), for they have none of the properties of the N(NO) and N:CO groupings. The formulation $\begin{matrix}NAr{:}N\\ \diagdown\!\!\diagup\\ N{-}\!\!-O\end{matrix}\!\!>CO$, as *anhydrides of oximinoarylazocarboxylic acids*, on the other hand, explains their stability to heat, and to H_2O, EtOH, NH_2Ph, etc., and the fact that *p*-nitrobenzenediazonium nitroformate when treated with KOH+MeOH or KOH+EtOH gives quantitatively the *K* salts of Me and Et *N*-nitroso-*p*-nitrophenylhydrazinecarboxylates (cf. preceding abstract). E. W. W.

Supercrystallinity of *p*-azoxybenzoic acid.—See this vol., 1108.

Constitution of *o*-hydroxyazo-compounds. K. von Auwers (Annalen, 1933, **505**, 283—295).—Polemical (cf. this vol., 828, 946). Arguments in favour of the azoid structure are advanced. H. A. P.

Action of chlorine on the nitrobenzeneazoacetoacetates. F. D. Chattaway and D. R. Ashworth (J.C.S., 1933, 1143—1146).—The action of Cl_2 on nitrobenzeneazoacetoacetates (αβ-diketo-*n*-butyrate-α-nitrophenylhydrazones) differs considerably from that of Br (cf. this vol., 705); the course of the reaction is affected by the position of the NO_2-group and by the solvent. Thus, p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CAc{\cdot}CO_2Et$ (I) and Cl_2 in AcOH give *Et* α-*chloroglyoxylate*-2-*chloro*-4-*nitrophenylhydrazone*, m.p. 120°, also obtained similarly from *Et* 2-*chloro*-4-*nitrobenzeneazoacetoacetate*, m.p. 109°. In dry $CHCl_3$, *Et* α-*chloroglyoxylate*-*p*-*nitrophenylhydrazone* (II), m.p. 192°, results, but in AcOH–NaOAc the N-*Cl*-derivative (III), m.p. 67°, of (II) is formed. (III) and KI in aq. AcOH give (II). Cl could not be introduced into the Ac group of (I). *Et* 2 : 6-*dichloro*-4-*nitrobenzeneazoacetoacetate*, m.p. 104°, and Cl_2 in AcOH afford *Et* α-*chloroglyoxylate*-2 : 6-*dichloro*-4-*nitrophenylhydrazone*, m.p. 124°. o-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CAc{\cdot}CO_2Et$ (IV) and Cl_2 in $CHCl_3$ give *Et* o-*nitrobenzeneazo*-γ-*chloroacetoacetate*, m.p. 149°, whilst *Et* 4-*chloro*-2-*nitrobenzeneazoacetoacetate* (V), m.p. 127°, affords *Et* 4-*chloro*-2-*nitrobenzeneazo*-γ-*chloroacetoacetate*, m.p. 131°. In AcOH–NaOAc, (IV) and (V) furnish *Et* α-*chloroglyoxylate*-4-*chloro*-2-*nitrophenylhydrazone*, m.p. 108°. *Et* α-*chloroglyoxylate*-m-*nitrophenylhydrazone*, m.p. 158°, is obtained from m-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CAc{\cdot}CO_2Et$ and Cl_2 in $CHCl_3$; in AcOH or AcOH–NaOAc, viscous liquids result. The above benzeneazoacetoacetates are prepared from the requisite diazonium salt and $CH_2Ac{\cdot}CO_2Et$ (cf. *loc. cit.*). *Et* p-*nitro*-, m.p. 135°, 2-*chloro*-4-*nitro*-, m.p. 134°, and 2 : 6-*dichloro*-4-*nitro*-, m.p. 127°, -*benzeneazo*-γ-*chloroacetoacetates*, prepared from the appropriate diazonium salt and $CH_2Cl{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, are converted by EtOH–KOAc into Et 4-hydroxy-1-*p*-nitrophenyl-, -1-2′-*chloro*-4′-*nitrophenyl*-, m.p. 188°, and -1-2′ 6′-*dichloro*-4′-*nitrophenyl*-, m.p. 197°, -*pyrazole*-3-*carboxylate*, respectively. *Et* 2-*chloro*-4-*nitro*-, m.p. 130°, and 2 : 6-*dichloro*-4-*nitro*-, m.p. 112°, -*benzeneazo*-γ-*bromoacetoacetates* are prepared from the corresponding azoacetoacetates and Br. Et α-aminoglyoxylate-*p*-nitrophenylhydrazone, -2 : 6-*dichloro*-4-*nitrophenylhydrazone*, m.p. 182°, -4-*chloro*-2-*nitrophenylhydrazone*, m.p. 141°, and -m-*nitrophenylhydrazone*, m.p. 158°, are obtained from the corresponding α-Cl-derivatives and EtOH–NH_3. H. B.

Rearrangements of phenyl ethers. Action of aluminium chloride on phenyl butyl ethers. R. A. Smith (J. Amer. Chem. Soc., 1933, **55**, 3718—3721).—Equal wts. of $PhOBu^{\beta}$ (I) and $AlCl_3$ at room temp. for a few days give > 50% of *p*-*tert*.-$Bu{\cdot}C_6H_4{\cdot}OH$, also obtained similarly from *tert*.-BuOPh (II), and when (II) is boiled for a few hr. *sec*.-BuOPh (III) and $AlCl_3$ give *p*-*sec*.-$Bu{\cdot}C_6H_4{\cdot}OH$. (I) and (III) do not rearrange when boiled for 10 hr. H. B.

Aromatic compounds of fluorine. XVII. Fluoronitroanisoles. G. Schiemann and T. B. Miau (Ber., 1933, **66**, [*B*], 1179—1187; cf. A., 1932, 1247).—Treatment of *o*-fluoroanisole (I) (improved prep.) with HNO_3 of differing concn., also in presence of AcOH and, particularly, of Ac_2O, affords 2-*fluoro*-4-*nitroanisole* (II), m.p. 104·6°. Repetition of the procedure of Holmes and Ingold (A., 1926, 831) leads only to (II) in addition to (I), and the compound, m.p. 52—52·5°, should be deleted from the lit. The constitu-

tion of (II) is established by converting 4-nitro-*o*-anisidine, m.p. 116° (prepared by reducing 2 : 4-dinitroanisole with H_2S–NH_3 or by successive nitration and hydrolysis of acet-*o*-anisidide), into 5-*nitro*-2-*methoxybenzenediazonium fluoborate*, decomp. 173°, which affords (II) when heated. Treatment of (I) with H_2SO_4–HNO_3 (*d* 1·51) at −5° to 0° yields 2-*fluoro*-4 : 6-*dinitroanisole* (III), b.p. 164—165°/10 mm., also obtained similarly from (II); prolongation of, or rise in temp. during, the reaction causes partial hydrolysis with production of 2-*fluoro*-4 : 6-*dinitrophenol* (IV), m.p. 102°. Similarly, *o*-fluorophenetole affords 2-*fluoro*-4 : 6-*dinitrophenetole*, b.p. 168°/13 mm., and (IV). The fluorodinitroanisole of Holmes and Ingold (*loc. cit.*) is probably impure (II) or partly hydrolysed (III). *p*-Fluoroanisole is transformed by conc. H_2SO_4–HNO_3 (*d* 1·51) into 4-*fluoro*-2 : 6-*dinitroanisole*, m.p. 81·7—82·7°, and 4-fluoro-2 : 6-dinitrophenol, m.p. 50—50·2°. Contrary to Holmes and Ingold (*loc. cit.*), elimination of F is not observed during reduction of fluoronitro-compounds. Thus (II) is converted by conc. HCl–$SnCl_2$ into 2-*fluoro*-p-*anisidine*, m.p. 82·6° (*hydrochloride*, decomp. 180—200°), whilst (III) gives 6-*fluoro*-4-*nitro*-o-*anisidine*, m.p. 108·5° (*Bz* derivative, m.p. 99—100°).

[With W. WINKELMULLER.] 4-Nitro-*o*-phenetidine is transformed into *o-nitro*-2-*ethoxybenzenediazonium fluoborate*, decomp. 171°, which, when heated, gives 2-*fluoro*-4-*nitrophenetole*, m.p. 77°, in poor yield. H. W.

Oxidation of *s*-tri-iodophenol. W. H. HUNTER and M. L. MORSE (J. Amer. Chem. Soc., 1933, **55**, 3701—3705).—Oxidation of *s*-$C_6H_2I_3$·OH (I) with $K_3Fe(CN)_6$ (10 equivs.) in dil. KOH gives a large amount of Lautemann's Red (chromopolydihalogenophenylene oxide), a small quantity of 2 : 6 : 2′ : 6′-*tetra-iododiphenoquinone* (II) [isolated through the corresponding *quinol*, m.p. 260—265° (decomp. at 245°)], and an unstable compound (not isolated); phenoxyquinones are not produced. Oxidation with PbO_2 in C_6H_6 gives amorphous material and 50% of unchanged (I). Oxidation does not occur with $NaNO_2$ in AcOH or N_2O_3 in CCl_4; replacement of I by NO_2 occurs. The product from (I) and CrO_3–AcOH contains 86% of 2 : 6-di-iodo-*p*-benzoquinone [+ a little (II) and amorphous material]; *s*-$C_6H_2Cl_3$·OH and *s*-$C_6H_2Br_3$·OH give 97 and 74%, respectively, of the dihalogenoquinone. The type of radical formed from (I) is discussed (cf. A., 1926, 839). H. B.

Mono- and di-bromo-derivatives of *m*-cresol. II. R. C. HUSTON and W. J. PETERSON (J. Amer. Chem. Soc., 1933, **55**, 3879—3882).—Br (1 mol.) is added to *m*-cresol (1 mol.) in cold oleum (23% SO_3), the mixture kept for 24 hr., diluted with H_2O, and then heated to 180°; steam distillation (mixture kept at 180—210°) gives (mainly) 2-bromo-*m*-cresol (I), m.p. 58·5—59° [Me ether, m.p. 39·5—40° (lit. 35·5—36·5°); *benzoate*, m.p. 59—60°; *benzenesulphonate*, m.p. 70—71°; p-*toluenesulphonate*, m.p. 85—85·5°], 6-bromo-*m*-cresol (II) (*benzoate*, m.p. 87·5—88°; *benzenesulphonate*, m.p. 92—93°; p-*toluenesulphonate*, m.p. 72·5—73°), and 2 : 6-*dibromo*-m-*cresol* (III), b.p. 114—116°/4 mm. (*benzoate*, m.p. 89·5—90°; *benzenesulphonate*, m.p. 94—95°; p-*toluenesulphonate*, m.p. 122—123°). (I), (III), and 2 : 4 : 6-tribromo-*m*-cresol (*benzoate*, m.p. 84—85°; *benzenesulphonate*, m.p. 117—117·5°; p-*toluenesulphonate*, m.p. 113—114°) are obtained from Br (1 mol.) and *m*-cresoldisulphonic acid in alkaline solution and subsequent distillation of the acidified product in superheated steam. (III) is also prepared by deamination of its 4-NH_2-derivative and by bromination of *m*-cresol-*p*-sulphonic acid in alkaline solution (and subsequent steam distillation). (I) and (II) are also prepared from the amino-*m*-cresols. (I) is brominated in CCl_4 to (probably) 2 : 6- and 2 : 4-dibromo-*m*-cresol (*benzoate*, m.p. 81—81·5°; *benzenesulphonate*, m.p. 92—92·5°; p-*toluenesulphonate*, m.p. 89·5—90°). H. B.

β-Arylaminocrotonarylamides. I. J. K. THOMSON and F. J. WILSON (J.C.S., 1933, 1262—1263).—Contrary to Jadhav (A., 1930, 1426), *s*-diarylcarbamides and not β-arylaminocrotonarylamides are obtained (in poor yield) from $CH_2Ac{\cdot}CO_2Et$ and *p*-OMe·C_6H_4·NH_2, *p*-OEt·C_6H_4·NH_2, *o*-, *m*-, and *p*-$C_6H_4Cl{\cdot}NH_2$, and *m*-4- and *p*-xylidines. The following (also prepared from NH_2Ar and $COCl_2$ in PhMe) are described: s-*dianisyl*-, m.p. 234—235°; *s*-diphenetyl-, m.p. 232—233° (lit. 225—226°); s-*di*-o-, m.p. 238—239°, -m-, m.p. 245—246°, and -p-, m.p. 306—307° (sealed hard-glass tube; in soft-glass tubes the m.p. is much lower and is accompanied by decomp.), -*chlorophenyl*-; s-*di*-2 : 4-, m.p. 263—265°, and -2 : 5-, m.p. 285° (sealed tube), -*dimethylphenylcarbamides*. H. B.

β-Naphthol derivatives. I. Preparation and identification of some β-naphthol ethers. A. B. WANG (J. Chinese Chem. Soc., 1933, **1**, 59—63).—Interaction of β-$C_{10}H_7$·ONa and alkyl halides in boiling EtOH afford the following β-naphthyl alkyl ethers, the *picrates* of which (m.p. in parentheses) are described: Me (118°); Et (104·5°); Bu^{α} (67°); Bu^{β} (80·5°); sec.-*Bu*, m.p. 34° (85°); *n*-amyl (64°) *iso*amyl (90·5°); cyclo*hexyl*, m.p. 116° (125°); benzyl (122°). β-Naphthyl methylene ether, m.p. 134°, does not form a picrate. J. L. D.

Synthesis and resolution of *dl*-phenyl-2-methoxy-α-naphthylmethylamine. F. E. RAY and W. A. MOOMAW (J. Amer. Chem. Soc., 1933, **55**, 3833—3838).—*Ph* 2-*methoxy*-α-*naphthyl ketone* (I), m.p. 125° (corr.) [*phenylhydrazone*, m.p. 183·5° (corr.), obtained from (II) (below) and NHPh·NH_2 in EtOH–AcOH], is obtained from BzCl, β-$C_{10}H_7$·OMe, and $AlCl_3$ in CS_2, or by hydrolysis of its *ketimine* (II), m.p. 98—99° [the *hydriodide*, m.p. 180° (corr.), is prepared from Mg 2-methoxy-α-naphthyl iodide (III) and PhCN]. 1-*Iodo*-2-*methoxynaphthalene*, m.p. 88°, is prepared by methylation (Me_2SO_4, 10% alkali) of the iodonaphthol. (I) does not react with NH_2OH and is reduced (Na–Hg) to *phenyl*-2-*methoxy*-α-*naphthylcarbinol*, m.p. 98° (corr.), also prepared from (III) and PhCHO. MeOBz and (III) give (mainly) (I) and some *diphenyl*-2-*methoxy*-α-*naphthylcarbinol*, m.p. 202—203° (corr.). Reduction (2% Na–Hg and EtOH in Et_2O–C_6H_6) of (II) affords dl-*phenyl*-2-*methoxy*-α-*naphthylmethylamine* (IV), m.p. 102° (corr.) [hydrochloride, m.p. 237—240° (decomp.); iso*propylidene*, m.p. 162° (corr.), *benzylidene*, m.p. 98° (corr.), and *N-Ac*, m.p. 186·5—187°, derivatives], which is

resolved by *l*-malic acid into *d*-, $[\alpha]_D^{25}$ +197° in Et_2O, and *l*-, $[\alpha]_D^{5}$ −202° in Et_2O, forms. (IV) is much more stable than the 2-OH-analogue (cf. this vol., 389). β-$C_{10}H_7$·OMe does not react with PhCHO and NH_3 (cf. *loc. cit.*). H. B.

Substitution in resorcinol derivatives. Bromo-derivatives of resorcinol methyl ethers. M. S. Iyengar and H. S. Jois (J. Mysore Univ., 1931, 5, 232—234).—Bromination of dialkoxy-benzaldehyde or -benzoic acid yields, in addition to large quantities of 5-Br-derivatives, small quantities of Br_2-derivatives. Thus 2 : 4-$C_6H_3(OMe)_2$·CO_2H or 2 : 4-$C_6H_3(OMe)_2$·CHO also affords 4 : 6-dibromoresorcinol Me_2 ether; the (OEt)(OMe) compounds afford the 1-Et 3-Me ethers. Ch. Abs.

Preparation of 3 : 4-dihydroxytoluene from 3-amino-*p*-cresol by diazotisation. J. B. Aschkinazi (J. Appl. Chem. Russ., 1933, 6, 730—738).—3 : 4-$C_6H_3Me(OH)_2$ (I) is obtained in 82·5—87·5% yield by diazotising 3-amino-*p*-cresol and hydrolysing the product with 65% H_2SO_4 at 153°, and distillation with steam preheated at 160°. (I) may be determined by pptn. as the Pb salt. A solution of (I) in abs. EtOH becomes blue on pouring without mixing on to EtOH–NaOEt; under these conditions *o*-$C_6H_4(OH)_2$ gives a green coloration. R. T.

Co-ordination compounds of 2 : 2′-dihydroxydiphenyl. O. L. Brady and E. D. Hughes (J.C.S., 1933, 1227—1230).—The physical properties of 2 : 2′-dihydroxydiphenyl (I) suggest that it is R<O—H / O> (in this and subsequent formulæ, R= ·C_6H_4·C_6H_4·). (I) and TlOAc in aq. EtOH–NH_3 give the *Tl* derivative, R<O—H / O>Tl (II), m.p. 227°, which is converted by aq. NaOH or KOH (not aq. NH_3) into the *Tl*$_2$ salt, R(OTl)$_2$ (III). A cold aq. solution of (II) contains $Tl^{\cdot}$. (II) is decomposed by boiling $CHCl_3$ or C_6H_6 to (I) and (III); it is readily sol. in fused (I), $CHCl_3$ containing an excess of (I), and in fused mixtures of (I) and camphor or $C_{10}H_8$. In these last cases, further co-ordination probably occurs. (I) and $TlEt_2$·OH in C_6H_6 give the *mono(diethylthallium)* derivative, R<O—H / O>$TlEt_2$, m.p. 191° (decomp.), an aq. solution of which contains $TlEt_2$ ions; the mol. wt. in camphor is high, indicating association. (I), NH_2Me, and $Cu(OAc)_2$,H_2O in EtOH give the *compound*, R<O / O>Cu←NH_2Me, which also dissolves in $CHCl_3$+(I) or fused (I); NH_2Pr and piperidine afford *compounds* containing 1 mol. of R<O / O>Cu and 1 mol. of amine. The *compound* obtained from (I) and an ammoniacal solution of $Cu(OAc)_2$ contains 3 mols. of (I) and 2 mols. of NH_3 per 1 atom of Cu. This dissolves in $CHCl_3$ to an olive-green solution which decomposes slowly at room temp. and more rapidly at the b.p.; the decomp. is facilitated by $COMe_2$ and the resultant product appears to be a mixture of $(C_6H_4)_2O_2Cu$, $(C_6H_4)_2O_2Cu(NH_3)_2$, and $(C_6H_4)_2O_2Cu(H_2O)_2$. (I), $Cu(OAc)_2$, and an excess of aq. NH_3 give a *compound*, $[(C_6H_4)_2O_2H]_2Cu(NH_3)_2,2H_2O$, (approx. composition), which when dried over conc. H_2SO_4 affords a *complex*, $[(C_6H_4)_2O_2H]_2Cu(NH_3)_3.H_2O$ (approx. composition). H. B.

Relation of electromeric effects and relative polarisabilities of halogens. R. Robinson (J.C.S., 1933, 1114—1117).—A criticism of the views of Baddeley and Bennett (this vol., 499). When two electromeric processes are opposed and one of them is concerned with a hetero-enoid system terminating in a halogen atom, then the resistance offered by the latter is not a question of the extent of its electromeric displacement under normal conditions, but will depend on the deformability of the halogen atom. The order of polarisability or deformability is doubtless I>Br>Cl>F. H. B.

Influence of nuclear substituents on side-chain reactions.—See this vol., 1124.

Triphenylvinyl mercaptan. C. F. Koelsch and G. Ullyot (J. Amer. Chem. Soc., 1933, **55**, 3883—3884).—Mg triphenylvinyl bromide and S give *triphenylvinyl mercaptan* (I), m.p. 110—111° (*Me ether*, m.p. 109·5—110°; *benzoate*, m.p. 192—193°), which reacts only in the ·SH form, is hydrolysed (AcOH–H_2SO_4) to $CHPh_2$·COPh, and is oxidised (alkaline $KMnO_4$) to *di(triphenylvinyl) disulphide*, m.p. 179·5—180·5° [also formed from (I), NH_2OH, HCl, and NaOAc in EtOH]. H. B.

Preparation of 4 : 4′-tetraethyldiamino-2 : 2′-dimethoxytriphenylcarbinol. W. R. Brown and F. A. Mason (J.C.S., 1933, 1269—1270).—m-*Methoxydiethylaniline*, b.p. 146—148°/14 mm. (from *m*-NEt_2·C_6H_4·OH, Me_2SO_4, and MeOH–KOH), PhCHO, and conc. HCl give 4 : 4′-*tetraethyldiamino*-2 : 2′-*dimethoxytriphenylmethane*, m.p. 114°, which is oxidised by tetrachloro-*p*-benzoquinone in Et_2O to the carbinol, m.p. 115°. The carbinyl chloride resembles brilliant-green and shows no tendency to form the corresponding xanthen. *as*-Phthaloyl chloride, *m*-NMe_2·C_6H_4·OMe [? *m*-NEt_2·C_6H_4·OMe], and $AlCl_3$ give (probably) rhodamine-*B* and not the 4′ : 4″-tetra-alkyldiamino-2 2″-dimethoxydiphenylphthalide. H. B.

Constitution of triarylmethyl compounds. A. Hantzsch and A. Burawoy (Ber., 1933, 66, [*B*], 1435—1441).—In reply to Petrenko-Kritschenko (this vol., 1048), it is shown that colourless, ester-like triarylmethyl compounds and coloured triarylmethyl salts exist. The acid residue is non-ionic in the former, ionic in the latter. Coloured triarylmethyl ions are quinonoid, containing conjugated systems which are responsible for the bands causative of dark colour. All "carbonium" theories according to which the peripheral residues of the triarylmethyl ions possess the same function in each individual ion do not explain the colour or the regularities of the absorption and are therefore to be discarded, particularly since they depend on the improbable assumption that a C atom and not a positive group is the site of the charge. H. W.

Retropinacolin rearrangement. I. W. E. BACHMANN (J. Amer. Chem. Soc., 1933, **55**, 3857—3859).—Dehydration of CPh_3·CHPh·OH [acetate, m.p. 151° (lit. 131°)] with I in AcOH gives CPh_2:CPh_2. *αββδ-Tetra-p-tolylethyl alcohol*, m.p. 161—162°, similarly affords tetra-*p*-tolylethylene, m.p. 142° (lit. 151°), reduced (Na, amyl alcohol) to *s-tetra-p-tolylethane*, m.p. 278—279°, which is also prepared from 4 : 4′-dimethylbenzhydryl bromide and Mg in Et_2O–C_6H_6; *αββδ-tetra-anisylethyl alcohol*, m.p. 148—150°, yields tetra-anisylethylene; *9-phenyl-9-α-hydroxybenzylfluorene*, m.p. 159—160°, furnishes 9 : 10-diphenylphenanthrene (I); 10 : 10-*diphenyl-9-phenanthrol*, m.p. 205—206°, gives (I); 10-*diphenylene-9-phenanthrol*, m.p. 177—178°, affords 9 : 10-diphenylenephenanthrene. The alcohols are prepared by reduction of the corresponding pinacolins with $MgPr^{\beta}I$ in Et_2O–C_6H_6. H. B.

Direct carboxylation of carbon compounds. II. C. R. KINNEY and O. W. WARD (J. Amer. Chem. Soc., 1933, **55**, 3796—3798; cf. A., 1931, 1053).—Carboxylation of various substances occurs when they are heated with CO_2 under pressure in presence of a catalyst (Zn–Cu–Cr oxide on asbestos); the yields of acids (some of which are very impure) are usually 0·1—0·6%. The following changes are effected: PhMe ⟶ *p*-C_6H_4Me·CO_2H; CH_2Ph_2 ⟶ $CHPh_2$·CO_2H; $CHPh_3$ ⟶ CPh_3·CO_2H; CHPh:CH_2 ⟶ CHPh:CH·CO_2H; PhOMe ⟶ *p*-OMe·C_6H_4·CO_2H; PhBr ⟶ *p*-C_6H_4Br·CO_2H; $NPhMe_2$ ⟶ *p*-NMe_2·C_6H_4·CO_2H; $PhNO_2$ *p*-NO_2·C_6H_4·CO_2H; *o*-$C_6H_4(OH)_2$ ⟶ 2 : 3-$(OH)_2C_6H_3$·CO_2H; *p*-$C_6H_4(OH)_2$ ⟶ 2 : 5-$(OH)_2C_6H_3$·CO_2H; *m*-$C_6H_4(OH)_2$ ⟶ 2 : 4-$(OH)_2C_6H_3$·CO_2H (10·6% yield). PhOH gives a trace of an acid. H. B.

Molecular compounds of *p*-nitrophenylacetic acid. A. DANSI (Gazzetta, 1933, **63**, 484—489).—NH_4X, where X = *p*-NO_2·C_6H_4·CH_2·CO_2·, reacts with $CuCl_2$ to form the *Cu* salt, CuX_2. With HgCl, it yields the *compounds* HgX_2,$HgCl_2$ (I), m.p. 149—150°, and HgX_2,$HgCl_2$,$(NH_4X)_2$ (II), m.p. 139—140°. HX and $Hg(OAc)_2$ form HgX_2, decomp. 170—185°, which combines with $HgCl_2$ to form (II); the latter when heated at 190° condenses to the *compound* $C_{14}H_{10}O_4N_2Cl_2Hg_3$, decomp. 215—220°. The *o-isomeride* of (II) has m.p. 163°. E. W. W.

Dehydroperillic acid, an acid from Western red cedar (*Thuja plicata*, Don.). A. B. ANDERSON and E. C. SHERRARD (J. Amer. Chem. Soc., 1933, **55**, 3813—3819).—*Dehydroperillic acid* (I), $C_{10}H_{12}O_2$, m.p. 88° (*Me* ester, b.p. 112—113°/14 mm., m.p. 34·5—35°), is isolated (together with a phenolic compound, $C_{10}H_{12}O_2$, m.p. 82°) in 0·03—0·3% yield by steam distillation of sawdust (heartwood). (I) is reduced (H_2, Pd-black, EtOH) to an *acid* (II), $C_{10}H_{18}O_2$, b.p. 150—152°/16 mm., is oxidised (O_3) to CO_2, CH_2O, MeCHO, HCO_2H, AcOH, $H_2C_2O_4$, and (probably) β*γ*-diketovaleric acid [p-*nitrophenylosazone*, m.p. 294—295° (decomp.); p-*bromophenylosazone*, m.p. 220°], and is isomerised by aq. 3% HCl in AcOH to *p*-$C_6H_4Pr^{\beta}$·CO_2H. (I) is probably 4-iso*propenyl*-$\Delta^{1:4}$-cyclo*hexadiene*-1-*carboxylic acid*. (II) is considered to be a form of hexahydrocuminic acid. H. B.

Local anæsthetics. Amino-alcohol ethers with salicylic and other phenolic acids. E. FOURNEAU and J. MATTI (J. Pharm. Chim., 1933, [viii], **18**, 247—258).—Acetylsalicyl chloride with β-hydroxy-β-methyl-*n*-butyldimethylamine (I) in dry C_6H_6 yields the *acetylsalicylate hydrochloride* of (I), m.p. 171° (*salicylate hydrochloride*, m.p. 162°). Similarly were prepared the p- and m-*acetoxybenzoate hydrochlorides* of (I), m.p. 167° and 165°, respectively (p- and m-*hydroxybenzoate hydrochlorides*, m.p. 174° and 187°, respectively); 2-*acetoxy*-3-*methoxybenzoate hydrochloride* of (I), m.p. 174° [from 2-*acetoxy*-3-*methoxybenzoic acid*, m.p. 139° (*chloride*, m.p. 69°)] (2-*hydroxy*-3-*methoxybenzoate hydrochloride*, m.p. 158°); 4-*acetoxy*-3-*methoxybenzoate hydrochloride* of (I), m.p. 161° (4-*hydroxy*-3-*methoxybenzoate hydrochloride*, m.p. 178°); 2-*acetoxy*-4-*methylbenzoate hydrochloride* of (I), m.p. 150°; 2-*acetoxy*-3-*methylbenzoate hydrochloride* of (I), m.p. 161°; *acetylsalicylate hydrochloride* of 2-*dimethylaminomethyl*cyclo*hexanol*, m.p. 108°; 2-*hydroxy*-3-*methoxybenzoate hydrochloride* of *diethylaminoethyl alcohol* (II), m.p. 159°; 4-*acetoxy*-3-*methoxybenzoate hydrochloride* of (II), m.p. 140·5° (4-*hydroxy*-3-*methoxybenzoate hydrochloride*, m.p. 160°); 2-*acetoxy*-3-*methylbenzoate hydrochloride* of (II), m.p. 120°. F. O. H.

Course of hydrogenations with amalgam; β-phenylsorbic acid. R. KUHN and M. HOFFER (Ber., 1933, **66**, [*B*], 1263—1273).—Crotonylbenzene, CH_2Br·CO_2Me, and Zn in boiling C_6H_6 afford Me β-hydroxy-β-phenyl-Δ^{γ}-hexenoate (I), m.p. 58°, in 70—75% yield, converted by Br in CS_2 through the unstable dibromide into the compound $C_{13}H_{15}O_3Br$, m.p. 179—180° (corr., Berl). (I) is hydrolysed by KOH–MeOH–H_2O to β-*hydroxy*-β-*phenyl*-Δ^{γ}-*hexenoic acid* (II), m.p. 121—122° (corr., Berl), which, with Br in $CHCl_3$, affords the *bromolactone* (III), $C_{12}H_{11}O_2Br$, m.p. 110—110·3° (corr., Berl). Cautious thermal decomp. of (II) leads to β-*phenyl*-$\Delta^{\alpha\gamma}$-*pentadiene*, b.p. 85—86°/15 mm., which readily polymerises when exposed to air. Treatment of (I) with $POCl_3$ gives *Me* β-*phenyl*-$\Delta^{\alpha\gamma}$-*hexadienoate* (IV), b.p. 152—158°/12 mm., hydrolysed by KOH–MeOH to β-*phenyl*-$\Delta^{\alpha\gamma}$-*hexadienoic* (β-*phenylsorbic*) *acid* (V), m.p. 133—134° (corr., Berl). Treatment of (II) or, less advantageously, of (I) with HCl–AcOH yields β-*phenylsorbolactone*, CH<CPh·CH_2 / CHM O>CO, m.p. 100°, converted by Br in CS_2 into (III) and by HCl–MeOH into (IV) and β-*phenylsorbolactone*, CH_2<CPh=CH / CHMe·O>CO, m.p. 63°. Reduction of (V) suspended in H_2O with Na–Hg gives a mixture of β-phenyl-Δ^{γ}- and β-phenyl-Δ^{β}-hexenoic acids, the oxidation of which with $KMnO_4$ shows αβ- and αδ-addition to have occurred to the extent of 30% and 70%, respectively. The acids are so stable that a secondary isomerisation to the Δ^{α}-acid is highly improbable. The course of the change does not appear to be influenced appreciably by the purity of the amalgam. It is considered that the primary action is addition of Na or H at a C atom vicinal to a negative group giving a radical-like monohydro-compound in which the double linkings are particularly mobile. The ratio of αβ- to αδ-addition in a diene depends on the relative stability of the tautomeric monohydro-forms. H. W.

Amino-acids. IV. Dihydroxyphenylalanine and related amino-acids. V. DEULOFEU and G.

MENDIVELZUA (Z. physiol. Chem., 1933, **219**, 233—239; cf. A., 1932, 1144).—Protocatechualdehyde (I) and hippuric acid (II) when heated with Ac_2O and NaOAc give an azlactone (*Ac*$_2$ derivative, m.p. 137—138°), which on hydrolysis with 3% NaOH affords *benzdihydroxyphenylamidoacrylic acid*, m.p. 224—225° [*Et* ester (III), m.p. 168°]. Reduction of (III) with HI gives 3 : 4-dihydroxyphenylalanine (IV). In presence of Ac_2O and NaOAc, (I) also condenses with diketopiperazine (V) to give *bis*-(3 : 4-*diacetoxybenzylidene*)*diketopiperazine*, m.p. 291° (decomp.), which is reduced by HI to (IV). With hydantoin (VI) and thiohydantoin, (I) gives 3 : 4-*diacetoxybenzylidene-hydantoin*, m.p. 237—239°, and -2-*thiohydantoin*, m.p. 224—225°, respectively. Veratraldehyde (VII) and (II) afford the *azlactone*, m.p. 152°, which gives on hydrolysis *benz*-3 : 4-*dimethoxyphenylamidoacrylic acid* (VIII), m.p. 211—212°. Reduction of (VIII) with Na–Hg yields N-*benzoyldimethoxyphenylalanine*, m.p. 173—174°, which is hydrolysed by aq. $Ba(OH)_2$ at 100° to 3 : 4-dimethoxyphenylalanine (IX), m.p. 252—253° (*phenylcarbimido*-derivative, m.p. 171°). With (VI), (VII) gives 3 : 4-*dimethoxybenzylidenehydantoin* (X), m.p. 204—206°. Reduction of (X) with Na–Hg affords 3 : 4-*dimethoxybenzylhydantoin*, m.p. 164°, which on hydrolysis with $Ba(OH)_2$ yields (IX). (V) with (VII) gives *bis*-(3 : 4-*dimethoxybenzylidene*)*diketopiperazine*, m.p. 300—302° (decomp.), reduced by Zn dust and AcOH to the corresponding *benzyl* compound, m.p. 215—216°, which on hydrolysis affords (IX). 3-*Methoxy*-4-*acetoxybenzylidene-hydantoin*, m.p. 262—263°, and -2-*thiohydantoin*, m.p. 246—247°, are described. J. H. B.

Resolution of *cis*- and *trans-dl*-3-carboxy-1 : 1-dimethyl*cyclo*propane-2-propionic acids and *trans-dl*-caronic acid. J. OWEN and J. L. SIMONSEN (J.C.S., 1933, 1223—1225).—*cis-dl*-3-Carboxy-1 : 1-dimethyl*cyclo*propane-2-propionic acid (A., 1932, 739) is resolved by morphine (half-mol. method) into the d-*acid* (I), m.p. 104—105° (softens at 102°), $[\alpha]_{5461}$ +39° in $CHCl_3$ [*dimorphine* salt (+H_2O), m.p. 177—178° (sinters at 168°)], which is identical with the acid obtained (J.C.S., 1922, **121**, 2297) by oxidation of *d*-Δ^4-carene. The acid recovered from the more sol. dimorphine salt is treated with strychnine (= *l*-acid present); the *distrychnine* salt (+$4H_2O$), m.p. 189—190° (sinters at 185°), of the cis-l-*acid*, m.p. 104—105° (softens at 102°), $[\alpha]_{5461}$ −37·8° in $CHCl_3$, is thus obtained. *trans-dl*-3-Carboxy-1 : 1-dimethyl-*cyclo*propane-2-propionic acid (*loc. cit.*) is resolved by nor-*d*- and -*l*-*ψ*-ephedrines into the l-, m.p. 112°, $[\alpha]_{5461}$ −37·1° in EtOAc [Na salt, $[\alpha]_{5461}$ +11·6° in H_2O; *dinor*-d-*ψ*-*ephedrine* salt (+H_2O), m.p. 192—193° (sinters at 187°)], and d-*acids*, m.p. 112°, $[\alpha]_{5461}$ +37·4° in EtOAc (*dinor*-l-*ψ*-*ephedrine* salt, m.p. 192—193°). *trans-dl*-Caronic acid is similarly resolved into the d-, m.p. 211—212°, $[\alpha]_{5461}$ +34·8° in EtOH [*nor*-l-*ψ*-*ephedrine* salt, m.p. 199—200° (sinters at 195°)], and l-*acid* (II), m.p. 211—212°, $[\alpha]_{5461}$ −34·5° in EtOH [*nor*-d-*ψ*-*ephedrine* salt, m.p. 199—200° (sinters at 195°)]. (II) is identical with the acid obtained (A., 1929, 449, 819) by oxidation of *d*-Δ^3- and -Δ^4-carenes, and chrysanthemum-mono- and -di-carboxylic acids (Staudinger and Ruzicka, A., 1924, i, 510). The 1 : 1-dimethyl-2-*γ*-ketobutyl*cyclo*propane-3-carboxylic acids (*loc. cit.*) are too weakly acidic to form satisfactory salts. H. B.

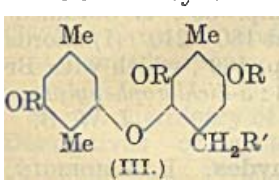
Synthesis of homocaronic acid. J. OWEN and J. L. SIMONSEN (J.C.S., 1933, 1225—1227).—Et Δ^{β}-*iso*hexenoate, $CHN_2{\cdot}CO_2Et$ (I), and Cu-bronze at 45—50° give a mixture of the Et esters of *cyclo*butane-1 : 2 : 3 : 4-tetracarboxylic acid and cis- (II), m.p. 135—136° (sinters at 125°), and trans-, m.p. 190—191°, -*homocaronic acid* (3-*carboxy*-1 : 1-*dimethyl*cyclo*propane*-2-*acetic acid*). (II) is identical with the acid $C_8H_{12}O_4$, m.p. 136—137° (J.C.S., 1923, **123**, 556), obtained by oxidation of *d*-Δ^3-carene. (II) is attacked by alkaline $KMnO_4$ and is converted by conc. HCl at 100° (sealed tube) into a *lactone*, $C_8H_{12}O_4$, m.p. 101—102°, which could not be reduced [Na–Hg; HI (*d* 1·7) and red P] and is not oxidised by HNO_3 (*d* 1·22). (I) could not be condensed with Et Δ^{α}-*iso*hexenoate. H. B.

Action of sulphuric acid on derivatives of *cyclo*propane. C. F. H. ALLEN and R. BOYER (Canad. J. Res., 1933, **9**, 159—168).—The residue in the prep. of Ph *γ*-chloropropyl ketone (I) contained PrCl, Bu$^{\alpha}$Cl, PhBr, Ph_2, a *substance*, m.p. 177°, but no benzoyl*cyclo*propane (II). (II) is obtained from (I) with KCN (yield 93%) or CuCN (yield 60%) in MeOH. (II) with H_2SO_4 in AcOH gives *Ph γ-acetoxypropyl ketone*, b.p. 195—200°/40 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 165°), converted by NHPh·NH_2 into 1 : 2-diphenyldihydropyridazine. Me 2-benzoyl-3-phenyl*cyclo*propane-1 : 1-dicarboxylate (III) with H_2SO_4 in AcOH gives *γ*-hydroxy-β-benzoyl-*γ*-phenylpropane-αα-dicarboxylic acid (IV), m.p. 118°, which decomposes to give PhCHO and (benzoylmethyl)-malonic acid, m.p. 164—165° [also obtained from (III) with conc. H_2SO_4 in 80% yield]. The latter yielded β-benzoylpropionic acid at 180°. The yield of (IV) was not sufficient to exclude 2 : 3- as well as 1 : 3-ring scission. 1-Nitro-2-*p*-chlorobenzoyl-3-phenyl-*cyclo*propane with the same reagent gives 2-phenyl-5-*p*-chlorophenylfuran (which does not react with maleic anhydride), indicating that the ring has been opened at the 2 : 3-linking. 1-Nitro-2-benzoyl-1-phenyl*cyclo*propane is converted into the isomeride, m.p. 131°. With more conc. solutions N oxides are evolved, the products being indefinite. Both forms of 2 : 3-dibenzoyl-1-phenyl*cyclo*propane are either unattacked or give a bimol. *substance*, m.p. 205°. Me 2-benzoyl-1 : 3-diphenyl*cyclo*propane-1-carboxylate is unattacked by conc. H_2SO_4, whilst *cyclo*propyldiphenylcarbinol yields indefinite products. Et 1-cyano-*cyclo*propane-1-carboxylate with conc. H_2SO_4 gives the corresponding *Et amide*, m.p. 126°, hydrolysed to the *H amide*, m.p. 190° (and a little of a *substance*, m.p. 127°), and to *cyclo*propane-1 : 1-dicarboxylic acid. Three forms of 1-cyano-2-benzoyl-1 : 3-diphenyl*cyclo*propane (V) similarly all give the same *amide* (VI), m.p. 179°, and a little of an *isomeride* (VII), m.p. 198°. (VI) gives (VII) with Ac_2O, whilst (VII) gives (VI) with MeOH–HCl. (VI) with PCl_5 in xylene gives (V). It is concluded that H_2SO_4 opens the *cyclo*propane ring in a similar manner to HBr. An explanation is suggested for the anomalous behaviour of 1-phenyl-2-hydroxyphenylmethyl*cyclo*-

propane-1-carboxylic acid with H_2SO_4 in AcOH (A., 1924, i, 1205). A. A. L.

Lichen substances. XXIX. Salazic acid. III. Y. ASAHINA and J. ASANO. **XXX. Cuprarie acid.** Y. ASAHINA and M. YANAGITA. **XXXI. Components of certain *Usnea* species, particularly with respect to compounds of the salazic acid group.** Y. ASAHINA and T. TUKAMOTO (Ber., 1933, **66**, [*B*], 1215—1217, 1217—1220, 1255—1263; cf. this vol., 823).—XXIX. It is proposed to designate the first (I) and second (II) reduction products of salazic acid ($C_{18}H_{14}O_8$ and $C_{18}H_{14}O_7$, respectively) hyposalazic acid and hyposalazolide. The Me_3 derivative of (I) is therefore Me hyposalazate Me_2 ether, whilst the Me_2 derivative, m.p. 283°, of (II) is hyposalazolide Me_2 ether. The first and second reduction products of stictic acid are hyposalazic acid Me ether and hyposalazolide Me ether, respectively. The name hypoprotocetraric acid is applied to the reduction product $C_{18}H_{16}O_7$ (Me_3 derivative, m.p. 170°) of cetraric acid, also obtained from protocetraric acid.

β-Orcinol Me_2 ether is converted by Br in AcOH at 0° into the Br_1-derivative, b.p. 165°/25 mm., transformed by the K derivative of β-orcinol Me_1 ether, Cu powder, and $Cu(OAc)_2$ in H_2 into the compound (III) (R=Me; R′=H), m.p. 95°, identical with deoxyhyposalazinol Me_3 ether. Hyposalazinol is therefore (III) (R=R′=H) and its conversion by molten KOH into β-orcinol and 3 : 5-dihydroxy-*p*-toluic acid is due to reductive fission, not to hydrolysis.



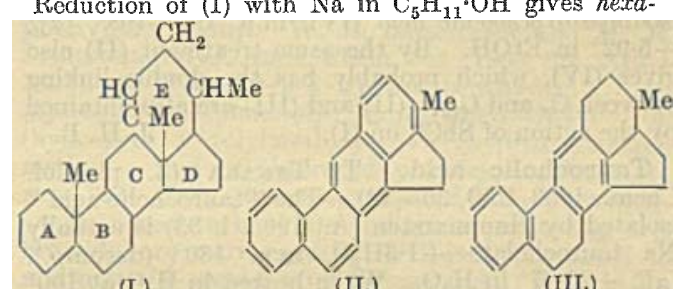
(III.)

XXX. Extraction of Japanese *Parmelia caperata*, Ach., with $COMe_2$, after removal of matter sol. in Et_2O, leads to capraric acid (IV), $C_{18}H_{14}O_9$, decomp. about 250° after becoming discoloured at 220°, identical with the acid obtained by Hesse (A., 1897, i, 631; 1898, i, 680; 1916, i, 264). The application of the name " capraric acid " by Koller *et al.* (A., 1930, 1590) to the *Ac* derivative of (IV) is deprecated. Catalytic hydrogenation of (IV) (Pd–C) yields hypoprotocetraric acid, m.p. 240—243° (decomp.) after softening at 220° (Me_3 ether, m.p. 170°). Protracted treatment of (IV) with boiling EtOH affords cetraric acid, thus further establishing the identity of (IV) with protocetraric acid. (IV) is slowly transformed by boiling AcOH into its Ac_1 derivative, decomp. about 250° after softening at about 220°.

XXXI. The thalli are extracted with boiling Et_2O, the extract is evaporated to dryness, and the residue is treated with boiling C_6H_6, when it generally yields a sol. (*A*) and an insol. portion (*B*). The thalli are next extracted with hot $COMe_2$ and the extract is conc.; if salazic acid (V) is present the matter which separates is thoroughly extracted with Et_2O, leaving an insol. or sparingly sol. product (*C*). (*A*) is usually a mixture of usnic acid (VI) and atranorin (VII), separated into its components by treatment with EtOH–NaOAc, in which (VI) dissolves, whereas (VII) is insol. (*B*) affords protocetraric (? ramulic) acid (VIII), $C_{18}H_{14}O_9$, decomp. about 240° after darkening at about 210° (also $+1H_2O$); the corresponding *anil*, $C_{18}H_{14}O_8$:NPh has m.p. 225° (decomp.). Protracted ebullition with EtOH transforms (VIII) into cetraric acid, whereas MeOH affords protocetraric acid Me ether (probably identical with Hesse's methylprotocetraric acid). Hydrogenation of (VIII) gives hypoprotocetraric acid, $C_{18}H_{16}O_7$, identical with that obtained from cetraric acid. (*C*) from thalli free from (V) yields a neutral product, m.p. about 211°, closely related to or probably identical with Hesse's barbatin (IX). (*C*) from thalli which are coloured red or rust-red with alkali consists of (V) or its *Me_1 ether* (X), decomp. 210—220°. The formation of hypoprotocetraric in addition to hyposalazic acid by reduction of (V) is confirmed.

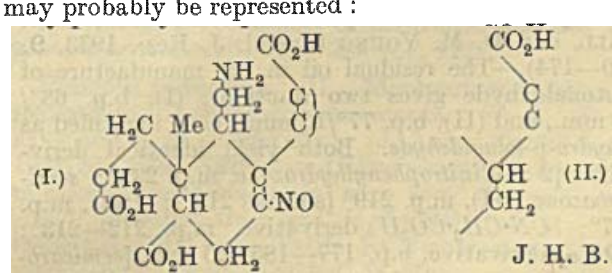
The following substances are isolated from individual lichens: (V), (VI), (VII), and (VIII) from *Usnea montis*, Fuji, *Motyka in litt.*; (V), (VI), (VIII), and barbatic acid (XI) from *U. florida*, Hoffm., *v. perplexans*, Wain, from Formosa; (VI), (VIII), and (X) from an *Usnea* from Java; (VI), (IX), and (XI) from *U. longissima*, Ach., from Japan; (VI), (XI), and (IX) from *U. longissima* from Europe; (VI), (XI), (VII), and (IX) from an *Usnea* sp. from Japan; (VI) and evernic acid from an *Usnea* sp. from Sakhalin. H. W.

Constitution of bile acids. LII. Point of attachment of the side-chain. H. WIELAND and E. DANE (Z. physiol. Chem., 1933, **219**, 240—244; cf. this vol., 1049).—Dehydrogenation of dehydronorcholene (I) with Se (3 hr. at 150—160° and 25 hr. at 320°) gives *methylcholanthrene* (II), $C_{21}H_{16}$, m.p. 174°. Reduction of (I) with Na in C_5H_{11}·OH gives *hexahydromethylcholanthrene* (III), $C_{21}H_{22}$, m.p. 157°. The unsaturated pentacyclic hydrocarbon $C_{22}H_{34}$ could not be obtained by thermal decomp. of 12-ketonorcholanic acid, as is to be expected from the *trans*-linking of rings C and D. The attachment of the side-chain at C_{17} is thus confirmed. J. H. B.



(I.) (II.) (III.)

Bile acids. XL. M. SCHENCK (Z. physiol. Chem., 1933, **220**, 61—68; cf. this vol., 713).—Treatment of the gel (I), $C_{24}H_{36}N_2O_9$ with NaOH affords N_2 in nearly quant. yield. Van Slyke analysis of deoxybilianic acid aminocarboxylic acid (II) gives N_2 considerably in excess of theory in 24 hr. (I) and (II) may probably be represented:



J. H. B.

Conversion of cholesterol into 6-keto*allo*-cholanic acid. O. STANGE (Z. physiol. Chem., 1933, **220**, 34—38).—Treatment of 6-hydroxycholestane with PCl_5 in $CHCl_3$ gave 6-*chlorocholestane* (I), m.p. 147°, $[\alpha]_D^{18}$ +45·1° in $CHCl_3$. Oxidation of (I) with CrO_3 in AcOH yielded 6-chloro*allo*cholanic acid, which, on hydrolysis with KOH at 160—170°, afforded 6-*hydroxy*a*llocholanic acid* (II), m.p. 240° (*Me* ester, m.p. 101°). The 6-keto*allo*cholanic acid obtained from (II) by CrO_3 oxidation was identical with Wieland and Dane's product from hyodeoxycholic acid (cf. this vol., 64), although the OH-derivatives differed and are therefore epimeric. This affords a simple proof of the identity of ring II of cholesterol with ring III of the bile acids. J. H. B.

Conversion of a bile acid into a hydrocarbon derived from 1 : 2-benzanthracene. J. W. COOK and G. A. D. HASLEWOOD (Chem. and Ind., 1933, 758—759).—Dehydrogenation (Se) of dehydronorcholene gives "methylcholanthrene" (I), m.p. 171° (cf. Wieland and Dane, this vol., 1161), and a product, m.p. 132—134°, not oxidised to a quinone. (I) is oxidised ($Na_2Cr_2O_7$–AcOH) to an anthraquinonyl acid, m.p. about 270°, which at 400° in CO_2 gives a quinone, m.p. 229°, insol. in alkali. The structure assigned by Wieland to (I) cannot be correct. F. R. S.

Intermediate products in the Hammarsten reaction of cholic acid. K. YAMASAKI (Z. physiol. Chem., 1933, **220**, 42—49).—Treatment of cholic acid (I) in AcOH with conc. HCl in absence of air gives *apo*cholic acid (II), dihydroxycholenic acid (III), and iso*dihydroxycholenic acid* (IV), m.p. 197—198°, $[\alpha]^{20}$ +5·92° in EtOH. By the same treatment (II) also gives (IV), which probably has the double linking between C_8 and C_{14}. (II) and (III) are also obtained by the action of $SbCl_3$ on (I). J. H. B.

Taurocholic acid. T. TANAKA (Z. physiol. Chem., 1933, **220**, 39—42).—The "taurocholic acid" isolated by Hammarsten (A., 1905, i, 33) is actually Na taurocholate +1·5H_2O, m.p. 180° (decomp.), $[\alpha]_D^{20}$ +23·87° in H_2O. When heated in H_2O at 100° it gives an *isomeride* (+2H_2O), m.p. 230—231° (decomp.), $[\alpha]_D^{20}$ +24·21° in H_2O. J. H. B.

Nutria-bile acid. P. BRIGL and O. BENEDICT (Z. physiol. Chem., 1933, **220**, 106—112).—A stone" from the stomach of the nutria (*Myocaster coypus*, Mol.) contained *nutria-glycocholic acid* (I), m.p. 226—228° (decomp.), $[\alpha]_D$ +47·8° in MeOH. Hydrolysis with *N*-KOH for 30 hr. gives glycine and *nutria-cholic acid* (II), $C_{24}H_{40}O_5$, m.p. 198°, which gives no Mylius or Hammarsten reactions. (II) loses 0·5 mol. of H_2O at 100° in vac. and 1·5 mols. at 134°. (I) was also obtained from nutria-bile. J. H. B.

Dihydro-*p*-tolualdehyde. C. F. H. ALLEN, W. L. BALL, and D. M. YOUNG (Canad. J. Res., 1933, **9**, 169—174).—The residual oil in the manufacture of crotonaldehyde gives two fractions, (I), b.p. 68°/10 mm., and (II), b.p. 77°/10 mm., both identified as *dihydro*-p-*tolualdehyde*. Both yield identical derivatives {2 : 4-*dinitrophenylhydrazone*, m.p. 239°; *semicarbazone* (III), m.p. 219° (shrinks 215°); *azine*, m.p. 157°; *CN·CH₂·CO₂H* derivative, m.p. 212—213°; *COMe₂* derivative, b.p. 177—185°/25 mm. [*semicarbazone*, m.p. 206—210° (decomp., shrinks 196°)]}. Only (II) is regenerated from (III) or the $NaHSO_3$ compounds. (I) is possibly a mixture of (II) with other substances. Both give *p*-$C_6H_4Me·CO_2H$ (IV) by autoxidation (prevented by quinol) with HNO_3, and with O_3, whilst $KMnO_4$ in $COMe_2$ gives terephthalic acid and a little (IV). The mechanism of formation of the aldehyde is discussed and the $\Delta^{1:4}$-constitution is suggested. A. A. L.

Influences of substitution on velocity of hydrolysis of benzylidene chloride.—See this vol., 1124.

3 : 5-Dichlorobenzaldehyde. F. ASINGER and G. LOCK (Monatsh., 1933, **62**, 344—348).—3 : 5-*Dichlorobenzaldehyde* (I), m.p. 65°, b.p. 235—240°/748 mm. (*oxime*, m.p. 112°; *phenylhydrazone*, m.p. 106·5°; $NaHSO_3$ additive *compound*), is prepared by side-chain chlorination of 3 : 5-dichlorotoluene (from *o*-$C_6H_4Me·NHAc$) and hydrolysis of the product with 8% oleum at room temp. With PCl- (I) gives 3 : 5-*dichlorobenzylidene chloride*, m.p. 36·5°, and with 50% KOH at 100° it gives 3 : 5-dichlorobenzoic acid and 3 : 5-*dichlorobenzyl alcohol*, m.p. 82°, from which 3 : 5-*dichlorobenzyl chloride*, m.p. 36°, is obtained. With NaOAc and Ac_2O in N_2 at 180—210°, (I) affords 3 : 5-*dichlorocinnamic acid*, m.p. 186°, which with Br in $CHCl_3$ gives *αβ-dibromo*-β-3 : 5-*dichlorophenylpropionic acid*, m.p. 209° (corr.). J. W. B.

Action of metals on aldehydes. P. SCHORIGIN, V. ISSAGULIANZ, and A. GUSSEVA (Ber., 1933, **66**, [*B*], 1431—1435).—Treatment of PhCHO (I) in boiling PhMe with activated Mg leads to benzoin (II) in 20% yield when (I) : Mg = 1 : 0·5 and $CH_2Ph·OBz$ (III) in 77% yield when (I) : Mg = 1 : 0·05. Under the experimental conditions (II) does not arise from (III). Anisaldehyde yields anisil presumably from primarily formed anisoin, whereas piperonal does not react. Al–Hg and (I) yield (II) in about 80% yield, whereas Zn, Al, and Fe are inactive and Cu yields unstable, green crystals. Aliphatic aldehydes with Mg (0·5—0·05 atom) or Al–Hg react: $CH_2R·CHO + CH_2R·CHO \longrightarrow CH_2R·CH{:}CR·CHO + H_2O$. *iso*Valeraldehyde yields γ-methyl-α-*iso*propyl-Δ$^{\alpha}$-pentenal, whilst *n*-octaldehyde affords α-n-*hexyl*-Δ$^{\alpha}$-*decenal*, b.p. 148—149°/5 mm. H. W.

Basic properties of hydrazones. VII. G. OTTOLINO (Gazzetta, 1933, **63**, 513—516).—One of the products from PhCHO, HCl, and CHPh:N·NHPh (cf. A., 1932, 51, 609) is *αα′-diphenyl-pp′-dihydrazinotriphenylmethane*, $CHPh(C_6H_4·NPh·NH_2)_2$ (I), m.p. 120°. When treated with Ac_2O, HNO_2, and *p*-$NO_2·C_6H_4·CHO$, (I) gives respectively benzaldehydediphenylhydrazone (II), *p*-nitrosodiphenylamine, and *p*-nitrobenzaldehydediphenylhydrazone. The action of PhCHO on (II) gives the *dibenzylidene* derivative of (I), m.p. 226°, or, under different conditions and in presence of a trace of HNO_3, a *compound*, m.p. 165°, probably the corresponding quinonoid quaternary *chloride*, $CHPh{:}N·NPhCl{:}C_6H_4{:}CPh·C_6H_4·NPh·N{:}CHPh$. CHPh:N·NPhMe, HCl, and PhCHO form a compound, m.p. 155° (cf. A., 1922, i, 475), now formulated $CHPh{:}N·NMe·C_6H_4·CHPh·C_6H_4·NMe·NH_2$, converted

by p-NO_2·C_6H_4·CHO in AcOH into pp′-*bis*-(α-*methyl*-β-p″-*nitrobenzylidenehydrazino*)*triphenylmethane*, m.p. 162°, with an *isomeride*, m.p. 138°. E. W. W.

Tetraconiferylaldehydesulphonic acid (tetraligninsulphonic acid). P. Klason (Svensk Kem. Tidskr., 1933, **45**, 221—226).—A review. R. P. B.

***cyclo*Pentanone and *cyclo*hexanone.** D. Vorlander (Trans. Faraday Soc., 1933, **29**, 910—912).—Mechanical double refraction measurements of bisarylidene*cyclo*-pentanones and -hexanones indicates a relation between mol. stability of the direction of movement and liquid-cryst. properties (cf. this vol., 10). E. S. H.

Supposed enolising power of organic magnesium compounds. E. P. Kohler and D. Thompson (J. Amer. Chem. Soc., 1933, **55**, 3822—3823).—Contrary to Grignard and Blanchon (A., 1931, 465), *cyclo*hexenyl acetate (I) could not be obtained from $MgPr^{\beta}Br$ (II) and *cyclo*hexanone (III), and hydrolysis of (I) always gave (III). Decomp. of the product from (II) and (III) with aq. NH_4Cl gives *cyclo*hexanol (68%) and *cyclo*hexylidene*cyclo*hexanone (26%). Grignard and Blanchon appear to have mistaken reduction for enolisation. H. B.

Stereochemistry of dicyclic ring systems. IX. Derivatives of *cyclo*pentano*cyclo*heptane. W. Hückel and L. Schnitzspahn (Annalen, 1933, **505**, 274—282).—The unsaturated ketone, $C_{10}H_{14}O$, b.p. 123°/12 mm., m.p. < −18° [*semicarbazone*, m.p. 195—200°; *oxime*, m.p. 134° (*Bz* derivative, m.p. 118°)], from *cyclo*decanedione and dil. aq. NaOH (cf. A., 1930, 76; the "α- and β-forms," m.p. 37° and 52°, appear to be impurities), is shown to be homogeneous and to have the structure of a *cyclo*penteno-*cyclo*heptanone, $CH_2<\begin{matrix}CH_2\cdot C(=CH\cdot CH_2)\cdot CO\cdot CH_2\\CH_2\cdot C\cdot CH_2\cdot CH_2\end{matrix}>CH_2$ or $CH_2<\begin{matrix}CH{=}C{-}CO{-}CH_2\\CH_2\cdot CH\cdot CH_2\cdot CH_2\end{matrix}>CH_2$. Hydrogenation (Pd–C) gives a mixture of cis- and trans-cyclo*pentano*cyclo*heptanone*, b.p. 235°/760 mm. [cis-*oxime*, m.p. 119°; trans-*oxime*, m.p. 140° (*Bz* derivative, m.p. 98—99°)], oxidised by aq. $KMnO_4$ to δ-ketosebacic acid. The configurations of the oximes are determined by reduction (Na in EtOH) to two cis- (*Bz* derivatives, m.p. 194° and 154°; *Ac* derivatives, m.p. 161° and 115°, respectively) and one trans-cyclo*pentano*cyclo*heptylamine*, b.p. 97°/10 mm. (*Bz*, m.p. 173—174°, and *Ac*, m.p. 114—115°, derivatives). The *trans*-amine gives the *alcohol* (*H phthalate*, m.p. 132—133°) with HNO_2 and a *trimethylammonium iodide*, m.p. 192° (decomp.), converted by Ag_2SO_4 and $Ba(OH)_2$ into cyclo*pentano*cyclo*heptene*, b.p. 63·5°/8 mm., oxidation of which with O_3 or $KMnO_4$, and distillation of the products with Ac_2O yields (? trans-)*hexahydroindan-4-one* (*semicarbazone*, m.p. 183°), synthesised for comparison by oxidation (CrO_3–AcOH) of 4-hydroxyhexahydroindane. H. A. P.

Reactions of *aci*-nitro-salts and silver fulminate. H. Wieland and A. Höchtlen (Annalen, 1933, **505**, 237—247).—Interaction of CPh_3Cl with $(CHPh{:}NO_2)_2Hg$ gives α-*nitro*-αβββ-*tetraphenylethane*, m.p. 169—170° (decomp.) (aci-*K* salt). BzBr and $CN\cdot CPh{:}NO_2Ag$ (I) give *Ph* ω-*nitro*-ω-*cyanobenzyl ketone*, m.p. 118° (decomp.). With $CHPh_2Br$ (I) gives α-*nitro*-αββ-*triphenylpropionitrile*, m.p. 146—147° (decomp.), which with hot 10% KOH in MeOH gives *triphenylacrylonitrile*, m.p. 166—167°, and KNO_2, and with $SnCl_2$–HCl in hot AcOH gives the α-NH_2 (?) compound, m.p. 177°. In presence of air CPh_3Cl and (I) give triphenylmethyl peroxide, and in its absence $CPh_3\cdot NCO$, CO_2, N_2, *phenyltriphenylmethyldiazomethane*, $CPh(N_2)\cdot CPh_3$, m.p. 145° (decomp.) (identified by thermal fission to tolane, CPh_3, and N_2), and a *compound*, $C_{14}H_{11}ON_3$, m.p. 156—158° (decomp.), isomerised by KOH in EtOH to an *acid*, m.p. 182°. The $\cdot CPh_3$ group could not be introduced into $CHBr{:}NO_2Ag$ on account of its ready decomp. into AgBr, HCO_2H, and N_2. BzBr and C:NOAg (II) give *dibenzoylcarbamide*, m.p. 208—209°, presumably through intermediate formation of Bz·NCO. With $CHPh_2Br$ (II) gives *benzhydryl cyanate*, b.p. 160—164°/11 mm. (dibenzhydrylcarbamide, m.p. 269—270°; *Et benzhydrylcarbamate*, m.p. 129°), as also does AgNCO. CPhCl:NOH reacts only very slowly with (II) in C_6H_6, and in C_5H_5N forms *benzhydroxamylpyridinium chloride*, m.p. 117°; in presence of a little $NPhMe_2$, however, a *compound*, $C_8H_6O_2N_2$ (? phenylfuroxan), m.p. 96—97°, is formed. H. A. P.

Pinacol–pinacolin rearrangement. IV. Rearrangement of pinacols containing the diphenylene group. W. E. Bachmann and H. R. Sternberger (J. Amer. Chem. Soc., 1933, **55**, 3819—3821).—9-Hydroxy-9-α-hydroxybenzhydryl-, -9-(*hydroxydi*-m-*tolylmethyl*)-, m.p. 143·5—144·5°, -9-(hydroxydi-*p*-tolylmethyl)-, -9-(hydroxydianisylmethyl)-, and -9-(*hydroxydi*-p-*ethoxyphenylmethyl*)-, m.p. 147—150°, *-fluorenes*, prepared from Me 9-hydroxyfluorene-9-carboxylate and the requisite Mg aryl bromide, are rearranged by AcCl in C_6H_6–AcOH to mixtures of 9-aroyl-9-arylfluorenes and 9 : 9-diaryl-10-phenanthrones, and not single compounds (cf. Meerwein, A., 1913, i, 485; Bergmann and Schuchardt, A., 1931, 1059). 9 : 9-*Di*-m-*tolyl*-, m.p. 198—198·5°, and 9 : 9-*di*-p-*ethoxyphenyl*-, m.p. 135—135·5°, -10-*phenanthrones* are new. 2-*Di*-p-*methyl*-, m.p. 193—194°, and 2-*di*-p-*methoxy*-, m.p. 136—137°, *-benzhydryldiphenyl-2′-carboxylic acids* are prepared from the corresponding phenanthrones and EtOH–KOH. The relative migration aptitudes of the groups are Ph 1, *m*-tolyl 0·33, diphenylene 0·31, *p*-tolyl 0·046, *p*-OEt·C_6H_4· 0·012, anisyl 0·006; the order is the reverse of that for *s*-pinacols (cf. A., 1932, 515). H. B.

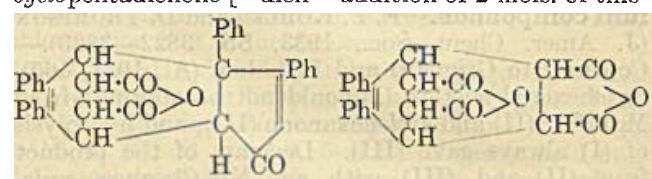
Electrolytic reduction of aromatic ketones in glacial acetic acid.—See this vol., 1127.

Benzoin reduction. II. Mechanism of ketone formation. *m*-Chlorobenzanisoin. S. S. Jenkins and E. M. Richardson (J. Amer. Chem. Soc., 1933, **55**, 3874—3879).—m-*Chlorobenzanisoin* (*anisoyl-m-chlorophenylcarbinol*) (I), m.p. 86·5° (all m.p. are corr.), prepared from *m*-$C_6H_4Cl\cdot CHO$ and *p*-$OMe\cdot C_6H_4\cdot CHO$ in aq. EtOH–KCN or from *m*-chloromandelamide and *p*-$OMe\cdot C_6H_4\cdot MgBr$, is oxidised

(Fehling's solution) to 3-*chloro*-4′-*methoxybenzil*, m.p. 88°, and is reduced (4% Na–Hg, EtOH) to α-m-*chlorophenyl*-β-*anisylethylene glycol*, m.p. 101·5—102·5°. Dehydration of this with AcOH–conc. H_2SO_4 gives m-*chlorophenyl* p-*methoxybenzyl ketone*, m.p. 73—74° (anti-*oxime*, m.p. 74—75°, rearranged by PCl_5 in Et_2O to p-*methoxyphenylacet*-m-*chloroanilide*, m.p. 86·5°), also prepared from *p*-methoxyphenylacetamide and *m*-C_6H_4Cl·MgI in Et_2O and H_2, and by reduction of (I) with Sn and conc. HCl in EtOH containing a little $CuSO_4$. *Anisyl* m-*chlorobenzyl ketone*, m.p. 70—71° (anti-*oxime*, m.p. 106·5—107·5°, rearranged to m-*chlorophenylacet*-p-*anisidide*, m.p. 148·5°), is also formed in the reduction (Sn) of (I) and is synthesised from *m*-C_6H_4Cl·CH_2·MgBr (II) and anisamide. These results substantiate the mechanism of reduction of *as*-benzoins previously advanced (A., 1932, 516). (II) and *p*-OMe·C_6H_4·CHO give β-m-*chlorophenyl*-α-*anisylethyl alcohol*, m.p. 42—43°, dehydrated (AcOH–conc. HCl) to 3-*chloro*-4′-*methoxystilbene*, m.p. 96°. *Anis*-m-*chlorobenzylamide* and m-*chlorobenz*-p-*methoxybenzylamide* have m.p. 161° and 92·5°, respectively. H. B.

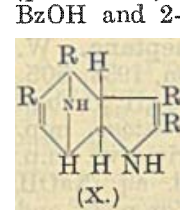
β-Phenyl-β-anthronylpropionic acid. 3-Anthronylindan-1-one. L. Gravel (Natural. Canad., 1933, **57**, 221—255).—β-Phenyl-β-anthronylpropionic acid (cf. Meerwein, A., 1919, i, 25) [*chloride* (I), m.p. 115—116°; *Me*, m.p. 111—112°, and *Et* ester, m.p. 88—89°; *amide*, m.p. 181—182°; *anilide*, m.p. 168—169°; *Ag* salt] is dehydrated by conc. H_2SO_4 at 103—110° to 3-*anthronylindan*-1-*one* (II), m.p. 161—162° [2-*Br*-derivative (III), m.p. 170—171°; *hydrazone* (+1H_2O), m.p. 176°; *phenylhydrazone*, m.p. 224—225° (+1PhMe); *oxime* (+1PhMe), m.p. 181—184°], identified by oxidation (HNO_3, *d* 1·2) to anthraquinone and *o*-$C_6H_4(CO_2H)_2$. (I) with $AlCl_3$ in C_6H_6 or (better) CS_2 gives (II) and in addition an *isomeride*, m.p. 188°, which on account of its conversion into (III) with Br is regarded as the enolic form of (II); in C_6H_6 Ph β-phenyl-β-anthronylethyl ketone, m.p. 115—116° (*loc. cit.*), is also obtained. The following are also described: *Me*$_2$, m.p. 58—59°, b.p. 175°/3 mm., and *Et*$_2$ o-*chlorobenzylidenemalonate*, m.p. 30°, b.p. 182—183°/5 mm.; *Me*$_2$, m.p. 148—149°, and *Et*$_2$ β-o-*chlorophenyl*-β-*anthronyl*isosuccinate, m.p. 119—120°; *Et*$_2$ β-*phenyl*-β-*anthronyl*isosuccinate, m.p. 104—105°; and β-o-*chlorophenyl*-β-*anthronyl*propionic acid, m.p. 159—161°. H. A. R.

Reactions of anhydroacetonebenzil. II. C. F. H. Allen and E. W. Spanagel (J. Amer. Chem. Soc., 1933, **55**, 3773—3780).—Anhydroacetonebenzil (4-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone) (I) and AcOH–conc. H_2SO_4 give 4 : 7-endo*keto*-3 : 5 : 6 : 8-*tetraphenyl*-4 : 7 : 8 : 9-*tetrahydroindenone* (II) [the compound, $C_{34}H_{24}O_2$, of Japp and Burton (J.C.S., 1887, **51**, 426)] (*dioximes*, m.p. 176° and 229°); with Ac_2O–conc. H_2SO_4, (II) and a little of an *acetate*, $C_{19}H_{16}O_3$, m.p. 91° [hydrolysed by oil. aq. NH_3 to (II) and by EtOH–KOH to a *compound*, m.p. 280°], result. Short heating of (II) at 210° gives 3 : 5 : 6 : 8-*tetraphenyl*-8 : 9-*dihydroindenone* (III), m.p. 167° [*oxime*, m.p. 130° (not sharp); *phenylhydrazone*, m.p. 250°, probably identical with (V) (below), since heating in a sealed tube is necessary for its formation], and 2 : 3 : 5 : 6-*tetraphenylhydrindone* (IV), m.p. 176° [*oxime*, m.p. 225°; *phenylhydrazone* (V), m.p. 250° (cf. *loc. cit.*)]; (III) passes into (IV) when heated. (III) and S at 325° give a little PhSH; (IV) is similarly dehydrogenated to 2 : 3 : 5 : 6-*tetraphenylindenone* (VI), m.p. 166° (*oxime*, m.p. 292°; p-*bromophenylhydrazone*, m.p. 226°). (II) heated with maleic anhydride (VII) until evolution of CO ceases gives the *anhydride* (VIII), m.p. 301°, also formed [together with (IV)] from (III) and (VII). (I) and excess of (VII) at 170—230° give CO and the *dianhydride* (IX), shrinks at 334°, becomes liquid at 346°, and decomp. 356° (corresponding *Me*$_4$ ester, m.p. 188°), the formation of which shows that dehydration of (I) affords 3 : 4-diphenyl-*cyclo*pentadienone [" dien "-addition of 2 mols. of this



(VIII.) (IX.)

yields (II)]. (VI) is oxidised (CrO_3–AcOH) to 2-*phenylglyoxyl*-4 : 5-*diphenylbenzophenone*, m.p. 183° (*quinoxaline*, m.p. 184°), cleaved by cold aq. Na_2O_2 to BzOH and 2-*benzoyl*-4 : 5-*diphenylbenzoic acid*, m.p. 250° (*compound*, $C_{26}H_{17}O_2N$, m.p. 225°, formed with NH_2OH), which with a little $CuCO_3$ at 225° gives a poor yield of 3 : 4-*diphenylbenzophenone*, m.p. 133°. Rearrangement of the *oxime*, m.p. 156°, of this with PCl_5 in Et_2O, hydrolysis of the resultant product to the amine, and deamination of this gives *o*-$C_6H_4Ph_2$.



(X.)

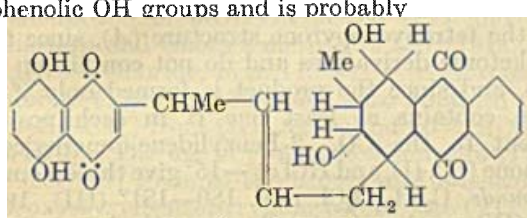
The above work suggests that the dipyrroles should be formulated as (X). H. B.

Action of oxalyl chloride on the ethers of the cresols, carvacrol, and substituted phenols. N. Schapiro (Ber., 1933, **66**, [*B*], 1370—1372).—*o*-C_6H_4Me·OMe, $AlCl_3$, and $(COCl)_2$ in CS_2 yield 4 : 4′-*dimethoxy*-3 : 3′-*dimethylbenzil*, m.p. 177°, converted by *o*-$C_6H_4(NH_2)_2$ in AcOH into the *quinoxaline* $C_{24}H_{22}O_2N_2$, m.p. 139·5—140°, and oxidised by H_2O_2 in AcOH or, preferably, in C_5H_5N–NaOH to 4-methoxy-3-methylbenzoic acid, m.p. 193° after softening at 192°. *p*- and *m*-C_6H_4Me·OMe yield only resins. *o*-C_6H_4Me·OEt affords 4 : 4′-*diethoxy*-3 : 3-*dimethylbenzil*, m.p. 181—182° (quinoxaline, $C_{26}H_{26}O_2N_2$, m.p. 172—173°), oxidised to 4-ethoxy-3-methylbenzoic acid, m.p. 198—199°. Carvacrol Me ether gives an unidentified oil. *o*-C_6H_4Cl·OMe fairly smoothly yields 3 : 3′-*dichloro*-4 : 4′-*dimethoxybenzil*, m.p. 226·5—227·5°, oxidised to 3-chloro-4-methoxybenzoic acid, m.p. 213°. *o*-NO_2·C_6H_4·OMe, under the same reaction conditions, is smoothly hydrolysed to *o*-NO_2·C_6H_4·OH. H. W.

Substituted aminoquinones. M. Covello (Gazzetta, 1933, **63**, 517—524).—A mixture of triaminophenol in EtOH+H_2O and maleic anhydride in C_6H_6 treated in N_2 with $NaCO_3$ solution forms 2 : 4 : 6-*trimaleimidophenol*, m.p. 200°, converted by dil. HCl

into *phenol*-2 : 4 : 6-*tris*-N-*maleiamidic acid*, decomp. 150° (*Ag* salt), and by HNO_3 (*d* 1·48) into 2 : 6-*dimaleimidobenzoquinone*, decomp. 180° (*phenylhydrazone*, decomp. 100°). E. W. W.

Constituents of alkanet root (*Anchusa tinctoria*, Lam.). I. Constitution of alkannin. M. V. Betrabet and G. C. Chakravarti (J. Indian Inst. Sci., 1933, **16A**, 41—51).—Alkannin (I) (decomp. 220°), prepared from the Ac_4 derivative (II), is $C_{30}H_{26}O_8$ [*Ba* and *Pb* derivatives; *tetrabenzoate*, m.p. > 260° (decomp.)]. (I) with Me_2SO_4 gives *dimethoxyalkannin* (*dibenzoate*), whilst $ClCO_2Et$ gives *dicarbethoxyalkannin*, decomp. > 270°, and bromination affords *di-*, *tetra-*, decomp. 260°, and *hexa-bromoalkannin*, according to conditions. *Tetrabromoalkannin tetra-acetate*, decomp. about 280°, is obtained by treating (II) with Br. (I) is not oxidised by H_2O_2, fuming HNO_3 reacts energetically giving $H_2C_2O_4$, $(\cdot CH_2\cdot CO_2H)_2$, and a NO_2-compound, m.p. 287°, whilst oxidation with dil. HNO_3 produces $H_2C_2O_4$, a neutral *compound*, m.p. 320°, and a NO_2-compound, m.p. 297°. Nitration of (II) gives *dinitroalkannin tetra-acetate*, decomp. 260°. 2-Methylanthracene is produced when (I) is distilled with Zn dust. (I) contains two alcoholic and two phenolic OH groups and is probably



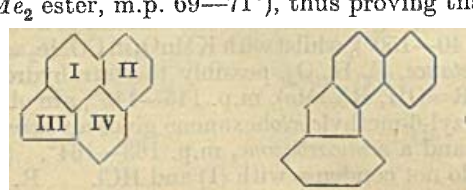
which explains why its absorption spectrum differs so much from that of either naphthazarin or the hydroxyanthraquinones. S. C.

Halogen derivatives of the benzophenone and anthraquinone series.—See B., 1933, 857.

1-Amino-10-anthrones and 1-aminoanthraquinone compounds.—See B., 1933, 857.

Preparation of depsides with the aid of azides. R. O. Pepe (Anal. Asoc. Quím. Argentina, 1933, **21**, 53—60).—An account of work already abstracted (A., 1930, 1039). R. K. C.

Strophanthin. XXVIII. Further degradation of strophanthidin and periplogenin derivatives. W. A. Jacobs and R. C. Elderfield (J. Biol. Chem., 1933, **102**, 237—248; cf. A., 1932, 1138).—The Me_3 ester of the tribasic acid, $C_{21}H_{32}O_6$ (now called dephanthanic acid), from strophanthidin with MgPhBr or MgMeI gives the *hexaphenyl-*, amorphous, or *hexamethyl-tricarbinol*, cryst., respectively, both oxidised by hot CrO_3–AcOH to $COPh_2$ and *dephanthic acid*, $C_{17}H_{26}O_4$, m.p. 243—245° after softening at 200° (*Me*$_2$ ester, m.p. 69—71°), thus proving that the



group in position 14 is CH_2. If the accepted structure for ring III of strophanthidin is correct, this substance must contain the C skeletons (*A*) or (*B*), which, however, are not in agreement with the formation of a dimethylphenanthrene as a primary product of Se-dehydrogenation. Alternative structures are discussed on the assumption of the possibility of migration of the ethylenic linking during dehydration of dihydrostrophanthidin. The unsaturated lactone, $C_{24}H_{30}O_8$, from undephanthontriacid Me_2 ester is hydrogenated (PtO_2) in AcOH to a saturated, neutral *lactone*, $C_{24}H_{32}O_8$, m.p. 225—227°, and *undephanthantriacid Me*$_2$ ester, $C_{24}H_{31}O_8$, m.p. 201°; the H ester and $SOCl_2$ give the *chloride*, cryst., whence the *amide* *Me*$_2$ ester, m.p. 205° after softening at 110—111° (could not be degraded), was obtained. The corresponding *azide*, similarly prepared, gives the urethane, whence 25% KOH–EtOH at 100° forms the very stable *lactam*, $C_{21}H_{29}O_5N$, m.p. 264—266° (*Me* ester, m.p. 226—228°). The unsaturated lactone, $C_{23}H_{30}O_6$, from undeplogondiacid Me ester gives by similar reduction a neutral *substance*, ? $C_{23}H_{32}O_6$, m.p. 189—190° after softening, and a *deoxy-acid*, $C_{23}H_{31}O_6$, m.p. 212°, whence by way of the chloride, azide, and urethane, a small amount of the *amine*, $C_{21}H_{33}O_4N$ (*hydrochloride* of *Et* ester, m.p. 110—120°), was obtained. R. S. C.

Action of heat on resin acids. Fanica (Bull. Inst. Pin, 1933, 151—165, 181—189).—The following are obtained by heating at 230° in CO_2: from Aleppo colophony in one experiment *α-pyroabietic acid* (I), m.p. 172—173°, $[\alpha]_{5790}$ +60° [*NH*$_4$ (unstable), *Ni*, *Co*, *Cu*, *Mn*, *Fe*^{III}, and *Ba* salts; *anilide*, m.p. 148°], but in a second experiment an *acid* (II), m.p. 176—182°, $[\alpha]_{5790}$ −30°; from French colophony an *acid*, m.p. 185—187°, $[\alpha]_{5790}$ −25°; from β-pimaric acid an impure *acid* (III), m.p. 164—165°, $[\alpha]_{5790}$ −38·3°; from α-alepic acid an *acid*, m.p. 172—173°, $[\alpha]$ +70·7°; from abietic acid, m.p. 171—172°, $[\alpha]_{5790}$ −100·2°, *β-pyroabietic acid*, m.p. 185—190°, $[\alpha]_{5790}$ −52·8°, possibly identical with (II), (III), a known colophonic acid (A., 1906, i, 100), and the acid of Fonrobert *et al.* (B., 1929, 403). α-Pimaric acid is only slightly affected by this treatment. The abietic acids from Aleppo and French colophony give the same *nitrosite*, m.p. 150—160° (decomp.) (15 and 25% yields, respectively), and *nitrosochloride*, m.p. 148° (25 and 35% yields, respectively). (I) forms no additive compounds (except with ICl), gives with fuming HNO_3 a *substance*, $C_{40}H_{57}O_4(NO_2)$, m.p. 218—220°, $[\alpha]_{5790}$ +102°, with H_2SO_4 at 0° a *sulphonic acid*, decomp. 213—214°, $[\alpha]_{5790}$ +81·7° in AcOH (*Na H* salt), and with Se at 200—250° a 43·5% yield of retene. R. S. C.

Rhamnol. A. Windaus and M. Deppe (Ber., 1933, **66**, [*B*], 1254—1255).—Rhamnol (I), m.p. 134°, $[\alpha]_D^{18}$ −35·2° in $CHCl_3$, is purified through its 3 : 5-*dinitrobenzoate*, m.p. 202—204°, $[\alpha]_D$ −10·8° in $CHCl_3$. (I) loses its H_2O of crystallisation with great difficulty at 100°/vac., thus causing a low % of C to be observed. Treatment of rhamnol acetate (II) with Br–AcOH yields a small amount of *tetrabromide* of high m.p., but mainly a dibromide which with Zn dust regenerates (II), m.p. 118—119°, $[\alpha]_D^{18}$ −38·2° in $CHCl_3$. In particular, analyses of the ester show the formula $C_{20}H_{32}O$ usually ascribed to (I) to be incorrect.

It probably belongs to the sitosterol group and contains 29 C; this is probably also true of cupreol, cinchol, and quebrachol. H. W.

Cerebronic acid. VIII. P. A. LEVENE and K. HEYMANN (J. Biol. Chem., 1933, **102**, 1—6; cf. A., 1929, 1479).—Fractionation of crude phrenosin gives 3% of a product (I), m.p. 200° (decomp.), $[\alpha]^{20}$ +3·6° in C_5H_5N, whence cerebronic acid (II), m.p. 100—101°, $[\alpha]_D^{23}$ +2·9° in C_5H_5N, was obtained. This, when oxidised, gives a mixture including acids (possibly mixtures), $C_{23}H_{46}O_2$, m.p. 76° (Et ester, b.p. 175°/0·4 mm.), and $C_{24}H_{48}O_2$, m.p. 76—78° (Et ester, b.p. 191—194°/0·4 mm.). (II) and (I) are thus mixtures, although the latter forms large crystals. R. S. C.

Tetrahydroxybufostan, a tetrahydric alcohol $C_{27}H_{48}O_4$ from winter-bile of toads. H. MAKINO (Z. physiol. Chem., 1933, **220**, 49—54).—From the winter-bile of *Bufo vulgaris japonica* there were isolated cholesterol and *tetrahydroxybufostan* (I), $C_{27}H_{48}O_4$, m.p. 230°, $[\alpha]_D^{20}$ +37·5° in EtOH (Ac_4 derivative, m.p. 52—55°). Oxidation of (I) with CrO_3 in AcOH gives a *triketomonocarboxylic acid*, m.p. 221—222°, $[\alpha]^{20}$ +31° in EtOH [*Et* ester (*trioxime*, m.p. 218°); *Me* ester, m.p. 198—199° (*trioxime*, m.p. 214—215°)]. The primary OH of (I) is probably in the Pr^{β} group. J. H. B.

Fission of wogonin by alkali; formation of iretol. S. HATTORI and K. HAYASHI (Ber, 1933, **66**, [*B*], 1279—1280).—Iretol, m.p. 186° (decomp.), BzOH, and AcOH are formed when wogonin, m.p. 203° after softening at 200°, is boiled with KOH–H_2O in H_2 (cf. A., 1931, 493). H. W.

Resin acids of American turpentine gum. Preparation of the pimaric acids from *Pinus palustris*. S. PALKIN and T. H. HARRIS (J. Amer. Chem. Soc., 1933, **55**, 3677—3684).—Improved methods of isolation and separation of *d*- (I), m.p. 218—219°, $[\alpha]_D^{20}$ +73·3° in EtOH, and *l*-pimaric acid (II), m.p. 150—152°, $[\alpha]_D^{20}$ −274·5° in EtOH, from the gum of *P. palustris* are given. (I) differs markedly (in m.p. and rotation) from the *d*-pimaric acid from *P. maritima*, but the properties of the *l*-acid from both sources are almost identical. (I) is reduced (H_2, Pd–$BaSO_4$, EtOAc) to a dihydro-acid, m.p. 249—250° (cf. Ruzicka and Balas, A., 1923, i, 818); (II) similarly gives a mixture from which a dihydro-acid, m.p. 144—146°, is isolated. Crystallographic data for (I) and (II) are given. H. B.

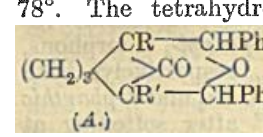
Oxidations by selenium dioxide in the terpene series. G. DUPONT, J. ALLARD, and R. DULOU (Bull. Soc. chim., 1933, [iv], **53**, 599—603).—The oxidation of pinene to verbenone (33% yield) by SeO_2 (modified prep.) (A., 1932, 1253) is confirmed. Nopinene gives similarly (best in ligroin or H_2O) a 25% yield of pinocarvone. CH_2Ph_2 gives $COPh_2$. R. S. C.

Santenone. O. ASCHAN (Svensk Kem. Tidskr., 1933, **45**, 209—221).—Crude santenone forms two *semicarbazones*, α (m.p. 235—236°) and β (m.p. 221—222°), which give on hydrolysis α-, b.p. 191°, m.p. 55—56°, and β-*santenone*, b.p. 189·5—190·5°, m.p. 46°, respectively. The corresponding *oximes* have m.p. 74° and 50—51°. The α and β forms are regarded as stereoisomerides. R. P. B.

First product of condensation of furfuraldehyde with phenol. A. E. PORAI-KOCHITZ, N. A. KUDRJAVTZEV, and B. E. MASCHKILEIZON (J. Appl. Chem. Russ., 1933, **6**, 685—690).—Furfuraldehyde (I) reacts with PhOH in alkaline media with production of unidentified tarry and resinous substances. In boiling feebly acid solutions 71%, and in alkaline solution in presence of $NaHSO_3$ 5%, yields of o- or p-*hydroxyphenylfurylcarbinol*, m.p. about 150° (*benzyl ether*, m.p. 161—162°; its *Ac* ester, m.p. 285—287°; Ac_2 ester), are obtained. R. T.

Preparation of tetrahydropyrone. R. CORNUBERT and P. ROBINET (Bull. Soc. chim., 1933, [iv], **53**, 565—569).—The prep. of Et_2 acetonedioxalate, chelidonic acid, pyrone, and tetrahydropyrone is modified, the yields obtained being 81, 98, 89, and (?) 100%, respectively. R. S. C.

[Confirmation of the constitution of] so-called tetrahydropyrones. R. CORNUBERT and (in part) P. ROBINET (Bull. Soc. chim., 1933, [iv], **53**, 610—633).—Partly a detailed account of work previously published (A., 1932, 272). The condensation products of cyclic ketones (1 mol.) and PhCHO (I) (2 mols.) have the tetrahydropyrone structure (*A*), since they form ketonic derivatives and do not contain an OH group, and since the product is formed only if the ketone contains at least one H in each position adjacent to the CO. 2-Benzylidene-6-methyl*cyclo*hexanone (II), (I), and HCl at −15° give three isomeric *compounds*, $C_{28}H_{27}O_2Cl$, m.p. 180—181° (III), 199—200° (IV), and not stated, respectively, probably containing a tetrahydropyrone ring and the grouping CHClPh·C. (II) and HCl in ligroin give the *hydrochloride*, $C_{14}H_{17}OCl$, m.p. 90·5°, which with (I) and HCl gives a compound, m.p. 200—205° after sintering at 192°, probably (IV). The liquid benzylidene compound from 2-methyl*cyclo*hexanone (A., 1932, 58) gives similarly a compound, m.p. 172—173°, probably (III). Hydrogenation (Ni) of 2-benzylidene-6 : 6-dimethyl*cyclo*hexanone gives 2-*benzyl*-6 : 6-*dimethyl*cyclo*hexanone* (V), b.p. 179°/29 mm. (*oxime*, m.p. 145°; *semicarbazone*, m.p. 201—202°). 2 : 6-Dimethyl*cyclo*hexanone and $NaNH_2$ in hot Et_2O give a Na salt, which with CH_2PhBr gives much 2-*benzyl*- (VI), b.p. 174°/22 mm. (*oxime*, m.p. 155—156°; *semicarbazone*), and a little 2 : 6-*dibenzyl*-2 : 6-*dimethyl*cyclo*hexanone*, b.p. 240—245°/19 mm., m.p. 78°. The tetrahydropyrone (*A*; R=H, R′=Me)



(*A*.)

[*semicarbazone*, m.p. 230° (rapid heating)] with Na and EtOH gives a substance, m.p. 127—128° [*loc. cit.* (i), b.p. 127—128°] (also obtained by KOH in $Bu^{\beta}OH$, together with a small amount of a *substance*, m.p. 140—150°), whilst with $KMnO_4$ in $COMe_2$ acids and a *substance*, $C_{21}H_{22}O_3$, possibly the tetrahydropyrone (*A*; R=OH, R′=Me), m.p. 145—146°, are obtained. 2-Benzyl-6-methyl*cyclo*hexanone gives an *oxime*, m.p. 115°, and a *semicarbazone*, m.p. 163—164°. (V) and (VI) do not condense with (I) and HCl. R. S. C.

(*a*) Case of ketonic activity of acetic anhydride and (*b*) condensation of salicylaldehyde with

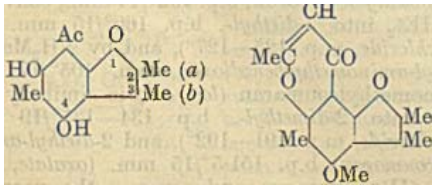
benzoylacetone. R. J. W. Le Fevre and J. Pearson (J.C.S., 1933, 1197—1200).—The compound obtained from COPhMe, Ac_2O, and $FeCl_3$ by Dilthey's method (A., 1916, i, 829) is considered to be 4 : 6-diphenyl-2-methylpyrylium ferrichloride (I) (cf. Schneider and Ross, A., 1922, i, 1171) and not the 2 : 6-diphenyl-4-methyl derivative (II) (cf. Dilthey, *loc. cit.*), since nitration (fuming HNO_3) of the corresponding *perchlorate*, m.p. 265—266° (decomp.), gives a mixture of products which on oxidation ($KMnO_4$; 6*N*-H_2SO_4) affords some *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$; (II) should give *m*-$NO_2$-derivative almost entirely (cf. this vol., 163). COPhMe, Bz_2O, and $FeCl_3$ at 50° give a little 2 : 4 : 6-triphenylpyrylium ferrichloride. COPhMe and Ac_2O do not react at 100° whilst treatment of the product from COPhMe, CH_2BzAc (III), and HCl with $FeCl_3$ affords (I). It is unlikely that (III) is an intermediate in Dilthey's method of prep. of (I); the mechanism is considered to be: $2COPhMe \longrightarrow COPh{\cdot}CH{:}CPhMe \xrightarrow{Ac_2O}$

$COPh{\cdot}CH{:}CPh{\cdot}CH{:}CMe\ OAc \longrightarrow Cl +$

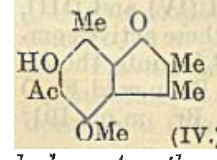
$COPh{\cdot}CH{:}CPh{\cdot}CH{:}CMe \rightarrow CPh\langle^{CH{\cdot}CPh}_{CH{:}CMe}\rangle O\}Cl \rightarrow$ (I).

Condensation of *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ (IV) and (III) by Chatterji and Ghosh's method (J.C.S., 1918, **113**, 446) gives a chloride, m.p. 115—120° [corresponding perchlorate (V), m.p. 135—140°, also obtained (with m.p. 103—105°) from (III), (IV), and 70% $HClO_4$ in Et_2O–HCl]. The use of twice the amount of (IV) in Ac_2O (solvent) leads to the isolation of 3-benzoyl-2-*o*-hydroxystyrylbenzopyrylium perchlorate (VI), m.p. 234—235°, which raises the m.p. of (V), and is converted by alkali into the corresponding *ψ*-base or *spiro*pyran. Reaction proceeds by way of the 3-benzoyl-2-methylbenzopyrylium salt, which then reacts rapidly with (IV) to give (VI). COMeEt, (IV), and 70% $HClO_4$ in Et_2O–HCl give 2-*o*-hydroxystyryl-3-methylbenzopyrylium perchlorate, m.p. 261—262° (lit. 257—258°), even when a large excess of COMeEt is used; the intermediate 2 : 3-dimethylbenzopyrylium salt reacts more rapidly with (IV) than does COMeEt. H. B.

Usnic acid. III. Usnetol, usnetic acid, and pyrousnic acid. F. H. Curd and A. Robertson (J.C.S., 1173—1179; cf. this vol., 831).—Usnetol is shown to be (I) by conversion into (II) and by synthesis of its 4-*Me ether* (III) and of O-*methylisousnetol* (IV), which resembles (III) in colour and $FeCl_3$ and H_2SO_4 reactions. Arguments are presented that usnetic acid (V) is (I) with a $CH_2{\cdot}CO_2H$ group for Me in position (*a*) or (*b*), pyrousnic acid (VI) being derived therefrom by loss of the Ac. The formulæ of Schopf

(I.) 

(II.)

et al. (A., 1928, 294) for these and derived substances are refuted. *dl*-Usnic acid (prepared from the *d*-acid by refluxing in xylene) and 50% aq. KOH at 210° in H_2 give $COMe_2$, AcOH, and (VI), m.p. 199—200° (decomp.) after sintering at 195° [also obtained similarly (with AcOH) from (V)]. (VI) and CH_2N_2 in Et_2O give the *Me* ester, m.p. 186° (decomp.), which with MeI–$COMe_2$–K_2CO_3 gives *Me* O-*dimethylpyrousnate*, m.p. 63—64°, obtained similarly from (VI) and hydrolysed to O-*dimethylpyrousnic acid*, m.p. 126—127°. *d*- or *dl*-Usnic acid and 75% aq. KOH give (VI) and *usnetinic acid*, $C_{11}H_{10}O_5$, m.p. 180—181° (decomp.) (cf. Schopf, *loc. cit.*). Me *O*-methylusnetate, 

(IV.) m.p. 117—118° [from (V) and CH_2N_2 in Et_2O], affords O-*methylusnetic acid*, m.p. 164—165°. (I) with MeI–K_2CO_3–$COMe_2$ affords (III), m.p. 127—128°, which with EtOAc and Na at 160° gives 6-*hydroxy*-4-*methoxy*-7-*acetoacetyl*-2 : 3 : 5-*trimethylcoumarone*, m.p. 126—127°, whence by a little HCl in hot AcOH 7-*methoxy*-2 : 8 : 4′ : 5′-*tetramethyl*-5 : 6-*furano*-(2′ : 3′)-*chromone* (II), m.p. 192°, was obtained. Methylphloroglucinol α-Me ether, MeCN, $ZnCl_2$, and HCl in Et_2O lead to 2 : 4-*dihydroxy*-6-*methoxy*-3-*methylacetophenone*, m.p. 224°, whence CHMeAcCl in hot $COMe_2$ forms 6-*hydroxy*-4-*methoxy*-5-*acetyl*-2 : 3 : 7-*trimethylcoumarone* (IV), m.p. 109—110° (*oxime*, m.p. 161—162°). Methylphloroglucinol β-Me ether, m.p. 115—116° (prepared from Me 2 : 6-dihydroxy-4-methoxybenzoate), gives similarly 2 : 6-*dihydroxy*-4-*methoxy*-3-*methylacetophenone*, m.p. 197—198° [giving with MeI–K_2CO_3–$COMe_2$ the 2-OH-4 : 6-$(OMe)_2$-compound], α-3-*hydroxy*-5-*methoxy*-2-*acetyl*-4-*methylphenoxyethyl Me ketone*, m.p. 151—152°, and thence (III). R. S. C.

Spatial configuration of the valencies in tricovalent carbon compounds. E. S. Wallis and F. H. Adams (J. Amer. Chem. Soc., 1933, **55**, 3838—3851).—Partly an account of work previously reviewed (A., 1932, 611; this vol., 153). 12-Chloro-12-phenyl-β-benzoxanthen hydrochloride (Gomberg and Schoepfle, A., 1917, i, 551) and $SH{\cdot}CH_2{\cdot}CO_2H$ in C_6H_6 give dl-12-*phenyl*-12-β-*benzoxanthenylthiolacetic acid* (I), m.p. 187—188°, which is resolved by brucine into *l*- (II), m.p. 183—184°, $[\alpha]_D^{20}$ −48·5° in $COMe_2$, and impure *d*-, m.p. 179°, $[\alpha]_D^{20}$ +28·9° in $COMe_2$, forms. (II) racemises slowly when kept alone or in $COMe_2$ at 20° and rapidly in boiling C_6H_6. (I) and Na in liquid NH_3 in absence of air give (after decomp. with dry NH_4Br) 12-*phenyl*-β-*benzoxanthen*, m.p. 153° [the substance, m.p. 171°, described as this by Kauffmann and Egner (A., 1914, i, 39) is probably a fluorene derivative]. (II) similarly affords products of $[\alpha]_D^{20}$ −2·3° (in C_6H_6) to −11·7° (in $COMe_2$), showing that $[CAr_3]^-$ can exist in an optically active state and that the three covalencies and the central C atom are not co-planar. The anion racemises fairly readily; when the solution is kept for some time before decomp. with NH_4Br, an inactive product results. dl-α-*Phenyl*-α-*methylpropylthiolacetic acid*, m.p. 137—138°, obtained in poor yield from CPhMeEtCl and $SH{\cdot}CH_2{\cdot}CO_2H$ in PhMe, could not be resolved; its alkaloid salts show a tendency to decompose into unsaturated hydrocarbons and alkaloid thiolacetates.

(II) and $AgNO_3$ in aq. $COMe_2$ give *dl*-12-phenyl-12-

β-xanthenol, m.p. 170—171° [the *Me*, m.p. 148°, and *Et*, m.p. 118°, *ethers* are prepared from (II) and MeOH– and EtOH–$AgNO_3$, respectively], indicating the optical instability of $[CAr_3]^+$. A cation of this type can, however, maintain an asymmetric configuration, since *d*-, m.p. 160°, $[\alpha]^{20}_{5461}$ +7·2° in CCl_4, and *l*-, m.p. 161—162°, $[\alpha]^{20}_{5461}$ −7·6° in CCl_4, -phenyldiphenylyl-α-naphthylcarbinols are obtained by the action of aq. $COMe_2$–$AgNO_3$ on *l*- (III) and *d*- (IV) -phenyldiphenylyl-α-naphthylthiolacetic acid, respectively; the *d*-, m.p. 125—126°, and *l*-, m.p. 125·5—126°, -Et ethers are prepared from EtOH–$AgNO_3$ and (IV) and (III), respectively (cf. A., 1932, 611). All these active compounds are converted by $SOCl_2$ in C_6H_6 into the *dl*-carbinyl chloride. (III) or (IV) and Br in cold Et_2O give an inactive *compound*, $C_{29}H_{21}Br$, m.p. 191° (decomp.).

The optical instability of neutral free radicals (electron septet) is shown by the formation of an inactive product from (III), CPh_3Cl, and Hg in Et_2O, the production of optically inactive βγ-dimethylhexane from *d*-β-bromobutane and Na in dry Et_2O (and by electrolysis of *d*- and *l*-α-methylbutyric acids), and the prep. of inactive αβγδ-tetraphenylbutane, m.p. 178° (lit. 255°), from l-αβ-*diphenylethyl bromide*, $[\alpha]^{22}_{D}$ −27·1° in EtOH (from *d*-$CH_2Ph{\cdot}CHPh{\cdot}OH$ and HBr in C_6H_6 at 0°), and Na in Et_2O. H. B.

Constituents of the leaves of *Ginkgo biloba*, L. III, IV. S. Furukawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 273—277, 278—285; cf. A., 1932, 1138).—III. The diacetate of substance *A* is hydrolysed by H_2SO_4 in aq. EtOH to an *isomeride*, $C_{11}H_{14}O_5$, m.p. 225·5—226·5°, and by aq. KOH to an oil. *A* and Me_2SO_4 yield a *substance*, $C_{11}H_{15}O_5{\cdot}OMe$, m.p. 100° (decomp.) [*Ag* salt; *Me* ester, m.p. 110° (decomp.)]. *A* is unattacked by HNO_3 in AcOH; alkaline $KMnO_4$ or CrO_3 in AcOH yield oily acids; fusion with KOH yields an *acid*, m.p. 150°. The EtOH mother-liquors of *A* yield a *substance*, $C_{11}H_{14}O_6,H_2O$, m.p. 291—292° (decomp.) [Ac_3 derivative, m.p. 180° (decomp.)].

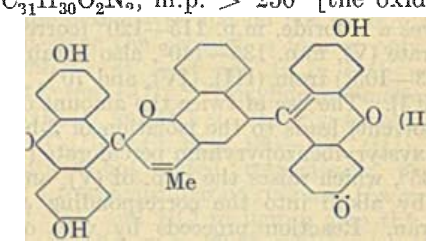
IV. Substance *B* and CH_2N_2 yield a *Me* derivative, m.p. 277—278° (*Ac* derivative, m.p. 218—219°, resolidifies, m.p. 257—259°). Demethyl-*B* yields a Ac_3 derivative, m.p. 237—238°. Treatment of *B* with 40% KOH yields *p*-hydroxyacetophenone, anisic acid, a *substance*, m.p. 266—267°, phloroglucinol, and a little (?) *p*-methoxyacetophenone. *B* is probably 5 : 8-dihydroxy-4′-methoxyflavone, since one OH (at 5) is unattacked by CH_2N_2, the 5 : 7-$(OH)_2$ derivative is acacetin, and the 5 : 6-position in excluded by consideration of the absorption spectrum.

Curves of the absorption spectra of *B* and its derivatives are given and compared with those of acacetin, monoacetylmonomethylacacetin, apigenin acetate, 4′-hydroxy-, 7-hydroxy-, 7-hydroxy-4′-methoxy-, and 6 : 4′-dimethoxy-flavones. 6 : 4′-*Dimethoxyflavone*, m.p. 194·5—195°, is obtained from 2 : 4 : 4′-trimethoxybenzoylacetophenone by treatment with HI. R. K. C.

Yellow colouring matter of Khapli wheat, *Triticum dicoccum*. III. Constitution of tricin. J. A. Anderson (Canad. J. Res., 1933, **9**, 80—83).—Tricin (I) (A., 1931, 1426; 1932, 1256) is identical with 5 : 7 : 4′-*trihydroxy*-3′ : 5′-*dimethoxyflavone*, m.p. 288—289° (corr.) [Ac_3 derivative, m.p. 251—254° (corr.)], synthesised by demethylation of 5 : 7-dihydroxy-3′ : 4′ : 5′-trimethoxyflavone with 96—98% H_2SO_4 at 60°. When fused with H_2O–KOH at 200—210°, (I) gives phloroglucinol and syringic acid. J. W. B.

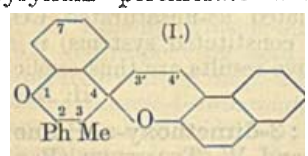
Dye of yellow dahlias. L. Schmid and L. Haschek (Monatsh., 1933, **62**, 317—322).—The yellow dye $C_{15}H_{10}O_5$ (I), isomeric with apigenin (II), isolated from the dahlia (A., 1932, 621) affords *p*-hydroxyacetophenone by treatment with 20% KOH. Its Me_2 ether (III) (obtained in 60% yield by use of CH_2N_2) similarly gives *p*-methoxyacetophenone. With Ac_2O and C_5H_5N (I) gives a Ac_3 derivative, m.p. 182°, hydrolysed by 10% HCl in EtOH to a substance chemically and spectroscopically identical with (II), which is also obtained by demethylation of (III) with HI (*d* 1·7). J. W. B.

6-Aldehydo-4-methyl-α-naphthapyrone and dyes derived from it. R. N. Sen and G. C. Mukherjee (J. Indian Chem. Soc., 1933, **10**, 271—273).—4-Methyl-α-naphthapyrone, EtOH–$CHCl_3$, and aq. NaOH at 80—100° give 6-*aldehydo*-4-*methyl*-α-*naphthapyrone* (I), m.p. 280° (*phenylhydrazone*, m.p. 125°; *semicarbazone*, m.p. 260°; *oxime*, m.p. > 280°), which with $NPhMe_2$ and conc. HCl at 100° affords a *leuco-base*, $C_{31}H_{30}O_2N_2$, m.p. > 250° [the oxidised (PbO_2) base dyes silk greenish-blue]. (I), *m*-$C_6H_4(OH)_2$, and conc. H_2SO_4 at 100—130° give the *compound* (II), m.p. > 280°, the Na salt of which dyes silk bright orange. H. B.



Heterocyclic bases from coumarans and phenyldioxan [benzdioxan]. E. Fourneau, P. Maderni, and (Mme.) Y. de Lestrange (J. Pharm. Chim., 1933, [viii], **18**, 185—191).—Br and *o*-allylanisole, in C_6H_6 at 0°, do not yield nuclear Br-derivatives of coumaran (Adams and Rindfusz, A., 1919, i, 340), but α-(o-*anisyl*)-βγ-*dibromopropane*, b.p. 128—131°/0·4—0·5 mm. (I), and a little 2-methylcoumaran. (I) reacts slowly with $NHMe_2$ giving a mixture of bases separable into the *hydrochlorides*, m.p. 134° and 153°, of the stereoisomeric α-(o-*anisyl*)-γ-*dimethylamino*-Δ^{α}-*propenes*, and α-(o-*anisyl*)-βγ-*bis-dimethylaminopropane dihydrochloride*, m.p. 226—227°. $SOCl_2$ and 3-hydroxymethylbenzdioxan yield 3-*chloromethylbenzdioxan*, b.p. 132°/14 mm., converted by $NHEt_2$ into 3-*diethyl*-, b.p. 160°/15 mm. (II) (*hydrochloride*, m.p. 125—127°), and by NH_2Me into 3-*methyl-aminomethylbenzdioxan*, b.p. 105°/17 mm. 2-Bromomethylcoumaran (*loc. cit.*) is similarly converted into 2-*dimethyl*-, b.p 134—135°/19 mm. (*hydrochloride*, m.p. 191—192°), and 2-*diethyl-aminomethylcoumaran*, b.p. 151·5°/15 mm. (*oxalate*, m.p. 123°). (II) suppresses and reverses the vaso-constrictive action of adrenaline, and causes marked lowering of temp. in rabbits. A. C.

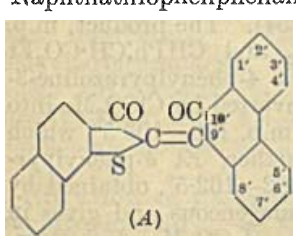
Styrylpyrylium salts. XV. Correction. Production of α-benzopyrones by the Kostanecki reaction. I. M. HEILBRON, R. N. HESLOP, and G. F. HOWARD (J.C.S., 1933, 1263—1264; cf. this vol., 614).—The course of the Kostanecki reaction is governed by factors which are not yet understood. The substances called 2-ethyl- and 7-methoxy-2-ethyl-chromone are proved by mixed m.p. and degradation to be 3 : 4-dimethyl- and 7-methoxy-3 : 4-dimethyl-coumarin, respectively, whence the following revised structures are assigned (the new name is given second): 4-phenyl-2-ethylbenzopyrylium perchlorate and its 7-OMe derivative,



2-phenyl-3 : 4-dimethylbenzopyrylium perchlorate and its 7-OMe derivative; 4-phenyl-3′-methylbenzo-β-naphtha-*spiro*pyran and its 7-OMe derivative, 2-*phenyl*-3-*methylbenzo*-β-*naphtha*isospiro-*pyran* (I) and its 7-*OMe* derivative. The ionising power of these pyrans is thus normal. R. S. C.

Synthesis of rotenone and its derivatives. IV. Dehydrodihydrorotenonic and tephrosic acids. A. ROBERTSON (J.C.S., 1933, 1163—1165; cf. this vol., 712).—The structures of dehydrodihydrorotenonic acid (I) (and thus of dehydrorotenone) and of tephrosic acid (II) (this vol., 397) are confirmed by synthesis. 4 : 5-*Dimethoxyphenoxyacetic*-2-*pyruvic acid oxime*, $+H_2O$, double m.p. 80° and 160—165° (prepared in 10% aq. NaOH at 50°), and Ac_2O at 100° give 4 : 5-*dimethoxyphenoxyacetic acid*-2-*aceto-nitrile*, m.p. 174° [*Me* ester (III), m.p. 92°]. 2 : 6-Dimethoxybenzonitrile and $MgBu^{\beta}Br$ (less well $MgBu^{\beta}I$), first in hot Et_2O and then in xylene at 100°, give 2 : 6-*dimethoxy*isovalerophenone, b.p. 178°/15 mm. (*semicarbazone*, m.p. 207°), reduced (Clemmensen) to tetrahydrotubanol Me_2 ether, b.p. 142—145°/15 mm., demethylated by HI–Ac_2O at 140—145°. (III), tetrahydrotubanol, $ZnCl_2$, and HCl in Et_2O afford a ketimine, hydrolysed to *Me tetrahydroderrisate*, m.p. 185°, and a little tetrahydroderrisic acid. This acid with hot Ac_2O–AcOH yields 7-acetoxy-6′ : 7′-dimethoxy-8-*iso*amylchromeno-(3′ : 4′ : 2 : 3)-chromone, hydrolysed by HCl–AcOH to the corresponding 7-OH compound [=(I)]. (III) and *m*-$C_6H_4(OH)_2$ give by the Hoesch reaction 4 : 5-dimethoxyphenoxyacetic acid-2-resacetophenone [=(II)] and its Me ester. R. S. C.

Indigoid dyes. II. 1 : 2-Naphthathiophen-phenanthreneindigotin. III. P. C. DUTTA (Ber., 1933, **66**, [*B*], 1226—1230, 1230—1232).—II. 1 : 2-Naphthathiophenphenanthreneindigotins (cf. *A*) are



darker than the corresponding thionaphthenphenanthreneindigotins (A., 1932, 753); they do not yield even or darker shades on wool. Phenanthrenequinone and 1 : 2-naphthoxythiophen in boiling AcOH afford 1 : 2-*naphthathiophen*-9′-*phenanthreneindigotin*, m.p. 291°. The following derivatives are described: -2′-*nitro*-, m.p. > 300°; -4′-*nitro*-, m.p. 281°; -2′ : 7′-*dinitro*-, m.p. > 295°; 4′ : 5′-*dinitro*-, m.p. > 295°; -2′-*bromo*-, m.p. > 295°; -*dibromo*-, m.p. > 295°; -*bromonitro*-, m.p. > 300°; -2′-amino-, m.p. > 295°; -4′-*amino*-, m.p. > 300°; -2′-*hydroxy*-, m.p. > 295°.

III. The following indigoid dyes are derived from 1 : 2-naphthoxythiophen by condensation in AcOH in presence of a little mineral acid: 1 : 2-*naphthathiophen*-3′-*indoleindigotin*, m.p. > 295°, its -5′-*chloro*-, m.p. > 295°, -5′-*bromo*-, m.p. > 295°, and -5′ : 7′-*dibromo*-, m.p. > 300°, derivatives: 1 : 2-*naphthathiophen*-2′-*acenaphthyleneindigotin*, m.p. 282°, and its 5′-*nitro*-, m.p. > 295°, derivative; 1 : 2-*naphthathiophen*-1-*aceanthyleneindigotin*, m.p. > 295°; di-1 : 2-naphthathiophenethyleneindigotin, m.p. > 295° after decomp. at 280°. H. W.

Polyhalogenated ketones. III. Pyrrole. G. SANNA (Gazzetta, 1933, **63**, 479—484; cf. A., 1931, 630).—The Mg derivative of pyrrole with $CHCl_2$·COCl in Et_2O forms 2-*dichloroacetylpyrrole*, m.p. 90°; this with 5% KOH or aq. NH_3 at 95° gives brown Cl-free condensation products, probably ter- and bi-mol., respectively. Using CCl_3·COCl, 2-*trichloroacetyl-pyrrole*, m.p. 67°, is formed. E. W. W.

Isomerisation products of pyridine salts of unsaturated acids. O. LUTZ, R. KLEIN, and A. JIRGENSON (Annalen, 1933, **505**, 307—310; cf. A., 1910, i, 879).—Titration of a mixture of 1 mol. of acid with 3 mols. of C_5H_5N after keeping at 18° for 20 days indicates that addition of C_5H_5N occurs readily with maleic, fumaric, itaconic, and crotonic acids, very slowly with aconitic, and not at all with citraconic, mesaconic, allylmalonic, and cinnamic acids. The *betaines* of *pyridiniumsuccinic*, m.p. 192° (decomp.), and β-*pyridiniumbutyric acid*, m.p. 79·5—80°, are described. H. A. P.

Fission of pyridinium salts and new mode of formation of α-ketoaldehydes. F. KRÖHNKE (Ber., 1933, **66**, [*B*], 1386—1392; cf. this vol., 501).—*Phenacylpyridinium iodide*, m.p. 214° (decomp.), is obtained from the bromide (I) and aq. KI. (I) affords a *phenylhydrazone*, m.p. 160—165° (decomp.), and *p-nitrophenylhydrazone*, m.p. 125° (gas evolution) and decomp. about 212°. The primary product of the action of Br–H_2O on (I) is the yellow perbromide (II) (*loc. cit.*), isomerised by heating at 80°, by long preservation in presence of traces of moisture, or immediately by seeding to the stable, red *perbromide* B (III), m.p. 92°, also obtained directly from the reagents in dil. solution at 50°. (II) or (III) when warmed with abs. EtOH passes into *perbromide* C, $C_{13}H_{12}ONBr_2$, m.p. 154—157°. Further action of Br–H_2O leads to ω-*bromophenacylpyridinium bromide* (IV), m.p. 220° (decomp.) (isolated from action in AcOH), which yields a *perchlorate*, m.p. 181° after softening, and a *perbromide*, $C_{13}H_{11}ONBr_4$, m.p. 137°. The final product is regarded as $CBr_2Bz{\cdot}N(C_5H_5)Br$, the ready hydrolysis of which to C_5H_5N salt, BzOH, and HCO_2H is accompanied by slight fission of the C_5H_5N ring. (IV) is very slightly hydrolysed in acid or neutral solution, more readily in alkaline solution to BzOH, CH_2O, and C_5H_5N,HBr. Boiling H_2O converts (IV) into BzCHO, readily oxidised by Br–H_2O through $BzCO_2H$ to BzOH and CO_2. (IV) and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ in

aq. HBr afford phenylglyoxaldi-*p*-nitrophenylhydrazone, decomp. < 312°. *p*-Bromophenacyl bromide and quinoline in Et_2O–EtOH afford p-*bromophenacylquinolinium bromide* (V), m.p. 242° (corresponding *perchlorate*; *perbromide*, m.p. 162·5° after softening at 157°). (V) and hot Br–AcOH yield *p*-bromophenylglyoxal hydrate, m.p. 133—134° after softening. $CHBr_2Bz$ and excess of C_5H_5N in Et_2O slowly give EtOBz and *methylenedipyridinium bromide* (VI), m.p. 255—258° (decomp.) after becoming discoloured (corresponding *perchlorate*, m.p. 236° after softening; *perbromide*; *periodide*). (VI) is not affected by boiling H_2O and mineral acids, but is converted by 0·25*N*-$Ba(OH)_2$ or Ag_2O into CH_2O and C_5H_5N. Catalytic reduction (PtO_2–H_2O) rapidly causes absorption of $7H_2$ and formation of MeOH and piperidinium bromide. (VI) is quantitatively formed from (IV) and warm C_5H_5N, slowly from CH_2Br_2 and C_5H_5N in Et_2O. H. W.

Derivatives of 3 : 3-dimethylindolinone. II. K. Brunner [with M. von Mikoss and J. Riedl] (Monatsh., 1933, **62**, 373—404).—3 : 3-Dimethylindolinone (I) in conc. H_2SO_4 at 100° gives its 5-*sulphonic acid*, $+2H_2O$ and anhyd., m.p. 245—247° (decomp.) [*Ca*, *Na* $+2H_2O$ and anhyd., salts; chloride (II), m.p. 197°; *amide*, m.p. 254—255°], isolated as its *Ba* salt $+4H_2O$ and anhyd. Reduction of (II) with Sn+HCl (*d* 1·19) gives 5-*thiol*-3 : 3-*dimethylindolinone*, m.p. 156—157°, which with $CH_2Cl{\cdot}CO_2H$ and KOH–EtOH affords the corresponding 5-*thioglycollic acid*, m.p. 193·4° (corr.) (*Na* salt) [also obtained from the 5-NH_2 derivative of (I) (A., 1932, 65) by diazotisation, conversion into the *xanthate*, m.p. 200—202°, reduction with NaOH–Zn, and treatment with $CH_2Cl{\cdot}CO_2H$]. With 32% oleum at 100° (I) gives its 5 : 7-*disulphonic acid*, $+H_2O$ and anhyd. (isolated as its *Ba* $+4H_2O$; Na $+3H_2O$, and *K* salts), in which both SO_3H groups are replaceable by Br–H_2O or NO_2 (fuming HNO_3), but not by H_2O, 9% NH_3, or 20% HCl, and only one by Na–Hg reduction. 1 : 3 : 3-Trimethylindolinone even with 37·7% oleum gives only its 2-*sulphonic acid*, $+2H_2O$ and anhyd., decomp. 220° (*Ba* $+4H_2O$ and anhyd.; *Na* $+0{\cdot}5H_2O$ and anhyd.; *K* $+1{\cdot}5H_2O$ and anhyd., salts), the SO_3H group being eliminated by heating with HCl at 180°, Br–H_2O at room temp., or fuming HNO_3 at 80°. Similarly is obtained 3 : 3 : 7-trimethylindolinone-5-sulphonic acid (*Na* salt $+4{\cdot}5H_2O$) as its *Ba* salt. With P_2S_5 in xylene at 140° (I) gives 3 : 3-*dimethylthioindolinone*, m.p. 108—109° [tautomeric with the 2-thiol form; *Ag* salt; *mercurichloride*, m.p. 227—228°; *Me thioether*, m.p. 65° (MeI on Ag salt at 86°, or by NaOH–MeOH on the *methiodide*, m.p. 165°); *thioglycollic acid*, m.p. 151°; *Ac*, m.p. 39—40°, and *Bz*, m.p. 80°, derivatives]. Similarly are obtained 3 : 3 : 7-, m.p. 153—154° [oxidised by 5% $K_3Fe(CN)_6$ to the *disulphide*, m.p. 127—128°], and the 2-*thioglycollic acid*, m.p. 90°; 3 : 3 : 5-, m.p. 167° (*Ag* salt; *thioglycollic acid*, m.p. 136°; *disulphide*, m.p. 165°), and 3 : 3 : 6-, m.p. 135—136°, -*trimethylthioindolinone*. J. W. B.

Reversible addition of aromatic compounds to conjugated systems. R. C. Fuson, A. P. Kozacik, and J. T. Eaton (J. Amer. Chem. Soc., 1933, **55**, 3799—3803).—2-m-*Bromostyryl*-, m.p. 96° (*dibromide*, m.p. 185—186°), and 2-p-*bromostyryl*- (I), m.p. 137—138° (*dibromide*, m.p. 194—195°), -*quinolines*, prepared from 2-methylquinoline and $C_6H_4Br{\cdot}CHO$ by the method previously described (this vol., 721) for the *p*-Cl-analogue (II), react with C_6H_6, $AlCl_3$, and HCl (cf. *loc. cit.*) to give 2-ββ-diphenylethylquinoline. PhBr is formed during the reaction with (I), showing that $\cdot C_6H_4Br$ [or $\cdot C_6H_4Cl$ with (II)] is replaced by Ph. *o*- and *p*-Chlorocinnamic acids, C_6H_6, and $AlCl_3$ give $CHPh_2{\cdot}CH_2{\cdot}CO_2H$; with PhCl, $AlCl_3$, and HCl, both acids give ββ-*di*-p-*chlorophenylpropionic acid*, m.p. 188—189°, oxidised (aq. $KMnO_4$) to 4 : 4′-dichlorobenzophenone. It is suggested that condensation of PhR with β-arylated αβ-unsaturated CO-compounds (and similarly constituted systems) is a reversible process; the above results are thus explicable. H. B.

2-Methoxy- and (?) 2 : 3-dimethoxy-acridine. W. Borsche, F. Runge, and W. Trautner (Ber., 1933, **66**, [*B*], 1315—1318).—*o*-$C_6H_4Cl{\cdot}CO_2H$ (I), *p*-anisidine, K_2CO_3, and Cu-bronze in tetrahydronaphthalene give 4-*methoxydiphenylamine*-2′-*carboxylic acid*, m.p. 186°, converted by conc. H_2SO_4 at 100° into 2-hydroxyacridone, which with Me_2SO_4 and KOH yields 2-*methoxyacridone* (II), m.p. 263—265°. (II) is reduced by Na and EtOH to 2-*methoxydihydroacridine*, oxidised by $K_2Cr_2O_7$ and H_2SO_4 to 2-*methoxyacridine*, m.p. 103—104° (*chromate*; *hydrochloride*; *sulphate*). (I), 4-aminoveratrole, Cu-bronze, and K_2CO_3 in boiling amyl alcohol yield 3 : 4-*dimethoxydiphenylamine*-2′-*carboxylic acid* (III), m.p. 180—181°, which is not condensed by H_2SO_4. (III) is converted by PCl_5 in boiling CS_2 (cf. Dirscherl *et al.*, this vol., 956) into 2 : 3-*dimethoxyacridone* (IV) (*hydrochloride*) and by a somewhat greater proportion of PCl_5 in boiling C_6H_6 into 9-*chloro*-2 : 3-*dimethoxyacridine*, m.p. 187° [*hydrochloride*, m.p. 226° (decomp.); *picrate*]. Reduction of (IV) leads to *dimethoxydihydroacridine*, m.p. 163—165°, oxidised to 2 : 3-*dimethoxyacridine* ($+1H_2O$) (V), m.p. 107° (*chromate*). Treatment of (V) with AcOH–HI yields 2 : 3-dihydroxyacridine [*hydrochloride* ($+H_2O$), m.p. 235° (decomp.)]. H. W.

Formation and degradation of pyrazoline derivatives. K. von Auwers and O. Ungemach (Ber., 1933, **66**, [*B*], 1198—1204; cf. A., 1929, 1080; 1932, 862, 1143).—The action of $CH_2N_2{\cdot}CO_2Et$ on Et tiglate slowly yields *Et* 4 : 5-*dimethylpyrazoline*-4 : 5-*dicarboxylate*, b.p. 169—176°/10 mm., showing (in conjunction with previous observations) that Δ^1-pyrazolinecarboxylic esters are stable only when they cannot pass into isomerides with conjugated linkings. Doubts are cast on the structures assigned by Muller *et al.* to the compounds obtained from butadiene and diazo-compounds (A., 1932, 754). The product, m.p. 100°, obtained from CH_2N_2 and $CHPh{:}CH{\cdot}CO_2Et$ appears to be exclusively Et 4-phenylpyrazoline-3-carboxylate (I), since it is converted by $ClCO_2Me$ into a crude 1-CO_2Me derivative, m.p. 103—103·5°, which is almost homogeneous. Further, Et 4-phenylpyrazole-3(5)-carboxylate, m.p. 162—162·5°, obtained by oxidation of (I), appears homogeneous and gives in high yield the corresponding 1-CO_2Me derivative, m.p. 75—76°, and 1-$CO{\cdot}NHPh$ compound, m.p. 105—106°. (I) is transformed by dry distillation into Et

trans-β-methylcinnamate, b.p. 132—135°/13 mm. (acid, m.p. 96—98°). CH_2N_2 condenses with nitriles to unstable cyanopyrazolines which readily lose HCN to form pyrazoles; thus CHPh:CH·CN and CH_2N_2 ultimately yield 4-phenylpyrazole, m.p. 230°. Treatment of the crude product with Br leads to 3(5)-*cyano*-4-*phenylpyrazole*, m.p. 149·5—150°, hydrolysed to 4-phenylpyrazole-3(5)-carboxylic acid, m.p. 248—249°. H. W.

Addition of diazomethane to acetylenecarboxylic esters. K. VON AUWERS and O. UNGEMACH (Ber., 1933, **66**, [*B*], 1205—1210).—Addition of CH_2N_2 to Me phenylpropiolate in Et_2O gives a mixture of Me 4-phenylpyrazole-3(5)-carboxylate, m.p. 184—187° (corresponding acid, m.p. 233—234°, whence 4-phenylpyrazole, m.p. 230·5—231°), and *Me* 3(5)-*phenylpyrazole*-4-*carboxylate* (I), m.p. 110—111·5° (corresponding acid, m.p. 252—253·5°, whence 3(5)-phenylpyrazole, m.p. 75—77°). Et 3(5)-phenylpyrazole-4-carboxylate, m.p. 85—86°, is converted by boiling $ClCO_2Et$ into *Et*$_2$ 3-*phenylpyrazole*-1 : 4-*dicarboxylate*, m.p. 57·5—58·5°, and by PhNCO into 4-*carbethoxy*-3-*phenylpyrazole*-1-*carboxyanilide*, m.p. 136—137°. Et tetrolate and CH_2N_2 yield Et 4-methylpyrazole-3(5)-carboxylate, m.p. 156·5—157·5° (corresponding acid, m.p. 217°, whence a methylpyrazole which decolorises only a trace of Br in AcOH and hence is an almost homogeneous 4-derivative), and Et 1 : 4-dimethylpyrazole-5-carboxylate containing a small proportion of Et 1 : 4-dimethylpyrazole-3-carboxylate. The behaviour of Et 4-methylpyrazole-3(5)-carboxylate towards Me_2SO_4 and NaOH is described.

With olefinic and acetylenic carboxylic esters addition of CH_2N_2 occurs to esters CHR:C*H CO_2Et in such a manner that N becomes attached to the C* when R is alkyl or aryl. With esters CR:C*·CO_2R' this rule applies only when R=alkyl, whereas when R=aryl addition of N can occur at both C atoms. H. W.

Homodeoxyveronal [diethylmalonethylenediamide] and its homologues. A. W. DOX (J. Amer. Chem. Soc., 1933, **55**, 3871—3873).—$CR_2(CO_2Et)_2$, $(\cdot CH_2\cdot NH_2)_2$, and EtOH–NaOEt at 100—110° give dialkylmalonethylenediamides, $CR_2<^{CO\cdot NH\cdot CH_2}_{CO\cdot NH\cdot CH}$, the *diethyl*-, m.p. 306°, *dibutyl*-, m.p. 290°, and *hexylmethyl*-, m.p. 188°, -derivatives are described. The properties of *ethyl*-, m.p. 350—355° (decomp.), *propyl*-, m.p. 242—245° (decomp.), and sec.-*butyl*-, m.p. 335—340° (decomp.), -*malonethylenediamides*, prepared similarly from $CHR(CO_2Et)_2$, suggest the structure $CHR<^{CO\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot CO}_{CO\cdot NH\cdot CH_2\cdot CH\cdot NH\cdot CO}>CHR$ for these derivatives. Malonethylenediamide (homodeoxybarbituric acid), m.p. 280° (decomp.), obtained when $CH_2(CO_2Et)_2$ is heated with $(\cdot CH_2\cdot NH_2)_2$, dissolves in H_2O to a colloidal solution. The above compounds possess no hypnotic activity. H. B.

Nitration of phenobarbital [5-phenyl-5-ethylbarbituric acid]. M. M. RISING and A. PIERCE (J. Amer. Chem. Soc., 1933, **55**, 3895—3896; cf. this vol., 958).—Nitration of 5-phenyl-5-ethylbarbituric acid gives 5-*m*-nitrophenyl-5-ethylbarbituric acid, m.p. 279—280° (corr.), oxidisable to *m*-$NO_2\cdot C_6H_4\cdot CO_2H$. H. B.

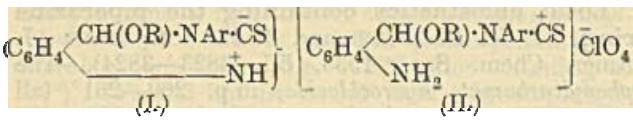
Local anæsthetics containing the piperazine ring. J. H. GARDNER and J. H. SCHNEIDER (J. Amer. Chem. Soc., 1933, **55**, 3823—3824).—The *phenylcarbamate hydrochloride*, m.p. 260—261° (all m.p. are corr.), and *cinnamate hydrochloride*, m.p. 261—262°, of 1 : 4-di-β-hydroxyethylpiperazine and the *phenylcarbamate hydrochloride*, m.p. 250—251°, *benzoate hydrochloride*, m.p. 251—252°, and *cinnamate hydrochloride*, m.p. 254—255°, of 1 : 4-*di*-γ-*hydroxypropylpiperazine*, m.p. 142—143° [prepared from piperazine and $CH_2Cl\cdot CH_2\cdot CH_2\cdot OH$ by Pyman's method (J.C.S., 1908, **93**, 1802)], all possess local anæsthetic activity; they give highly acid solutions. H. B.

Pyrimidines. CXXXV. Uracil glycol. T. B. JOHNSON and E. DYER. **CXXXVI. Mechanism of formation of tetrahydropyrimidines by the Biginelli reaction.** K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1933, **55**, 3781—3783, 3784—3791).—CXXXV. Et uracil-5-carboxylate and Br–H_2O give *Et* 5-*bromo*-6-*hydroxyhydrouracil*-5-*carboxylate*, m.p. 178° (corr.; decomp.), converted by Ag_2CO_3 in H_2O into *Et* 5 : 6-*dihydroxyhydrouracil*-5-*carboxylate* (+H_2O), softens at 72°, melts partly at 110°, and decomp. 125°, m.p. (anhyd.) 135—136° (corr.; decomp.) [*monoacetate*, m.p. 178° (corr.; decomp.)]. This is hydrolysed (under the mildest conditions) to *iso*barbituric acid (I), which is also formed in other processes designed to give uracil glycol (5 : 6-dihydroxyhydrouracil) (II). The instability of (II) is in marked contrast to the comparative stability of its 5-Me derivative (thymine glycol). Attempted addition of HOBr to uracil-5-carboxylic acid gives 5 : 5-dibromo-6-hydroxyuracil. (I) is produced during reduction (H_2, PtO_2) of *iso*dialuric acid (in EtOH) and diacetyl*iso*dialuric acid (in AcOH) [in Ac_2O–AcOH, the Ac derivative of (I) results]. Uracil is not attacked by AcO_2H.

CXXXVI. Condensation of $CO(NH_2)_2$, PhCHO, and $CH_2Ac\cdot CO_2Et$ to Et 2-keto-4-phenyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate (III) (Biginelli, A., 1893, i, 645) is catalysed by I, conc. HCl, or conc. H_2SO_4, and the yield of (III) is proportional to the amount of catalyst used. Reaction proceeds through the intermediate $CHPh(NH\cdot CO\cdot NH_2)_2$ or $NH_2\cdot CO\cdot NH\cdot CMe{:}CH\cdot CO_2Et$ (IV), which then reacts with $CH_2Ac\cdot CO_2Et$ or PhCHO to give (III). (IV) is also hydrolysed to $CO(NH_2)_2$ and $CH_2Ac\cdot CO_2Et$ under the conditions used. It is improbable that CHPh:CAc·CO_2Et is an intermediate. The isomerides (A., 1932, 1144) obtained from citral (V) are both reduced (H_2, Pt, AcOH) to *Et* 2-*keto*-6-*methyl*-4-β*s*-*dimethylheptyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 131—134°; the (V) used contained at least two isomerides. H. B.

Ionic dissociation of 2-thion-1 : 2 : 3 : 4-tetrahydroquinazolines. C. V. GHEORGHIU (Compt. rend., 1933, **197**, 622—624).—The colourless 4-hydroxy(or ethoxy)-3-aryl-2-thion-1 : 2 : 3 : 4-tetrahydroquinazolines (A., 1931, 842) give violet to red solutions, insensitive to O_2, in warm C_6H_6, PhMe, xylene, and C_5H_5N, the depth of colour varying with temp. and concn. The solids become red near their

m.p. and give intensely red solutions in acids. These phenomena are attributed to ionic dissociation (I)

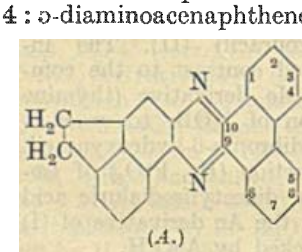


(I.) (II.)

and carbonium salt formation (II) (cf. A., 1926, 1163). In alcohols and ketones (except COPhMe) colourless solutions are formed, probably owing to addition of the solvent. H. A. P.

Benzo- and naphtho-pyrazolyl-*o*-benzoic acids. A. CORBELLINI and A. CECCHI (Gazzetta, 1933, **63**, 489—494).—*o*-(2′-Aminobenzoyl)benzoic acid (*Et* ester, m.p. 71—72°) on diazotisation and $SnCl_2$ reduction condenses to o-3-*indazolylbenzoic acid*, m.p. 184—186·5°. o-(2-*Amino*-3-*naphthoyl*)*benzoic acid*, m.p. 279—279·5° (uncorr.), prepared by hydrolysis of its *lactam*, m.p. 277·5° (uncorr.), which is derived by the action of $AlCl_3$ on β-naphthylphthalimide, is similarly converted into o-(3-ββ-*naphthindazolyl*)*benzoic acid*, m.p. 238—238·5°, not identical with the product, m.p. 269—271°, from 2 : 2′-diamino-1 : 1′-dinaphthyl (A., 1932, 524). E. W. W.

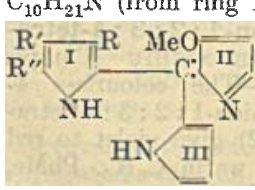
Dye derived from phenanthraquinone; acenaphthenophenanthrazines. P. C. DUTTA (Ber., 1933, **66**, [*B*], 1220—1223).—The following *acenaphthenophenanthrazines* (cf. *A*) are obtained by condensation of phenanthraquinone derivatives with 4 : 5-diaminoacenaphthene, generally in boiling AcOH



(A.)

or EtOH; -2-*nitro*-, m.p. 274°; -4-*nitro*-, m.p. 257—258°; -2 : 7-*dinitro*-, m.p. > 310°; -4 : 5-*dinitro*-, m.p. > 300°; -2 : 7-*diamino*-, m.p. >300°; -4 : 5-*diamino*-, m.p. >300°; -2-*amino*-, m.p. 269—270°; -4-*amino*-, m.p. 204° -2 : 7-*dihydroxy*-, m.p. > 300°; -2-*hydroxy*-, m.p. > 300°; -4-*hydroxy*-, m.p. > 300°; -2-*bromo*-, m.p. 273°; -dibromo-, m.p. > 300°; -*dibromonitro*-, m.p 272°; -*bromodinitro*-, m.p. > 300°. The dyes are lighter than fluorenophenanthrazines (A., 1932, 1043), but darker than the corresponding phenanthraphenazines and phenanthranaphthazines (this vol., 167). H. W.

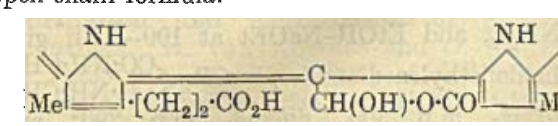
Prodigiosin, the red pigment of *Bacillus prodigiosus*. IV. F. WREDE and A. ROTHHAAS (Z. physiol. Chem., 1933, **219**, 267—274; cf. this vol., 516).—On catalytic hydrogenation (Pd-C in AcOH) prodigiosin (I) takes up 14 H. Alkaline $KMnO_4$ oxidation of the product gave oxamic acid (II) and an *oil*, $C_{11\,(or\ 12)}H_{20\,(or\ 22)}O_4$, b.p. 125 /1 mm. Acid $KMnO_4$ oxidation yielded the pyrrolidine $C_{10}H_{21}N$ (from ring I) (II), succinic acid (III), and



a substance resembling proline, not containing OMe, and therefore not derived from ring II. (III) is readily obtained from pyrrolidine, therefore ring III is an unsubstituted pyrrole. αββ′-Triethylpyrrolidine (*chloroaurate*, an oil; *chloroplatinate*, m.p. 206°, decomp. 224°) differs from the corresponding (I) product (*chloroaurate*, m.p. 105°; chloroplatinate, m.p. 212°), hence ring I is not a 2 : 3 : 4-triethylpyrrole (cf. Raudnitz, this vol., 958). The probable constitution of (I) is as annexed, where $R+R'+R''=C_6H_{15}$. The position of MeO in ring II is not yet decided. J. H. B.

Tetrazine. D. WOOD, jun., and F. W. BERGSTROM (J. Amer. Chem. Soc., 1933, **55**, 3648—3652).—Tetrazine (I) reduces aq. $AgNO_3$, $HgCl_2$, $AuCl_3$, or H_2PtCl_6 sometimes to the metal; salts (cf. Müller, A., 1915, i, 509) or additive compounds of (I) are not produced. (I) can be recovered from its solution in liquid NH_3 provided this is kept at > −40°; above this temp. decomp. occurs. (I) and KNH_2 in liquid NH_3 at −40° give a red *salt*, $K_2C_2N_4$ (?), which explodes violently when exposed to MeI vapour and from which (I) is regenerated by treatment with NH_4Br. Traces of dihydrotetrazine are formed from NH:CH·OEt,HCl and N_2H_4,H_2O in aq. KOH or N_2H_4 in liquid NH_3. H. B.

Chlorophyll. XXXIV. Chemistry of the chloroporphyrins. Chloroporphyrin e_7 lactone, phæoporphyrin a_7, and their decarboxylation to hydroxymethylrhodoporphyrin lactone and chloroporphyrin e_5. H. FISCHER, J. HECKMAIER, and W. HAGERT (Annalen, 1933, **505**, 209—237; cf. this vol., 959).—Chloroporphyrin e_5 (I) is formed in good yield by decarboxylation of phæoporphyrin a_7 (II) with 60% H_2SO_4 at 100°. Its Me_2 ester (III) (CH_2N_2 in Et_2O) readily gives an *oxime*, also obtained from the Me ester (IV) and NH_2OH, and subsequent treatment with CH_2N_2; it also shows evidence of reaction with N_2H_4, but not NH_2·CS·NH·NH_2. The Me_2 ester (V) (MeOH–HCl) does not react with ketonic reagents. Esterification of (IV) with CH_2N_2 in MeOH gives (V) [not (II)], and its Bz derivative is unaffected by CH_2N_2. (I) is decarboxylated by heating with Ph_2 and 60% H_2SO_4 to rhodoporphyrin; in AcOH or C_5H_5N there is little or no change. The following lactone formula is therefore assigned to (I), (IV), and (V), the ester (II) having the corresponding open-chain formula.



Chloroporphyrin e_7 lactone (VI) [*Me* ester, m.p. 285° (CH_2N_2 or MeOH–HCl)], previously obtained by oxidation of chloroporphyrin e_6 (VII) with $K_3Fe(CN)_6$ and considered to be an isomeride of (II) (cf. this vol., 724), is obtained from (VII) in 90% yield by action of I in AcOH. It gives (II) with O_2 in C_5H_5N, and a little of the Me ester of (II) is formed by long boiling with MeOH and HCl. Decarboxylation by 60% H_2SO_4 gives *hydroxymethylrhodoporphyrin lactone* (*Me* ester, m.p. 254°) [(I): CH_2 in place of CH·OH], reduced by HI to chloroporphyrin e_4 (VII), and readily oxidised to (I). (VI) is only slightly attacked by HI.

(VII) is formed in quant. yield by heating chloroporphyrin e_6 Me_3 ester with AcOH; with HCO_2H some phæoporphyrin a_5 is also formed. The reverse change is brought about by CH_2N_2 in MeOH. The change of (VII) into (I) is effected by O_2 in KOH–

MeOH or quantitatively by the action of I in AcOH on the Me_2 ester. Interaction of rhodoporphyrin Me_2 ester with MgMeI gives the corresponding *carbinol*, $C_{35}H_{42}O_3N_4$, m.p. 294°. The corresponding tert.-*alcohol*, $C_{36}H_{44}O_3N_4$, m.p. 324° (block), is similarly prepared from the Me_2 ester of (VII). Decarboxylation of chlorin *e* at 100°/high vac. gives a residue that with HI gives (VII) and phylloporphyrin, indicating partial removal of the 6-CO_2H in addition to the $\cdot CH_2\cdot CO_2H$ residue. Chlorin e_4 absorbs $0{\cdot}5H_2O$ on keeping in air. H. A. P.

Chlorophyll. XXXVI. Verdoporphyrin and degradation of chlorophyll by alkali. A. TREIBS and F. HERRLEIN. **XXXVII. Chlorophyll *b*. III. Proof of the isocyclic ring in chlorophyll *b*.** H. FISCHER, A. HENDSCHEL, and L. NÜSSLER (Annalen, 1933, **506**, 1—19, 83—106).—XXXVI. Reduction (H_2, PtO_2, Et_2O) of verdoporphyrin (I), probably $C_{32}H_{32}O_4N_4$ (cf. A., 1929, 941) (prep. from phæophytin and MeOH–KOH described) [K_2 salt; *dihydrochloride*; *diacetate*; *Me* ester; Me_2 ester, m.p. 280° (corr.) (*hæmin*, sinters at 261°), which has two active H atoms (Zerevitinov)], and oxidation (air) of the resulting leuco-compound gives rhodoporphyrin (II). Verdoporphyrin (III) (A., 1931, 1431) [Me_2 ester, probably $C_{34}H_{36}O_4N_4$, m.p. 276° (corr.)] is often obtained instead of (I) in the above prep.; in two cases, (I) and the unstable allo*porphyrin* (IV), $C_{33}H_{34}O_5N_4$ (?) [Me_2 ester (V), m.p. 269° (corr.)], were isolated. (IV) when heated with C_5H_5N or alkali gives (II). (V) passes gradually into chloroporphyrin e_5. The spontaneous rearrangement of (I) into (II) is not an isomerisation (cf. *loc. cit.*) but a reduction process; (I) often rearranges into (III). (I), (II), and pyrro- and phyllo-porphyrins have been isolated from the products of the alkaline degradation of methylchlorophyllide. Structures are suggested for (I) and chlorin *e*.

XXXVII. Phæophorbide *b* (I) and CH_2N_2 in MeOH–C_5H_5N and N_2 or O_2 give rhodin *g* Me_3 ester (II) (about 50%) and some *chlorin* ester (III), m.p. 191° (contains 3 OMe groups). (III) is also formed to some extent from rhodin *g* (which could not be decarboxylated in C_5H_5N) and MeOH–CH_2N_2. (III) is hydrolysed (22% HCl) to a *chlorin* (IV), $C_{36}H_{38}O_8N_4$, m.p. 209°, which contains 1 OMe and is degraded by boiling $(\cdot CH_2\cdot OH)_2$ to a product resembling chloroporphyrin e_4. Fusion of the Fe salt of (IV) with *m*-$C_6H_4(OH)_2$ gives a substance resembling chloroporphyrin e_6 (V), whilst reduction (HI–AcOH at 60°) of (III) affords a porphyrin, the *Me* ester, $C_{37}H_{42}O_7N_4$, m.p. 240°, of which is spectroscopically identical with (V). (I) and EtOH–diazoethane in N_2 give about 70% of *rhodin* g *Et*$_3$ ester (+$COMe_2$), m.p. 223°. Phæoporphyrin b_6 (VI) [oxime (+H_2O) (*Me* ester, m.p. 229°, by the action of CH_2N_2); *oxime*, m.p. 230°, of Me ester, m.p. 256° (this vol., 839; prepared using MeOH–HCl); *Me* ester, m.p. 277°, using Et_2O–CH_2N_2] and MeOH–CH_2N_2 in N_2 for 24 hr. afford a *porphyrin*, $C_{36}H_{36}O_{6(7)}N_4$, m.p. 273° [also formed by the reduction of the cyanohydrin of (I) with HI (*d* 1·96) at 45°], which is spectroscopically identical with phæoporphyrin a_5; the use of conc. Et_2O–MeOH–CH_2N_2 for 5 days gives a porphyrin, m.p. 237°, spectroscopically identical with (V). (VI) and MeOH–KOH in N_2 afford [after esterification (CH_2N_2)] *rhodinporphyrin* g_7 *Me*$_3$ ester (VII), $C_{37}H_{40}O_7N_4$, m.p. 265° (*oxime*, m.p. 277°), also formed by mild reduction (HI–AcOH at 55°) of (II). Successive treatment of (VI) with HBr–AcOH and MeOH–HCl gives a *Me* ester, $C_{36}H_{38}O_6N_4$, m.p. 259°. The *oxime* of phæoporphyrin b_5 ester has m.p. 230°. The conversion of (VII) into (VI) (as ester, m.p. 277°) by C_5H_5N–Na_2CO_3 and the formation of (II) from (I) show definitely that chlorophyll *b* contains the isocyclic ring (cf. Stoll and Wiedemann, A., 1932, 1266). H. B.

Chemistry of chlorophyll. K. F. ARMSTRONG (Chem. and Ind., 1933, 809—816).—A review.

Fluorescence of the porphyrins. II. H. FINK and W. HOERBURGER (Z. physiol. Chem., 1933, **220**, 123—136; cf. this vol., 959).—p_H–Fluorescence curves were determined for ætioporphyrin I, eight mono- and ten di-carboxylic acids derived from the ætioporphyrins. It is concluded that the porphyrins exist as ampholytes in aq. solution. The fluorescence is due chiefly to dissociated pigment. J. H. B.

Calorimetric determinations with polynuclear pyrrole derivatives. I. Experimental data for porphyrins, chlorins, phæophorbides, and purpurins. A. STERN and G. KLEBS (Annalen, 1933, **505**, 295—306).—Determination of the heat of combustion is a valuable adjunct to elementary analysis in the chlorophyll series, as it indicates the stage of oxidation. The following vals. of Q_v (in kg.-cal.) are recorded: ætioporphyrin I and II, 4304·0, 4310·2; octaethylporphyrin, 4915·0; γ-phylloporphyrin Me ester, 4314·4; pyrroporphyrin XV Me ester, 4150·0; rhodoporphyrin XV and XXI Me_2 esters, 4373·2, 4371·5; verdoporphyrin Me_2 ester, 4283·2, 4298·4; protoporphyrin, 4238·7 (Me_2 ester, 4561·4); mesoporphyrin IX Me_2 ester, 4623·6; coproporphyrin Me_4 ester, 4987·5; *iso*uroporphyrin Me_8 ester, 5741·6; chlorin e_6 Me_3 ester, 4693·3, e_4 Me_2 ester, 4513·0; chloroporphyrin e_6 Me_2 ester, 4684·3, e_5 Me_2 ester, 4411·7 (CH_2N_2), 4486·6 (MeOH–HCl), e_4 *Me*$_2$ ester, 4506·3; chlorin p_6 Me_3 ester, 4461·3; methylphæophorbide *a*, 4524·5; phæoporphyrin a_5 Me_2 ester, 4579·6; pyrrophæophorbide *a* Me ester, 4342·0; phylloerythrin Me ester, 4343·7; deoxophylloerythrin Me ester, 4455·7; methylphæophorbide *b*, 4415·4; dimethylphæopurpurin-7, 4601·0; and phæopurpurin-18 Me ester, 4197·5. H. A. P.

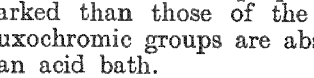
Blue sodium salt of rhodamine-*B* and related substances. W. R. BROWN and F. A. MASON (J.C.S., 1933, 1264—1269).—Attempted alkylation or acylation of the blue Na_2 salt of rhodamine-*B* (I) [the salt could only be obtained by Wacker's method (Z. Farbenind., 1907, 201)] resulted in the immediate regeneration of (I). Blue alkali salts could not be prepared from other rhodamines. 4′-Diethylamino-2′-hydroxy-*o*-benzoylbenzoic acid (II) (improved prep. given) [*Me* ester, m.p. 124°; the Me ether could not be prepared either by direct alkylation or from *m*-$NEt_2\cdot C_6H_4\cdot OMe$ (III), *o*-$C_6H_4(CO)_2O$, and $AlCl_3$] condenses with $NPhMe_2$, $NPhEt_2$ (III), m-*ethoxydiethylaniline* (IV), b.p. 148°/15 mm. (from *m*-$NEt_2\cdot C_6H_4\cdot OH$ and *p*-$C_6H_4Me\cdot SO_3Et$ in aq. NaOH),

and benzylethylanilinesulphonic acid in presence of $POCl_3$ and C_6H_6 or PhMe to give pairs of P-containing substances; one type dissolves in alkali to a green solution, whilst the other gives a violet solution. Acidification of the alkaline solutions of the products from (III) and (IV) gives (I). Condensation of (II) and $NPhEt_2$, $NPhMe_2$, and α-$C_{10}H_7$·NMe_2 with Ac_2O affords 4′ : 4″-*tetraethyldiamino-*, m.p. 136—137°, and 4″-*dimethylamino*-4′-*diethylamino-*, m.p. 130—131°, -2′-*acetoxydiphenylphthalides* and 4″-*dimethylamino*-4′-*diethylamino*-2′-*acetoxyphenyl*-α-*naphthylphthalide*, m.p. 122—123°, respectively; these are hydrolysed (cold EtOH–KOH) to the 2′-OH-derivatives, which are stable and act as indicators of the *ortho*phthalein type. 4′ : 4″-*Tetraethyldiamino*-2′-*acetoxy*-2″-*methoxy-*, m.p. 176—177°, and -2″-*ethoxy-*, m.p. 206—208°, -*diphenylphthalides*, similarly prepared from (II) and (III) and (IV), respectively, are deacetylated and dealkylated by warm EtOH–KOH with the formation of the rhodamine; with cold dil. MeOH–$Ba(OH)_2$, a purple solution is formed (this changes slowly at room temp. and rapidly on warming, to the typical rhodamine red solution). The last observation suggests that von Baeyer's formula for the above blue salt is correct. (II) could not be condensed with *N*-ethylcarbazole, *m*-NO_2·C_6H_4·NMe_2, NHPhAc, *o*-C_6H_4Me·NHEt, and *o*-C_6H_4Me·NEt_2. H. B.

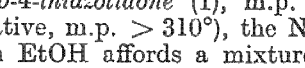
Azine dyes derived from α- and β-naphthathiofuran-1 : 2-diones. P. C. Dutta (Ber., 1933, **66**, [*B*], 1223—1226).—The following *dyes* are prepared by the condensation of α- and β-naphthathiofuran-1 : 2-diones with various *o*-diamines: β-, m.p. 205°, and α-, m.p. 226°, -*naphthathiofuranophenazine*; β-, m.p. 247° after softening at 226°, and α-, m.p. 237°, -*naphthathiofuranonaphthazine*; β-, m.p. 248°, and α-, m.p. 272°, -*naphthathiofuranoacenaphthazine*; β-, m.p. 271°, and α-, m.p. 266°, -*naphthathiofurano*-6-*chloro*-1-*methylphenazine*; β-, m.p. > 295°, and α-, m.p. > 295°, -*naphthathiofuranoquinoxalineazine*; β-, m.p. > 295°, and α-, m.p. > 295°, -*naphthathiofuranophenazineazine*. The size of the mol. has little influence on the depth of colour of these compounds, which is greatly intensified by the introduction of chromophores. The tinctorial properties of the α- are less marked than those of the β-compounds. Although auxochromic groups are absent, they dye wool from an acid bath. H. W.

Alkyl derivatives of mono-substituted thiazolidones. I. F. B. Dains and F. Eberly (J. Amer. Chem. Soc., 1933, **55**, 3859—3862).—*N*-Chloroacet-*p*-bromoanilide (from *p*-C_6H_4Br·NH_2 and CH_2Cl·COCl in $COMe_2$–C_5H_5N) and KCNS in EtOH give 2-p-*bromoanilino*-4-*thiazolidone* (I), m.p. 224° (*o-benzylidene* derivative, m.p. > 310°), the Na salt of which with EtI in EtOH affords a mixture of 2-p-*bromoanilo*-3-*ethyl*-4-*thiazolidone* (II), m.p. 91° [5-*benzylidene* derivative, hydrolysed (acid) to *p*-C_6H_4Br·NH_2 and 2 : 4-*diketo*-*o*-*benzylidene*-3-*ethyltetrahydrothiazole*, m.p. 95·5°], and 2-N-*ethyl*-p-*bromoanilino*-4-*thiazolidone* (III), m.p. 121° [5-*benzylidene* derivative, m.p. 225°, hydrolysed to 2 : 4-diketo-5-benzylidenetetrahydrothiazole (IV); 5-o-*chlorobenzylidene* derivative, m.p. 192°, hydrolysed to 2 : 4-*diketo*-5-o-*chlorobenzylidene*-*tetrahydrothiazole*, m.p. 172°]. (II) is hydrolysed (H_2SO_4) to *p*-C_6H_4Br·NH_2 and NH_2Et and is synthesised from *p*-C_6H_4Br·NH·CS·NHEt and CH_2Cl·COCl in $COMe_2$–C_5H_5N. (III) is hydrolysed by 50% H_2SO_4 to *p*-C_6H_4Br·NHEt (V) (N-*Bz*, m.p. 88°, and *phenylcarbamyl*, m.p. 108°, derivatives), and by 20% NaOH to p-*bromophenylethylcyanamide*, *p*-C_6H_4Br·NEt·CN, m.p. 78°, which is prepared from (V), Br, and KCN. The Na salt of (I) and MeI or Me_2SO_4 give 2-p-*bromoanilo*-3-*methyl*-4-*thiazolidone*, m.p. 111° (5-*benzylidene* derivative, m.p. 166°, hydrolysed to 2 : 4-*diketo*-5-*benzylidene*-3-*methyltetrahydrothiazole*, m.p. 133°), and 2-N-*methyl*-p-*bromoanilino*-4-*thiazolidone*, m.p. 197° [5-*benzylidene* derivative, m.p. 256°, hydrolysed to (IV)]; the latter is hydrolysed (50% H_2SO_4) to *p*-C_6H_4Br·NHMe (N-*Bz*, m.p. 77°, and *phenylcarbamyl* derivative, m.p. 137°). The Na salt of (I) and CH_2PhCl give only 2-N-*benzyl*-p-*bromoanilino*-4-*thiazolidone*, m.p. 153° (5-*benzylidene* derivative, m.p. 192°), which is hydrolysed to N-*benzyl*-p-*bromoaniline*, m.p. 55° (also prepared from *p*-C_6H_4Br·NH_2 and CH_2PhCl). 2-N-*Benzyl*-p-*chloroanilino*-4-*thiazolidone*, m.p. 129°, is similarly obtained from 2-*p*-chloroanilino-4-thiazolidone. The N-*chloroacetyl* derivative, m.p. 184°, of dibromo-*p*-toluidine and KCNS afford 2-(*dibromo*-p-*toluidino*)-4-*thiazolidone*, m.p. 250°, the Na salt of which with MeI gives approx. equal amounts of 2-(*dibromo*-p-*tolylimino*)-3-*methyl*-4-*thiazolidone*, m.p. 132°, and 2-(N-*methyldibromo*-p-*toluidino*)-4-*thiazolidone*, m.p. 194°. The thiazolidones studied correspond with the stable 2-arylamino-derivatives of Wheeler and Johnson (A., 1902, i, 758). The results of the alkylations disprove the formulation of Beckurts and Frerich (A., 1916, i, 744). H. B.

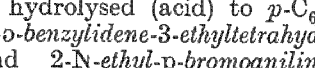
Structure and synthesis of *iso*pilocarpine. II. N. A. Preobrashenski, A. F. Vompe, and V. A. Preobrashenski (Ber., 1933, **66**, [*B*], 1187—1193).—*d*-Homo*iso*pilopic acid, b.p. 160·8°/0·01 mm., $[\alpha]_D$ +50·98°, is converted by $SOCl_2$ at 50—60° into the corresponding chloride, which, by successive action of CH_2N_2 and HCl in Et_2O, is transformed into d-*chloromethyl homoisopilopyl ketone* (I),



, m.p. 72·5—73·5°, $[\alpha]_D^{16\cdot75}$ +71·31° in $C_2H_2Cl_4$. (I) is transformed by K phthalimide in boiling EtOH into d-*phthalimidomethyl homoisopilopyl ketone*, m.p. 121·5—122·5°, $[\alpha]_D^{18}$ +36·87° in $C_2H_2Cl_4$, hydrolysed by boiling 20% HCl to d-*aminomethyl homoisopilopyl ketone hydrochloride* (II), m.p. 158—160°, $[\alpha]_D^{15}$ +57·58° in H_2O. (II) and KCNS in H_2O yield 2-*thiol*-4(5)-d-*homoisopilopyliminazole* (*thiolisopilocarpidine*),

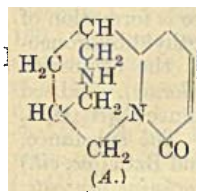


, m.p. 206·5—208° (decomp.), $[\alpha]_D$ +85·36° in MeOH, oxidised by $FeCl_3$ to *iso*pilocarpidine (III),



, isolated as the nitrate, m.p. 112—113·5° (decomp.), $[\alpha]_D^{17}$ +27·63° in H_2O, identical with that obtained by Späth *et al.* (A., 1925, i, 575) from the natural alkaloid. Methylation of (III) leads to *iso*pilocarpine (nitrate, m.p. 158—158·5°, $[\alpha]_D^{14}$ +55·62° in H_2O). H. W.

Constitution of cytisine. E. SPATH and F. GALINOVSKY (Ber., 1933, **66**, [*B*], 1338—1344; cf. A., 1932, 1146; Ing, this vol., 77).—Cytisine (I) is converted by successive electrolytic reduction and acetylation into N-*acetyltetrahydrodeoxycytisine*, m.p. 70—71°, transformed by MeI at 100° into the *methiodide*, m.p. 249—250° (vac.; decomp.). The corresponding quaternary base is subjected to the Hofmann degradation and the product is reduced; repetition of the degradation and reduction followed by a further degradation leads to NMe_3 and a product reduced to 1-*acetyl*-3-*methyl*-5-n-*amylpiperidine* (II). (II) is hydrolysed by fuming HCl at 150° and the product is dehydrogenated (Pd sponge at 180—190°) to 3-*methyl*-5-n-*amylpyridine* (III) (*picrate*, m.p. 145°). Oxidation of (III) with $KMnO_4$ gives 3-methylpyridine-5-carboxylic acid, m.p. 214—216°, with a small amount of pyridine-3 : 5-dicarboxylic acid, m.p. < 300° (decomp.). The *sec.* N of (I) is therefore present in a piperidine ring. Since oxidation of (I) does not afford methylsuccinic or α-methylglutaric acid, whereas in defined circumstances $(\cdot CH_2 \cdot CO_2H)_2$ is produced, (I) is regarded as (*A*). H. W.

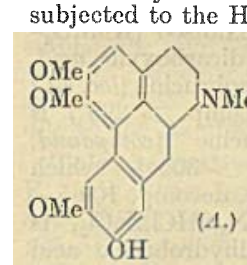


(*A*.)

Hydroxy- and amino-esters of yohimbic acid. D. E. WORRALL (J. Amer. Chem. Soc., 1933, **55**, 3715—3718).—β-*Chloroethyl* (I), m.p. 119—120°, β-*hydroxyethyl*, m.p. 132—135° [O-*sulphate* (II), m.p. 288—289°], γ-*hydroxypropyl*, m.p. 135—138° (*methiodide*), and βγ-*dihydroxypropyl*, m.p. 111—112° (*methiodide*), *yohimbates*, prepared from yohimbic acid (III), the appropriate alcohol, and HCl, are derivatives of the hydrated form of (III); they lose 1 H_2O (in vac. over P_2O_5) which is regained on exposure to air. (II) is hydrolysed (dil. alkali) to the unsaturated β-*hydroxyethyl* apo*yohimbate*, $C_{22}H_{28}O_4N_2$, m.p. 117—118° (*hydrochloride*, m.p. 292—294°). (I) and the appropriate amine give β-*diethylaminoethyl*, m.p. 76—78° (IV) [*dimethiodide*, m.p. 217—218°; *dihydrochloride*, m.p. 198—200° (decomp.)], β-*allylaminoethyl*, m.p. 124—126° [*methiodide*; *dihydrochloride*, m.p. 263—264° (decomp.)], and β-*piperidinoethyl*, m.p. 129—131° [*dimethiodide*, m.p. 218—219°; *dihydrochloride*, m.p. 212—214° (decomp.)], *yohimbates*. Hydrolysis (2% EtOH–KOH) of the product from (IV) and conc. H_2SO_4 gives β-*diethylaminoethyl* apo*yohimbate*, m.p. 80—82° (*dimethiodide*, m.p. 179—180°). H. B.

Structure of cuscohygrine. Synthesis of ethyl homohygrinate. W. E. SOHL and R. L. SHRINER (J. Amer. Chem. Soc., 1933, **55**, 3828—3833).—1-Methylpyrrole, $CHN_2 \cdot CO_2Et$, and Cu-bronze give Et 1-methyl-2-pyrrylacetate, b.p. 115—118°/10 mm., which is reduced (H_2, PtO_2, EtOH–AcOH) to *Et* 1-*methyl*-2-*pyrrolidylacetate*, b.p. 88—89°/10 mm., 78°/6 mm. [*picrate*, m.p. 112—113°; *methiodide*, m.p. 121—122°; *chloroaurate* (+$2H_2O$), m.p. 133—134°]. The latter is identical with Et homohygrinate prepared by esterification (EtOH–HCl) of the acid obtained from cuscohygrine (I), NO, and EtOH–NaOEt using Hess and Fink's method (A., 1920, i, 497). The methylene*di*-*iso*nitroamine isolated by Hess and Fink (*loc. cit.*) does not arise from (I) but from the EtOH. (I) and Br in Ac_2O–AcOH give a *compound*, $C_{13}H_{25}ON_2Br_3$, converted by $COMe_2$ into the dihydrobromide, m.p. 239° (decomp.), of (I). (I) does not give the CHI_3 reaction (*Me* β-*diethylaminoethyl ketone*, b.p. 84°/30 mm., 53°/4 mm., from $NHEt_2$,HCl, aq. CH_2O, and $COMe_2$, gives CHI_3 with NaOI), and does not condense with PhCHO, indicating that it is di-(1-methyl-2-pyrrolidylmethyl) ketone (Liebermann and Cybulski, A., 1895, i, 310) and not Me di-(1-methyl-2-pyrrolidyl)methyl ketone (Hess). H. B.

***N*-Methyl-laurotetanine, a new alkaloid from *Litsea citrata*.** E. SPATH and E. E. SUOMINEN (Ber., 1933, **66**, [*B*], 1344—1348).—The crude bases obtained by extraction of the powdered bark of *Litsea citrata*, Bl., with NH_3–Et_2O are treated with Ac_2O, thus leading to separation of the *sec.* and *tert.* (I) bases. Treatment of (I) with KOH removes *O*-Ac, rendering possible the separation of phenolic (II) from non-phenolic *tert.* bases. Fractional treatment of (II) with HCl leads to separation of a portion (III), b.p. 205—215°/0·01 mm., transformed by CH_2N_2 in MeOH into glaucine in good yield. (III) is treated successively with $CHMeN_2$ and MeI and then subjected to the Hofmann degradation; the resinous methine base thus produced affords a methiodide (IV), m.p. 272—274° (decomp.), identical with that derived from laurotetanine. Degradation of (IV) leads smoothly to 3 : 4 : 6-trimethoxy-7-ethoxy-1-vinylphenanthrene, m.p. 140—141°, oxidised to 3 : 4 : 6-trimethoxy-7-ethoxyphenanthrene-1-carboxylic acid, m.p. 236—237°, which is decarboxylated by Cu powder in quinoline to 3 : 4 : 6-trimethoxy-7-ethoxyphenanthrene, m.p. 114—115°. (III) is therefore mainly *A*. H. W.

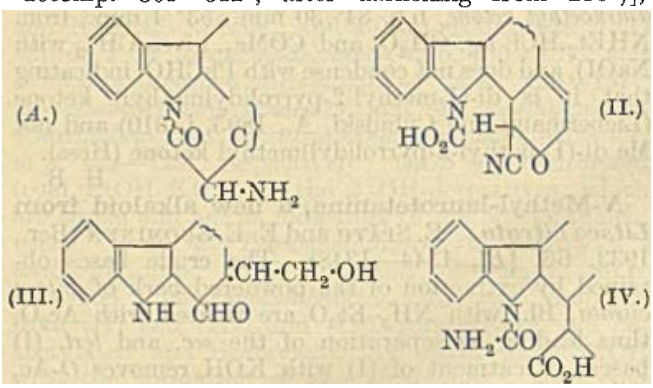


(*A*.)

Successive degradation of α-*iso*cinchonine (cinchoniline) to cinchotoxine derivatives. T. DUBAS, A. KONOPNICKI, and J. SUSZKO (Rocz. Chem., 1933, **13**, 464—472).—The anhyd. sulphate of α-*iso*cinchonine (I) (N-*oxide*, m.p. 152—153°), when heated during 5 hr. at 140° under reduced pressure, yields α-*iso*cinchonicine, m.p. 98—100° [N-*Ac*, m.p. 164—165°, N-*NO*-, m.p. 128—130°, *Br*- (II), m.p. 57—58°, and N-*Me* derivative (III), m.p. 81—82° (*hydriodide*, m.p. 218—220°; *methiodide*, m.p. 229°; *Br*-derivative, m.p. 60°)], which on hydrolysis with 5% HCl at 100° during 5 hr. gives α-hydroxydihydrocinchotoxine, the *Br*-, an oil [*hydrobromide*, m.p. 241° (decomp.)], and N-*Me* derivative, an oil (*methiodide*, m.p. 130°; p-*nitrophenylhydrazone*, m.p. 85—90°; *picrate*, m.p. 211°), of which are obtained analogously by hydrolysis of (II) and (III). The chemical behaviour of (I) is analogous to that of α-*iso*quinidine (IV), and the [α] of various derivatives of (I) and (IV) vary similarly, pointing to the similarity in structure of the two compounds. R. T.

***Strychnos* alkaloids. XIII. Degradation of oximinostrychnine.** H. WIELAND and K. KAZIRO (Annalen, 1933, **506**, 60—76).—Oximinostrychnine (I) (A., 1932, 629) (p-*toluenesulphonyl* derivative,

decomp. > 290°) is reduced ($SnCl_2$, conc. HCl or Zn, $ZnCl_2$, and dil. HCl) to 12-*aminostrychnine* (as *A*), m.p. 83—86° [*dihydrochloride*, becomes brown at 170° and blackens at 250° (1 : 1-*compound* with $ZnCl_2$, decomp. 305—312°, after darkening from 250°)],



which with HNO_2 gives 12-*diazostrychnine*, decomp. 107—108° to 189—190° (according to catalytic effect of impurities). This is converted by warm dil. H_2SO_4 into 12-*hydroxystrychnine* (*A*, >CH·NH_2=>CH·OH), m.p. 205°, reduced (H_2, PtO_2, AcOH) to 12-*hydroxydihydrostrychnine*, m.p. 282—284° (decomp.) (*Br*-derivative, m.p. 290—292°), which is oxidised ($KMnO_4$–$COMe_2$) to a small amount of a dicarboxylic *acid*, $C_{21}H_{24}O_5N_2$, decomp. 296°. Oximinobrucine (*loc. cit.*) (*p-toluenesulphonyl* derivative, decomp. > 290°) is similarly reduced to aminobrucine [*compound*, $C_{23}H_{27}O_4N_3$,2HCl,$ZnCl_2$, decomp. > 300°], which affords the unstable 12-*diazobrucine*, decomp. 100·5—101°. The *compound*, $C_{23}H_{29}O_4N_3$,2HCl,$ZnCl_2$, is prepared similarly from oximinodihydrobrucic acid nitrosoamine (*loc. cit.*).

The hydrochloride of (I) and $SOCl_2$ give (mainly) the *hydrochloride*, decomp. > 300°, of the *carbamic acid* (II), $C_{21}H_{21}O_3N_3$, m.p. 260—263° (decomp.), and the *base*, $C_{20}H_{21}ON_3$ (II, >N·CO_2H=>NH), m.p. 258—259°. (II) is hydrolysed [aq. $Ba(OH)_2$] to CO_2, HCN, and the *aldehydo-base* (III), $C_{19}H_{22}O_2N_2$, m.p. 217°, (+$CHCl_3$) decomp. 135—138°, and then re-solidifies [*hydrochloride*, decomp. about 310°; *methiodide*, m.p. > 300°; *oxime*, decomp. 245°; Ac_2 derivative (*hydrochloride*, m.p. > 300°; *oxime*, decomp. 206—207°)]. (I) and $SOCl_2$ give (II) and the *carbamide* (IV), $C_{21}H_{23}O_4N_3$, decomp. 275—276° (*hydrochloride*, decomp. 270—272°), which is hydrolysed (*N*-NaOH) to *norstrychnic acid*, $C_{20}H_{22}O_3N_2$ (II, where >N·CO_2H=>NH and CN=CO_2H), m.p. 295—296° (decomp.). H. B.

***Strychnos* alkaloids. LXXVI. Methoxymethyldihydroneo-brucidine and -strychnidine. Decahydrogenation of strychnidine.** H. Leuchs, H. Beyer, and H. S. Overberg (Ber., 1933, **66**, [*B*], 1378—1386; cf. this vol., 617).—Hydrogenation (PtO_2) of the ether $C_{25}H_{34}O_4N_2$ (I) (cf. A., 1927, 889) leads only to the H_4-derivative, m.p. 133—135°, $[\alpha]_D^{20}$ −7·6°/*d* in EtOH. The "nitromethoxymethyldihydroneobrucidine" (*loc. cit.*) is *N-methylneobrucidinium nitrate*. Oxidation of (I) with CrO_3 (=15 O) gives methoxymethyldihydroneodiketonucidine (*perchlorate*), whereas oxidation with $KMnO_4$ affords dihydroxymethoxymethyldihydroneobrucidine *Y* form (II), m.p. 184—186°, $[\alpha]_D^{20}$ −20·1°/*d* in EtOH, and *Z* form (III), m.p. 114—117° (decomp.), $[\alpha]_D^{2}$ +54·9°/*d* in EtOH. (III) or (III +II) and CrO_3 give dihydroxymethoxymethylneodihydrodiketonucidine, $C_{19}H_{26}O_6N_2$, m.p. 228—230°, $[\alpha]_D^{21}$ +228·6°/*d* in H_2O [*monoxime*, m.p. 268—271° (decomp.); *monosemicarbazone*, m.p. 272—276° (decomp.), $[\alpha]^{25}$ +240°/*d* in H_2O], hydrogenated (PtO_2 or Clemmensen) to the H_2-derivative, m.p. 227—229°, $[\alpha]_D^{21}$ +99·6°/*d* in H_2O; with $Ba(OH)_2$ and H_2O there is formation of CO_2. Hydrogenation of methoxymethyldihydroneostrychnidine (PtO_2–dil. HCl) affords the *compound* $C_{23}H_{38}O_2N_2$, m.p. 119—120° (*diperchlorate*), oxidised ($KMnO_4$=4 O in $COMe_2$) to the substance $C_{23}H_{36}O_4N_2$ (*perchlorate*, $[\alpha]^{25}$ −59·1°/*d* in H_2O). The substance, m.p. 215—218°, from strychnic acid and BzCl (*loc. cit.*) is not a mixed anhydride, but is *strychnine benzoate*. Hydrogenation of strychnidine (PtO_2–*N*-HCl) gives *decahydrostrychnidine* I, m.p. 264—265°, $[\alpha]_D$ −62·5°/*d* in $CHCl_3$ [*diperchlorate*, decomp. 285—290°, $[\alpha]_D^{24}$ +27·6°/*d*; *dimethiodide*, $[\alpha]^{24}$ +15·3°/*d* in H_2O; O(?)-*Ac* derivative (*diperchlorate*, $[\alpha]^{20}$ +63·4°/*d*)], and *decahydrostrychnidine* II, m.p. 269—271° (vac.), $[\alpha]_D$ +22·6° in $CHCl_3$ (*diperchlorate*, $[\alpha]^{22}$ +21·5°/*d*). *Octahydrostrychnidine dimethiodide* has $[\alpha]_D^{24}$ + 11·5°/*d* in H_2O. H. W.

Colour reactions of strychnine and strychnine nitrate. H. Fujiwara (J. Biochem. Japan, 1933, **18**, 153—162).—Colour reactions of strychnine (I) and its nitrate, brucine, and many other alkaloids, etc. with HCl and H_2SO_4 alone and in presence of Na_2MoO_4 or Na phosphomolybdate are described. A reagent of H_2SO_4–Na_2MoO_4 is sp. for (I). F. O. H.

Catalytic hydrogenation of halogenomorphides. Dihydrodeoxymorphine-*D*. L. F. Small, K. C. Yuen, and L. K. Eilers (J. Amer. Chem. Soc., 1933, **55**, 3863—3870).—Reduction (H_2, Pd–$BaSO_4$, MeOH or dil. HCl) of α- (I) and β-chloromorphides and bromomorphide (II) gives (mainly) *dihydrodeoxymorphine*-D (III), m.p. 188—189°, $[\alpha]_D^{23}$ −76·8° in MeOH [*hemihydrate*, m.p. 162—164° (decomp.), $[\alpha]_D^{28}$ −78·6° in EtOAc] [*hydrochloride*; *hydriodide*; *sulphate* (+2H_2O); *H oxalate*; *salicylate*; *methiodide*], and smaller amounts of tetrahydrodeoxymorphine and oil (IV). (IV) is the main product from (II) in MeOH (not in dil. HCl). (III) is also prepared by reduction (H_2, PtO_2, AcOH) of deoxymorphine-*C* (this vol., 961) and by demethylation of dihydrodeoxycodeine-*D* (A., 1931, 1077) [which is formed by methylation (CH_2N_2) of (III)]. (III) is unaffected by prolonged electrolytic reduction. Electrolytic reduction of (I) or (II) gives *deoxymorphine*-A (V), m.p. 257—258° (decomp.) [*salicylate*, m.p. 248—250° (decomp.)], whilst reduction with Zn–Hg and 6*N*-HCl affords (V) and β-*iso*morphine. Reduction (Sn, conc. HCl) of (I) gives (cf. Schryver and Lees, J.C.S., 1900, **77**, 1024) a small amount of the *hydrochloride*, m.p. 263·5° (decomp.), $[\alpha]_D^{20}$ −78·1° in H_2O, of a non-cryst. base. H. B.

Optical activity of alkaloid salts of geometrically isomeric unsaturated acids. P. Neogi and A. B. Sen-Gupta (J. Indian Chem. Soc., 1933, **10**, 373—381).—Comparison of the sp. rotation (I) (usually in EtOH) of various neutral alkaloid salts

of pairs of *cis*- and *trans*-ethylenic acids shows that, with the exceptions observed by Hilditch (J.C.S., 1908, **61**, 704), the salt of the *cis*-form possesses the higher val.; the relationship is reversed for the amyl esters (Walden, A., 1896, ii, 633). The vals. of (I) decrease with dilution; this may be due to compound formation between the solvent and solute. The following *salts* are described: quinine maleate, m.p. 182—183° (decomp.), fumarate, m.p. 187—188° (decomp.), crotonate, m.p. 136°, *iso*crotonate, m.p. 160—162°, mesaconate, m.p. 215—216° (decomp.), and citraconate, m.p. 96—98°; cinchonidine maleate, m.p. 182° (decomp.), fumarate, m.p. 186° (decomp.), mesaconate, m.p. 216—217° (decomp.), and citraconate, m.p. 173—175° (decomp.); strychnine maleate ($+2H_2O$), m.p. 210° (decomp.), fumarate ($+4H_2O$), m.p. 240° (decomp.), crotonate, m.p. 215—217° (decomp.), *iso*crotonate, m.p. 250—252° (decomp.), mesaconate ($+3H_2O$), m.p. 230° (decomp.), and citraconate ($+2H_2O$), m.p. 185°; quinidine maleate, m.p. 98—99° (decomp.), and fumarate, m.p. 154° (decomp.); brucine mesaconate ($+5H_2O$), m.p. 205—207° (decomp.), and citraconate ($+4H_2O$), m.p. 209—210° (decomp.). H. B.

Arsenated derivatives of phenobarbital [5-phenyl-5-ethylbarbituric acid]. M. T. Bush and J. R. Johnson (J. Amer. Chem. Soc., 1933, **55**, 3894—3895).—5-*m*-Nitrophenyl-5-ethylbarbituric acid (I), m.p. 279—280° (all m.p. are corr.) [the position of the NO_2-group (cf. Bousquet and Adams, A., 1930, 351) is shown by the changes (I) ⟶ *m*-nitrophenylethylmalonic acid ⟶ α-*m*-nitrophenylbutyric acid, m.p. 115·5—116·3°, ⟶ *m*-NO_2·C_6H_4·CO_2H], is reduced to the 5-*m*-aminophenyl derivative (II), which is converted by the method of Bousquet and Adams (*loc. cit.*) into a 5-(nitro-*m*-aminophenyl)-5-ethylbarbituric acid (III), decomp. 330—340°. Elimination of NH_2 from (III) gives a new 5-nitrophenyl-5-ethylbarbituric acid, decomp. 327—330°. (II) and (III) have been converted into the corresponding arsinic acids and thence into the arseno-compounds. H. B.

Optically active arsinic acid possessing molecular dissymmetry. Resolution of *dl-spiro*bis-3 : 5-dioxan-4 : 4′-di(phenyl-*p*-arsinic acid). C. S. Gibson and B. Levin (Proc. Roy. Soc., 1933, **A**, **141**, 494—501).—*p*-CHO·C_6H_4·AsO_3H_2, $C(CH_2·OH)_4$, and 30% H_2SO_4 at 100° (bath) give dl-spiro*bis*-3 : 5-*dioxan*-4 : 4′-*di*(*phenyl*-p-*arsinic acid*) (I),

$AsO_3H_2·C_6H_4·CH\langle^{O·CH_2}_{O·CH}\rangle C\langle^{CH_2·O}_{CH·O}\rangle CH·C_6H_4·AsO_3H_2$-*p*,

undecomposed at 290°, purified through its dl-α-*phenylethylamine* salt, decomp. 204° (previous softening). (I) is resolved using nor-*d*- and -*l*-ψ-ephedrine into the l- (II), undecomp. at 300° (slight previous sintering) (*nor*-d-ψ-*ephedrine* salt, decomp. 225°, $[\alpha]^{20}_{5461}$ −24·67° in H_2O), and d-*acids* (*nor*-l-ψ-*ephedrine* salt, decomp. 225°, $[\alpha]^{20}_{5461}$ +23·69° in H_2O), the Na_4 salts of which have $[\alpha]^{20}_{5461}$ −70·6° and +69·74° in H_2O, respectively. (II) is not racemised by boiling with an excess of aq. NaOH, but with SO_2, EtOH–conc. HCl, and a little I gives dl-spiro*bis*-3 : 5-*dioxan*-4 : 4′-*di*(*phenyl*-p-*dichloroarsine*) (III), m.p. 163°, which is oxidised (H_2O_2, aq. NaOH) to (I). It is suggested that the production of (III) may involve the opening (and subsequent re-closure) of the dioxan rings, thus accounting for the racemisation. H. B.

Hydroxy-derivatives of 10-alkyl(aryl)-9 : 10-dihydrophenarsazine. G. A. Razuvaiev and V. S. Malinovski (J. Appl. Chem. Russ., 1933, **6**, 669—676).—The following compounds have been prepared from the dihydroxides (I) of 10-alkyl- and from the oxide (II) of 10-phenyl-9 : 10-dihydrophenarsazine: *tribromo*-, m.p. 271—272°, and 3-*nitro*-10-*methyl*-, m.p. 154—155° (decomp.); *tetrabromo*-, m.p. 219—221°, and *nitro*-10-*phenyl*-, m.p. 139—141° (decomp.); *nitro*-10-*ethyl*-, m.p. 134—136° (decomp.), -10-*propyl*-, m.p. 147° (decomp.), and -10-iso*amyl*-9 : 10-*dihydrophenarsazine*, m.p. 146—147°. The above NO_2-derivatives regenerate (I) or (II) on reduction with $Fe(OH)_2$, Fe and $FeCl_3$, or $NaHSO_3$, and on treatment with alkalis. (I) and (II), on reduction with SO_2, yield the corresponding 10-alkyl(phenyl)-9 : 10-dihydrophenarsazines, together with $NHPh_2$ and the appropriate alkyl- or phenyl-arsine oxides. R. T.

Evidence for an asymmetrical tervalent arsenic atom. C. F. H. Allen and F. B. Wells (J. Amer. Chem. Soc., 1933, **55**, 3894).—7-Chloro-7 : 12-dihydrobenzophenarsazine and Ag *d*-bromocamphorsulphonate give two "dimerides," [α] +35·11° and +59·52°, whence [α] (calc. for As radical) −24·68° and +22·65°, respectively. The activity may be due to the As atom. H. B.

Tolyl derivatives of germanium. J. K. Simons, E. C. Wagner, and J. H. Müller (J. Amer. Chem. Soc., 1933, **55**, 3705—3712).—*Ge tetra*-o- (I), m.p. 175—176° (all m.p. are corr.), -m- (II), m.p. 146°, and -p- (III), m.p. 227° (229° on the Dennis m.p. bar), *-tolyls* are prepared from $GeCl_4$ and the product from $C_6H_4Me·MgBr$ and $ZnCl_2$ in PhMe or xylene (cf. Kraus and Foster, A., 1927, 268). *Ge triphenyl* m-*tolyl*, m.p. 136·5—138·5°, is similarly obtained from $GePh_3Br$ and *m*-$C_6H_4Me·MgBr$. $GeCl_4$ and *p*-$C_6H_4Me·MgBr$ give Ge tri-*p*-tolyl bromide (IV), m.p. 130°, and a little (III). *Ge tri*-m-*tolyl chloride*, m.p. 84—85°, is isolated in a slightly impure state from the mother-liquors from the prep. of (II); the *bromide*, b.p. 222—223°/1 mm., m.p. 78—78·9°, is prepared from (II) and Br in CCl_4. (I) and Br in CCl_4 give Ge tri-*o*-tolyl bromide, b.p. 205—210°/1 mm.; the crude *chloride*, b.p. 216—222°/1 mm. [from the mother-liquors from the prep. of (I)], and an excess of EtOH–$AgNO_3$ afford *Ge tri*-o-*tolyl hydroxide*, b.p. 212—214°/1 mm. *Ge tri*-m- and -p-*tolyl oxides* have m.p. 125—125·2° and 147—148°, respectively. Excess of HBr passed through $GePh_4$ in $CHCl_3$ at room temp. gives $GePh_3Br$; (IV) is obtained similarly from (III). H. B.

Mono- and di-substituted organo-mercury derivatives of acetylene. R. J. Spahr, R. R. Vogt, and J. A. Nieuwland (J. Amer. Chem. Soc., 1933, **55**, 3728—3731).—*Di*-(*alkyl*- and *-aryl-mercuri*)-*acetylides*, $(:C·Hg·R)_2$, where R is *Pr*$^{\beta}$, m.p. 110·5—111·5°, sec.-*Bu*, m.p. 105·5—106°, iso*amyl*, m.p. 106—107°, cyclo*hexyl*, m.p. 172—173°, β-*methoxyethyl*, m.p. 129·5—130·5° (decomp.), p-*aminophenyl*, m.p. 188—190° (decomp.), and o-*nitrophenyl*, ex-

plodes > 300°, are prepared by the method previously described (this vol., 815) using 10% EtOH–KOH instead of aq. KOH. The alkali acts as a catalyst. The extent of the reaction $(:C\cdot Hg\cdot R)_2$ (I) $+C_2H_2 \longrightarrow 2CH{:}C\cdot Hg\,R$ depends primarily on the solubility of the (I). Δ^{α}-Heptinene and $HgPr^{\beta}Br$ in 10% EtOH–KOH give *α-isopropylmercuri-Δ^{α}-heptinene*. Di-(*o*-hydroxyphenylmercuri)acetylide could not be prepared. H. B.

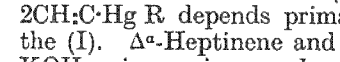
Preparation of aryl derivatives of mercuric oxide by means of aromatic iodo-compounds. A. N. Nesmejanov and L. G. Makarov (J. Gen. Chem. Russ., 1933, **3**, 257—261).—The possibility of preparing aromatic Hg derivatives by the action of aromatic I-derivatives on HgO in presence of alkali hydroxides or freshly pptd. Ag_2O according to a reaction analogous to Meyer's synthesis of iodonium bases was investigated. PhI, *p*-C_6H_4MeI, *o*-, *m*-, and *p*-C_6H_4ClI, *o*-, *m*-, and *p*-$NO_2\cdot C_6H_4I$, were used and in each case the corresponding Hg derivatives obtained. The advantage of this method lies in the ease with which any salt of the derivatives can be prepared by simple pptn. with the corresponding anion. M. Z.

Catalytic decomposition of organo-metallic compounds. II. G. A. Razuvaiev and M. M. Koton. **III. Catalytic decomposition of organic compounds of lead and tin.** M. M. Koton (Ber., 1933, **66**, [*B*], 1210—1213, 1213—1215; cf. this vol., 730).—II. Study of the catalytic decomp. of *p*-substituted derivatives of $HgPh_2$ in presence of Pd leads to the sequence, $1\text{-}C_{10}H_7\cdot < C_6H_4Me < C_6H_4Br < C_6H_4\cdot OEt < C_6H_4\cdot OMe < Ph < CH_2Ph$, which differs from that of Kharasch (A., 1932, 409) for the action of HCl on *as.* Hg derivatives. The products are Hg and the Ph_2 derivatives except in the case of $Hg(C_{10}H_7\text{-}1)_2$ (I), which yields $C_{10}H_8$, H being derived from a second $C_{10}H_7$. The order of catalytic activity towards $HgPh_2$ is Pd>Ni>Au>Ag>Cu in EtOH and Pd>Au>Ag>Ni>Cu in tetrahydronaphthalene (II). In EtOH the products are of the type R·R except in the case of (I), whereas in (II) they are of the type RH.

III. The temp. of decomp. of $PbPh_4$ with and without H_2 pressure is lowered by metals in the sequences Pd>Ni>Au>Ag>Cu and Pd>Au>Ag>Ni, respectively. The similar series for $SnPh_4$ are Pd>Ni>Ag>Au>Cu and Pd>Ag>Au>Ni. Decomp. occurs according to $RPh_3+2H_2=4C_6H_6+R$ (I) and $RPh_4=2Ph_2+R$ (II). Under H_2 pressure in presence of Ni and Pd, respectively, reaction occurs exclusively in accordance with (I) and (II). In absence of H_2 reaction (II) takes place solely. In EtOH reaction (II) is catalysed by metals in the sequences Pd>Au>Ag>Ni for $PbPh_4$ and Pd>Ag>Ni>Au for $SnPh_4$. H. W.

Free phenyl radicals in the gas phase. M. F. Dull and J. H. Simons (J. Amer. Chem. Soc., 1933, **55**, 3898).—When $PbPh_4$ is heated at 215—220°/0·01 mm. using the method previously described (this vol., 930), a little $HgPh_2$ is produced presumably owing to the formation of free Ph radicals. H. B.

Monoarylguanidines. IV. Benzoselenazolylguanidine. G. B. L. Smith, J. P. Miale, and C. W. Mason (J. Amer. Chem. Soc., 1933, **55**, 3759—3762). —*o*-$NH_2\cdot C_6H_4\cdot SeH$ [as Zn salt, prepared by reduction (Zn, AcOH) of $(o\text{-}NO_2\cdot C_6H_4\cdot Se\cdot)_2$] and dicyanodiamidine in aq. HCl give the *hydrochloride*, m.p. 247—249°, of *benzoselenazolylguanidine* (I), *o*-



m.p. 198—200° (*nitrate*, m.p. 193—198°; *sulphate*, m.p. 287—289°; *picrate*, m.p. 267—270°). Crystallographic data are given. Potentiometric titration shows that (I) is a weak base and thus resembles its analogues (A., 1929, 1186; 1932, 176). H. B.

Synthesis of metallo-organic compounds of titanium. G. A. Razuvaiev and I. F. Bogdanov (J. Gen. Chem. Russ., 1933, **3**, 367—368).—Unsuccessful attempts were made to synthesise the organo-metallic derivatives of Ti by the action of $TiCl_4$ on $HgPh_2$, on a mixture of Na and PhCl, and on Grignard's reagent in the absence of a solvent. M. Z.

Constitution of casein. M. L. Demanez (Compt. rend. Soc. Biol., 1933, **112**, 1561—1562).—The two casein fractions separated by differential solubility in acid–EtOH behaved similarly in the precipitin test. Nutr. Abs. (*b*)

Proteins. X. Silk fibroin. II. Action of hypobromite on silk. S. Goldschmidt, K. Martin, and W. Heidinger. **III. Action of hydrochloric acid on silk.** S. Goldschmidt, G. Freyss, and K. Strauss (Annalen, 1933, **505**, 255—261, 262—273; cf. A., 1930, 940).—II. The action of alkaline KOBr on silk does not vary with its origin except in the case of Tussah, which differs in composition from true silk. Attack is very rapid at first, but soon lessens; after 8—10 min. the composition of the insol. cryst. decomp. product remains unchanged, and glycine (I) and alanine (II) in the const. mol. ratio 1 : 1·7—1·75 are then the sole hydrolysis products. The presence of polycarboxyamino-acids was not detected.

III. With 5*N*-HCl silk gives a cryst. decomp. product of const. composition, giving on hydrolysis (I), (II), and tyrosine (III) in the mol. ratio 1 : 1·7 : 0·13. This is further decomposed by trypsin to (III) and an amorphous substance of high mol. wt., insol. in H_2O, dil. acids, and alkalis, but sol. in conc. HCl. The KOBr product is also decomposed by trypsin, but silk is unaffected. (III) and its Bz derivatives are destroyed by NaOBr. From the composition and *X*-ray examination of the cryst. decomp. products it is concluded that the polypeptide chains are composed of individual NH_2-acids. H. A. P.

Water content and rate of heat denaturation of crystallisable ovalbumin. H. A. Barker (J. Gen. Physiol., 1933, **17**, 21—34).—Ovalbumin (I) dried over P_2O_5 is equilibrated with saturated salt solutions of different v.p. The temp. of denaturation of (I) is approx. a linear function of the relative humidity (II). The log. of relative velocity of denaturation varies linearly with (II). Heat-denatured (I) takes up approx. 80% as much H_2O at a given v.p. as native crystallisable (I). H. D.

Labile sulphur in proteins. H. Zahnd and H. T. Clarke (J. Biol. Chem., 1933, **102**, 171—186;

cf. A., 1931, 26).—Determination of cystine- (I) -labile S by reduction with $SnCl_2$ to cysteine (II), oxidation with Br and HCl, and subsequent determination of SO_4'' as $BaSO_4$ gave vals. lying between 97 and 107% of the calc. amounts. Vals. obtained for casein, gelatin, cottonseed globulin, zein, edestin, ovalbumin (III), fibrin, and horse hæmoglobin were compared with those in lit. In (III) the labile S val. is considerably > the cystine-S val. by the Folin–Looney (A., 1922, ii, 539) procedure and somewhat > by Sullivan's (A., 1930, 1604). (I) is extracted to a small extent by BuOH from HCl but not from H_2SO_4. (II) is extracted to 50%. Colorimetric determination of (II) in the aq. and BuOH solutions fails to give complete recovery. With (I) this applies to the Sullivan procedure only. On prolonged extraction of a neutral hydrolysate of (III) with BuOH, >70% of the total S passes into the BuOH. From labile S and colorimetric (I) determinations it is shown that all the labile S (15% of the total) is in the (I) form. The aq. solution contains 22% of the original S. Approx. 66% of this is labile, of which only 25% is in the (I) form. 25% of the S in the $COMe_2$-insol. fraction of the benzoylated hydrolysate of (III) was labile, but reacted negatively to the Folin test, showing the absence of ·S·S· or ·SH. H. D.

Nucleoproteins. III. Methods. S. J. von Przylecki (Biochem. Z., 1933, **264**, 334—347).—The methods in general use for investigation of nucleoproteins are discussed and the difficulties encountered in carrying them out are emphasised in a series of experiments dealing with the influence of salts on the solubility of nucleoglobin at p_H > isoelectric point, the influence of the protein component on the solubility of nuclein in presence of acids and salts, the changes induced by repeated dissolution and pptn., the production of mixed ppts., etc. P. W. C.

Nucleic acid in sake press cake and in beer yeast. M. Kimura (J. Soc. Chem. Ind. Japan, 1933, **36**, 50—51B).—Nucleic acid from sake press cake contains 12·77% N, 4·82% P; that from yeast has 12·40% N, 5·6% P. Both contain pentose groups. The former on hydrolysis gives guanine, adenine, cytosine, and uracil, and is essentially the same as that from yeast. H. A. P.

Microbomb for determination of organic halogens. F. E. Beamish (Ind. Eng. Chem. [Anal.], 1933, **5**, 348—349). E. C. S.

Cause of error in the determination of iodine in organic substances poor in carbon by fusion with potassium hydroxide. A. Guerbet (J. Pharm. Chim., 1933, [viii], **18**, 262—263).—The fusion of org. substances such as $CHI_2·SO_3Na$ with KOH produces KIO_3 which, if present in excessive amounts (*i.e.*, with an I equiv. > one sixth of the total I), partly escapes the action of HNO_2. If acidification of the aq. extract of the melt yields free I, Na_2SO_3 must be added until free I is no longer present. F. O. H.

Determination of phosphorus and arsenic in organic compounds by means of the bomb calorimeter. F. Garelli (Chim. et Ind., 1933, **29**, Spec. no., 262—263).—For determination of P, a small quantity of the substance is placed, with 0·2—0·4 c.c. of PhMe or decahydronaphthalene, in a stainless steel bomb containing 10 c.c. of H_2O; after combustion the P is pptd. as $MgNH_4PO_4$. In the case of As, dil. aq. NH_3 is used in the calorimeter, and the bomb is washed several times with 2*N*-NaOH and with H_2O after combustion; the As is determined as $Mg_2As_2O_7$. J. W. S.

Condensation of furan compounds. II. Coloured derivatives of the furylidene series, and a method of determining small quantities of acetone based on them. V. V. Tschelincev and E. K. Nikitin (J. Gen. Chem. Russ., 1933, **3**, 319—328).—A new and accurate colorimetric method of determining $COMe_2$, in concns. as low as 0·0001%, is described. $COMe_2$ when treated with a 2½—3-fold excess of furfuraldehyde gives difurfurylideneacetone, m.p. 61°, which develops a characteristic reddish-violet colour in H_2SO_4 solution. This reaction is sp. and is not given by any other aldehyde or keto-compound. M. Z.

Micro-determination of acetyl, benzoyl, and *C*-methyl groups. R. Kuhn and H. Roth (Ber., 1933, **66**, [*B*], 1274—1278).—An apparatus is described for the determination of *O*- or *N*-Ac or -*Bz* by alkaline or acid hydrolysis or of *C*-Me by oxidation with CrO_3 (cf. Kuhn *et al.*, A., 1931, 1437) AcOH or BzOH formed is distilled under atm. pressure and titrated with 0·01*N*-NaOH is presence of phenolphthalein. H. W.

Application of the method of Hagedorn and Jensen to the determination of other sugars. W. Weise and T. von Brand (Biochem. Z., 1933, **264**, 357—360).—Extension of the Hagedorn–Jensen method to determinations of *l*-arabinose, *l*-xylose, *d*-galactose, *l*-mannose, *d*-fructose, maltose, and lactose is described. P. W. C.

Application of volumetric methods to the study of non-aqueous cystine solutions. T. F. Lavine and G. Toennies (Amer. J. Med. Sci., 1933, **185**, 302).—NaOMe is used as the base, thymol-blue as indicator, and $CHCl_3$ as diluent for MeCN solutions of cystine perchlorate. Ch. Abs.

Gravimetric determination of phenols as "aristols." M. François and (Mlle.) L. Seguin (Bull. Soc. chim., 1933, [iv], **53**, 711—723; cf. A., 1931, 1438).—Treatment of guaiacol (I) (in glycerol and aq. NaOH) with an excess of I (in aq. KI and Na_2SO_4) gives an "aristol" of the (probable) composition $[C_6H_2I(OH)(OMe)]_2,C_6H_4(OMe)·OH$; isolation of this affords a method for the determination of (I). α- and β-$C_{10}H_7·OH$ similarly give "aristols" of the (probable) composition $(C_{10}H_6OI)_2,C_{10}H_8O$. Determination of guaiacol carbonate is effected by treatment with conc. aq. NH_3 in EtOH [whereby (I) and $CO(NH_2)_2$ result] and evaporation of the excess of NH_3; the (I) is then treated as above. β-$C_{10}H_7·OBz$ and β-$C_{10}H_7$ salicylate are first hydrolysed by NaOH. Full details are given. H. B.

Colorimetric determination of acetylsalicylic acid. G. Deniges (Bull. Trav. Soc. Pharm. Bordeaux, 1932, **70**, 182—183; Chem. Zentr., 1933, i, 1661).—Acetylsalicylic acid (approx. 5 mg.) is treated with aq. NH_3 (3—4 drops), H_2O (5 c.c.), 1% aq. $CuSO_4,5H_2O$ (2 drops), and then 3% H_2O_2 (3—4

drops); an orange-red colour is produced. After boiling and adding 4 drops of 3% H_2O_2 a more intense dark brown colour appears. Either can be used for the colorimetric determination. As a control the sample is boiled for < 30 sec. with modified Millon's reagent, formation of a ppt. being avoided by addition of 0·25 vol. of AcOH. A. A. E.

Microchemical detection of coumarin. M. Wagenaar (Pharm. Weekblad, 1933, **70**, 1007—1011).—Coumarin may be detected microchemically by sublimation, pptn. by acid from a solution in alkali (1 : 500), or better (sensitivity 1 : 1000), as the dichroic "periodide" (I in KI) or the anisotropic mercurichloride. The formation of an insol. Tl salt is not a satisfactory microchemical method. S. C.

Determination of pyridine bases in the presence of ammonia. F. H. Rhodes and K. R. Younger (Ind. Eng. Chem. [Anal.], 1933, **5**, 302—304).—C_5H_5N and quinoline, but not their homologues, can be titrated potentiometrically in presence of NH_4 salts (I). To remove (I), the material, made alkaline with NaOH, is extracted five times with xylene, which is then extracted six times with 10% HCl, and the small quantity of NH_3 in the extract is oxidised with NaOBr and NaOH. The bases are distilled into 2*N*-HCl, and determined by potentiometric titration. The bases extracted from a sample of bath liquor of a by-product coke-oven plant contained approx. 50% of C_5H_5N, and approx. 25% of picolines. E. C. S.

Determination of hordenine as silicotungstate. M. M. Janot and P. Faudemay (Bull. Sci. pharmacol., 1932, **39**, 288—293; Chem. Zentr., 1933, i, 1486—1487).—The compound $4C_{10}H_5ON,12WO_3,Si(OH)_4,2H_2O$, is pptd. in the cold in presence of Na_2SO_4. The accuracy is ±1%. A. A. E.

Identification of cocaine and novocaine. C. C. Fulton (Amer. J. Pharm., 1933, **105**, 326—339, 374—380).—The sensitivity of the pptn. tests for these substances, the nature of the ppt. obtained (when cryst.), tests for their identification in presence of each other, and methods of separation are described. R. S. C.

Detection of phosphatides. W. Diemair, A. Schloemer, and K. Täufel (Z. physiol. Chem., 1933, **220**, 86—88).—Various so-called tests are not sp. for phosphatides. J. H. B.

Biochemistry.

Apparatus for graphical recording of oxygen consumption and carbon dioxide elimination. G. Mansfeld (Klin. Woch., 1933, **12**, 668—671; cf. A., 1932, 955).—Modified apparatus is described. Nutr. Abs.

Nature of oxygen linking in oxyhæmoglobin. R. D. Barnard (Proc. Soc. Exp. Biol. Med., 1932, **20**, 43—44).—Tests for H_2O_2 give negative results. The peroxide formula is rejected in favour of an ozonic linking. Ch. Abs.

Crystallised synthetic carboxyhæmoglobin. A. Herzog (Biochem. Z., 1933, **264**, 431—433).—The method of crystallising is described. P. W. C.

Prosthetic group of blood-pigment, its isolation in crystalline form, and its conversion with native globin into hæmoglobin. A. Herzog (Biochem. Z., 1933, **264**, 412—430).—The prep. of *hæmoprosthetin*, $C_{33}H_{31}O_4N_4Fe$ (I), from hæmin, oxy- and carboxy-hæmoglobin is described. (I) by treatment with NaCl, AcOH, and MeOH gives Teichmann's crystals and by coupling with native globin gives various modifications of hæmoglobin, the absorption curves of which correspond with those of the natural modifications. (I), and not hæmatin, $C_{34}H_{33}O_5N_4Fe$, is the prosthetic group of blood-pigment, the thirty-fourth C of the latter being introduced during its prep. It follows that hæmin has 34, hæmato-, meso-, proto-, and hæmo-porphyrins and the corresponding hæms have 33, whilst ætioporphyrin and ætiohæm have 31 C atoms per mol. (cf. this vol., 622). P. W. C.

Sensitising action of synthetic porphyrins. W. Hausmann and F. M. Kuen (Biochem. Z., 1933, **265**, 105—109; cf. A., 1911, ii, 138; 1917, i, 69; 1932, 1284).—Since synthetic meso- (I), *iso*uro- (II), and copro-porphyrin (III) act photodynamically on blood-agar the action is to be ascribed to the substances themselves, and not to impurities. In the ultra-violet the action of (I) is very pronounced. (II) and (III) have a feeble effect in the region near λ 365 mμ and only an extremely slight effect in visible light. The sensitising effect of hæmatoporphyrin in visible light is destroyed by serum. W. McC.

Physico-chemical properties of hæmocyanins. J. Roche and P. Dubouloz (Bull. Soc. Chim. biol., 1933, **15**, 954—968).—The absorption curves of the oxyhæmocyanins from the octopus (I), the snail (II), and the crab (III) are similar, but unlike oxyhæmoglobulin, each show two bands having max. at 3450 and 2780 Å. Reduction causes a marked decrease in the absorption between 4000 and 3000 Å. The absorption spectra of the Cu complexes [hæmocuprin (IV)] from (I), (II), and (III) separated by the method of Schnitz (A., 1931, 753) are identical. The hæmocyanins are considered as being composed of (IV) (which is responsible for the absorption between 4000 and 3000 Å.) combined with a protein the constitution of which varies according to the hæmocyanin. A. L.

Histone of bird erythrocytes. T. Leipert and E. Leberl (Biochem. Z., 1933, **265**, 115—123).—In the histone hydrochloride obtained from the picrate 45·1% of the total N is basic and is distributed thus: arginine (guanidine group free) 25·02; histidine (NH free) 3·03; lysine (one NH_2 free) 17·05%. Of every 100 N atoms 4·28 are present as $CO{\cdot}NH_2$, whilst 8·37 react with HNO_2. Titration by the methods of Sørensen and Willstatter indicates 10·05—10·15 basic groups (I), but the Cl content indicates 17·37 preformed (I). Methylation products contain 0·27—1·7% OMe and 3·66—5·27% NMe. W. McC.

Determination of amino-acids and peptones in blood-serum. E. CHERBULIEZ and I. TRUSFUS (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 154—155).—NH_2-acids and peptones in blood-serum are determined by addition of solid and saturated aq. $(NH_4)_2SO_4$, filtration from pptd. proteins, addition of a 1% solution of triketohydrindene, boiling, extraction of the ppt. with amyl alcohol, removal of extraneous colouring matter by 0·5% NaOH, and colour-matching of the resulting alcoholic solution against a standard glycine solution. R. S. C.

Colorimetric determination of plasma-proteins. M. ANDERSCH and R. B. GIBSON (J. Lab. Clin. Med., 1933, **18**, 816—820).—The colour produced by Folin and Wu's phenol reagent is intensified if the solutions are first heated for 0·5 hr. at 100°. CH. ABS.

Determination of protein in serum. R. S. HUBBARD and G. E. SLY (J. Lab. Clin. Med., 1933, **18**, 946—949).—A further modification of the author's micro-Kjeldahl method for determining proteins in blood-serum, based on the separation of albumin and globulin as recommended by Howe. The solutions containing the proteins are oxidised with the acid oxidising reagent of Folin and Wu and the NH_3 is nesslerised in the presence of K Na tartrate. The error is $\pm$1·6%. NUTR. ABS. (*m*)

Biological effects of high pressures. Effects of very high pressures on proteins. J. BASSET, M. MACHEBŒUF, and G. SANDOR (Compt. rend., 1933, **197**, 796—798).—When blood-serum (horse) is submitted to increasing high pressure for 30 min., opalescence is observed at 5000, increased viscosity at 9000, and complete coagulation at 13,000 atm. Separate examination at p_H 7·2 of isotonic solutions of the serum-globulins and -albumins shows that only the former are coagulated by pressure. Electrometric titration shows that the buffering power of the globulins is unchanged by pressure, whence it is suggested that the observed effects are physical and are due to an irreversible dehydration or modification of the spatial arrangement of the peptide chains. J. W. B.

Simplified colorimetric determination of blood-urea clearance. D. D. VAN SLYKE and C. L. COPE (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1169—1174).—The urea in blood and dil. urine is converted into NH_3 with urease; proteins and other interfering substances are removed, and the NH_3 is determined colorimetrically. CH. ABS.

Simultaneous determination of blood-carbon dioxide capacity and -urea-nitrogen. W. Z. FRADKIN and J. SIEGEL (J. Lab. Clin. Med., 1933, **18**, 949—954).—After liberation of CO_2 from serum by acid phosphate urease is added. An apparatus is described. CH. ABS.

Blood-uric acid and uric acid excretion on different diets. W. VON MORACZEWSKI, S. GRZYCKI, H. JANKOWSKI, and R. SLIWINSKI (Klin. Woch., 1933, **12**, 738—741; cf. A., 1932, 772).—Blood-Ca is lowered by nuclein (I) when given with a protein- or fat-rich diet. Ingestion of caseinogen increased uric acid (II) production with retention or increased tolerance; this increase was reduced by (I). Diets high in carbohydrate or fat showed the lowest vals. for blood-(II). (I) with these diets increased both blood- and urine-(II). NUTR. ABS.

Lipins of normal [human] plasma. G. G. VILLELA and C. SILVA (Mem. Inst. Oswaldo Cruz, 1933, **27**, 1—15).—Vals. are (mg. per 100 c.c.): lecithin 182; fatty acids (men) 314, (women) 350; cholesterol 151, 194. CH. ABS.

Comparison of the methods of Kanner and Grigaut for determination of free cholesterol of serum. O. KANNER and M. CHANCOGNE (Compt. rend. Soc. Biol., 1933, **113**, 57—59).—Grigaut's criticisms are rebutted and errors in his method, leading to too high results, are pointed out. NUTR. ABS. (*m*)

Micro-extractor for determination of cholesterol in blood. G. G. VILLELA (Mem. Inst. Oswaldo Cruz, 1933, **27**, 17—20).—A modified apparatus for Meyer's method is described. NUTR. ABS. (*m*)

Hyperglycæmia in the normal dog. Free sugar. Protein-bound sugar. F. RATHERY and I. COSMULESCO (Compt. rend. Soc. Biol., 1933, **113**, 248—250, 250—253).—The hyperglycæmic response of different dogs to the administration of similar amounts of glucose is very variable; there is little correlation between the changes in free and "protein-bound" sugar. NUTR. ABS. (*m*)

Use of Somogyi's filtrate to increase the specificity of the gasometric blood-sugar method. D. D. VAN SLYKE and V. H. KUGEL (J. Biol. Chem., 1933, **102**, 51—55).—When the gasometric method is applied to Somogyi's $ZnSO_4$ blood-filtrate (A., 1930, 801), it yields results of the same type as the Benedict (A., 1925, i, 994) and Folin (A., 1928, 786) methods. H. G. R.

Determination of lactic and pyruvic acids [in blood]. W. B. WENDEL (J. Biol. Chem., 1933, **102**, 47—50).—The method of Friedemann *et al.* (A., 1927, 800) has been modified for use with small quantities of blood. H. G. R.

Variations in certain constituents of the blood of relatively normal individuals. E. M. GREISHEIMER and F. P. ARNY (J. Lab. Clin. Med., 1933, **18**, 680—683).—Average fasting vals. are (mg. per 100 c.c.): glucose 84·01$\pm$0·33, serum-Ca 10·591$\pm$0·016, inorg. PO_4 3·419$\pm$0·020, serum-Cl 577·06$\pm$0·72, urea-N 13·53$\pm$0·13, total non-protein-N (men) 34·87$\pm$0·23, (women) 32·90$\pm$0·26, uric acid (men) 3·417 0·034, (women) 3·070$\pm$0·029. CH. ABS.

Colorimetric determination of the hydrogen-ion concentration of the blood. V. C. MEYERS, E. MUNTWYLER, D. BINNS, and W. H. DANIELSON (J. Biol. Chem., 1933, **102**, 19—28).—With increasing CO_2 tension and with decreasing protein concn., the p_{H_c} 20—38° correction (I) decreases. Colorimetric (I) for human plasma has an average of 0·30 p_H. H. G. R.

Determination of the uncombined water in blood-corpuscles. M. A. SLAWINSKI (Bull. Soc. Chim. biol., 1933, **15**, 982—991).—The author's method of determining suspension concns. (A., 1929,

1142) is applied to blood, and the vol. of free H_2O in the corpuscles of horse blood is found to be 51%. A. L.

Determination of total base of serum. W. S. HOFFMAN (Proc. Soc. Exp. Biol. Med., 1933, **30**, 834—838).—The author's method for urine is modified so that the total base in 1 c.c. of serum can be determined. NUTR. ABS. (*m.*)

Iron in human blood. A. SACHS, V. E. LEVINE, and A. APPELSIS (Arch. Int. Med., 1933, **52**, 366—377).—The Fe content of whole blood is $50{\cdot}01 \pm 2{\cdot}56$ and $42{\cdot}67 \pm 2{\cdot}13$ mg. per 100 c.c. for men and women, respectively. The error in calculating the hæmoglobin from blood-Fe is negligible and both the Fe- and the Fe-colour-indices are preferable to the colour- and the hæmoglobin-colour-indices. H. G. R.

Seasonal variations in the serum-calcium of rabbits. S. HERMANN and M. ZENTNER (Arch. exp. Path. Pharm., 1933, **172**, 5—9; cf. A., 1932, 81).—The ratio of total to free Ca (Ca quotient) in rabbit's serum has a max. val. in winter and a min. val. in spring. The total Ca follows a parallel course. F. O. H.

Determination of chlorides in blood. J. W. CAVETT and C. E. HOLDRIDGE (J. Lab. Clin. Med., 1933, **18**, 944—946).—Cl' in blood and plasma is determined by direct titration with $Hg(NO_3)_2$ of the Folin–Wu filtrate, using Na nitroprusside as indicator. NUTR. ABS. (*m.*)

Electrometric determination of halogens [in serum].—See this vol., 1132.

Non-solvent space of serum and bound chlorine of serum-protein. A. HAYASIDA (J. Biochem. Japan, 1933, **18**, 107—124).—Determinations of the $[Cl']$ and total Cl content of serum (I) indicate that the non-solvent space (II) (cf. A., 1920, ii, 603) of (I) is approx. 20% by vol. and that the protein-bound Cl concn. is $0{\cdot}006M$, *i.e.*, approx. 6% of the total Cl. Dilution of serum with H_2O increases (II), but with aq. KCl the increase in (II) diminishes with increasing [KCl]. F. O. H.

Pharmacodynamic analysis of blood transfusion and hæmotherapy. E. PRIBRAM (Arch. exp. Path. Pharm., 1933, **172**, 444—458).—The physico-chemical characteristics of blood and its constituents are investigated with reference to the interaction on mixing during transfusion. The action of the surface-active substances, assisted by the hydrophilic elements, is important. Thus the action of K–lecithin in presence of hæmoglobin and loosely combined CO_2 of the donor's blood is correlated with the influence of tissue respiration and the action of the heart muscle on the initiation of corpuscular degeneration. Increases in the dispersivity of the plasma and in the turgor of the tissues produce an increased absorption leading to better nutrition, hæmatopoiesis, and oxidation. The rate of decomp. of leucocytes also affects the oxidation–reduction processes leading to an increase in cell respiration. F. O. H.

Theory of blood clotting. II. Syneresis of blood in presence of acids and alkalis. S. PRAKASH (Kolloid-Z., 1933, **65**, 88—92; cf. A., 1932, 870).—The syneresis (I) of clotted blood is increased by the presence of small amounts of AcOH or glycine, by adsorption of $H^{\cdot}$, but at higher concn. the anion is adsorbed preferentially and (I) is normal or reduced. HCl, urea, glucose, and glycerol decrease the amount of (I). Rise of temp. reduces the time of clotting and increases the amount of (I). When clotting is slower the particles develop surface hydration and (I) is less. E. S. H.

Effect of iodoacetic acid on coagulating systems and fermentative processes. Blood-glycolysis and -coagulation. B. STUBER and K. LANG (Pflüger's Archiv, 1932, **230**, 465—474; Chem. Zentr., 1933, i, 2130).—$< 0{\cdot}1M$-$CH_2I{\cdot}CO_2Na$ (I) retards blood-coagulation (II); $> 0{\cdot}1M$-(I) arrests it. $0{\cdot}005$—$0{\cdot}05M$-(I) promotes (II). Other coagulation processes are similarly affected. (II) depends on the intensity of glycolysis and the physico-chemical condition of the fibrinogen. Halogenoacetic acids, by arresting glycolysis and increasing the lability of the fibrinogen, have two mutually opposed effects. Tryptic cleavage of proteins, but not lipolysis, is similarly affected by (I). A. A. E.

Reaction between inhibitors of blood-coagulation and calcium ions in aqueous solution. I. K. MULLI, T. PILLEWIZER, and W. LAVES (Arch. exp. Path. Pharm., 1933, **172**, 384—388).—Colorimetric and electrical conductivity measurements indicate that in aq. media "germanin," "liquoid" (cf. A., 1932, 293), "novirudin," and Na citrate form complexes with $Ca^{\cdot\cdot}$, a reaction to which they probably owe their inhibitory activity. F. O. H.

Inhibition of blood-clotting by bile acids *in vitro*. II. H. ELBEL (Biochem. Z., 1933, **265**, 36—40; cf. this vol., 296).—The increase in the amount of ultra-filterable Ca in serum produced by adding bile acids (I) may be due to the stimulating effect of (I) on the combination of lecithin and protein. The inhibition of clotting by (I) is possibly related to this effect. W. McC.

Formation of globulin from albumin by heparin. H. A. OELKERS (Klin. Woch., 1933, **12**, 191; Chem. Zentr., 1933, i, 2427).—Contrary to Fischer, an increase in the globulin fraction by the action of heparin on blood-protein was not observed. The colloid-osmotic pressure of serum is unchanged by heparin. A. A. E.

Felton antibody: its distribution and purity as determined by salting-out methods. A. M. BROWN (J. Hyg., 1933, **33**, 252—258). CH. ABS.

Nature of antibodies. A. EASTWOOD (J. Hyg., 1933, **33**, 259—281).—A discussion. CH. ABS.

Protein–crystalloid complex as an antigenic unit. A. C. KURTZ, H. C. SOX, and W. H. MANWARING (Proc. Soc. Exp. Biol. Med., 1932, **30**, 138—140).—Experiments support the theory that each protein–crystalloid complex functions as a single antigenic unit, and not that according to which the protein is the mechanical carrier of independent superficial unit "determinants." CH. ABS.

Influence of formaldehyde on various antibody functions. H. BRAUN (Z. Immunitat., 1933, **78**, 46—61; Chem. Zentr., 1933, i, 2131).—Various

antisera lose by treatment with CH_2O the property of complement formation and hæmolysis, but retain that of coagulation and agglutination. A. A. E.

Reactivity of synthetic lecithin and its antisera. H. MAIER (Z. Immunität., 1933, **78**, 1—21; Chem. Zentr., 1933, i, 2130).—Experiments with lecithin and distearyl-lecithin are described. A. A. E.

Cholesterol content of fish muscle. S. NAMIKI (J. Biochem. Japan, 1933, **18**, 163—171).—Ordinary muscle from *Teleostei* contains 0·035—0·077% of cholesterol, whilst the red muscle contains 0·103—0·146%. The total P content is approx. the same (0·22—0·34%) for the two types of muscle. F. O. H.

Preparation of intact total phosphatide-cerebroside. H. H. ESCHER (Helv. Chim. Acta, 1933, **16**, 943—958).—Brain or spinal marrow is coarsely subdivided and dehydrated by successive treatments with EtOH or $COMe_2$. The product is extracted at 37° with mixtures of 95% EtOH and light petroleum, b.p. 35—70° (1 : 1, 1 : 3, and 1 : 10 successively). By means of H_2O, EtOH is removed from the extract, which is conc. at 37°/vac., and pptd. with $COMe_2$. The solid is triturated with successive quantities of $COMe_2$, whereby fats, cholesterol and its esters, and lipochromes are removed without considerable loss of total phosphatide-cerebroside, which forms additive compounds with $COMe_2$. The material is pressed into thin sheets from which $COMe_2$ is removed at 37°/1—2 mm., after which it can be preserved indefinitely in CO_2. H. W.

Micro-determination of phosphatides in tissues and blood. B. NORBERG and T. TEORELL (Biochem. Z., 1933, **264**, 310—315).—A method for the determination of phosphatide in 0·1 g. of tissue or 0·5 c.c. of blood depending on the pptn. of phosphatide + protein with $CCl_3{\cdot}CO_2H$ and extraction of the ppt. with EtOH–Et_2O is described. P. W. C.

Fatty acids from the larva-fat of the beetle *Pachymerus dactris*, L. G. COLLIN (Biochem. J., 1933, **27**, 1373—1374).—Fat extracted from the larvæ found in the nuts of *Manicaria saccifera* gave on saponification the following fatty acids: lauric (24%), myristic (21%), palmitic (8%), oleic (32%), linoleic (3%), stearic, oleic, or linoleic (present in residual fractions) (12%). As compared with the kernel-fat of the nuts, the lower fatty acids are diminished, whilst oleic and linoleic acid are increased. W. O. K.

Component fatty acids of rat-body fats. A. BANKS, T. P. HILDITCH, and E. C. JONES (Biochem. J., 1933, **27**, 1375—1382).—The fatty acids include palmitic (I) (25—30%), myristic (II) (4—5%), stearic (III) (2—3%), and unsaturated (65—70%) acids (oleic with a small quantity of probably palmitoleic acid). Linoleic acid (IV) is almost entirely absent. When the diet contains cod-liver oil, highly unsaturated C_{20} and C_{22} acids may occur and the proportion of (IV) is only slightly increased. The fatty acids of the perinephric fat of the wild rabbit include (I) (23%), (II) (4·5%), (III) (4%), and unsaturated (68·5%) acids [chiefly (IV) with some linolenic acid]. Fully saturated components (almost wholly tri palmitin) occurred in the body-fat of the rat (2—3%) and in the perinephric fat of the rabbit (6—7%). W. O. K.

New group of animal pigments (lyochromes). III. P. ELLINGER and W. KOSCHARA (Ber., 1933, **66**, [*B*], 1411—1414; cf. this vol., 847).—Nascent PbS is a very suitable adsorbent for lyochromes. Lactoflavin *b* passes when heated at 60° into an almost colourless compound of purine character and a pigment with lyochrome properties. Purification of the mother-liquors from the crude crystallisates of lactoflavin *a*—*c* followed by pptn. with $AuCl_3$ leads to *lactoflavin* d (I), $C_{16}H_{20}O_6N_4$ or $C_{17}H_{20}O_7N_4$, m.p. 270—273° (decomp.), oxidation of which with CrO_3 affords $8CO_2$ and $0{\cdot}5NH_3$ per mol. of (I). The murexide test is negative. A cryst. *pigment* (24% N) is obtained as by-product. Pigment concentrates as present in conc. C_5H_5N eluates when made alkaline to litmus with NaOH and exposed to sunlight yield a *pigment* $C_{14}H_{14}O_2N_4$, m.p. 315—317° (decomp.). H. W.

Flavins as biological hydrogen acceptors. T. WAGNER-JAUREGG and H. RUSKA (Ber., 1933, **66**, [*B*], 1298—1302).—Flavin (I) solutions become decolorised when preserved in vac. in contact with yeast, finely-divided muscle, or powdered liver, kidney, heart, or brain, particularly in presence of $AcCO_2H$, lactic, succinic, or citric acid, or aldehydes. The colour returns on exposure to air. The hydrogenating enzyme can be dissolved by H_2O from ox-liver and purified by addition of acid glycine buffer (p_H 3·7) or saturated $(NH_4)_2SO_4$ and dialysis. Impure but not pure (I) solutions are decolorised by this prep. in vac. Yeast extracts, autolysates, and juices prepared with phosphate buffer (p_H 7·4) do not decolorise (I) solutions even in presence of lactic acid, whereas the yeast residues show the reaction. Reduction is restricted by HCN but not by CO. H. W.

Colouring matter of *Halla parthenopæa*, Costa. F. P. MAZZA and G. STOLFI (Arch. Sci. biol., 1931, **16**, 183—197; Chem. Zentr., 1933, i, 1462).—The red colouring matter of the epidermis is the 5 : 6-quinone of 2 : 3-dihydroindole-2-carboxylic acid, $C_9H_7O_4N$. Oxidation with H_2O_2 affords pyrroletricarboxylic acid; *p*-bromophenylhydrazine in AcOH gives $C_{15}H_{12}O_3N_3Br$. Aq. SO_2 gives 5 : 6-dimethoxyindole and its -2-carboxylic acid, m.p. 202° (decomp.). A. A. E.

Biological reversible oxidation–reduction system: the pigment of *Arion rufus*. E. A. H. FRIEDHEIM (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 162—164).—A pigment is extracted which forms a reversible oxidation–reduction system, E_0 at p_H 7·0 being —27 mv. R. S. C.

Astacene in Crustacea. R. FABRE and E. LEDERER (Compt. rend. Soc. Biol., 1933, **113**, 344—346).—Astacene, m.p. 243°, obtained from different varieties of lobsters, is the only known carotenoid pigment which occurs solely in animals. NUTR. ABS. (*b*)

Presence of carotene in the frog. F. G. DIETEL (Klin. Woch., 1933, **12**, 601—602).—A yellow pigment, extracted with $COMe_2$ and Et_2O from the ovaries, skin, and liver of two species of frog (*Rana*

temporaria and *esculenta*), was identified spectroscopically as carotene. NUTR. ABS. (*b*)

Carotene in the retina and the probable relationship between carotenoid deficiency and night blindness. H. VON EULER and H. HELLSTROM (Svensk Kem. Tidskr., 1933, **45**, 203—205).—Ox retina, extracted in Na light, yields an EtOH+$CHCl_3$ extract which exhibits absorption in the blue region of the spectrum with max. at 450 and 484 mμ and in the ultra-violet (255—527 mμ) with a max. at 265 mμ; when freed from EtOH it gives a positive response with $SbCl_3$–$CHCl_3$. Extraction with H_2O+$CHCl_3$ gives a dark red aq. layer having absorption bands at 586—572, 505—478, and 467—440, with max. at 489 and 455 mμ. Hence it appears that the night blindness associated with xerophthalmia is not essentially a consequence of *A*-avitaminosis, but depends on a deficiency of carotenoids in the retina. The relation between carotenoids and the visual purple is discussed. F. O. H.

Quantitative extraction of histamine from tissues by electrodialysis. R. G. MACGREGOR and W. V. THORPE (Biochem. J., 1933, **27**, 1394—1399).—The minced tissue is electrodialysed and the histamine passing into the cathode chamber is determined physiologically. The results are in agreement with those obtained by the EtOH-extraction method (Best *et al.*, A., 1927, 371) and added histamine is quantitatively recovered. W. O. K.

Choline in opotherapeutic powders. M. R. DU NOYER and E. KAHANE (Bull. Soc. Chim. biol., 1933, **15**, 938—943).—The Florence reaction for choline (I) is given by all opotherapeutic powders and cannot therefore be used in the identification of testicle powder. (I) is probably formed by enzymic hydrolysis of lecithin. A. L.

Determination of glutathione in tissues. Y. OKUDA and M. OGAWA (J. Biochem. Japan, 1933, **18**, 75—86).—The tissue is extracted with 0·5*N*-sulphosalicylic acid and the extract is filtered. Reduced and total glutathione are determined in the filtrate by titrating with 0·0001*N*-KIO_3 in presence of KI before and after reduction by Zn dust. The difference between the two results gives the content of the oxidised form. F. O. H.

Determination of gelatin. G. FARKAS (Biochem. Z., 1933, **264**, 361—366).—Gelatin dissolves in picric acid on warming and may then be separated from other proteins. It re-separates on cooling to 8° and is then determined in terms of the N content. P. W. C.

Determination of the gelatin content of different kinds of flesh. F. THAN (Biochem. Z., 1933, **264**, 367—370).—Using the method of the preceding abstract, the % of the total N as gelatin is for three types of ox and calf flesh 9—10, 12—13, and 20—21%, for tendons 80%, and for pig's flesh is rather less. P. W. C.

Isolated cell- and tissue-constituents. M. BEHRENS. II. Hæmosiderin of horse-spleen. T. ASHER (Z. physiol. Chem., 1933, **220**, 97—105; cf. A., 1932, 957).—Hæmosiderin in the form of granules containing Fe may, owing to its high sp. gr. (1·6—2·6), be isolated mechanically from powdered spleen. The granules have a varying composition and consist of a protein stroma containing $Fe(OH)_3$ and some $CaHPO_4$. J. H. B.

Distribution of iron in animal tissues. S. KATSUNUMA and H. NAKAMURA (Nagoya J. Med. Sci., 1932, **6**, 101—106).—Various animal tissues were examined by a colorimetric method, using a methylene-blue standard. CH. ABS.

Iron distribution in the earlier stages of growth of soya-bean and chick embryo. S. KATSUNUMA and H. NAKAMURA (Nagoya J. Med. Sci., 1932, **6**, 107—112).—The tegument and embryo of soya-bean contained much, and the cotyledon little, Fe. During sprouting the largest amount of Fe was found in the root, most being in the lower and least in the middle portion. During the development of hen's eggs the Fe content of the embryo increases 20 times at the expense of Fe in other portions. CH. ABS.

Classification of the biological elements; biochemistry of beryllium. W. R. FEARON (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 531—535).—The periodic table can be divided for the upper section only to contain thirty-four biological elements. Be has been detected in the lichens *Parmelia saxatilis* and *Xanthoria parietina*. H. G. R.

Magnesium and other inorganic constituents of some marine invertebrates. R. A. MCCANCE and H. L. SHIPP (J. Marine Biol. Assoc., 1933, **19**, 293—296).—Analyses for H_2O, Na, K, Ca, Mg, and Fe are given. C. W. G.

Fluorine content of bones and teeth. R. KLEMENT (Naturwiss., 1933, **21**, 662—663).—The bones and teeth of land mammalia contain < 0·1% F (0·030—0·065%), whilst those of sea animals contain more (0·57—1·62%). Fossilised bones are especially rich in F (2·36—2·73%). The significance of hydroxy- and fluor-apatite in bone tissue is discussed (cf. this vol., 296). F. O. H.

Determination of chloride in tissues. F. W. SUNDERMAN and P. WILLIAMS (J. Biol. Chim., 1933, **102**, 279—285).—The tissue is digested in *N*-KOH and HNO_3 added to the turning point of Me-orange; excess of $AgNO_3$ is added and titrated with NH.CNS. H. D.

Fixed mineral matter of seminal elements during spermatogenesis. A. POLICARD (Compt. rend., 1933, **197**, 710—711).—The mineral content (I) of the nuclei of the seminal elements of the rat is high (no Fe) until mitosis causes a low (I) in the resulting spermatids. During development of the latter, (I) increases progressively and its distribution tends towards that in the spermatozoa. A. C.

Eggs of gastropods. T. KUMON (J. Biochem. Japan, 1933, **18**, 145—151).—Analytical data (total N, distribution of N, H_2O content, mineral constituents, etc.) of the vitellin, mucous layer, and capsule protein of the eggs of *Hemifusus tuba*, Gmel., and of the eggs at various stages of development are given. F. O. H.

Chemical composition of the human fœtus. M. H. GIVENS and I. G. MACEY (J. Biol. Chem., 1933,

102, 7—17).—Up to 4 months the fœtus requires total ash (I) 0·55 g., Ca 0·1 g., and Mg 0·028 g., increasing to 54 -112 g., 13—33 g., and 0·277—0·78 g., respectively, at maturity. (I) varies between 4 and 21% of the dry body-wt., and contains 6—30% Ca and 0·6—0·9% Mg. H. G. R.

Composition of the new-born rat during early development. A. ROCHE and I. GARCIA (Compt. rend. Soc. Biol., 1933, **112**, 1686—1688).—There is a steady increase with age from 0 to 25 days in the wt. of the rat and in the % of N in the fresh material. During the first 4 days the N and P content of the dry material falls and subsequently rises irregularly. At birth the rats contained on an average 85·3% H_2O, 1·54% N, and 0·37% P. NUTR. ABS. (*b*)

Composition of muscle, liver, and blood of the dog. T. CAHN and J. HOUGET (Compt. rend. Soc. Biol., 1933, **112**, 1319—1321).—The most const. constituents are H_2O, lipin-P, acid-sol. P, total P, and total fat (I). (I) is more const. in liver and blood than in muscle. Despite variations, the composition of each tissue is characteristic. NUTR. ABS. (*m*)

Methods for standardisation of biological stains. III. Nitro- and azo-dyes. A. R. PETERSON, H. J. CONN, and C. G. MELIN (Stain Tech., 1933, **8**, 121—130).—Methods for analysis and biological testing are given for the following dyes: Martius-yellow, orange G, Janus-green B, Me-orange, orange II, Sudan III and IV, Bismarck-brown Y and R, Congo-red, and Erie-garnet B. H. W. D.

Block staining of nervous tissue with silver. III. Pericellular end-bulbs or boutons. H. A. DAVENPORT (Stain Tech., 1933, **8**, 143—147).—Fixation in 20—40% C_5H_5N or in 10% chloral hydrate followed by 10—40% C_5H_5N gave the most consistent staining of pericellular structures in the cat's spinal cord. H. W. D.

Phloxine with orange-G as a differential counterstain. L. A. MARGOLENA (Stain Tech., 1933, **8**, 157).—Phloxine and orange-G, following hæmatoxylin, may be used for differential staining of plant or animal tissues. H. W. D.

Determination of small amounts of unsaturated fatty acids in biological fluids. R. WILLHEIM and F. SCHOLL (Biochem. Z., 1933, **264**, 302—309).—A colorimetric method is described for the determination of oleic acid in 0·2 c.c. of serum using the red colour obtained when oleic acid is treated with a solution of cellulose in conc. H_2SO_4. P. W. C.

Source of lipins in thoracic-duct lymph in fasting. Endogenous lipin secretion and reabsorption in bowel. H. R. RONY, B. MORTIMER, A. C. IVY (J. Biol. Chem., 1933, **102**, 161—170, and Proc. Soc. Exp. Biol. Med., 1933, **30**, 827—828; cf. A., 1932, 878).—The average content in total fatty acids of the thoracic-duct lymph of dogs fasted 2—14 days is 0·63%. Pilocarpine (I) and secretin markedly increase the lipin content, whereas thyroxine, pituitrin, and glucose are without effect. When the bile is excluded from the intestine the lipin content of the lymph is low and does not rise on injection of (I). The lymph fat cannot be increased by (I) in enterectomised animals. It is concluded that during fasting the intestinal mucosa secretes fats which are absorbed after hydrolysis, resynthesised, and passed into the lacteals. H. D.

Gastric juice. I. Proteins of human gastric juice. II. Urea-splitting enzyme and pepsin in relation to proteins. L. MARTIN (J. Biol. Chem., 1933, **102**, 113—130, 131—136; cf. this vol., 750).—I. A small quantity of sugar-containing protein is pptd. from the gastric juice (I) at p_H 6·8—7. By ½ saturation of the filtrate with $MgSO_4$ or addition of AcOH and $COMe_2$ to 2 and 33·3%, respectively, at p_H 3·5 a heat-coagulable protein, named gastroglobulin (II), is pptd. It is crystallised by the brucine–C_5H_5N method, at its isoelectric point, and from EtOH. Pptn. of a protein substance which reduces $CuSO_4$ after hydrolysis occurs on addition of H_2WO_4 to the filtrate or dialysate from (II). The compounds obtained by treating the hydrolytic products with $NHPh{\cdot}NH_2$ are described.

II. The urea-splitting (III) and peptic (IV) activities of the ppts. and filtrates from ½ saturation of (I) with $MgSO_4$ at different p_H, both dialysed and undialysed, were determined. The non-dialysed (III) was found in connexion with (II), the NH_3 and non-protein-N formed being directly proportional to the quantity of (II). Dialysis tends to increase the activity. (IV) was found only in connexion with (II). H. D.

Neurolytic properties of cerebrospinal fluid. R. GRECO (Ann. Inst. Pasteur, 1933, **51**, 265—275).—Nerve substance is destroyed *in vitro* by cerebrospinal fluid within 40 hr. This action, which is probably enzymic, does not take place after warming to 60—70° or in the presence of $CHCl_3$, but is unaffected by thymol or pilocarpine. P. G. M.

Inorganic constituents of mixed and parotid gland saliva activated by reflex stimulation in the dog. H. BAXTER (J. Biol. Chem., 1933, **102**, 203—217).—The [Cl′] and [Ca″] and the alkalinity of the saliva from the mixed glands of dogs were < those for the parotid alone. No difference in [K·] was observed. 5% NaCl, 0·125% HCl, and bread and meat powder introduced into the mouth can produce the same vol. of excreted saliva in the same dog, with different concns. of inorg. constituents. Decreasing concns. of NaCl and HCl produce decreasing vols. of parotid and mixed salivas containing decreasing [Cl′] and alkalinity, whilst the [P], [K·], and [Ca″] remain approx. the same. Parotid saliva, excreted in consequence of pilocarpine injections, is less conc. in Cl′, Ca″, and K· than is that produced at the same rate by meat extract, whilst the alkalinities are the same. H. D.

Effect of pilocarpine and "Neu-Cesol" on the amylase content of human saliva. A. GERNHARDT (Z. klin. Med., 1933, **123**, 16—22; Chem. Zentr., 1933, i, 2120).—Pilocarpine and "Neu-Cesol" (Merck), injected subcutaneously, increase both the quantity and the ptyalin content of human saliva. A. A. E.

Saponin nature of snake venom. G. BAYER and H. ELBEL (Z. Immunität., 1933, **78**, 82—85; Chem. Zentr., 1933, i, 2427).—Experiments on the

resistance of hedgehogs to intravenous injections indicate that snake venom is not of saponin nature. A. A. E.

Formation of bile acids. VI. Rice embryo and bile acid excretion. K. TANAKA and T. TANAKA (J. Biochem. Japan, 1933, **18**, 15—22).—Oral administration of irradiated ergosterol (I)-containing sterol mixture (II) from rice embryo (III) to dogs with biliary fistulæ produces a temporary increase (21—24%) in the bile-acid secretion. The increase is more marked (13—43%) with the unsaponifiable fraction of the oil of (III), but does not occur with (II) freed from (I). Hence (I) and vitamin-*D* are concerned with the formation of bile acids. F. O. H.

Possibility of experimentally changing the concentration of alkali metals in bile. E. NEUBAUER (Arch. exp. Path. Pharm., 1933, **172**, 393—401).—For short periods (4—5 hr.) the concns. of K, Ca, and Mg and the ratio of their concns. in the bile of rabbits remain approx. const. Administration of Na dehydrocholate (I) lowers [Ca] and [Mg], that of the Mg salt lowers [Ca] and, after a preliminary diminution, increases [Mg], whilst that of the K salt lowers the Ca and Mg contents. Inorg. K, Ca, and Mg salts have no effect on the content of these cations in the bile, and hence an anion such as (I) is necessary for their passage through the liver into the bile. F. O. H.

Concentration and precipitation of bilirubin in the gall-bladder and bile ducts. N. W. ELTON and E. DEUTSCH (Arch. Pathol., 1933, **15**, 818—827).—Comparison of the icteric index, *n*. the direct Van den Bergh reaction, and the total bilirubin (I) % of biles (cat, dog) shows that a crit. concn. exists at which bilirubin tends to ppt. in the bile. Further removal of H_2O from the bile is accompanied by progressive passage of (I) (and possibly cholesterol) into the form of a suspensoid colloid or minute crystals. NUTR. ABS. (*m*)

Biological value of milk of normal and thyroidectomised goats irradiated by the mercury lamp. C. KUCERA and M. SOOS (Compt. rend. Soc. Biol., 1933, **113**, 619—621).—Irradiation of the milk of normal (but not of thyroidectomised) goats produces favourable effects on development and metamorphosis of tadpoles. NUTR. ABS. (*m*)

Effect on peptic digestibility *in vitro* of artificial feeding as used for American infants. A. LAUTZ (Amer. J. Dis. Children, 1933, **45**, 985—995).—The peptic digestibility of cow's milk is unaffected by dilution, heating, or addition of acids in the usual amounts. It is increased by increasing the caseinogen : lactalbumin ratio and is reduced by addition of gelatin, cereals, or sugar or by increasing the fat content. CH. ABS.

Possibility of increasing the milk secretion of cows by feeding with irradiated feeding stuffs. F. BÍLEK and L. HYNEK (Zemed. Archiv., 1931, **22**, 449—454; Bied. Zentr., 1933, **A**, **3**, 427).—Addition of irradiated yeast to the winter rations of cows increased the secretion of milk without affecting its fat content. The somewhat better results obtained with irradiated linseed cake are attributed to the activation of the phytosterol therein. The effect persisted 8 days after feeding. Irradiated foods had no beneficial action on cows receiving ample supplies of fresh green fodder. A. G. P.

Specificity of caseinogens. M. L. DEMANEZ (Compt. rend. Soc. Biol., 1933, **112**, 1560—1561).—Whilst the caseinogens of the cow, ewe, and goat are quasi-identical with respect to their antigenic properties, those of the woman and the mare are distinct. NUTR. ABS. (*b*)

Milk of cows inoculated with anthrax serum. F. I. DENISOV (Trans. Omsk Inst. Dairying, 1931, **1**, No. 3, 3—33).—The fall in yield is accompanied by an increase in fat, lactose, Cl, albumin, acidity, and total solids, and a decrease in caseinogen. CH. ABS.

Influence of certain agents on the lability of the "reducing factor" (vitamin-*C* ?) in milk. A. T. R. MATTICK and S. K. KON (Nature, 1933, **132**, 446—447).—Exposure to light rapidly destroys the labile, reducing factor in milk. This is significant in view of the marked fluctuations in reducing power previously observed (this vol., 969). L. S. T.

Iodometric determination of sugars in human milk. M. POLONOVSKI and A. LESPAGNOL (Compt. rend. Soc. Biol., 1932, **107**, 301—303; Chem. Zentr., 1933, i, 1486).—Gynolactose (I) combines with about 33% of the amount of I corresponding with an equal wt. of lactose or the third sugar of human milk; the Cu-reducing power is, however, the same. The (I) content of milk sera is determined by hydrolysis and iodometry. A. A. E.

Physiological variations in the concentration of various sugars in human milk. M. POLONOVSKI, A. LESPAGNOL, and H. WAREMBOURG (Compt. rend. Soc. Biol., 1932, **107**, 303—305; Chem. Zentr., 1933, i, 1473).—Variations in concn. of the three forms of lactose are at first inconsiderable; after several months that of gynolactose and the sugar sol. in MeOH appears to fall. A. A. E.

Effect of increased blood-glucose on milk-sugar. C. H. WHITNAH, W. H. RIDDELL, and R. E. HODGSON (J. Dairy Sci., 1933, **16**, 347—353).—Administration of glucose increased the blood-sugar in lactating cows. Milk drawn at the period of greatest increase had a higher lactose (I) content than that on preceding or following days. The (I) increase in milk was not proportional to the blood-sugar increase, and the latter is not a factor controlling the (I) content. A. G. P.

Monthly variation in the fat content of milk from Welsh farms. P. M. HICKSON and S. B. THOMAS (Welsh J. Agric., 1933, **9**, 240—248).—Analyses for fat of 7372 random samples from the bulk milk of > 1000 herds show that afternoon milk (I) generally has a higher fat content (II) than morning milk (III). There is very little seasonal fluctuation in the (II) of (I), whereas marked seasonal fluctuations occur in the (II) of (III). NUTR. ABS. (*m*)

[Changes in] amount and properties of fat globules in Siberian cow's milk during the lactation period. A. ZHURAVSKAYA (Trans. Omsk Inst. Dairying, 1931, **1**, No. 3, 34—60).—With

advance of the lactation period *d* (milk) and the Reichert–Meissl val. (butter) decrease, whilst *n* (butter) slightly increases. CH. ABS.

Quantity and fat content of milk during milking in women. C. VINCENT and J. VIAL (Compt. rend. Soc. Biol., 1933, **112**, 1422—1424).—During simultaneous milking of the two breasts the variations in the amount (I) of milk and the % (II) of fat are bilateral and simultaneous. At first (I), (II), and the wt. (III) of fat increase in parallel. Then there is a check in the rate (IV) of milk secretion and in the rise in (II), following which there is a steep rise in (I) and (II). Towards the end of milking (IV) and (III) decrease, whilst (II) attains its max. NUTR. ABS. (*m*)

Composition of human milk. Influence of the method of extraction on the fat percentage. S. T. WIDDOWS and M. F. LOWENFELD (Biochem. J., 1933, **27**, 1400—1410).—The concn. of fat in human milk depends on the method of extraction, being smallest in the case of dripped milk, higher in milk extracted by gentle suction with the pump, and still higher in milk obtained by digital pressure. It varies inversely with the quantity of milk in the breast and depends also on other factors. W. O. K.

Colloidal calcium phosphate of milk. G. T. PYNE and J. J. RYAN (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 471—476).—The colloidal PO_4''' (I) appears to be mainly $Ca_3(PO_4)_2$. The acidity obtained for fresh milk to which a sol. oxalate has been added depends largely on (I). H. G. R.

Micro-determination of calcium in milk. M. SATO and K. MURATA (J. Agric. Chem. Soc. Japan, 1933, **9**, 334—336).—Milk (1 c.c.) is heated with conc. H_2SO_4–HNO_3 (1 : 1, 3—4 c.c.); when HNO_3 is removed, H_2O_2 is added dropwise. The solution is heated for 2—3 min., diluted to 50 c.c., made slightly alkaline with 10% aq. NH_3, acidified with AcOH, and boiled. CaC_2O_4 is then pptd. with boiling aq. $(NH_4)_2C_2O_4$, treated with H_2SO_4, and titrated with 0·01*N*-$KMnO_4$. CH. ABS.

Calcium and inorganic phosphorus in human and cow's milk. A. F. HESS and H. R. BENJAMIN (Proc. Soc. Exp. Biol. Med., 1933, **30**, 1358—1361).—Four fractions (I) were determined both for Ca and P in milk: a filterable absorbable fraction, a filterable remainder, a non-filterable absorbable fraction, and a non-filterable remainder. The Ca (I) of human milk, unlike those of cow's milk, are very similar to those of human and bovine sera. The differences in the Ca partitions of the milks cannot account directly for the difference in antirachitic potency. NUTR. ABS. (*m*)

Phosphorus compounds of milk. C. BOMSKOV (Z. Kinderheilk., 1933, **54**, 779—780).—Hochheimer's technique (this vol., 300) is criticised. His figure for org. P in cow's milk is too low. NUTR. ABS. (*m*)

Organic phosphorus compounds in goat's and mare's milk. C. BOMSKOV and J. NISSEN (Z. Kinderheilk., 1933, **54**, 775—778).—The mean vals. for 14 samples of goat's milk were: total P 97·87, total acid-sol. P 85·53, inorg. + labile P 60·70, pyro-P 4·67, hexose phosphate P 0, residual P 19·85 mg. per 100 c.c. Two samples of mare's milk gave, respectively, total P 87·56, 60·39, total acid-sol. P 74·31, 46·78, inorg. + labile P 53·55, 33·85, pyro-P 13·30, 7·58, hexose phosphate P 2 08, 3·01, residual P 5·69, 1·85 mg. NUTR. ABS. (*b*)

Spectrographic examination of urine in ultra-violet light. G. HUWER (Strahlenther., 1933, **46**, 393—396; Chem. Zentr., 1933, i, 2425).—Prolan fractions (Zondek) gave typical absorption curves, with max. at 290, min. at 265 mμ. The EtOH fraction of urine gave the same absorption. Deproteinised serum gave similar curves. The substance causing the absorption has not been identified. A. A. E.

Determination of porphyrin in urine. H. T. SCHREUS and C. CARRIÉ (Klin. Woch., 1933, **12**, 146—148; Chem. Zentr., 1933, i, 1660).—A spectroscopic method depends on the fact that the intensity of the absorption bands of porphyrin solutions is proportional to the porphyrin content. A. A. E.

Physiology and pathology of porphyrin excretion. H. T. SCHREUS and C. CARRIÉ (Klin. Woch., 1933, **12**, 745—748).—Vals. < 0·1 mg. per day of coproporphyrin in the urine of normal subjects fed on a mixed diet are physiological. Fever from any cause increases porphyrinuria; salvarsan has a similar effect. In the first days of infancy also the urinary porphyrin is high. In all these conditions increased breakdown of blood corpuscles takes place and is assumed to be the cause of increased porphyrinuria. The hæmatin is probably transformed in the liver into coproporphyrin III, the intermediate stage being protoporphyrin. NUTR. ABS. (*b*)

Determination of urinary indican by means of the Pulfrich photometer. M. K. ZACHERL (Z. physiol. Chem., 1933, **220**, 113—122).—The indican is converted by means of $FeCl_3$ in conc. HCl into indigotin, which is extracted by $CHCl_3$ and determined by step-photometer. J. H. B.

Ergothioneine in urine. M. X. SULLIVAN and W. C. HESS (J. Biol. Chem., 1933, **102**, 67—72).—Ergothioneine has been isolated from normal urine. Colorimetrically 90 mg. per litre were found, but ≯ 5—6 mg. could be isolated. H. G. R.

Determination of urinary protein. G. CZONICZER (Biochem. Z., 1933, **264**, 348—351).—The protein of 5 c.c. urine is pptd. and separated in a centrifuge tube and its amount calc. from the total N (Kjeldahl). P. W. C.

Blood- and urine-ammonia. Formation of ammonia in the kidney. M. POLONOVSKI, P. BOULANGER, and G. BIZARD (Bull. Soc. Chim. biol., 1933, **15**, 863—917).—Endogenous NH_3, like exogenous NH_3, is converted into a substance which acts as a "buffer" in the control of the urinary NH_3 level (I) and as a defence against NH_3 toxicity. The renal formation of NH_3 for the elimination of acidosis and the appearance of NH_3 which enters the blood and is not excreted into the urine ("ammoniophaneresis") are distinct phenomena, the latter being neither increased by a lowering of the blood-p_H nor diminished by alkalosis. Whilst insulin and adrenaline are antagonistic in their action on the blood-sugar of

dogs, both produce an increase in (I) probably due to increased utilisation of glucose. Injection of phloridzin or salipurposide (A., 1931, 1199) induces glycosuria, but not an increase in (I). The increase in (I) due to the injection of NH_4 salts is proportional to the degree of elevation of blood-NH_3, but not to the elimination of acid. These and other findings lead to the differentiation of excretory and secretory functions of the kidney. The liberation of NH_3 is enzymic in each case, whilst the secretory function also occurs in the pancreas. F. O. H.

Diathermy test for sugar and albumin in urine. H. E. Kimble (Arch. Phys. Ther., 1933, **14**, 237).—The presence of albumin is indicated by coagulation giving a white line between the plates inserted in urine acidified with AcOH; alkaline $BiONO_3$ is then added, and when the liquid between the plates boils sugar is indicated by the formation of a black ring. Ch. Abs.

Sumner's method for [determining] sugar in urine. J. J. Short (J. Lab. Clin. Med., 1933, **18**, 641—643).—The presence of sugar in strongly acid urine or samples containing $> 0{\cdot}6\%$ is not always detected; the alkalinity of the reagent should be increased by 50%. Ch. Abs.

Mercury-reducing substances of normal urine. B. Gwozdz (Bull. Soc. Chim. biol., 1933, **15**, 969—981).—The reducing power (I) of the oxyproteic acid fraction (II) of urine expressed as the difference between that due to the pigment [pptd. by $Cu(OAc)_2$ from (III)] and that of the $Hg(OAc)_2$ ppt. (III) from the solution obtained after $Ba(OH)_2$ treatment (cf. Giedroyc, A., 1926, 636) is 17·36% of the total (I) when a meat diet (IV) is given and 8·6% when a milk diet (V) is followed. (II) contains 83·4% of the total neutral S on (IV) and 45·7% on (V). A. L.

Evaluation of the Rupp–Schied–Thiel method as a test for thiocyanate in urine. M. X. Sullivan and W. C. Hess (J. Washington Acad. Sci., 1933, **23**, 419—425).—CNS′ is separated from urine as Ba salt in hot EtOH, thereby eliminating ergothioneine-like material and oxyproteic acids which interfere with the method. H. G. R.

Colorimetric determination of chlorides in blood and urine. B. B. Westfall (Amer. J. Med. Sci., 1933, **185**, 148).—Ag_2CrO_4 is added, the mixture is filtered, and CrO_4'' is determined colorimetrically in the filtrate with *s*-diphenylcarbazide. 0·0004 mg. of NaCl can be determined to $\pm 3\%$. Ch. Abs.

Relation of dietary fat and fat derivatives in the fæces of young dairy calves. C. Y. Cannon, D. L. Espe, and J. B. Waide, jun. (Proc. Amer. Soc. Animal Produc., 1932, 85—90).—The dry fæces of calves fed with skim milk contained 5·3% of fat (daily excretion 2·3 g.); fæces of those fed with milk (fat 4%) contained 22·5% of fat (daily excretion 13·5 g.). The most const. fraction of fæcal fat was the free fatty acids and the most variable was the soaps. Ch. Abs.

Effect of acidosis and alkalosis on the total base, chloride, and carbon dioxide contents of muscle. E. F. Yang and H. Wu (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1165—1167).—In the rabbit the muscle-base and -Cl varied with plasma vals. and not with p_H changes. Ch. Abs.

Carbohydrate metabolism in Addison's disease. O. Porges and D. Adlersberg (Arch. exp. Path. Pharm., 1933, **172**, 433—443).—Addison's disease is frequently accompanied by a mild hypoglycæmia (I) which tends to be emphasised by a deficiency of carbohydrate (II) in the diet. Oral administration of glucose produces a hyperglycæmia followed by a marked (I), especially when the subject has been previously fed on a (II)-free diet. Adrenal cortex preps. restore the (II) metabolism to normal. With morbid cases the acetonuria due to a (II)-free diet resembles that occurring with normal men. F. O. H.

Composition of foodstuffs in relation to nutritional anæmia in cattle. W. M. Neal and R. B. Becker (J. Agric. Res., 1933, **47**, 249—255).—With increase of growth of wire-grass, Ca, Mg, P, Fe, and protein decrease. In areas where nutritional anæmia occurs, forages contain less of the above elements. H. G. R.

Blood-diastase in cancer. L. L. Tureen (Arch. Path., 1933, **15**, 834—842).—Individuals exhibit marked fluctuations. As a diagnostic test for cancer the determination of blood-diastase is not significant. Ch. Abs.

Arginase and arginine in the metabolism of tumours. G. Klein and W. Ziese (Z. Krebsforsch., 1932, **37**, 323—346; Chem. Zentr., 1933, i, 2277).—Edlbacher's observation, that in animals with implanted malignant tumour the muscle-arginase is increased, is confirmed. The total arginine of the tumour tissue is normal, but the free arginine in tumour and muscle of cancerous animals is thrice as high as in normal muscle. A. A. E.

Reducing substance in tumours. L. J. Harris (Nature, 1933, **132**, 605).—The indications (this vol., 872) that the high reducing capacity of tumours in the dichlorophenol-indophenol test is due mainly to a substance other than vitamin-*C* have been confirmed. The powerful reducing substance present in high concn. in the growing cell of the tumour tissue (Jensen rat sarcoma in guinea-pigs) is named "reducytin." L. S. T.

Influence of cations on the fermentation power of tumour cells. III. Action of potassium. IV. Action of lithium. A. Lasnitzki (Biochem. Z., 1933, **264**, 285—291, 292—301).—III. Addition to K- and Ca-free medium of 0·0025 mol. of KCl per litre causes an increase in fermentation intensity with Jensen sarcoma of 70%, and addition of the same amount of KCl together with 0·0018 mol. of $CaCl_2$ per litre, an increase of 115%.

IV. Li cannot replace K with respect to the above activity. P. W. C.

Effect of irradiated ergosterol on the mineral constituents of cancerous tissue. F. Brikker and J. Lasaris (Z. Krebsforsch., 1932, **37**, 423—431; Chem. Zentr., 1933, i, 2276).—In mouse carcinoma the K : Ca ratio was 0·78 in animals treated with vigantol, and 2·72 in untreated animals. Vigantol administration also appears to retard the growth of implanted tumours. A. A. E.

Action of iodo- and bromo-acetic acid on tumours. I. A. A. KRONTOVSKI, M. K. JAZIMIRSKA-KRONTOVSKA, and H. P. SAVITZKA (Z. Krebsforsch., 1932, **37**, 457—491; Chem. Zentr., 1933, i, 2277).—$CH_2I{\cdot}CO_2H$ and $CH_2Br{\cdot}CO_2H$ diminish the sugar requirement and the formation of lactic acid in tissue cultures of sarcoma and carcinoma. A. A. E.

Effect of radiation on blood. G. W. PHILLIPS (Lancet, 1933, **225**, 745—747).—No characteristic changes are produced in blood by radiation treatment of malignant disease with Ra or with *X*-rays. L. S. T.

Alleged cancer-producing qualities of tomatoes. M. J. A. DES LIGNERIS (Lancet, 1933, **225**, 698—699).—Askanazy and Bellow's production of peritoneal sarcoma in rats by means of tomato juice could not be repeated. Injections of tomato juice, in combination with tar painting, did not accelerate the formation of skin tumours. L. S. T.

Detection of oxalic acid in urinary calculi. H. SCHMALFUSS, H. WERNER, and R. KRAUL (Klin. Woch., 1932, **11**, 791; Chem. Zentr., 1933, i, 1486).—A small quantity of powdered material is dissolved in 10% HCl and the filtrate is shaken with Et_2O, the residue from which (0·1—1 mg.) is fused on white porcelain with resorcinol (0·4—2 mg.). After cooling, the residue is treated with conc. H_2SO_4 (10 mg.) and heated several times for 3 sec. with 20-sec. intervals. In presence of $H_2C_2O_4$ a deep blue, and then a green, colour appears. For the separation of $H_2C_2O_4$ and H_3PO_4 the solution is strongly acidified to Congo-red and the $H_2C_2O_4$ extracted with Et_2O. A. A. E.

Biological degradation products of chlorophyll in animal concrements. A. TREIBS (Z. physiol. Chem., 1933, **220**, 89—96).—Intestinal "stones" contained 75% of lithofellic acid and 0·02% of phylloerythrin (I). A hair-ball contained (I). A horse intestinal stone consisted chiefly of NH_4MgPO_4 with protophorbide *a*, *lithoporphyrin* [which readily yields (I)], and *lithocholin*. Horse fæces contained (I) and probably methylphæophorbide *a*. J. H. B.

Etiology of gallstones. E. L. WALSH (Arch. Path., 1933, **15**, 698—713).—Dissolution of human mixed cholesterol gallstones in dog's bile probably depends on the difference in the ratio of non-saponifiable to saponifiable substances in the bile. CH. ABS.

Azotæmia and dental affections. E. A. ZAWELS and H. W. REILLY (Semana med., 1933, i, 1924—1927).—Dental infections are often accompanied by high blood-non-protein-N. CH. ABS.

Chemical factors of saliva related to immunity and susceptibility to dental caries. W. A. PRICE (J. Dent. Res., 1933, **13**, 195).—Before treatment of caries by supplement of vitamin and mineral-rich foods, addition of powdered bone to the saliva increased the inorg. P content by 3·07%. After treatment there was a decrease. NUTR. ABS. (*b*)

Variation in salivary proteins. F. KRASNOW and E. B. OBLATT (J. Dent. Res., 1933, **13**, 239).—A higher salivary protein (I) occurred more often in caries-immune (II) than in caries-susceptible (III) individuals. (I) of (III) was more const. and more (I) was sedimented from saliva of (III), which suggests that (I) of (II) is possibly more stable. In (III) there was a high correlation between (I), P, p_H, and titratable alkalinity of the saliva. NUTR. ABS. (*b*)

Some chemical factors of saliva apparently related to alveolar decalcification and pyorrhœa alveolaris. W. A. PRICE (J. Dent. Res., 1933, **13**, 195—196).—A case of pyorrhœa alveolaris was treated with a diet rich in vitamins and minerals. Before treatment filtered saliva treated with powdered bone gained 33·57% Ca and 2·18% P. After treatment salivary Ca decreased 68·13% and P 19·4%. NUTR. ABS. (*b*)

Blood-phosphorus insufficiency in pyorrhœa. C. J. GROVE and C. T. GROVE (J. Dent. Res., 1933, **13**, 191—192).—The P content of blood-serum in pyorrhœa (I) (2·2—3·4 mg. per 100 c.c.) was much < normal (3·45 mg.); the average Ca content (10·99 mg. per 100 c.c.) was > normal (9—10 mg.). Deficiency of blood-P may influence bone degeneration as in (I). The intestinal contents should be kept acid (by medicament) to improve absorption of Ca and P. NUTR. ABS. (*b*)

Diabetic coma refractory towards insulin. S. J. THANNHAUSER and H. FULD (Klin. Woch., 1933, **12**, 252—258; Chem. Zentr., 1933, i, 2128).—A case of diabetic coma uninfluenced by large doses of insulin is described. Insulin intervenes in carbohydrate metabolism only in presence of an enzyme-like substance in the liver which produces glycogen from sugar. A. A. E.

Diabetic lipæmia. Rôle of fats in diabetes mellitus. Hæmolipocrit method for the determination of fat in blood-serum. D. H. COLLINS (Quart. J. Med., 1933, **2**, 267—279).—The hæmolipocrit method for the volumetric determination of fat in blood-serum is described, vals. for diabetic and non-diabetic sera being recorded. Increase of serum-fat is associated with glycosuria, acetonuria, and the severer cases of diabetes, but no definite relationship appears between serum-fat and either blood-sugar or body-wt. NUTR. ABS. (*m*)

Effect of pancreatectomy in the dog on blood-lipase content. N. FIESSINGER, M. ALBEAUX-FERNET, and A. GAJDOS (Compt. rend. Soc. biol., 1933, **112**, 549—550).—The blood of depancreatised and normal dogs contains an atoxyl-resistant and quinine-sensitive lipase, not necessarily of pancreatic origin. NUTR. ABS. (*m*)

Experimental adrenaline epilepsy in guinea-pigs treated with yohimbine, ergotamine, or peptone. J. TINEL and G. UNGAR (Compt. rend. Soc. Biol., 1933, **112**, 542—543; Chem. Zentr., 1933, i, 2167). A. A. E.

Toxic substance from protein degradation. H. LIEB and E. SCHADENDORFF (Arch. exp. Path. Pharm., 1933, **172**, 343—358).—The urine of epileptics and men suffering from scalds contains a thermostable substance (I) which produces necrosis on subcutaneous injection and is also present in peptone in an inactive form, being liberated by heating at 100° with H_2O. (I), which is enzyme-free, non-dialysable,

sol. in 70% EtOH, and pptd. by Hg acetate or 50—60% $(NH_4)_2SO_4$, is a polypeptide or peptone. It is hydrolysed by trypsin-free erepsin (when the toxicity is lost) and contains dialysable Ca, the toxicity being proportional to the $Ca^{\cdot\cdot}$ combined with (I). $Mg^{\cdot\cdot}$ has no influence on the necrosis produced. When preceded by adrenaline injection, Ca-free (I) is toxic, due to the retardation of absorption and subsequent combination with tissue-Ca. F. O. H.

Experimental fever in man. II. Energy exchange in fever: thermogenesis and metabolism. E. DELCOURT-BERNARD (Rev. belge Sci. med., 1933, 5, 229—292).—In cases (I) exhibiting rigor, the metabolism tends to diminish beforehand, rises markedly (112%) during rigor, and remains approx. 30% high afterwards until the temp. begins to fall. In cases (II) without rigor the mean rise is 16%. On deducting the extra metabolism due to shivering, the increase in (I) is similar to that of (II). Fat combustion increases, especially in the middle and later periods of experiment, in (I) or (II). Carbohydrate combustion increases in (I), in which it is proportional to intensity of shivering, but diminishes in (II). Protein metabolism varies. NUTR. ABS. (*m*)

Iodine and goitre in the Far East. J. F. MCCLENDON (J. Biol. Chem., 1933, **102**, 91—99).—Japan is the only non-goitrous country, owing to the large amount of I ingested in the diet as seaweed. The I content of 79 species of seaweed is given. H. G. R.

Catechin (inhibitory substance) of the thyroid gland and its therapeutic use in exophthalmic goitre. E. HERZFELD and A. FRIEDER (Deut. med. Woch., 1933, **59**, 84—86; Chem. Zentr., 1933, i, 2127).—The properties and use of "tyronorman" are discussed. A. A. E.

Influence of Lugol's solution on the effect of adrenaline in exophthalmic goitre and beri-beri. W. C. AALSMEER (Klin. Woch., 1932, **11**, 2111—2113; Chem. Zentr., 1933, i, 2167).—The effect on blood-pressure is neutralised by Lugol's solution. Beri-beri is probably a dysfunction of the thyroid gland. A. A. E.

Human iodine metabolism. II. Blood- and urinary iodine after a single intravenous injection of inorganic iodine in hypothyreosis. A. W. ELMER (Deut. Arch. klin. Med., 1933, **174**, 449—455; Chem. Zentr., 1933, i, 2127).—Variations in I excretion show that in thyroid insufficiency the I is utilised much less and more slowly than normally. A. A. E.

Post-operative amino-acid excretion in Graves' disease. W. KRECH (Arch. klin. Chirurg., 1933, **174**, 662—666).—After operations on the thyroid (I) in Graves' disease, the urinary output of NH_2-N increased; in other (I) conditions there was a post-operative fall in NH_2-N. The urinary NH_2-N curve seemed to bear no relation to changes in temp. The differences between Graves' disease and other (I) conditions are attributed to the defect in the former of protein synthesis and the effect of pre-operative I medication on the storage of protein in the (I). NUTR. ABS. (*b*)

Post-operative changes in blood-fat. F. FROCHNOW and L. FINDEISEN (Arch. klin. Chirurg., 1933, **175**, 121—137).—The total blood-fat (I) in operative as distinct from metabolic diseases varies in the fasting condition from 230 to 310 mg. per 100 c.c. In cholelithiasis and cholecystitis (I) varies from 214 to 354 mg. per 100 c.c. The lowest vals. are 200 mg. (tubercular peritonitis) and the highest 530 mg. (xanthomatosis). The normal individual variations are 13% (fasting), and 20—22% (fed). No significant change of (I) occurs with Et_2O narcosis alone, but hyperlipæmia arises as soon as operative work begins. Variation of (I) as a result of operations under local anæsthesia is very small and post-operative hypolipæmia is rarely observed. NUTR. ABS. (*m*)

Rose-Bengal test of hepatic function. Spectroscopic method. T. L. ALTHAUSEN, G. R. BISKIND, and W. J. KERR (J. Lab. Clin. Med., 1933, **18**, 954—958).—The dye present in the blood-plasma is determined spectroscopically. CH. ABS.

Carbohydrate metabolism in obstructive jaundice. S. NISHIGAKI (J. Chosen Med. Assoc., 1933, **23**, 34—36).—In rabbits and chickens, experimental obstructive jaundice produced by ligature of the common duct to prevent passage of bile into the duodenum causes immediate hyperglycæmia followed by a prolonged hypoglycæmia (I). The effects of administering insulin to the jaundiced animals indicate that a hypersecretion of pancreas hormone, secondary to the disturbed liver function, is the main factor in causing (I). NUTR. ABS. (*m*)

Copper in the normal and pathological liver. A. POLICARD (Compt. rend. Soc. Biol., 1933, **112**, 1418—1419).—In atrophic cirrhosis (man) Cu (determined histospectrographically) is much more abundant than in normal liver, being particularly localised in the fibrous tissue septa, although irregularly distributed. In pigmentary cirrhosis the Cu content is also above normal. The livers of white rats contain only minute traces of Cu. NUTR. ABS. (*m*)

Pharmacology of inflammation. IX. Action of water- and salt-mobilising agents on the inflammatory reaction. W. LIPSCHITZ and E. REUTER (Arch. exp. Path. Pharm., 1933, **171**, 650—667).—Intravenous injection into rabbits of NaCl solution (3·7%) decreases the inflammatory reaction produced by the application of mustard oil to the skin 1 hr. or 16 hr. later. Injection of glucose solution (25%) has a similar action even after a 16-hr. interval when the blood chemistry has become approx. normal. Administration of salyrgan, which results in a marked increase in H_2O and NaCl excretion, has only an uncertain effect in decreasing inflammation. W. O. K.

Experimental leucocytosis and blood-sugar regulation. P. LORTHIOIR (Compt. rend. Soc. Biol., 1933, **113**, 401—403).—Experimental leucocytosis in rabbits evoked by injection of colchicine causes the blood-sugar to increase and the glucose tolerance to decrease. NUTR. ABS. (*m*)

Change produced in the fat tissue by insulin in malnutrition. H. BLOTNER (J. Amer. Med. Assoc., 1933, **100**, 1235—1237).—In a case of non-diabetic malnutrition during a period of gain in wt. (21 lb.) induced by insulin administration, the

depth of the subcutaneous fat increased from 3 to 16 mm. and the average diameter of each fat cell from 35 to 79·8 μ, but there was no change in the glycogen content of the skin. NUTR. ABS. (*m*)

Standards of basal metabolism for children of retarded growth. A. TOPPER (Amer. J. Dis. Child., 1933, **45**, 1203—1210).—In children with retarded growth the basal rate exceeds the normal when referred to standards of total height, sitting height, wt., and surface area, but agrees with standards according to age. NUTR. ABS. (*m*)

Metabolism studies with glycine in progressive muscular dystrophy. S. KOSTAKOW and A. SLAUCK (Deut. Arch. klin. Med., 1933, **175**, 302—310).—In progressive muscular dystrophy, treatment with glycine, which is sometimes beneficial, is followed by increase in creatinuria. NUTR. ABS. (*m*)

Effect of adrenaline in certain muscular disorders. J. ST. C. ELKINGTON and M. W. GOLDBLATT (Lancet, 1933, **225**, 693—694).—The injection of adrenaline produced a rise in blood-lactate (I) in all the various myopathies examined. Resting lactic acid in the blood remained within normal limits. Differences obtained in (I) increments and in the hyperglycæmias for various kinds of muscular disorder are recorded. L. S. T.

Blood-non-protein-nitrogen and -creatinine in nephritis and prostatic obstruction. A. CANTAROW and R. C. DAVIS (J. Lab. Clin. Med., 1933, **18**, 502—506).—In individuals with obstructive urinary lesions the blood-creatinine is increased to approx. the same extent as in renal disease. CH. ABS.

Andrewes' diazo-reaction and Becher's xanthoproteic reaction in the blood. C. P. WALDORP (Semana méd., 1933, i, 1817—1826).—Blood (5 c.c.) is mixed with $CCl_3{\cdot}CO_2H$ (5 c.c.) and Becher's reaction applied to the filtrate; a Sahli colorimeter and 0·03874% $K_2Cr_2O_7$ solution are employed. Becher's reaction is positive in normal blood, and increased in nephritis. Andrewes' reaction is negative in normal blood, but positive in renal insufficiency. CH. ABS.

Unsaturated fatty acids in experimental renal damage and oxygen deficiency. J. ROF and A. THURNHERR (Z. ges. exp. Med., 1933, **88**, 693—704).—The I val. (I) of the renal fat of rabbits increases after poisoning with $HgCl_2$ or large doses of salyrgan, but decreases after cantharidin poisoning. Rats and rabbits exposed to decreased atm. pressure (O_2 lack) show a rise in the (I) of the fat of all the organs when the decrease in pressure is moderate, a fall when the decrease is more marked; the total fat content of the kidneys is halved. Rats on fat-free diet are more susceptible to O_2 lack and show a more rapid and marked fall in (I) of the fat than rats on stock diet. NUTR. ABS. (*m*)

Inorganic sulphur of blood in azotæmia. C. B. UDAONDO, M. SCHTEINGART, and D. ZANALDA (Compt. rend. Soc. Biol., 1933, **113**, 462—463).—The normal inorg. S of human blood varies between 0·8 and 1·4 mg. per 100 c.c. In patients with N retention, the inorg. S of the blood lies between 2·0 and 8·0 mg. per 100 c.c. There is no direct relation between the blood-urea and blood-S. NUTR. ABS. (*m*)

Clinical manifestations of variations in blood-magnesium. A. D. HIRSCHFELDER (Proc. Soc. Exp. Biol. Med., 1933, **30**, 996—997).—Oral administration (I) of 20—30 g. of $MgSO_4$ does not significantly raise the blood-Mg of normal individuals. About 40% is excreted in the urine in 24 hr. In nephritis similar doses raise the serum-Mg from near normal to very high levels (9·8—11·3 mg. per 100 c.c.). The low serum-Mg vals. (0·9—1·37 mg. per 100 c.c.) found in nephritis, epilepsy, and parathyroid tetany are raised by (I) of $MgSO_4$. NUTR. ABS. (*m*)

Adrenaline content of the adrenal gland during upper intestinal obstruction. V. MIURA (J. Chosen Med. Assoc., 1933, **23**, 133—156).—A decrease is not due to starvation; it can be partly prevented by intraperitoneal, but not by intravenous, injection of adrenaline. CH. ABS.

So-called "pellagra-producing" diet. T. D. SPIES and J. GRANT (Amer. J. Physiol., 1933, **104**, 18—22).—A diet low in minerals, protein, and vitamins-*C*, -*D*, and -B_2 (I), beneficial to pellagra patients, was fed to rats 7 weeks old. Symptoms of (I) deficiency developed. The identity of (I) with the pellagra-preventive factor was thus contradicted. The symptoms were prevented or cured by doses of yeast or ventriculin, but not by caseinogen. It is suggested that (I) is the anti-anæmic factor. NUTR. ABS. (*b*)

Cereal food poisoning and its relation to the etiology of pellagra. R. STOCKMAN and J. M. JOHNSTON (J. Hyg., 1933, **33**, 204—223).—Monkeys fed on maize meal, with butter, milk, and fruit, developed, in some cases, paresis, depression, and nervous degeneration as observed in human pellagra. The symptoms could be induced by feeding or injecting the Na salt of an acid separated from the maize. Rabbits and guinea-pigs were slightly susceptible and frogs were killed by injection of the salt. Only one sample of rice had the same deleterious effect; rye, wheat, and oats were toxic. The theory that pellagra is caused by toxic factors present in cereals is confirmed. NUTR. ABS. (*b*)

Acid–base equilibrium and pregnancy. H. VIGNES and M. LEVY (Compt. rend., 1933, **197**, 794—796).—Determinations of the p_H val. of the plasma and the Cl ratio (Cl_P/Cl_C) in the plasma and red corpuscles in 14 cases of pregnancy indicate that the acid–base equilibrium is displaced in the direction of alkalosis, the p_H val. increasing and the Cl_P/Cl_C ratio decreasing. J. W. B.

Hyperventilation and acid–base equilibrium in pregnancy. I. BERCONSKY and J. J. ROSSIGNOLI (Rev. asoc. med. Argentina, 1932, **45**, 103).—During pregnancy pulmonary ventilation is increased 53%; CO_2 tension is decreased and O_2 tension increased in the alveolar air, the alkaline reserve of the plasma is diminished, and p_H is normal. In some cases of pelvic disease changes in the same direction were observed. Causes of hyperventilation are discussed. CH. ABS.

Contents of parovarian cysts. K. DIERKS and M. BECKER (Arch. Gyn., 1933, **152**, 679—689; Chem. Zentr., 1933, i, 2833).—H_2O, Cl, Ca, PO_4, sugar, and N distribution have been determined. Amylase was present in traces; lipase, ovarian hormone, and gonadotropic hormone were absent. A. A. E.

Renal hypertrophy in rats fed on a high-protein diet. H. E. C. WILSON (Biochem. J., 1933, **27**, 1348—1356).—Gelatin fed to rats produces a greater increase in the kidney wt. than does either caseinogen or liver. Glycine, glutamic acid, and wheat-gluten all cause an increase which is approx. proportional to the additional N consumed. The hypertrophy may be associated with some intermediate process in protein catabolism, possibly deamination by the kidney. A. W.

Evaluation of the phosphorus deficiency of the rickets-producing diet. A. T. SHOHL, H. B. BROWN, E. C. CHAPMAN, C. S. ROSE, and E. M. SAURWEIN (J. Nutrition, 1933, **6**, 271—284).—On a high-Ca, low-P diet adequately supplemented with vitamin-*A* and -*D* the growth of rats was retarded. Over a long period retention of Ca was high and of P low. The fat-free bones contained normal proportions of Ca and P. P deficiency was the limiting factor causing delayed growth. A. G. P.

Phosphorus and rickets. II. Role of the phosphate ion in the antirachitic activity of inorganic phosphorus compounds. R. LECOQ and H. VILLETTE (J. Pharm. Chim., 1933, [viii], **18**, 192—197; cf. A., 1932, 642).—Na_2HPO_3 (up to 3% of diet) has no antirachitic activity in rats. The activity of salts derived from P_2O_5 increases with the no. of mols. of H_2O combined with P_2O_5 in the corresponding acid. Thus the active doses of P are 0·1, 0·2, and 0·3% of diet when given in the forms of Na_2HPO_4, $Na_4P_2O_7$, and $NaPO_3$, respectively. The calcifying action of Na, K, and NH_4 phosphates increases with the acidity of the salt. The activity, referred to P content, of NH_4 phosphates is slightly <, of K phosphates almost equal to, that of the corresponding Na salt. A. C.

Plasma-phosphatase in rickets and other disorders of growth. J. SMITH (Arch. Dis. Child., 1933, **8**, 215—220).—The average plasma-phosphatase val. (I) of normal breast-fed, healthy infants is 0·248 unit (range 0·20—0·30). Infants suffering from rickets, and others on rachitogenic diets (II), have increased (I). Addition of vitamins-*A* and -*D* to the (II) causes the val. to fall to normal. Conditions characterised by cessation of growth are associated with abnormally low (I). NUTR. ABS. (*m*)

Hydrogen-ion concentration in the organs and body-fluids of scorbutic guinea-pigs. R. MCCARRISON and G. SANKARAN (Indian J. Med. Res., 1933, **20**, 971—974).—In the scorbutic group fed on autoclaved milk and crushed oats, the urine was more acid and the blood, bile, testes, and thyroid tended to have a diminished alkalinity, whilst the spleen, heart, and liver tended to be less acid than corresponding organs of the normally fed group. NUTR. ABS. (*b*)

Blood picture of guinea-pigs during scurvy and recovery. B. DIBLICEK and C. KUCERA (Compt. rend. Soc. Biol., 1933, **113**, 632—634).—Scurvy is accompanied by a 32% reduction in the red blood-corpuscles (I), and an increase of blood-platelets and poikilocytosis, this being most marked during the scorbutic crisis. Recovery results from feeding germinated pulses, decitrated lemon-juice, or green food and is accompanied by an increase in (I), up to 17% above the original. The white-cell count follows the (I) count, falling to 32% of the normal; recovery is accompanied by an increase of eosinophile leucocytes at the expense of lymphocytes; the basophile leucocytes do not vary. Excess (II) of vitamin-*C* causes a transitory acute leucocytosis.

Hæmoglobin (III) is lowered by 3—10% during scurvy. (II) causes a 10—20% increase in (III) and as much as 25% during pregnancy. Although pulses germinated for 5—9 days are the most potent in curing macroscopic symptoms, those germinated for 10—15 days have the most marked effect on the blood picture. NUTR. ABS. (*m*)

Minerals in silicotic lungs. W. R. JONES (J. Hygiene, 1933, **33**, 307—329).—The bulk of the mineral residue (I) from silicotic lungs consists of minute fibres of sericite (II) which is present in the inhaled dust. Quartz (III) is also present in (I), but is not the chief cause of silicosis (IV). Fibrous minerals such as (II), sillimanite, or tremolite etc. which are liberated in air during drilling and blasting and not the relatively large particles of (III) are of prime importance in producing (IV). L. S. T.

Excretion of antigenic substances with the urine in infectious diseases, particularly tuberculosis and syphilis. F. KLOPSTOCK (Klin. Woch., 1933, **12**, 249—252; Chem. Zentr., 1933, i, 2269).—A method of extraction is described, and the results of complement-combination tests are recorded. A. A. E.

Amine theory of infantile toxæmia. S. ROSENBAUM and A. CHASSEL (Jahrb. Kinderheilk., 1933, **139**, 131—142).—In the intestine or blood of dogs suffering from intoxication (I) due to exsiccation and injection of *coli* endotoxin there is no increase in amines, but increase occurs always in the intestine (but only occasionally in the blood) of infants with symptoms of (I). The urine or cerebrospinal fluid of such infants contains no amines. The amine theory of toxæmia in infancy hence receives no support. NUTR. ABS. (*m*)

Diagnostic utilisability of peptolytic enzymes in trans- and ex-udates. J. AMMERSCHLAGER (Deut. Arch. klin. Med., 1933, **175**, 124—128; Chem. Zentr., 1933, i, 2708).—In pathological exudates of the chest and stomach a " peptolytic " enzyme which decomposes glycyltryptophan is present. Its differential diagnostic val. is limited. A. A. E.

Energy of activation and temperature coefficient of a biological reaction (respiration of the larvæ of *Diphyllobothrium latum*). E. A. H. FRIEDHEIM, B. SUSZ, and J. G. BÆR (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 177—182).—The energy of activation for this process between 20° and 37° is 25,000 g.-cal., and the temp. coeff. 3·8 for 10°. The reaction involved is, therefore, not simple addition of O_2, but resembles a catalytic reaction. Above 37° the velocity of respiration decreases rapidly. R. S. C.

Standard metabolism of Australian aborigines. C. S. Hicks and R. F. Matters (Austral. J. Exp. Biol., 1933, **11**, 177—183).

Basal metabolism in different races of fowls. G. Iftimesco, G. Nichita, I. Popesco, and N. Tuschak (Compt. rend. Soc. Biol., 1933, **113**, 492—494).—The data (six different breeds) confirm the increase of metabolism per unit wt. with diminishing size, and its constancy when expressed per unit of surface area. Nutr. Abs. (*m*)

Basal metabolism of small birds. F. G. Benedict and E. L. Fox (Pflüger's Archiv, 1933, **232**, 357—388).—The average metabolic rate (I) of canaries (II) and parrots (III) at 28° at night at least 10 hr. after the last feed is 718 g.-cal. per sq. m. per 24 hr.: under similar conditions that of sparrows is 656 g.-cal.; at 16° the average val. for (II) and (III) is 1077 g.-cal. and for sparrows (IV) 914 g.-cal. The rectal temp. averages about 42°. (I) is slightly higher in males and is considerably higher during the day, even although the birds are kept in the dark. Muscular activity has a great effect on (I). The reaction to reduced temp. is much more marked in (II) and (III) than in (IV). The (I) of small birds (average about 700 g.-cal.) is low when the high cell temp. is taken into account, and compares with the val. for the mouse (640 g.-cal.). Nutr. Abs. (*m*)

Simple eudiometer. L. Plantefol (Bull. Soc. Chim. biol., 1933, **15**, 992—1012).—With the apparatus described R.Q. may be determined with an accuracy of 0·03. A. L.

Tendency of different animal species to ketonuria and ammonuria. H. Trimbach (Compt. rend., 1933, **197**, 708—710).—The degree of ketonuria (I) appears to vary inversely as the size of the animal. In the rat (I) is ten and six times as great as in the calf and pig, respectively, on a cow's milk diet and about twice as great as in the pig on a purely carbohydrate diet, *i.e.*, at the level of sp. min. N output. The variations of urinary NH_3 in different species on the same diet are also considerable, but not parallel to those of (I). A. C.

Ketogenic diet in normal individuals. F. L. Apperly and J. H. Norris (Amer. J. Med. Sci., 1933, **185**, 802—810).—The blood changes produced by ketogenic diets in three normal subjects showed that, despite a profound ketosis, alkalæmia (I) was almost constantly present, accompanied by a fall in plasma- and red-cell-CO_2. (I) may be the result of a hyperpnœa produced by the direct stimulation of the respiratory centre by certain ketone derivatives, and this may outweigh the tendency to acidosis produced by the keto-acids. Nutr. Abs. (*m*)

Effect of cholesterol ingestion on tissue-lipins of rats. A. Chanutin and S. Ludewig (J. Biol. Chem., 1933, **102**, 57—65).—With a diet containing 2·5% of cholesterol (I), (I) ester and total lipin (II) were increased in the liver, reaching a max. after 25 days with production of fatty livers; free (I) increased after the third week, but other organs showed no change. Fats inhibit and carbohydrates accelerate deposition of (I) in the liver and markedly increase (II). H. G. R.

Metabolism during secretion in liver, kidney, and salivary glands. R. Ferrari and R. Hober (Pflüger's Archiv, 1933, **232**, 299—321).—The ability of the frog's liver which is being perfused with Ringer's solution to concentrate and excrete colouring material (eriocyanin-*A* 0·0005%) in the bile is temporarily inhibited by addition of $CH_2I{\cdot}CO_2H$ (I). The stellate cells which possibly take part in the secretion of bile and leucocytes are immune to the presence of CN′, but are prevented by (I) from storing trypan-blue. The formation of urine by renal glomeruli, re-absorption of Cl by the tubules, and secretion of phenol-red are all inhibited by both CN′ and (I). Addition of 0·001*N*-KCN to the perfusing fluid of the submaxillary salivary gland of the cat leads to increased production of lactic acid and H_3PO_4. (I) causes decrease in lactic acid and increase in H_3PO_4 production. CN′ and (I) lead to increased content of Cl and K. The secreting and storing of substances by liver, kidney, and glandular cells depend on the utilisation of carbohydrate and the catabolism of an org. P compound. Nutr. Abs. (*m*)

Composition of different regions of mounds of *Eutermes exitiosus*, Hill. F. G. Holdaway (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 160—165).—The proportion of excreted lignin was highest in the central (nursery) section of the mound and lowest in the external wall. The ratio cellulose : lignin decreased somewhat towards the centre, the average val. being 1 : 4. A. G. P.

Analysis of termite (*Eutermes exitiosus*) mound material. W. E. Cohen (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 166—169).—In the digestion of wood by termites lignin remains practically unchanged. Considerable decomp. of cellulose is shown by the increased alkali-sol. fraction. A. G. P.

Glycogen formation from lower fatty acids with an even number of carbon atoms. II. Glycogen formation from *n*-butyric acid. R. Stohr (Z. physiol. Chem., 1933, **220**, 27—33; cf. this vol., 855).—Female rats receiving $PrCO_2H$ and glucose show a considerably higher liver-glycogen content than controls with glucose only. This indicates a synthesis of carbohydrate from the acid. J. H. B.

Absorption of glucose from the intestine. I. S. Ravdin, C. G. Johnston, and P. J. Morrison (Amer. J. Physiol., 1933, **104**, 700—709).—In unanæsthetised dogs increase in the concn. and in the vol. of the same concn. of glucose results in increase in the amount (I) of glucose absorbed from jejeunal Thiry loops. No linear relationship exists between (I) and the time, (I), in increasing periods, being dependent on the concn. and vol. of the solution present during any given period. Nutr. Abs. (*m*)

Bile acids and carbohydrate metabolism. XXVI. Production of glycogen in the livers of splenectomised rabbits receiving adrenaline, cholic acid, and spleen extract. K. Fuziwara. **XXVII. Production from bile acids of glycogen in the livers of castrated and ovariotomised rabbits.** H. Takata (Biochem. Z., 1933, **265**, 76—79, 80—84; cf. this vol., 528).—XXVI. In

splenectomised rabbits (I) injection of a small amount of adrenaline causes increase (II) in the production (III) of glycogen in the liver from glucose simultaneously administered, but (II) is counteracted by injecting cholic acid (IV) at the same time. Oral administration of ox-spleen extract also causes (II).

XXVII. Although (IV), orally administered, increases (III) in the livers of castrated and ovariotomised rabbits, castration and, still more, ovariotomy decrease (III) and diminish the stimulating effect (V) of (IV). (V) is related to the function of the generative glands. W. McC.

Bile acids and carbohydrate metabolism. XXVIII. Ergosterol glycocholia and the sympathetic nervous system. T. TANAKA (J. Biochem. Japan, 1933, **18**, 33—43).—The bile-acid secretion of dogs with biliary fistulæ is increased by unilateral splanchnicotomy (I), whilst subsequent feeding with ergosterol (II), but not with its benzoate, further enhances the effect. (II) also diminishes the glycocholia due to administration of sugar (cf. this vol., 419), whilst subsequent (I) increases it again. F. O. H.

Excretion of citric acid by the rabbit kidney. H. LANGECKER (Arch. exp. Path. Pharm., 1933, **171**, 744—755).—The daily excretion of citric acid (I) in the urine of rabbits is: fasting 1·8—3·5 mg.; on oats, 1—7 mg.; and on green food, 13—50 mg.; *i.e.*, 0·5%, 1%, and 1·4—2%, respectively, of the total org. acid. Administration of $NaHCO_3$ with the acid-producing oats increases the excretion of (I), whilst HCl with the basic green food has the opposite effect. (I) or Na citrate administered by mouth does not increase the (I) excretion in the urine. W. O. K.

Comparative effect of tomato and orange juices on urinary acidity. L. G. SAYWELL and E. W. LANE (J. Nutrition, 1933, **6**, 263—270; cf. A., 1932, 1056).—Daily addition of 1 litre of juice to the human diet caused an increase in urinary p_H (average 1·2 units) and corresponding reduction in total acidity and NH_3 excretion. Higher proportions of org. acids were excreted and there was an increased alkaline reserve. Increased alkalinity of urine is associated with a higher ratio of sol. to insol. alkalinity in the ash. A. G. P.

Relation between change in volume and the chemical processes of contraction in muscle. O. MEYERHOF and H. HARTMANN (Naturwiss., 1933, **21**, 661).—The disagreement between the data from dilatometer experiments using enzyme preps. of muscle (I) (cf. this vol., 856) and those from the living (I) is due to a secondary swelling of (I) which accompanies contraction. When, however, the Ringer's solution in the measuring vessel is replaced by paraffin this swelling is eliminated and a good agreement is obtained with both normal and iodoacetate-poisoned (I). Hence the normal contraction of (I) is fully explained by changes in vol. due to changes in the constituents. F. O. H.

[Anaerobic formation and disappearance of pyruvic acid in muscle.] A. HAHN (Z. Biol., 1933, **94**, 97—98).—Polemical (cf. this vol., 742). E. S. H.

Acetylation. Fate of *p*-aminobenzoic acid in the rabbit. B. HARROW, A. MAZUR, and C. P. SHERWIN (J. Biol. Chem., 1933, **102**, 35—38).—*p*-$NH_2 \cdot C_6H_4 \cdot CO_2H$ is acetylated to the extent of 25% and this is increased by injection of insulin. The effect of the latter is inhibited by injection of reduced glutathione. H. G. R.

Action of surviving tissue on amino-acids. E. C. GLOVER (Compt. rend. Soc. Biol., 1932, **107**, 1603—1605).—Tissues with anaerobic glycolysis (brain, embryo, tumour) have no action on NH_2-acids; liver and kidney tissue produce NH_3 or urea. A. A. E.

Synthesis of creatine from tissue-protein. G. PARISET (Compt. rend., 1933, **197**, 704—706).—The sum of the creatine- (I) and creatinine-N (II) excreted by rabbits during starvation and of their bodies after death is considerably > their total (I) (II) content at the beginning of starvation. This demonstrates creatinoid synthesis from tissue-protein. A. C.

Effect of diet on egg composition. II. Mortality of embryos in eggs from hens on diet containing protein supplements of different origin. III. Relation of diet to the vitamin- and -*B*$_2$ content of eggs: vitamin-*A* content. N. R. ELLIS, D. MILLER, H. W. TITUS, and T. C. BYERLY (J. Nutrition, 1933, **6**, 225—242, 243—262; cf. this vol., 631).—II. Rations containing certain cereal products and protein concentrates, supplemented with lucerne, minerals, and cod-liver oil, were deficient in some substance (possibly vitamin-B_2) necessary to produce eggs capable of supporting embryonic life during the second week of incubation.

III. The effect of variations in the proportion of vitamins-B_1 and -B_2 in the diet on the vitamin content of eggs is examined. No relationship was apparent between vitamin status and hatchability. A. G. P.

Chemical mass-action and protein degradation in the living body. O. KRUMMACHER (Z. Biol., 1933, **94**, 119—134).—A discussion, partly mathematical, of the relations between concn. of protein, rate of hydrolysis, and rate of resorption in the alimentary tract. W. O. K.

Distinctive characters of specific minimum nitrogen output and of exogenous protein metabolism. E. F. TERROINE and G. BOY (Compt. rend., 1933, **197**, 702—704).—N metabolism is classified as (*a*) sp. min. N output determined on a carbohydrate diet (I), and (*b*) contingent N output which is exogenous on a protein-rich diet (II) and is determined by difference between (I) and (II). Creatinine (III) is found only in (*a*), creatine (IV) in (*b*). The distribution of excreted N in (*a*) varies considerably with the species of animal, but is approx. const. in (*b*) for the pig, rabbit, and rat. Similarly the coeffs. of protein and purine oxidation vary in (*a*) but not in (*b*), where the vals. are higher. Whilst the abs. val. of NH_3 production is higher in (*b*) than in (*a*), it is lower in relation to the sum of urea-, NH_3-, and NH_2-N. Whilst (III) excretion is const., that of (IV) increases with the dietary protein, indicating different processes for their production. A. C.

Comparative biological value of proteins in different animal species. A. RAJZMANN (Compt. rend., 1933, **197**, 706—707).—The mean biological vals. of the total proteins of cow's milk, beef muscle, pease-meal, and of caseinogen, expressed in the Terroine form of Martin and Robison's formula, are 92, 100, 61, and 77, respectively, for the rat; 100, 95, 58, and 81 for the rabbit; and 94, 99, 65, and 78 for the pig. The vals. for each protein vary considerably within each species. A. C.

Milk-energy formulæ for various breeds of cattle. O. R. OVERMAN and W. L. GAINES (J. Agric. Res., 1933, **46**, 1109—1120).—Milk-energy vals. (g.-cal. per g.) determined were: fat $9{\cdot}253\pm0{\cdot}065$; protein $5{\cdot}853\pm0{\cdot}127$; lactose $3{\cdot}693\pm0{\cdot}059$. Formulæ for calculating milk energy based on the % fat showed small differences for different breeds, but the single formula expressed in terms of 4% milk, $0{\cdot}4M+15F$ (M=wt. of milk, F—wt. of fat), may be used for all breeds. Variations in protein-energy ratio with changes in % fat showed more definite differences with breed. Vals. for crossbred cows were intermediate between those of the parent breeds. The utilisation of the above vals. in determining food requirements for milk production is examined. A. G. P.

Form and function of synovial cells in tissue cultures. II. Production of mucin. E. VAUBEL (J. Exp. Med., 1933, **58**, 85—95).—Max. mucin production occurs in media containing a min. of growth-stimulating substances. Liquefaction of plasma is attributed to a proteolytic enzyme. CH. ABS.

Human purine metabolism. F. CHROMETZKA (Z. ges. exp. Med., 1933, **86**, 483—528; Chem. Zentr., 1933, i, 2271).—A scheme indicating the mode of degradation of uric acid etc. is advanced. In gout this degradation is retarded; in diabetes insipidus the oxidisability of the purine bases may be inhibited. A. A. E.

Purine metabolism. II. Fate of guanine in the dog. F. W. ALLEN and L. R. CERECEDO (J. Biol. Chem., 1933, **102**, 313—316; cf. A., 1932, 84).—Guanine is partly converted into allantoin and partly broken down to yield urea. Adenine is toxic in doses $>1{\cdot}3$ g. H. D.

Effect of alkaline water on purine metabolism. E. HESSE and K. NAWRATH (Klin. Woch., 1932, **11**, 1538—1540; Chem. Zentr., 1933, i, 2271).—H_2O from Salzbrunn (Kronenquelle) contains HCO_3', CO_2, and cations which separately do not affect the purine metabolism of the dog, but together they cause increased elimination of allantoin and uric acid. A. A. E.

Neuromuscular excitability in relation to the biochemistry of minerals. III. Mineral composition of blood-serum and muscle press-juice or their ultrafiltrates in relation to neuromuscular excitability. Influence of parathyroidectomy on the Ca/Mg ratio of blood-serum. B. SJOLLEMA and L. SEEKLES (Biochem. Z., 1933, **204**, 316—333).—The authors' previous work (this vol., 532, 979), in which changes of neuromuscular excitability (I) were correlated with changes in the mineral content (II) of the diet, is extended, the (II) of the blood-serum (III), muscle press-juice (IV), and of their ultrafiltrates being investigated. Abnormal Na/K ratios of (III) are associated with only irregular changes of (I). The Ca/Mg ratio of (III) shows irregular fluctuations with increasing (I), whereas the Ca/P ratio is invariably decreased. In parathyroidectomised dogs the Ca/Mg and the Ca/P ratios of (III) decrease. The Ca/Mg ratio is changed in different directions in different forms of tetany and does not always run parallel with changes of (I). In (IV) the total Ca content with diets of abnormal Ca/P and Na/K content increases with increasing (I), the results being the reverse of those in (III). The total Mg content was not directly related to the excitability. P. W. C.

Function of calcium deposits as buffer reserves in acid–base regulation. Chalk glands of the earthworm. H. DOTTERWEICH (Pfluger's Archiv, 1933, **232**, 263—286).—The chalk glands (I) of *Lumbricus terrestris* have considerable buffering capacity against acids. After removal of (I) the p_H of the cœlomic fluid remains normal while the worms are kept in air, but falls much $>$ that of normal worms when the atm. contains 5% CO_2. An atm. containing 8—10% of CO_2 raises the Ca content of the tissues of undissected worms from 10·34 to 17·27 mg. per 100 g., but causes only a slight increase in excretion of Ca. (I) contain a buffer reserve of solid $CaCO_3$ which becomes $CaH_2(CO_3)_2$ as the p_H falls, the process being reversible. Allied phenomena in other invertebrates and other functions of (I) are discussed. NUTR. ABS. (*m*)

Calcium and phosphorus metabolism. XIX. Effect of diet on urinary acid and ammonia excretion in man. W. T. SALTER, R. F. FARQUHARSON, and D. M. TIBBETTS (J. Lab. Clin. Med., 1933, **18**, 669—679).—The daily urinary excretion of NH_3 by adults receiving potentially neutral diets is equiv. to 21 c.c. of N-acid. With acid-producing foods it rarely exceeds 80 c.c. A high-protein diet does not cause increased NH_3 excretion if sufficient alkali is added to neutralise the acid catabolites. CH. ABS.

Calcium retention on a diet containing leaf lettuce. M. G. MALLON, L. M. JOHNSON, and C. R. DARBY (J. Nutrition, 1933, **6**, 303—311).—In the metabolism of women subjects, utilisation of the Ca of fresh leaf lettuce was $>$ that of pasteurised whole milk. A. G. P.

Excretion of calcium and phosphorus on maize diet. I. I. NITZESCU, G. POPOVICIU, and R. OPREAN (Compt. rend. Soc. Biol., 1933, **113**, 326—328).—In children a maize diet decreases the urinary Ca and P and increases the fæcal elimination, with consequent constipation and with an average negative balance of 32·1% for Ca and 17·5% for P. Meat and wheat (I) diet results in an average negative Ca balance of 6·2% and a positive P balance of 11·6%, whilst less Ca is lost by the fæces. Treatment with ultra-violet light reduces the fæcal Ca and P. The best retention of Ca occurs on a diet (II) of maize, milk, and cheese. The retention is fair on (I) if milk is given, but poor on (II) if beans are added. The Ca : P ratio in the excreta on (I) is 0·6 and on the maize and beans diet 1·1. Maize is rachitogenic, especially when associated with beans, but this effect is compensated by treatment with ultra-

violet light and perhaps by the addition of cheese and milk to the diet. NUTR. ABS. (*m*)

Influence of bile acids on calcium metabolism. VII. Calcium and phosphorus balance in dogs receiving bile acids. I. OKII (J. Biochem. Japan, 1933, **18**, 45—61).—Intravenous injection of cholic acid or subcutaneous injection of ultra-violet-irradiated Me cholate (A., 1932, 615) into dogs produces an increased assimilation of both P and Ca. F. O. H.

Importance of mineral supplements and iodine for milch cows. G. VON WENDT and W. MULLER-LENHARTZ (Z. Fleisch. Milchhyg., 1932, **42**, 221; Bied. Zentr., 1933, **A**, **3**, 424).—The significance of Ca, Fe, and I in mineral supplements for heavily milking cows is discussed. A. G. P.

Feeding of iodine to poultry. J. SCHMIDT (Berlin. Tierartzl. Woch., 1932, **48**, 161; Bied. Zentr., 1933, **A**, **3**, 425).—Hens are less sensitive to I injury than are mammals. Supplementary feeding with 0·3—0·5 g. KI reduced the size of eggs, and larger doses (to 1·5 g.) interrupted the laying period. With 1·5 g. KI the male reproductive system was not affected. Eggs from hens receiving KI had higher I contents and better keeping qualities. A. G. P.

Amount of iodine in the thyroid glands of Australian merino sheep. M. C. DAWBARN and F. C. FARR (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 179—180).—In the area examined, the use of iodised salt licks did not increase the I content of the thyroid glands. A. G. P.

Effect of an iodised lick on the growth and wool of Australian merino sheep. E. W. L. LINES [with R. G. THOMAS] (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 181—188).—Ingestion of 185×10^{-6} g. I daily by means of iodised salt licks did not affect growth or wool production in sheep. A. G. P.

Ferri-globulin compound of intermediate iron metabolism. E. STARKENSTEIN and Z. HARVALIK (Arch. exp. Path. Pharm., 1933, **172**, 75—92).—The significance of Fe^{III}–protein compounds (A., 1930, 952) in the metabolism of Fe is discussed. The oxidative power (I) of the blood (defined as mg. of $FeCl_2$ oxidised by 100 c.c. in 5 min.) is approx. 500, being high in rabbits (490—550) and low in men (454). No difference occurs between defibrinated and oxalated blood. Erythrocytes suspended in 0·9% NaCl have a (I) of approx. 50, that of serum is nil, whilst that of washed corpuscles re-suspended in serum is markedly < that of the whole blood. Hence during the separation (I) is partly destroyed. (I) is related to hæmoglobin, whilst the protein of the Fe^{III} complex formed appears to be serum-globulin, the bound Fe being anionic. The complex can be separated by half-saturation with $(NH_4)_2SO_4$ or by dialysis; in the latter instance it is insol. in H_2O, whereas serum-albumin pptd. by $FeCl_3$ is sol. Blood treated with sufficient $FeCl_3$ yields an Fe–protein complex with a N : Fe ratio of 4 : 1. F. O. H.

Oxidation of iron in the blood. F. HENDRYCH and S. MORI (Arch. exp. Path. Pharm., 1933, **172**, 1—4).—The oxidation of Fe^{II} salts and the concomitant formation of a Fe^{III}–globulin complex (cf. preceding abstract) does not occur in completely reduced or CO-saturated blood. Gradual saturation or replacement with O_2 in the two types of blood does not yield oxidising activities proportional to the O_2 content; the vals. are < those expected, indicating that the affinity of O_2 for reduced hæmoglobin is > that for Fe^{II} salts. The oxidation of Fe^{II} by oxy-hæmoglobin is not inhibited by HCN or quinine. F. O. H.

Periodic variation of bone-marrow activity and blood formation. E. STARKENSTEIN (Arch. exp. Path. Pharm., 1933, **172**, 36—54).—Partial destruction of the bone-marrow of rabbits and dogs produces an anæmia which spontaneously disappears within a few weeks. The effect is far more marked in autumn and winter (I) than in spring and summer (II). During (II) the hæmoglobin, erythrocyte count, and colour index are lowest, probably due to the gradual utilisation of reserve material during (II) and the resulting lack of stimulation of organ function during (I). Parallel variations are shown in metabolic rate, in the excitability of the sympathetic nervous system, in the sensitivity to poisons, and in the reproductive processes. F. O. H.

Oxidation and reduction of iron in organs. E. STARKENSTEIN and F. JOHNE (Arch. exp. Path. Pharm., 1933, **172**, 93—103).—The reducing substances of liver (I) extractable with conc. HCl at 100° consist partly of those extracted with H_2O at 100°. Practically all the Fe in rabbit's (I) is H_2O-insol. and is extracted only by hot 5*N*-HCl. The Fe^{III} of Na Fe citrate is rapidly reduced by (I) to Fe^{II}, which is only partly H_2O-sol. The reducing action of (I) is mainly due to enzyme action; heat or treatment with 2*N*-HCl greatly reduces, whilst absence of O_2 accelerates the action. That of blood is small, whilst its oxidising action on $FeCl_2$, unlike that of (I), is marked and yields a H_2O-sol. form of Fe^{III}, which after a time becomes partly H_2O-insol. Both (I) and blood also reduce $K_3Fe(CN)_6$ to $K_4Fe(CN)_6$; the reverse process of oxidation does not occur. The non-reducible, complex Fe^{III} of (I) probably originates from Fe^{II} oxidised in other organs before being transported to (I). F. O. H.

Autoxidation of ferrous salts and stability of their solutions. E. STARKENSTEIN and R. NEIGER (Arch. exp. Path. Pharm., 1933, **172**, 104—118).—Neutral aq. Fe^{II} salts are not stable in presence of O_2, whilst acid solutions have a stability (I) dependent not only on the p_H, but also on the anion. With simple inorg. Fe^{II} salts, the (I) of the neutral solution depends on the readiness of hydrolysis of the Fe^{III} salt formed by oxidation (II); thus in decreasing order of (I) are obtained: Cl', SO_4'', AcO', HCO_3'. The Fe^{II} salts of complex-forming org. acids (citrate, gluconate, lactate) are even less stable. In neutral solution formation of Fe^{III} [which inhibits (II)] is followed by its removal as $Fe(OH)_3$. The course of (II) depends on the concn. of Fe^{II} salt and on the temp. With simple inorg. salts it is independent of light, whilst with Fe^{II} citrate (II) is irregular, due to the reducing action of light. F. O. H.

Role of zinc in nutrition. J. M. NEWELL and E. V. MCCOLLUM (J. Nutrition, 1933, **6**, 289—302).—

It is improbable that Zn is an essential nutritional factor in the growth of rats, although in its absence reproduction was adversely affected. The total Zn content of the bodies of rats was influenced by that of the diet. A. G. P.

Carotid-sinus polyuria. S. JANSSEN and J. SCHMIDT (Arch. exp. Path. Pharm., 1933, **171**, 672—690).—In anæsthetised dogs and rabbits, clamping of the two carotids leads after a short latent period (1—2 hr.) to an abnormally high content of NaCl (up to 1·5%) in the urine usually associated with polyuria. The effect is due to a nervous reflex originating at the carotid sinus. W. O. K.

Biological action of intermediate products of tissue decomposition. I. Influence of pancreatolysate on blood-sugar. S. G. GENESS and S. P. EPSTEIN (Arch. exp. Path. Pharm., 1933, **171**, 733—743).—Digests of pancreas administered to rabbits usually reduce the blood-sugar. The effect is especially marked with a fraction free from protein but containing the larger fission products. W. O. K.

Influence of vagotomy on the blood-sugar. F. HOGLER (Arch. exp. Path. Pharm., 1933, **172**, 325—342).—Unilateral or double vagotomy (I) has no marked influence on the blood-sugar (II) of rabbits, whilst with unilateral (I) ergotamine completely inhibits the alimentary hyperglycæmia (III) following ingestion of glucose or galactose. Thus whilst the vagi play no part in the maintenance of the fasting (II) they are concerned with the function of the liver in the removal of (III). F. O. H.

Suitability of infusions and tinctures of *Digitalis* as medicaments. S. ROSENKRANZ (Arch. exp. Path. Pharm., 1933, **172**, 26—35).—Aq. extraction of the leaves affords a complete extraction even of the normally insol. glucosides. Such extracts are, however, somewhat less active than aq. EtOH extracts (probably due to destruction of glucosides by the high temp. used), whilst their stability is low. An optimum extraction is given by 50—70% EtOH. Higher concns. of EtOH yield more active but less stable preps. Extraction with 70% EtOH and storage in the dark at low temp. ensures retention of activity for at least 3 months. F. O. H.

Physiological action of the principles isolated from the secretion of *Bufo arenarum*. K. K. CHEN, H. JENSEN, and A. L. CHEN (J. Pharm. Exp. Ther., 1933, **49**, 1—13).—From the secretion have been isolated cholesterol (I), *arenobufagin* (II), $C_{25}H_{31}O_6$, m.p. 220°, *arenobufotoxin* (III), $C_{25}H_{34}O_6,C_{14}H_{26}O_5N_4$, m.p. 194—195°, probably a compound of (II) with suberylarginine; *arenobufotenine A* (IV) (*flavianate*, $C_{12}H_{20}O_3N_2,C_{10}H_6O_8N_2S$, m.p. 130—131°), *arenobufotenine B* (V) (*flavianate*, $C_{14}H_{18}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 265°). (II) and (III) have digitalis-like actions, whilst (IV) and (V) are indole derivatives, which stimulate the guinea-pig's isolated uterus, but differ pharmacologically in certain other respects. The presence of adrenaline in the secretion is indicated. W. O. K.

Physiological action of the principles isolated from the secretion of the European green toad (*Bufo viridis viridis*). K. K. CHEN, H. JENSEN, and A. L. CHEN (J. Pharm. Exp. Ther., 1933, **49**, 14—25).—From the parotid secretion have been separated cholesterol (I) containing approx. 0·3% of ergosterol; *viridobufagin* (II), $C_{23}H_{34}O_5$, m.p. 255—255·5°; *viridobufotoxin* (III), $C_{23}H_{34}O_5,C_{14}H_{26}O_5N_4$(?), m.p. 199°, possibly a compound of (II) with suberylarginine; *viridobufotenine A* (IV) (*flavianate*, $C_{12}H_{18}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 170°); *viridobufotenine B* (V) (*flavianate*, $C_{12}H_{20}O_3N_2,C_{10}H_6O_8N_2S$, m.p. 131—132°). (II) and (III) have digitalis-like actions, whilst (IV) and (V) are indole derivatives and act on smooth muscle. (V) is probably identical with arenobufotenine A (see preceding abstract). (IV) was isolated from a 1930 batch of frogs, whilst in a 1931 batch (V) was obtained instead. W. O. K.

Physiological action of the principles isolated from the secretion of the Japanese toad (*Bufo formosus*). K. K. CHEN, H. JENSEN, and A. L. CHEN (J. Pharm. Exp. Ther., 1933, **49**, 26—35).—From the parotid secretion of *B. formosus*, the following compounds have been isolated, cholesterol (I); *gamabufagin* (II), $C_{27}H_{38}O_6$, m.p. 253—254°; *gamabufotoxin* (III), $C_{27}H_{38}O_6,C_{14}H_{26}O_5N_4$, sinters 146°, possibly a compound of (II) and suberylarginine; *gamabufotenine* (IV) (*flavianate*, $C_{12}H_{18}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 186—187°). (II) and (III) have digitalis-like actions, whilst (IV) is an indole derivative and has pressor activity. Adrenaline has been detected in the secretion (cf. Kotake, A., 1928, 1138; Wieland and Vocke, A., 1930, 1466). W. O. K.

Determination of veratrine. C. H. HUMMELSHEIM (Arch. exp. Path. Pharm., 1933, **172**, 227—244).—The pharmacological properties of veratrine (I) were compared with those of aconitine (II), quinine (III), and colchicine (IV). Both (I) and (II) in a concn. of $1 : 10^{-5}$ have an optimum effect on the frog's gastrocnemius after 10 min., but with (II) a second poisoning of the muscle does not occur. (III) is effective in concns. of 0·033—0·05%, whilst 0·2% of (IV) is without action. Aq. (I) is stable at room temp. A local anæsthesia is produced by 1% solutions of (II) but not of (I). The content of (I) in *Sabadilla* extracts can be determined by comparison of their action on the dorsal muscle of leech with that of standard solutions of (I). F. O. H.

Pharmacological action of amines related to ephedrine and tryptamine. K. K. CHEN and A. L. CHEN (J. Amer. Pharm. Assoc., 1933, **22**, 813—819).—The following compounds have been examined (cf. Chen *et al.*, A., 1929, 1105): *p*-methyl-, *p*-methoxy-, and 3 : 4-dihydroxy-norephedrine, 3 : 4-dihydroxy-ephedrine, tryptamine, *N*-methyl- and *N*-dimethyl-tryptamine, *N*-trimethyltryptamine methiodide, hypaphorine, and cinobufotenine flavianate, $C_{13}H_{20}O_2N_2,C_{10}H_6O_8N_2S$ (cf. Jensen and Chen, A., 1932, 1142). W. S.

Catalytic influence of iron salts on the decomposition of nicotine during smoking. E. STARKENSTEIN and W. STEJSKAL (Arch. exp. Path. Pharm., 1933, **172**, 119—136).—Treatment of cigars with a solution containing $Fe(NH_4)_2(SO_4)_2$ and other Fe salts (Bonicot solution) reduces the nicotine (I) in the

smoke by approx. 25%. This is due to catalytic acceleration of the decomp. of (I) on the interface of the C–Fe system formed during combustion. F. O. H.

(I.) Influence of morphine on the premedication value of tribromoethanol (avertin) in relation to nitrous oxide anæsthesia in the rat. (II.) Influence of morphine on the premedication values of ethyl α-methylbutylbarbiturate (pentobarbital) and ethyl*iso*amylbarbituric acid (amytal). O. W. Barlow and J. T. Duncan (J. Pharm. Exp. Ther., 1933, 49, 50—59, 60—66).—(I) In white rats the premedication efficiency of combined doses of avertin and morphine is > the sum of the effects of the two agents administered separately. Respiratory depression and toxicity with combined medication were also marked.

(II.) Somewhat similar results are obtained when morphine is combined with amytal or pentobarbital. W. O. K.

Comparison of the effects of morphine, pantopon, codeine, narcotine, and papaverine on the respiration of rats and rabbits. O. W. Barlow (J. Lab. Clin. Med., 1933, 18, 785—795).—The respiratory changes produced by the administration of various opium alkaloids differ only quantitatively from those produced by morphine. Ch. Abs.

Relation between the chemical structure of the opium alkaloids and their effect on the movement of the intestines of rabbits *in situ*. K. Kin (Keijo J. Med., 1932, 3, 501—529).—Alkaloids containing *iso*quinoline nuclei tend to stimulate, whilst those containing phenanthrene or C_6H_6 nuclei tend to inhibit, the peristaltic action of rabbits' intestines. Side-chain Ac, alcoholic OH, OMe, and $O{\cdot}CH_2{\cdot}O$ diminish, whilst phenolic OH increases, the effect of the nucleus. Stimulation decreases in the order: *apo*morphine, narceine, narcotine, heroine, codeine, morphine, papaverine, thebaine. Ch. Abs.

Physiological identification of strychnine in forensic toxicology. A. S. Negrao (Arch. Med. Legal, 1932, 5, 45—50).—White mice 14—16 days old are preferable to frogs for identification of strychnine. Injection of a min. of 0·001 mg. of the nitrate or sulphate induces tetany accompanied by a characteristic tremor in the tail. R. K. C.

Reduction in the toxicity of alkaloids by hexamethylenetetramine. J. Gautrelet (Bull. Acad. Med., 1932, 108, 1678—1681; Chem. Zentr., 1933, i, 2136).—Pretreatment of guinea-pigs with $(CH_2)_6N_4$ (I) protects them against an otherwise lethal dose of nicotine (II). The (I)–(II) mixture is inactivated by previous heating at body temp. The (II)-poisoned dog's heart *in situ* is revived by CH_2O or (I) methiodide. A. A. E.

Detection and determination of aloes in post-mortem cases. G. F. Hall and W. M. Keightley (Analyst, 1933, 58, 518—523).—The dried viscera are extracted with Et_2O and the aloes extracted by boiling with successive quantities of 60% EtOH. Proteins are removed with slightly acid $Pb(OAc)_2$, and excess of Pb with Na_2SO_4. Bile pigments, if present, are removed by treatment for 5 min. with 0·2*N*-NaOH and 0·5 g. of animal C per 25 c.c. Aloin is then determined by semi-quant. methods based on Schoutelen's (Year Book Pharm., 1893, 166) or a modification of Borntrager's (*ibid.*, 1880, 140) reaction. The former is not sp. in presence of cascara. E. C. S.

Detection of extractable poisons by freezing. O. Schmidt (Deut. Z. ges. gerichtl. Med., 1933. 20, 260—266; Chem. Zentr., 1933, i, 2727—2728).—Organs are kept at −10° to −15°; synthetic and vegetable poisons behave as crystalloidally dissolved substances, passing into solution again on melting. A. A. E.

Inhalation technique for the comparison of semi-volatile liquids. D. A. Bryce (J. Lab. Clin. Med., 1933, 18, 638—640).—An apparatus for the biological assay of liquids of b.p. 37—100° is described. Ch. Abs.

Determination of alcohol in blood by Widmark's method. H. Kaiser and E. Wetzel (Angew. Chem., 1933, 46, 622—625).—The method is satisfactory. The EtOH content of the blood for a given consumption of alcoholic liquors under controlled conditions varies considerably with the subject. S. C.

Determination of alcohol in blood. F. J. Holzer (Deut. Z. ges. gerichtl. Med., 1933, 20, 284—288; Chem. Zentr., 1933, i, 2727).—Widmark's procedure is modified. A. A. E.

Blood-alcohol after administration of alcohol. O. Graf and E. Flake (Arbeitsphysiol., 1932, 6, 141—167; Chem. Zentr., 1933, i, 2268).—Widmark's analytical procedure is modified; his results are confirmed. A. A. E.

Relation between blood-alcohol and the psychological effect of alcohol. O. Graf (Arbeitsphysiol., 1932, 6, 169—213; Chem. Zentr., 1933, i, 2268).—Determination of blood-EtOH indicates the degree of psychological disturbance only within wide limits. A. A. E.

Toxicological detection of veronal, luminal, and phanodorm. J. Peltzer (Chem.-Ztg., 1933, 57, 816).—The method is a combination of those previously described (A., 1927, 1219; 1931, 981, 1328) in which proteins are coagulated with $CCl_3{\cdot}CO_2H$ and the hypnotics are characterised with $CoCl_2$+MeOH–BaO and determined by means of the C_5H_5N–Cu derivatives. E. H. S.

Presence and detection of diethylbarbituric acid in cerebrospinal fluid. G. Vitte (Bull. Trav. Soc. Pharm. Bordeaux, 1932, 70, 255—256; Chem. Zentr., 1933, i, 1661).—In a case of veronal poisoning the substance was found in the cerebrospinal fluid; the procedure of separation is described. A. A. E.

Determination, identification, and elimination of barbituric acid derivatives in urine. Paget and Desodt (J., Pharm. Chim., 1933, [viii], 18, 207—214).—Urine is treated with $K_4Fe(CN)_6$ and $Zn(OAc)_2$, filtered, acidified, and barbituric acid derivatives are extracted with Et_2O. The microchemical reactions of Deniges are recommended for their identification. The mean urinary eliminations of veronal (250 mg. per day), rutonal (200 mg.), dial (100 mg.), and gardenal (200 mg.) by mental patients are 65, 49, 30,

and 25% of the ingested amounts, respectively. This order is not affected by the observed daily variations for each drug. A. C.

Behaviour of cyanamide in the animal body. F. HORN (Z. Biol., 1933, **94**, 159—170).—$NH{:}C(NH_2)_2$ (I) could not be detected in the urine of rabbits or of dogs poisoned with $CN{\cdot}NH_2$ (II). Both (I) and (II) cause somewhat similar blood-sugar changes, but the course of the temp. and the other clinical symptoms are different. It is probable therefore that the toxicity of (II) is not due to the formation from it of (I) in the animal body. The toxic symptoms of $NH_2{\cdot}C(:NH){\cdot}NH{\cdot}CO{\cdot}NH_2$ also differ from those of (II) poisoning. W. O. K.

Pharmacological action of the phosphorous acid esters of the phenols. M. I. SMITH, R. D. LILLIE, E. ELVOVE, and E. F. STOHLMAN (J. Pharm. Exp. Ther., 1933, **49**, 78—99).—The pharmacological action of Ph_3, *m*- and *p*-$(C_6H_4Me)_3$ phosphites qualitatively resemble those of the *o*-ester, but differ quantitatively. Part of the action is probably due to phenol liberated by hydrolysis of the unstable ester, and part to the direct effect of the ester itself or some derivative on the nervous system. W. O. K.

Spontaneous motion of spermatozoa and hydrogen-ion concentration. W. SCHLENK, jun. (Biochem. Z., 1933, **265**, 29—35).—The spontaneous motion of spermatozoa (I) of the rainbow trout in natural waters is controlled exclusively by $[H^{\cdot}]$. At $p_H > 7{\cdot}8$ no movement occurs, but at p_H 8 there is normal movement. The undiluted (I) have about 7·3 and so begin to move immediatelv in spring H_2O (p_H about 8·0). W. McC.

Formation of lipin-soluble salts in chloride–sulphate solutions. E. STARKENSTEIN and G. HAHNEL (Arch. exp. Path. Pharm., 1933, **172**, 55—74).—When aq. solutions of two inorg. salts are mixed and treated with a large excess of EtOH–Et_2O (2 : 1), the amount of material remaining in solution affords a criterion of the lipin-solubility (I) of the salt system. Addition of increasing amounts of NaCl or Na_2SO_4 to aq. $MgCl_2$ produces an increase in the (I) of $Mg^{\cdot\cdot}$, which, however, is not linearly related to the amount of Cl' or SO_4'' added. Addition of *N*- or 2*N*-HCl to $MgSO_4$ results in only a small increase in the (I) of $Mg^{\cdot\cdot}$; with 0·1*N*-HCl, however, the (I) of the $Mg^{\cdot\cdot}$ of a *N*/16 solution is complete. The results of the above and other systems are discussed with reference to their therapeutic action and to their occurrence in mineral H_2O. F. O. H.

Action of curative waters on the composition of the blood. I. Influence of Karlsbad water on serum-calcium. E. STRANSKY (Arch. exp. Path. Pharm., 1933, **172**, 149—160).—Rabbits, on a standard diet and drinking Karlsbad mineral H_2O for a period of 25 days, experience an increase in body-wt., in dry wt. of the serum, and in serum-Ca when compared with controls on pure H_2O. The level of ionised Ca and the ratio of total to free Ca in the serum are not significantly changed. F. O. H.

Arsenic in the ash of cadavers. H. JESSER and A. SCHREMPF (Deut. Z. ges. gerichtl. Med., 1933, **20**, 278—283; Chem. Zentr., 1933, i, 2728).—Ramberg's method for the detection of As is satisfactory. A. A. E.

Resorption of aluminium in the animal organism. Aluminium content of animal tissues. J. WÜHRER (Biochem. Z., 1933, **265**, 169—180).—The organs and body-fluids of dogs contain only traces of Al and no increase occurs following long-continued administration of Al [$AlCl_3$, $Al(OH)_3$]. In man orally administered Al is excreted almost quantitatively in the fæces. Only when large amounts of or readily sol. salts of Al are given is there any detrimental effect on health. W. McC.

Mineral metabolism and salyrgan diuresis. M. NOTHMANN (Arch. exp. Path. Pharm., 1933, **172**, 402—406).—Injection of salyrgan (I) into men produces a marked increase in the blood-K, a max. being attained after 24 hr., whilst the urinary excretion of K is also increased. The blood- and urine-P are unchanged. The increase in electrical excitability, the tetanus occurring during injection of (I), and the changes in the alkali reserve of the blood are probably due to the increased blood-K. F. O. H.

Influence of thallium salts and thyroid preparations on the plumage of ducks. R. PRAWOCHENSKI and J. SLIZYNSKI (Nature, 1933, **132**, 482).—Neither thyroid preps. nor TlOAc produce moulting in ducks. L. S. T.

Penetration through tissue of iodine in different solvents. M. S. BISKIND (Proc. Soc. Exp. Biol. Med., 1932, **30**, 35—37).—Aq. solutions had a greater speed of penetration through ventral frog skin than tinctures containing 3·8 times as much I. CH. ABS.

Effect of iodine in different solvents on the permeability of frog skin to Ringer solution. M. S. BISKIND (Proc. Soc. Exp. Biol. Med., 1932, **30**, 37—38).—Permeability was greatly increased by 95% EtOH, unaffected by 2% aq. mercurochrome, and greatly and equally reduced by aq. I and 7% U.S.P. tincture of I. CH. ABS.

Effect of potassium iodide on basal metabolism and respiratory quotient in thyroidectomised guinea-pigs. W. J. SIEBERT (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1146—1148).—KI (0·05 g. daily) lowered the metabolism and raised the R.Q. of the thyroidectomised guinea-pig. CH. ABS.

Toxicity of organic fluorides. W. P. YANT (Amer. J. Pub. Health, 1933, **23**, 930—934).—20% by vol. of CCl_2F_2 (I) in air has no permanent harmful effect on dogs and monkeys exposed for 121 hr. continuously or for 8 hr. on many successive days. 14—15% of $C_2Cl_2F_4$ (II) is without permanent effect after 21 exposures of 8 hr., but exposure to higher concns. or longer exposures daily cause congestion of all organs and are fatal. During exposure to (I) and (II) symptoms similar to alcoholic ataxia are evident, but disappear immediately after removal. The odour and irritant properties of (I) and (II) are sufficiently marked to give distinct warning of their presence in sub-lethal concns. E. C. S.

Spectrographic analysis of teeth of rats on diets containing fluorine. H. BLUMBERG, H.

KLEIN, and E. V. MCCOLLUM (J. Dent. Res., 1933, **13**, 188—189).—Traces of F were found in the teeth of rats on a control diet and greater concn. on a diet with 0·05% NaF with a deposition also in the skull bones. The production of defective enamel on diets containing F may be due to inclusion of F during dental growth. NUTR. ABS. (*b*)

Action of minute amounts of copper on the organism of mammals. Effect of minute concentrations of heavy metal on the degradation of glycogen *in vitro*. H. HANDOVSKY, D. VON COTZHAUSEN, and R. SCHALLEHN (Biochem. Z., 1933, **265**, 110—114).—Very low concns. (10^{-4} to 10^{-9} mol.) of $CuSO_4$ attack glycogen (I) in aq. solution *in vitro* with production of a reducing substance (II). If KCl (0·9%) is present the degradation increases by 100%, possibly because the degree of dispersion of (I) is increased. It is the $Cu^{\cdot\cdot}$ which is active. $Fe^{\cdot\cdot\cdot}$ is also active, but not $Mn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ag^{\cdot}$, or $Hg^{\cdot\cdot}$. The amount of (II) produced is independent of the concn. of (I) or $Cu^{\cdot\cdot}$. (II) and also added glucose or maltose fix the $Cu^{\cdot\cdot}$ and hence soon inhibit the effect. W. MCC.

Interaction of metallic containers and foodstuffs. III. Biological rating of metals. J. SCHWAIBOLD and F. FISCHER (Biochem. Z., 1933, **265**, 124—132; cf. A., 1931, 652).—Small doses (*e.g.*, 2 mg. per litre) of salts (in some cases also of corrosion products) of Zn, Ni, Pb, Ag, and Hg are poisonous to tadpoles. Brass is also poisonous, but Al, Sn, Au, and Pt are only slightly poisonous or harmless to them. Mice are more resistant ; they succumb to Pb and Cu, but are not affected by relatively high doses of $HgCl_2$. W. MCC.

Normal absorption and excretion of lead. I. In primitive life. II. In modern American life. III. Sources of normal lead absorption. IV. In infants and children. R. A. KEHOE, F. THAMANN, and J. CHOLAK (J. Ind. Hyg., 1933, **15**, 257—272, 273—288, 290—300, 301—305).—I. Pb is a natural constituent of the soil and vegetation of primitive Mexican regions and occurs in the blood (0·0—0·00006%), urine (I) (average 0·0138 mg. per litre), and fæces (II) (average 0·0035% of the ash) of the inhabitants who live on local produce. Analytical methods based on those of Fairhall (A., 1922, ii, 659) and using the colour developed by *s*-diphenylcarbazide for the final determination of Pb are described.

II. The normal daily intake of Pb by adults is approx. 0·16—0·28 mg., whilst the daily excretion is 0·02—0·08 mg. per litre of (I) and 0·03—0·10 mg. per g. of ash of (II). The greater part of the ingested Pb is unabsorbed and is found in (II). Thus daily oral administration of 1 and 5 mg. of $PbCl_2$ produces a daily absorption of 0·5 and 1 mg., respectively. Data for the distribution of Pb in normal human tissues indicate that the greatest content (0·001%) is in bone. The non-occurrence of Pb in normal (I) and (II) is refuted.

III. Small amounts (< 1 mg. per kg.) of Pb are of general occurrence in food. Analytical data and indications of the sources of contamination are given.

IV. The Pb excretion of normal American children [average 0·08 mg. per litre in (I) and 0·08 mg. per g. of ash of (II)] is > that of Mexican children living under primitive conditions (0·015 and 0·04 mg., respectively). Normal human milk contains 0·0—0·05 mg. per litre, whilst human fœtuses contain small but definite amounts (up to 0·41 mg.) of Pb. F. O. H.

(*a*) Lead absorption and excretion in certain lead trades. (*b*) Lead absorption and excretion in relation to the diagnosis of lead poisoning. R. A. KEHOE, F. THAMANN, and J. CHOLAK (J. Ind. Hyg., 1933, **15**, 306—319, 320—340).—(*a*) The excretion of Pb by workmen engaged in Pb trades is markedly > the normal and serves as a criterion of incipient Pb poisoning.

(*b*) Men absorbing abnormal amounts of Pb subsequently display an increased Pb excretion, which diminishes rapidly for a period of several weeks and then slowly until the normal excretory level is attained. F. O. H.

Stimulation of the excretion of lead by irradiation. L. PINCUSSEN (Klin. Woch., 1933, **12**, 275; Chem. Zentr., 1933, i, 2135).—Mice and rats which had received Pb salts orally contained 10—20% less Pb after irradiation with visible and thermal rays than those irradiated with ultra-violet rays or kept in the dark. A. A. E.

Effect of irradiation on the excretion of zinc. K. NAKADATE (Biochem. Z., 1933, **265**, 61—63; cf. Pincussen and Roman, A., 1931, 1330).—In rats to which $Zn(OAc)_2$ is administered irradiation causes decreased excretion of Zn, light of long λ having more pronounced effect than that of short λ. W. MCC.

Effect of some forms of radiant energy on the distribution of colloids in the organism. I. T. TEPLOV and E. A. DOBROKHOTOVA (Arch. sci. biol., U.S.S.R., 1932, **32**, 72—79).—In rabbits which had been injected intravenously with trypan-blue and irradiated, the dye was deposited mainly in the irradiated tissues. CH. ABS.

Metabolic changes produced by irradiation. XII. Effect of various types of radiation on the glutathione content of the organs of irradiated animals. L. PINCUSSEN and S. TAKAHASHI (Biochem. Z., 1933, **265**, 64—68; cf. A., 1932, 96).—Results given previously require multiplication by 1·23. Irradiation of rats with various kinds of visible light (I) (Na- and Hg-vapour lamps, Ne lamp) produces no increase (but sometimes a decrease) in the glutathione (II) content of their livers. Neither (I) nor infra-red (III) light has any effect on the (II) of the spleens. Short-wave (I) and ultra-violet light (IV) produce increase in the (II) of the lungs, whilst long-wave (I) and (IV) cause decrease. In the muscle (I) increases (II), but neither (III) nor (IV) has any effect. W. MCC.

Influence of diet on the sensitivity of animal tissues to radiation. E. UHLMANN (Strahlenther., 1933, **46**, 550—564).—Rabbits fed on an acid diet (exclusively oats) are more sensitive to irradiation with *X*-rays than those fed on a normal mixed diet (hay, oats, turnips, potatoes). NUTR. ABS. (*m*)

Action of light on the chemistry of the cell. I. Experiments with tissue slices. II. Ex-

periments with red blood-corpuscles. III. Influence of histamine. J. WOHLGEMUTH and E. SZÖRENYI (Biochem. Z., 1933, **264**, 371—388, 389—405, 406—411).—I. The O_2 utilisation of slices of tissue does not, but after incorporation of dye sensitisers (I) does, increase on irradiation with an electric bulb, but this additional respiration is accelerated by HCN and is as great at 20° as at 37·5°. Anaerobic formation of lactic acid (II) is unaffected by these conditions. Irradiation with visible or ultra-violet light in presence or absence of (I) injures tissue respiration, anaerobic formation of (II) in absence of (I) being increased and in presence of (I) decreased.

II. When red blood-corpuscles (I) are irradiated in presence of hæmatoporphyrin, methæmoglobin is formed, the process being accelerated by HCN, especially in presence of certain sensitisers. Hæmatoporphyrin increases the respiration of (I) in the dark, the increase being greater when the cells have been previously irradiated. If during a respiration experiment irradiation is started, the O_2 utilisation increases by 300—400%, the action being even greater with hæmolysed than with intact cells. This photo-oxidation is independent of the temp. and is not inhibited by HCN. No parallelism exists between photo-oxidative and photodynamic action of sensitisers. Neither normal oxidation nor the photo-oxidation by (I) is effected by glutathione.

III. Histidine causes a very small increase of liver respiration, but does not affect that of kidney and skin. Histamine increases the respiration of liver and skin by 200—300%, of kidney and brain by about 25%, but does not increase the respiration of Jensen sarcoma. P. W. C.

Spectral resolution of the mitogenetic radiation of the stimulated nerve. G. S. KALENDAROV (Arch. Sci. biol., U.S.S.R., 1932, **32**, 26—33).—On stimulation by section the sciatic nerve of frogs emits mitogenetic rays in the range 1200—2400 Å. The metabolism of stimulated nerves apparently includes glycolysis and the oxidation of carbohydrates and possibly of proteins. CH. ABS.

Yeast as a detector of mitogenetic radiation. S. V. KONSTANSOV (Arch. sci. biol., U.S.S.R., 1932, **32**, 34—38).—A criticism of Gurwitsch's original method. CH. ABS.

[Yeast as a detector of mitogenetic radiation.] A. G. GURWITSCH (Arch. sci. biol., U.S.S.R., 1932, **32**, 39; cf. preceding abstract).—A reply. CH. ABS.

Enzyme action and enzyme formation in living cells. H. VON EULER and G. GÜNTHER (Z. physiol. Chem., 1933, **220**, 69—85).—In barley heated at 43° for 30 min. before germination in order to disturb the enzymic equilibrium, certain grains showed delayed germination but no abnormality in enzymic activity. Catalase formation and stability are greatly dependent on conditions of germination. Similar treatment of yeast produced no marked heat-activation of catalase, but ultra-violet irradiation increased the activity by > 700%. J. H. B.

Peroxidase. D. B. HAND (Ergebn. Enzymforsch., 1933, 2, 272—281; Chem. Zentr., 1933, i, 2562—2563).—A discussion including reference to Fe–porphyrin compounds (I) in yeast and the relation of (I) in general to HCN and CO. A. A. E.

Determination of peroxidase in agricultural products. A. K. BALLS and W. S. HALE (J. Assoc. Off. Agric. Chem., 1933, **16**, 445—453).—The rate of decomp. of H_2O_2 by the enzyme is determined in the presence of pyrogallol (I). The enzyme solution is added to 0·625 g. of (I), 4·0 c.c. 0·1*N*-H_2O_2, 25 c.c. of phosphate buffer (p_H 8·0), and H_2O to make up to 250 c.c., beneath a layer of paraffin. Samples are removed at 0, 2, 5, and 10 min., run into 0·5 g. of (I) in H_2SO_4, KI is added, and liberated I titrated after 12—20 min. The rate of H_2O_2 decomp. may be converted into the "purpurogallin no." of Willstätter and Stoll (A., 1923, i, 262). The presence of catalase does not interfere, (I) absorbing in peroxidic form all liberated O_2. Peroxidase may be extracted from material for analysis by grinding with sand and a phosphate buffer solution of p_H 8. J. S. A.

Influence of short electrical waves on leucocyte oxidases. G. JORNS (Strahlenther., 1933, **46**, 384—388; Chem. Zentr., 1933, i, 2563).—No effect on oxidation mechanism was observed. A. A. E.

Oxidase and dehydrogenase systems of the crystalline style. C. BERKELEY (Biochem. J., 1933, **27**, 1357—1365; cf. this vol., 297).—The oxidase system (I) of the cryst. style of *Saxidomus giganteus* consists of a peroxidase, present in the style, and an autoxidisable substance associated with the diatoms of the food. (I) acting on glucose produces glucosone but no acid. A dehydrogenase system (II) is also present, consisting of a substance in the style and another in the diatoms. In vac., (II) produces glucosone from glucose in the presence of methylene-blue. It is suggested that (I) acts as H acceptor for (II). A. W.

Mechanism of dehydrogenation. A. BERTHO [with V. SCHMITT] (Ergebn. Enzymforsch., 1933, **2**, 204—238; Chem. Zentr., 1933, i, 2259—2261).—A discussion, with special reference to the formation of H_2O_2 in biological and other dehydrogenations. A. A. E.

Specificity of hydratases. Action of peas and yeast on crotonic acid. K. P. JACOBSOHN and F. B. PEREIRA (Compt. rend. Soc. Biol., 1933, **108**, 208—210; Chem. Zentr., 1933, i, 2119).—Crotonic acid is unattacked by peas or yeast at p_H 7·0; hence fumarase is considered sp. A. A. E.

Enzyme models. W. LANGENBECK (Ergebn. Enzymforsch., 1933, **2**, 314—335; Chem. Zentr., 1933, i, 2561—2562).—A discussion of org. catalysts having an enzyme-like action. The active group of carboxylase is probably NH_2; a reaction scheme is outlined. A. A. E.

Separation of enzymes from their mixtures. M. SREENIVASAYA and N. K. IYENGAR (Nature, 1933, **132**, 604—605).—The method described utilises the difference in mol. wt. of enzymes. The enzyme extract is cooled and centrifuged into three layers at approx. 6000 r.p.m. for 15 min. The top layer of ice-cold H_2O contains the most easily diffused enzymes and the bottom those of higher mol. or micellar wts. The

method has been successfully applied to the fractionation of inulinase and invertase; it also gives a comparative idea of relative mol. wts. L. S. T.

Effect of coagulation of accompanying proteins on the activity of amylase. A. Oparin, S. Manskaja, and M. Magaram (Biochem. Z., 1933, **265**, 21—28; cf. this vol., 634).—The resistance of amylase (I) to inactivation by heat (II) is reduced by non-dialysed but increased by dialysed solutions (III) of ovalbumin. Analogous to (I) is inactivation in the cold (IV) by acid. When (III) are boiled and the protein is pptd. with salt no (II) or adsorption of (I) occurs. (I) is protected from inactivation in the cold by addition of peptone, which, however, does not reactivate inactivated (I). 50—60% reactivation after (II) and (IV) is brought about by digesting the protein ppt. with pepsin. W. McC.

Specificity of emulsin. B. Helferich (Ergebn. Enzymforsch., 1933, **2**, 74—89; Chem. Zentr., 1933, i, 2261).—The behaviour of β-*d*-glucosidase in the "emulsin" of sweet almonds towards various glucosides is summarised and discussed. A. A. E.

Constituent enzymes of myrosinase. C. Neuberg and O. von Schoenebeck (Biochem. Z., 1933, **265**, 223—236; cf. A., 1926, 1060; this vol., 863).—By pptn. with $Hg(OAc)_2$, $Pb(OAc)_2$, or Pb phosphate, adsorption on kaolin, Al_2O_3, or $Fe(OH)_3$, and elution with aq. Na and K phosphates and carbonates or aq. NH_3 with or without glycerol, the sulphatase (I) can be almost completely separated from the thioglucosidase (II). (I) and (II) are inactivated by heat, (II) being more resistant than (I). No separation of (I) from (II) can be attained by dialysis. Both are stable in H_2O at p_H 5·5. At $p_H < 3$ (II) is completely and (I) is half inactivated. (II) is unaffected by strong alkalinity, which, however, partly inactivates (I). Units for measuring the action of (I) and (II) are proposed. W. McC.

Glycolysis. H. K. Barrenscheen and H. Beneschovsky (Biochem. Z., 1933, **265**, 159—168; cf. Nilsson, this vol., 425).—Muscle (pulp and extract) and possibly liver (but not blood, brain, or kidney) dephosphorylate synthetic phosphoglyceric acid to $AcCO_2H$, small amounts of lactic acid (I) being produced at the same time. *dl*-Glyceraldehydephosphoric acid (II) is degraded by tissues with production (in some cases at least) of (I), but if glycolysis is inhibited AcCHO is produced, although the degree of dephosphorylation is unchanged. Much of added (II) seems to be converted into a condensation product, possibly hexosediphosphoric acid. These results and theoretical considerations support the views of Nilsson and contradict those of Embden *et al.* (Klin. Woch., 1933, **12**, 213). W. McC.

Role of iron in glycolysis of blood and muscle. H. J. Ustvedt (Biochem. Z., 1933, **265**, 154—156; cf. Zuckerkandl and Klebermass-Messiner, this vol., 751).—αα′-Phenanthroline has no effect on the production of lactic acid in muscle and only temporarily (30 min.) inhibits glycolysis in blood (cf. Barrenscheen and Hübner, A., 1931, 378). W. McC.

Inhibition of glycolysis by oxidation. F. Lipmann (Biochem. Z., 1933, **265**, 133—140).—Glycolysis (I) (which is not dependent on the presence of ·SH) in muscle extract (II) is inhibited by oxidising agents (I, benzoquinone) presumably because the glycolytic enzyme (III) is oxidised. If 2 : 6-dichlorophenol-indophenol (IV) is added, (I), which is otherwise independent of the presence of O_2, is inhibited only if O_2 is present, the inhibition being then complete. (IV) is reduced in (II) when it is in N_2, but remains unchanged if (II) is in O_2. The inhibition by (IV) is reversible. In cells saturated with O_2 the inhibition of (I) is caused by reversible inactivation of (III). W. McC.

Action of co-enzyme. VI. Constitution of adenosinetriphosphoric acid. H. K. Barrenscheen, K. Braun, and W. Filz (Biochem. Z., 1933, **265**, 141—147; cf. A., 1932, 1064, 1287, 1288).—Lohmann's objections (A., 1932, 1274) to the authors' formula for adenosinetriphosphoric acid (I) cannot be maintained, since deamination experiments confirm the authors' results and contradict his. His "inosinepyrophosphoric acid" is a mixture of inorg. phosphate, inosic acid, unchanged (I), and (possibly) inorg. pyrophosphate. W. McC.

Co-enzyme of glycolysis from tumours. II. E. Bumm, H. Appel, and P. Couceiro (Z. physiol. Chem., 1933, **220**, 186—191).—Co-enzyme *T* (I) under various experimental conditions exercises quantitatively the same action on glycolysis as $AcCO_2H$ (II). (I) is probably identical with (II). J. H. B.

Isolation of co-enzyme *T* of glycolysis from normal tissue. H. Kraut and F. Borkovsky (Z. physiol. Chem., 1933, **220**, 173—185).—Ox-brain (grey matter) is a convenient source of co-enzyme *T* (I). The organ is dried with $COMe_2$ and extracted with 0·01*N*-NH_3 and the product immediately pptd. with EtOH. A glycolysis inhibitor present may be (incompletely) removed with $Al(OH)_3$ *Cγ*. The activity of (I) is determined by measuring manometrically the lactic acid formed from glucose by washed sections of rat's kidney under anaerobic conditions. J. H. B.

Separation of co-enzyme *T* and phosphatase. H. Kraut and F. Borkovsky (Z. physiol. Chem., 1933, **220**, 192—198).—Co-enzyme *T* (I) from grey brain-matter is associated with a phosphatase (II), together with an inhibitor (III) of (II) which masks its presence, but which may be removed by $Al(OH)_3$. (I) from rat sarcoma also contains (III), but in smaller amount. (I) and (II) may be separated by dialysis, or better by adsorption of (I) on $Al(OH)_3$ *Cγ*. J. H. B.

Phosphatases and phosphatase hæmolysis. S. Munemura (J. Biochem. Japan, 1933, **18**, 23—32).—The following mono-derivatives of H_3PO_4 were prepared: β-naphthyl, *tetrabromo-β-naphthyl*, m.p. 140°, thymyl, *bromothymyl* (*Na* salt), *dibromothymyl* (*Na* salt). All the above are hydrolysed by monophosphatases from animal tissues, the optimum p_H being approx. 10, excepting the enzyme from blood with an optimum of p_H 5. Dephosphorylation is also accompanied by the acquisition of hæmolytic activity (I), and hence the rate of hydrolysis can be followed in the above systems by the rate of hæmolysis of erythrocytes (goat, rabbit). The (I) of the dephosphorylated com-

pounds forms the series: di- > mono-bromothymol >tetrabromonaphthol>thymol, naphthol. F. O. H.

Effect of fluoride on the action of phosphatase. E. AUHAGEN and S. GRZYCKI (Biochem. Z., 1933, **265**, 217—222).—NaF does not inhibit the action of kidney-phosphatase on Na β-glycerophosphate or Na diphosphoglycerate, but at p_H 5 (although not at p_H 9) it partly inhibits the action of takaphosphatase (I), possibly because (I) contains two phosphatases, one sensitive to NaF and one not. W. McC.

Enzymic hydrolysis of hexoside phosphate. S. OHMIYA (J. Biochem. Japan, 1933, **18**, 125—143).—Taka-, rice bran-, kidney-, and intestine-monophosphatase hydrolyse Na glycerophosphate, Ca sucrose phosphate (I) (A., 1910, i, 157), and Ca glucose phosphate (II). Taka- and yeast-invertase hydrolyse sucrose and (I), no dephosphorylation occurring with the latter. Taka- and yeast-maltase hydrolyse maltose (III) and, without dephosphorylation, Ca (III) phosphate. Yeast α-methylglucosidase hydrolyses α-methylglucoside (IV) and (III), but not (IV) phosphate (V). The hydrolysis of (III) phosphate by maltase is strongly inhibited by (II) but not by (IV) or (V), whilst that of (I) by the invertase preps. is not influenced by (II), (IV), or (V). F. O. H.

Formation of ammonia and pyrophosphate decomposition in muscle. II. W. MOZOŁOWSKI and B. SOBCZUK (Biochem. Z., 1933, **265**, 41—49; cf. A., 1932, 875).—In pulped frog muscle which has been frozen in liquid air decomp. of creatinephosphoric acid precedes decomp. (I) of pyrophosphate and production (II) of NH_3. (I) then proceeds more rapidly than (II). Poisoning with $CH_2I{\cdot}CO_2H$ does not affect these processes. W. McC.

Transformation of the pyrophosphate fraction in muscle. O. FEINSCHMIDT and M. DMITRENKO (Biochem. Z., 1933, **265**, 69—75; cf. Ferdmann, this vol., 736).—A pentose derivative (I) is produced when frog muscle is ground with H_2O and also, in smaller amount, when $CCl_3{\cdot}CO_2H$ solution replaces H_2O. (I) is partly pptd. by $Ba(OH)_2$. At the same time decomp. (II) of the pyrophosphate [chiefly the free portion (III)] occurs. (II) also occurs during autolysis of the muscle pulp in H_2O at 25°, (III) and the pyrophosphate (IV) combined as adenosinetriphosphoric acid being involved. Other P compounds present are decomposed simultaneously, since the amount of orthophosphate (V) corresponds with more than that produced by (II). On thawing muscle which has been frozen in liquid air (III) and (IV) decompose with simultaneous increase in (V), but the increase is < corresponds with (II). W. McC.

Phosphamidase. M. ICHIHARA (J. Biochem. Japan, 1933, **18**, 87—106).—$PO(OH)_2{\cdot}NH_2$ (I) and $PO(OH)(NH_2)_2$ (A., 1894, i, 267; ii, 188), but not $PO(OH)(NH_2){\cdot}OPh$ (II), are readily hydrolysed both in acid and alkaline media by kidney, rice-bran, and taka-diastase enzyme preps. $PO(OH)_2{\cdot}NHPh$ and $PO(OH)(OPh){\cdot}NHPh$ are hydrolysed in a manner parallel to (I). $PO(OH)_2{\cdot}NH{\cdot}C_6H_4Cl$ (*p*) is hydrolysed at acid but not at alkaline reactions. (II) at $p_H < 2$ is spontaneously deaminated. Under suitable conditions such a deamination is followed by dephosphorylation due to monophosphatase in the enzyme prep. used. By adsorption methods the phosphamidase can be separated from the phosphatases. F. O. H.

Transformation of methylglyoxal when added to blood and muscle. E. AUHAGEN (Biochem. Z., 1933, **265**, 213—216).—The statements of Barrenscheen and co-workers (this vol., 187) regarding the transformation of AcCHO when added to blood (I) could not be confirmed either for (I) or for muscle extract. W. McC.

Milk-coagulating enzymes of gastric mucosa and their zymogens. H. TAUBER and I. S. KLEINER (Z. physiol. Chem., 1933, **220**, 205—208).—Propepsin (I), the zymogen of pepsin, differs from prochymosin (II). (I), unlike (II), cannot coagulate milk; (II) has a p_H optimum at 2·8, whilst (I) is active only at p_H 1. EtOH destroys (I) but not pepsin. The mucosa of the adult animal contains no (II), but only (I). Inactive (I) can be prepared in dry form and activated with HCl. J. H. B.

Crystalline ovalbumin. Hydrolysis by pepsin, papain–hydrocyanic acid, and pancreatic proteinase, and the subsequent action of some other enzymes on the hydrolysis products. H. O. CALVERY (J. Biol. Chem., 1933, **102**, 73—89).—Pure proteinase (I) of pancreas hydrolyses one third of the calc. no. of peptide linkings, whilst papain–HCN (II) hydrolysed a further one third. Amino- and carboxy-polypeptidase hydrolyse to the same extent as (I), and 60% of total N (III) was liberated as NH_2-N (IV). Dipeptidase (V) liberated a further 10—12%, and after complete enzymic hydrolysis 75% of (III) was present as (IV). Pepsin (VI) liberates 24—26% of (III) as (IV). Protaminase liberates a further 7% and the polypeptidases a further 24—25%; following their action the (V) in erepsin produces a further 24—25%. The total (IV) thus obtained is again 72—75% of (III). The action of (II) is twice as extensive as that of (I) or (VI) and there is no further action by either of these enzymes. H. G. R.

Gelatinase and Gates–Gilman–Cowgill method of pepsin determination. E. R. B. SMITH (J. Gen. Physiol., 1933, **17**, 35—40).—The Gates method (A., 1930, 1620) for pepsin determination is uninfluenced by the presence of gelatinase, whilst the Northrop viscosity method (A., 1932, 1166) gives higher vals.

Action of pancreatin on gelatin surfaces. II. M. BERGMANN and F. FOHR (Biochem. Z., 1933, **264**, 246—250).—Using the method previously outlined (A., 1932, 1064) the rate of dissolution (x) of gelatin by pancreatin in unbuffered solution at p_H 4·8 is given by the equation $x - kt\sqrt{F}$, where F is the enzyme concn. and t the time of digestion. The extent of digestion is greater at p_H 8 and is the same using seven different buffer solutions at p_H 7·8—8·2. P. W. C.

Influence of oxidising and reducing agents on the activity of papain. T. BERSIN and W. LOGE MANN (Z. physiol. Chem., 1933, **220**, 209—216).—Papain inactivated by $CH_2I{\cdot}CO_2H$ (I) is not reactivated by reduced glutathione. SeO_3'' also inhibits,

particularly in presence of (I). Various oxidising agents, such as H_2O_2, benzoquinone, and I, produce inactivation; reducing agents, as H_2S, SO_3'', and glutathione, but not quinol, reactivate the enzyme. Oxidised papain is also activated by succinodehydrogenase in presence of succinate. J. H. B.

Inactivation of cathepsin and papain by iodoacetic acid and by halogen. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, **220**, 199—204).—$CH_2I{\cdot}CO_2H$, but not $CN{\cdot}CH_2{\cdot}CO_2H$, inhibits completely the proteolytic action of cathepsin under conditions which preclude oxidation of the thiol activator. The inhibition is reversible and probably due to formation of an additive compound with the enzyme. It differs from inhibition by I and Br, in which the active enzyme group is partly destroyed and partly dehydrogenated. J. H. B.

Pancreatic protease of cat-fish. T. ÔYA and S. YOKOTA (J. Imp. Fish. Inst. Tokyo, 1933, **28**, 97—103).—Pancreatic extract from *Parasilurus asotus*, L., contains a trypsin-like enzyme (I), mostly as zymogen, which is activated by the extract from the intestinal mucosa. The optimum temp. and p_H for the action of the protease are 45° and about 7·7. The action of (I) on caseinogen is unimol. (temp. coeff. 1·5 from 18·5° to 45°). NUTR. ABS. (*m*)

Influence of bile acids on the enzymic hydrolysis of lecithin. H. TAKATA (J. Biochem. Japan, 1933, **18**, 63—74).—The dephosphorylation of lecithin by $CHCl_3$–H_2O extracts of rabbit's kidney (I) and liver (II) in borate buffer at p_H 7·5 is somewhat increased by addition of Na cholate (III). With an enzyme prep. from autolysed tissue (A., 1929, 847) the liberation of acid-sol. P (cf. A., 1931, 984) is inhibited by (III), the inhibition with (II) being > that with (I). During autolysis of (II), the presence of (III) accelerates the liberation of inorg. and acid-sol. P. F. O. H.

Lactase in bottom yeast. E. HOFMANN (Biochem. Z., 1933, **265**, 209—212).—After preliminary digestion (for ⩾ 3 days) with lactose a suspension of bottom yeast (from fresh yeast by the action of AcOH or after autolysis in presence of PhMe) hydrolyses lactoseureide (I) (80% in 24 hr.). No fermentation of (I) occurs. Amygdalin, but not salicin, is hydrolysed by the suspension. W. McC.

Enzymes of lactose fermenters. S. GRZYCKI (Biochem. Z., 1933, **265**, 191—194).—*Saccharomyces fragilis* (I) and another lactose fermenter (II) contain glycolase, glyoxalase, and carboxylase. Under conditions which lead to production of AcCHO with ordinary *Saccharomyces* (I) also produces it and converts it, when added, quantitatively into lactic acid (III). All the (III) then produced by (II) is dextrorotatory. (I) and (II) ferment $AcCO_2H$, 69—75% of the theoretical amount of MeCHO being produced. W. McC.

Phosphorylation produced by lactose fermenters. E. HOFMANN (Biochem. Z., 1933, **265**, 203—208).—Fresh *Saccharomyces fragilis* (I) produces fructose 1 : 6-diphosphate and smaller amounts of a hexose monophosphate (II) from lactose in presence of PhMe. (II) is hydrolysed by takaphosphatase, giving H_3PO_4 and sugar, and has about 10% of the reducing power (Fehling's solution) of an equiv. amount of glucose. W. McC.

Maltose as a respiration substrate for non-maltose-fermenting yeasts. A. J. KLUYVER and J. C. HOOGERHEIDE (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 605—609).—The rate of respiration (I) of *Saccharomyces cerevisiæ* at p_H 4·7 is practically unchanged by increasing the concn. of glucose (II) from 0·2 to 10·0%. With the non-maltose (III) fermenting yeasts, *S. marxianus*, Hansen, and *S. exiguus*, a 10% concn. of a commercial sample of (III) produces a (I) = or even > that with 10% of (II) when fermented for short periods, whilst fermentation for 4 hr. produces with (III) a steady decline in (I) until the val. for the yeast without sugar is attained. This, together with the finding that the (I) of yeasts in the presence of (III) previously purified by fermentation approximates to that occurring in the absence of (III), refutes the dualistic theory of (I) and fermentation advanced by Trautwein and Weigand (A., 1931, 1457). F. O. H.

Conversion of the alcoholic fermentation of sugar by yeast into a lactic acid fermentation. E. AUHAGEN and C. NEUBERG (Biochem. Z., 1933, **264**, 452—455).—The conditions are outlined under which yeast in presence of glutathione converts Mg hexose diphosphate into lactic acid, yield about 25% of theoretical. P. W. C.

Degradation of lactic acid by yeast enzymes. A. HAHN, E. FISCHBACH, and H. NIEMER (Z. Biol., 1933, **94**, 58—66).—The prep. of yeast extracts containing lactic acid dehydrase is described. In presence of methylene-blue as H-acceptor the dehydrase brings about degradation of lactic acid with formation of $AcCO_2H$ and MeCHO. Degradation also occurs in presence of o-$C_6H_4(NO_2)_2$, but not in absence of H-acceptor. O_2 has practically no influence. E. S. H.

Transformation of acetoacetaldehyde by yeast. S. GRZYCKI (Biochem. Z., 1933, **265**, 195—198; cf. Claisen and Stylos, A., 1888, 671).—Yeast converts $CH_2Ac{\cdot}CHO$ into β-butylene glycol, part of which is dextrorotatory. W. McC.

Glyceromonophosphoric acid. III. Simplified preparation of phosphoglyceric acid. C. NEUBERG and M. KOBEL (Biochem. Z., 1933, **264**, 456—460; cf. this vol., 637, 982).—The method for isolating the *l*-acid as the Ba salt from glucose fermentations by bottom yeast after addition of NaF and MeCHO is described. P. W. C.

Synthesis of alanine by yeast during alcoholic fermentation. C. FROMAGEOT and P. DESNUELLES (Bull. Soc. chim., 1933, [iv], **53**, 541—547).—Addition of NH_3, $AcCO_2NH_4$, and NaOH to a mixture of yeast and aq. sucrose at 27—28° gives a 3—65% yield of alanine, according to the variety of yeast used. R. S. C.

Influence of iodoacetic acid on the respiration and fermentation of yeast. A. J. KLUYVER and J. C. HOOGERHEIDE (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 596—605).—The O_2 con-

sumption and CO_2 evolution by *Saccharomyces cerevisiæ* in presence of 0·001—0·014% of $CH_2I{\cdot}CO_2H$ (I) indicate that with an increasing concn. of (I) both anaerobic (II) and aerobic fermentation (III) are rapidly inhibited, whilst the respiration (IV) remains unchanged (A., 1930, 954). Above a certain "crit." concn. (approx. 0·0025%) at which both (II) and (III) are reduced to zero, however, (IV) steadily decreases with increasing concn. of (I). This phenomenon is probably due to the inactivation of the oxidation–reduction catalyst by (I) primarily affecting the surplus dissimilation [*i.e.*, (III)], the glycolysis falling below the level necessary for the maintenance of the normal rate of (IV) when the critical concn. of (I) is surpassed. In certain species of yeast, *e.g.*, *S. marxianus*, Hansen, (III) is very low, and in agreement with the above theory, addition of low concns. of (I) immediately causes a reduction in (IV).

F. O. H.

Action of toluene on fermentation by yeast. W. A. Belitzer (Biochem. Z., 1933, **265**, 5—12).—The inhibiting action (I) of PhMe on the fermentation (II) of glucose by yeast is irreversible and is not due to loss by diffusion (caused by increased permeability of the cells) of some substance necessary for (I). (I) is only sometimes due to selective action of PhMe on the phosphatase of the yeast. Harden's views (A., 1912, ii, 284) concerning (I) on the auto-fermentation of yeast are supported and modified to cover (II).

W. McC.

Effect of age on the nitrogen content of yeast. N. Nielsen (Compt. rend. Trav. Lab. Carlsberg, 1933, **19**, No. 16, 11 pp.).—N content and growth (I) of yeast in beer wort give an S-curve. When (I) is small, relatively large amounts of N are absorbed and the decrease with increasing (I) is not due to N storage.

H. G. R.

Endocellular hydrogen donors of yeast and their variation with the age of the culture. F. Chodat and M. Junquera (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 199—203).—The amount of endocellular H-donors in yeast increases slightly with the age of the culture for 2—3 days and then decreases rapidly, being nearly 0 after 6 days. R. S. C.

Effect of ultra-violet rays on the fermentation efficiency of yeast in the alcoholic fermentation of molasses. W. L. Owen and R. L. Mobley (Zentr. Bakt. Par., 1933, II, **88**, 273—286).—Exposure of yeast to ultra-violet rays increased the rate of cell development and the fermentative activity. The effect was more marked when yeast on molasses wort or the wort alone was irradiated. The principal benefit of irradiation is the formation of a growth-promoting substance in the substrate which stimulates the yeast. A. G. P.

Lipins of yeast. I. Acetone-soluble fat. II. Phospholipins. M. S. Newman and R. J. Anderson (J. Biol. Chem., 1933, **102**, 219—228, 229—235).—I. The Et_2O solution of the EtOH–Et_2O extract of *Saccharomyces cerivisiæ* is separated into a phospholipin fraction (I) by pptn. with $COMe_2$, a $COMe_2$-sol. fraction (II) obtained by removal of the Et_2O, decantation from an oily product, and evaporation to dryness, and a $COMe_2$-insol. fraction (III) by dissolving the oily product in Et_2O, pptn. of (I) with $COMe_2$, and evaporating to dryness. (I) was purified by repeated pptn. from Et_2O with $COMe_2$. The saponified (II) contained a sterol fraction consisting of hydrocarbons $C_{19}H_{35}$—$C_{31}H_{66}$, glycerol, and fatty acids. The saturated fraction of the latter consisted of palmitic (IV) 75% and stearic (V) 25% acids. The unsaturated acids on catalytic reduction gave 25% (IV) and 75% (V).

II. The unsaponifiable matter from (I) was identical with that obtained from (II). The liquid fatty acids on catalytic reduction contained 60% (IV) and 40% (V). The solid acids consisted of equal parts of (IV) and (V). From the ratio of NH_2-N to total N in the aq. hydrolysate it is concluded that lecithin and cephalin are present in (I) in the ratio 4 : 1. Ba glycerophosphate, choline, and $NH_2{\cdot}C_2H_4{\cdot}OH$ were isolated from the aq. hydrolysate. H. D.

Metabolism of fat and lipin in yeast. W. Halden, F. Bilger, and R. Kunze (Naturwiss., 1933, **21**, 660—661).—Lipin formation in yeast is not associated with cellular degeneration, but is a metabolic phase following suppression of fermentation and budding. Thus the reduction of the H_2O content of a yeast suspension to 75—80% and exposure to EtOH vapour increases the ergosterol content from 0·2 to 7—8% in 10—14 days; the fat content increases to a much smaller extent. The EtOH is converted by a dehydrase into MeCHO which does not exert its normal toxic action owing to the rapid conversion into condensation products such as acetoin.

F. O. H.

Schaudinn's fixative for protozoa. D. H. Wenrich and Q. M. Geiman (Stain Tech., 1933, **8**, 158).—A solution half the strength of Schaudinn's, to which 2% of glacial AcOH is added immediately before use, is recommended. H. W. D.

Refractive indices of whole cells. E. S. Castle (J. Gen. Physiol., 1933, **17**, 41—47).—The n of the cell of *Phycomyces* was determined by allowing parallel light to fall on it and measuring the focal distance. The average of six cells was 1·38. H. D.

Physical basis of positive phototropism of *Phycomyces*. E. S. Castle (J. Gen. Physiol., 1933, **17**, 49—62).—By assuming that the primary action of light is on the protoplasm and that the absorbing substance is uniformly distributed within the cell, the possibility of photochemical action in the half of the cell furthest from the source of light being > that in the side nearer is demonstrated. The factors governing the phenomenon are the n and radius of the cell and the absorption coeff. of the intracellular pigment.

H. D.

Growth of *Aspergillus niger* at different hydrogen-ion concentrations, with and without the addition of growth-promoting substance *B*. N. Nielsen and V. Hartelius (Compt. rend. Trav. Lab. Carlsberg, 1933, **19**, No. 15, 23 pp.).—The optimum initial p_H for growth in the presence and absence of the growth-promoting substance (I) is 6—7 and 3, respectively; the highest p_H at which the fungus can germinate is 1·3 and 1·5. The ratio of the amounts of dry matter formed with and without the addition of (I) is 2·12 and 3·48 after 48 hr. with

initial p_H 2·6 and 6·3. There is no autolysis in cultures if the initial p_H is $< 2·1$. H. G. R.

Action of certain fungi on solutions of aldoses and other saccharine materials. VIII. A. Angeletti and D. Ponte (Annali Chim. Appl., 1933, **23**, 315—317; cf. this vol., 638).—*Penicillium crustaceum* (L.), Fries, acts on *d*-galactose solutions with formation of small amounts of citric acid, but lactose solutions are attacked only very slightly and without giving acid products, either by this species or by *P. luteum-purpurogenum*. Lactose is attacked directly, without previous hydrolysis. T. H. P.

Formation of fructose and kojic acid by acetic acid bacteria. T. Takahashi and T. Asai (Zentr. Bakt. Par., 1933, II, **88**, 286—295; cf. this vol., 189).—Bacteria isolated from various fruits produced fructose (I) and kojic acid (II) from mannitol (III); in some cases the yield of (I) was 80% of the theoretical. The mechanism of formation of (II) differs from that by *Aspergillus* and probably consists of a progressive oxidation, (III) —— (II) ⟶ (I). A. G. P.

Production of fructose and kojic acid from mannitol by acetic acid bacteria. II. Effects of p_H of culture solution and addition of calcium carbonate. T. Takahashi and T. Asai (J. Agric. Chem. Soc. Japan, 1933, **9**, 369—374).—Optimum p_H were 6·95—7·54 and 5·79—6·25, respectively. Fructose (I) was produced in the first, and kojic acid (II) mainly in the latter, stage of fermentation. Production of (II) from (I) was optimal at p_H 6·28—6·46 when $CaCO_3$ was added; succinic acid was then also produced. Ch. Abs.

Relation between enzymic activity, morphology, and resistance to stains of butyric acid bacteria, and the mechanism of residual respiration. M. G. Sevag (Z. Hyg., 1933, **114**, 756—768; Chem. Zentr., 1933, i, 2711—2712).—Butyric acid bacteria, which in the early stage of development are Gram-positive (I), degenerate to the Gram-negative form and lose practically all their enzymes. The enzymic activity and residual respiration are approx. proportional to the no. or wt. of (I) cells. When the enzymic activity of (I) bacilli is extinguished by KCN, the O_2 requirement becomes zero. A. A. E.

Mechanism of the activation of glucose in lactic fermentation. C. Fromageot and J. Roux (Biochem. Z., 1933, **265**, 13—20; cf. A., 1932, 195).—The rate of evolution of CO_2 liberated by the action of *B. bulgaricus* (I) on glucose (II) in absence of O_2 is proportional to the amount of (I) present, whereas changes in the concn. (III) (2·6—0·052%) of (II) have no effect. The period (IV) of induction varies little while (III) remains relatively high, but increases rapidly when it is low. When almost all the (II) is exhausted evolution of CO_2 ceases. The results, considered mathematically, confirm the authors' views concerning the mechanism of the activation of (II). (IV) corresponds with the conversion of (II) into a special form. W. McC.

Respiration and fermentation of lactic acid bacteria. J. G. Davis (Biochem. Z., 1933, **265**, 90—104; cf. Bertho and Glück, A., 1932, 654).—The H_2O_2 produced by *B. Delbrückii* is equiv. in amount to the O_2 consumed in oxidising the substrate and hence the R.Q. is 0·5. The rate of oxidation is accelerated 100—300% by addition of methylene-blue (I) or p-$C_6H_4(NH_2)_2$, the yield of H_2O_2 being reduced 25% (R.Q. 0·7—0·9). The acceleration [which is inhibited by $CH_2I·CO_2H$ (II)] is probably due to oxidation of lactate (III), since (II) inhibits neither oxidation of (III) nor increase in respiration by (I) in presence of (III). (II) restricts consumption of glucose after glycolysis whether (I) is present or not. The oxidation of $AcCO_2H$, which is even more rapid, is little affected by HCN and no H_2O_2 is produced. *B. cereale* (IV) produces no H_2O_2; its action is inhibited by HCN and CO, but (I) has no effect. Oxidative fermentation accompanies the action of (IV); the R.Q. is about 2, and $AcCO_2H$ is produced and partly converted into AcOH, acetoin, and EtOH. W. McC.

Gluconic acid fermentation. VII. T. Takahashi and T. Asai (J. Agric. Chem. Soc. Japan, 1933, **9**, 351—360).—Yeast extract containing glucose 10 and $CaCO_3$ 2·5% was fermented with *B. hoshigaki* var. *rosea* at 26—28° for 45 hr. The yields of ε-keto-gluconic (I), gluconic (II), glycollic acids and a uronic acid, $[\alpha]_D^{25}$ +67·5°, from 300 g. of glucose were, respectively, 2·5, 1·5, 30, and 59 g. A brown colouring matter was also formed. With other AcOH bacteria, which produced no colouring matter, (I), (II), glycuronic, succinic, lactic, and (?) acetic acids were produced. The yield of (II) is increased by addition of $CaCO_3$. Ch. Abs.

Fermentation of [structurally] *d*- and *l*-arabinose by bacteria. S. A. Koser and F. Saunders (Proc. Soc. Exp. Biol. Med., 1932, **30**, 218—220).—*l*-Arabinose is fermented rapidly by many types of bacteria which ferment the *d*-form with difficulty. Three strains of *Proteus vulgaris* fermented the *d*- and not the *l*-form. *Es. coli* and *Aer. aerogenes* ferment *d*-arabinose with difficulty. Ch. Abs.

Nature of the reaction of *B. coli* on Endo's medium. L. A. Margolena and P. A. Hansen (Stain Tech., 1933, **8**, 131—138).—The typical reaction is caused by MeCHO. H. W. D.

Effects of saliva on growth of *Bacterium coli*. O. W. Clough (J. Dent. Res., 1933, **13**, 183—184).—Fresh, but not treated, filtered saliva partly inhibits growth of *B. coli* and staphylococci, but not of pneumococci. Nutr. Abs. (*m*)

Production of an unsaturated compound by *Es. coli* in a synthetic medium. W. F. Lange (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1134—1137).—In a medium containing dextrin 10, K_2HPO_4 1, KH_2PO_4 1, $MgSO_4$ 0·1, $CaCl_2$ 0·1, $(NH_4)_2C_4H_4O_6$ 10 g., H_2O 1000 c.c., *Es coli* produced acidity not due to lactic, acetic, or acetoacetic acid. An unsaturated acid, corresponding with propiolic acid, was isolated; it is probably an intermediate product in the metabolism of dextrin. Ch. Abs.

Toxic bacterial pigment. A. G. van Veen and W. K. Mertens (Proc. K. Akad. Wetensch. Amster-

dam. 1933, 36, 666—670).—Certain bacteria from coconut food-products, when grown on filter-paper soaked in a glycerol-containing nutrient medium, produce a yellow pigment. On purification by salting out with Na_2SO_4, extraction with $CHCl_3$, EtOAc, etc., this yields a substance, m.p. approx. 200°, the min. lethal dose of which to rats is < 0·005 mg. when administered intraperitoneally. The poison is rich in N, is amphoteric, and readily dialyses. F. O. H.

Ultrafiltration in bacteriology. R. Le Guyon (Ann. Inst. Pasteur, 1933, 51, 377—406).—Diphtheria toxin and anatoxin cannot be separated from each other by ultrafiltration, and their mol. size is approx. equal. The exogenous toxin of the tubercle bacillus can be separated by ultrafiltration, whilst bacteriophage cannot be so separated. Pyocyanine is completely ultrafilterable. P. G. M.

Action of formaldehyde on diphtheria toxin. I. Significance of formaldehyde concentration, temperature, and hydrogen-ion concentration in the production of anatoxin. S. Schmidt (Z. Immunität., 1933, 78, 27—45; Chem. Zentr., 1933, i, 2421).

Immunising properties of partial antigens from diphtheria bacilli. III. V. N. Kruizhanovski (Arch. sci. biol., U.S.S.R., 1932, 32, 263—270). Ch. Abs.

Metabolism of purple sulphur bacteria in organic media. F. M. Muller (Arch. Mikrobiol., 1933, 4, 131—166).—In the absence of oxidisable S the bacteria develop in media containing a simple N-free org. substance. Radiant energy is essential for growth. In cultures containing lactate, pyruvate (I), acetate, succinate, malate, or butyrate (II), no metabolic products other than small amounts of CO_2 are formed. In the case of (II) additional CO_2 is taken up. The conversion of org. acid into (I) as a necessary stage in the synthesis of cell material is discussed. The photosynthetic processes involved may be represented as a sp. case of the general equation. A. G. P.

Influence of aërial-earth circuit on biological activity. II. A. Itano (Proc. Imp. Acad. Tokyo, 1933, 9, 309—312).—The potential of *Azotobacter chroococcum* cultures (I) is influenced by the aërial-earth circuit (II), and the differences in the fixation of N by (I) previously reported under varying conditions of (II) may be due to this. A. L.

Dehydrogenases during staphylolysis. Method of evaluating bacterial lysis. F. Chodat and F. Wyss-Chodat (Compt. rend., 1933, 197, 657—660).—Data are recorded from which it is claimed that the dehydrogenase activity of *Staphylococcus aureus*, as measured by reduction of methylene-blue in the presence of Na succinate, progressively decreases during lysis by phage. A. C.

Specific protein of the capsule of the anthrax bacillus. J. Tomcsik and H. Szongott (Z. Immunität., 1933, 78, 86—99; Chem. Zentr., 1933, i, 2124).—Agar cultures were extracted with KOH and pptd. with EtOH, and then by pptn. with $CuSO_4$ a fraction containing 10% N and free from carbohydrate was obtained. The supernatant liquid contained the carbohydrate, probably a polysaccharide. The ppt. gives no biuret, xanthoproteic, or Molisch reaction, but is nevertheless regarded as a protein. A. A. E.

Polysaccharides of lepra bacilli. M. S. Newman and R. J. Anderson (Z. physiol. Chem., 1933, 220, 1—4).—By the acetylation of the crude polysaccharides of the lepra bacillus, cryst. trehalose octa-acetate, and an amorphous *acetate*, $[\alpha]$ +142° in $CHCl_3$, of a *polysaccharide*, decomp. 225°, $[\alpha]_D$ +156° in H_2O, giving the reaction for pentoses, were obtained. J. H. B.

Solubility of *Pneumococcus* in saponin. III. Sensitisation by ergosterol. S. J. Klein (J. Bact., 1933, 26, 215—219).—Ergosterol (I) and cholesterol sensitise the organism to lysis by saponin. Irradiation of (I) reduces its activity in this respect. A. G. P.

Chemical and immunological studies of *Pneumococcus*. III. Cellular carbohydrate fractions. A. Wadsworth and R. Brown (J. Immunol., 1933, 24, 349—368).—Type-sp. carbohydrates all contained P and N; they differed from the sol. sp. substances of Heidelberger, Avery, and others, and from Tillett and Francis' C-fraction. Ch. Abs.

Decomposition of specific bacterial polysaccharides by a species of *Myxobacterium*. W. T. J. Morgan and A. C. Thaysen (Nature, 1933, 132, 604).—A micro-organism (I), probably a typical *Myxococcus*, Thaxter, which rapidly decomposes the sp. polysaccharide, $[\alpha]_{5461}$ +110°, of Shiga's bacillus, has been isolated from decayed vegetable debris. (I) also attacks the sp. polysaccharides of *B. dysenteriæ*, Flexner Y, *Pneumococcus* (Type II), and the tubercle bacillus, and destroys their power to form a sp. ppt. when mixed with the homologous immune serum. L. S. T.

Influence of foodstuffs on the respiratory metabolism and growth of human tubercle bacilli. R. O. Loebel, E. Shorr, and H. B. Richardson (J. Bact., 1933, 26, 139—166).—The O_2 consumption of the organism is increased by glycerol, Na lactate, and Na salts of higher fatty acids, lecithin, milk- and serum-fat. Glucose and glycogen produce smaller effects. The stimulation of respiratory activity is produced by much smaller concns. of the above substances than are required for abundant growth. A. G. P.

Influence of adverse conditions on the respiratory metabolism and growth of human tubercle bacilli. R. O. Loebel, E. Shorr, and H. B. Richardson (J. Bact., 1933, 26, 167—200).—Metabolism of the organisms under conditions of starvation, changing p_H, and anaerobic exposure is examined. A. G. P.

***In vitro* action of tuberculin.** M. Popper, A. Teitel-Bernard, C. Raileanu, and G. T. Dinischiotu (Arch. exp. Path. Pharm., 1933, 172, 429—432).—The O_2 uptake (I) of the blood of normal and tuberculous guinea-pigs and men with and without the addition of tuberculin (II) has been studied in the micro-respirometer. The addition of (II) scarcely affects (I) of normal guinea-pig's, or of new-born

human, blood. (II) raises (I) of blood from tuberculous guinea-pigs and man. H. W. D.

p_H value of bacteria. M. GUTSTEIN (Arch. Mikrobiol., 1933, 4, 241—247; cf. this vol., 427).—The internal reaction of the majority of Gram-positive bacteria is slightly acid and of Gram-negative organisms slightly alkaline. A. G. P.

Gram reaction and the electrical charge of bacteria. V. BURKE and F. O. GIBSON (J. Bact., 1933, 26, 211—214).—Gram reaction is unrelated to the electrical charge of the cells. A. G. P.

Bacteriophage in relation to nitrogen fixation by red clover. L. ALMON and P. W. WILSON (Arch. Mikrobiol., 1933, 4, 209—219).—The behaviour of cultures of *Rh. trifolii* towards the action of a sp. bacteriophage *in vitro* has no relationship to its N-fixing ability in association with the host plant. A. G. P.

Inactivation of bacteriophage by mercuric chloride; reactivation of inactivated phage. A. P. KRUEGER and D. M. BALDWIN (J. Gen. Physiol., 1933, 17, 129—133).—The inactivation of phage (I) by $HgCl_2$ proceeds by a pseudo-unimol. reaction; when $Hg^{"}$ is pptd. by H_2S an increase in the concn. of (I) occurs, indicating the possibility of a reversal of inactivation. H. D.

Nature of the effect of carbon dioxide under pressure on bacteria. J. S. SWEARINGEN and I. M. LEWIS (J. Bact., 1933, 26, 201—210).—The lethal action of CO_2 under pressure is ascribed to pptn. of colloidal matter within the cell substance. A. G. P.

Bactericidal power of sodium ricinoleate. H. VIOLLE (Compt. rend., 1933, 197, 714—716).—High doses of aq. Na ricinoleate are not toxic to laboratory animals. Its bactericidal power varies in different groups of organisms. In general, intestinal bacteria, fungi, and yeasts are not destroyed, whilst bacteria of the respiratory system are very sensitive to its action *in vitro*. A. C.

Action of metals on bacteria at a distance. G. A. NADSON and C. A. STERN (Zentr. Bakt. Par., 1933, II, 88, 320—334; cf. A., 1932, 778).—The toxic action of plates of Mg, Al, Ni, Cu, Ag, Sn, Pt, Au, and Pb on cultures of yeast and bacteria at a distance of 1—3 mm. increased with the at. wt. of the metal and is ascribed to electronic bombardment. A. G. P.

Oligodynamic action of silver with special reference to in- and re-activation. I. BUHRMANN (Z. Hyg., 1933, 115, 241—258).—The activity of various species of bacteria was inhibited by oligodynamic Ag solution at rates which increased with the [$Ag^{\cdot}$]. The catalytic acceleration of oxidation of leucomalachite-green base is an approx. measure of the activity of the Ag. The bactericidal action of metallic Ag is destroyed by the removal of sol. Ag salts from the surface by heating or washing with aq. $Na_2S_2O_3$ or by conversion into insol. compounds. Inactivated Ag regains its bactericidal power by treatment with oxidising agents the efficiency of which is in the order $KMnO_4 > H_2O_2 >$ aq. $Cl_2 > NaOCl >$ moist O_3. Org. and inorg. acids (except HCl), $NaBO_3$, and $(NH_4)_2S_2O_8$ are ineffective in this respect. Electrical polarisation of Ag plates activates the anode and inactivates the cathode. Activation of Au results from treatment with aq. Cl_2, and to a small extent with $KMnO_4$, but not with H_2O_2. A. G. P.

Endocrinology; chemistry of hormones. II. H. P. TEUNISSEN (Chem. Weekblad, 1933, 30, 590—597).—A review. S. C.

Chemical control of the circulation. ANON. (Nature, 1933, 132, 487—488).—A summary of the British Association discussion. L. S. T.

Appearance of an acetylcholine-like substance in the venous blood of the mammalian heart on stimulation of the vagus. W. FELDBERG and O. KRAYER (Arch. exp. Path. Pharm., 1933, 172, 170—193).—With dogs and cats in which intravenous injection of physostigmine has inhibited decomp. of acetylcholine (I) in the blood (cf. A., 1930, 800), stimulation (II) of the vagi produces in the coronary venous blood a substance probably identical with (I). The concn. during (II) is $1 : 10^{-7}$ to 10^{-8} and the abs. amount corresponds with 0·0002—0·006 mg. of (I), whilst its action is apparent, although decreasing in intensity, for several min. after (II). F. O. H.

Local hormonal mechanism of parasympathetic excitation. V. E. HENDERSON and M. H. ROEPKE (Arch. exp. Path. Pharm., 1933, 172, 314—324).—An acetylcholine-like substance is produced (from a labile precursor) in the glands subserved by the chorda tympani even when the excitation is insufficient to produce any apparent secretion. Either the toxicity or contractility of the bladder appears to be based on a similar local hormonal mechanism. F. O. H.

Purification of secretin. IV. E. HAMMARSTEN, E. JORPES, and G. ÅGREN. **V.** E. HAMMARSTEN, G. ÅGREN, H. HAMMARSTEN, and O. WILANDER (Biochem. Z., 1923, 264, 272—274, 275—284).—IV. The method for the prep. of large amounts of crude secretin for electrodialysis is described.

V. Secretin obtained in acid aq. extracts is purified by electrodialysis and forms with picrolonic acid a cryst. salt which after recrystallisation from anhyd. C_5H_5N shows const. and high activity. The mol. wt. (ultracentrifuge) is about 5000. The presence of peptide linkings is shown by protease digestion. Aromatic NH_2-acids are probably not present. The prep. contains 1 atom S per mol. The ninhydrin reaction is negative, the Ac_2 reaction strong, and arginine is probably present. P. W. C.

Effect of parathyroid hormone and sodium hydrogen phosphate on bones of guinea-pigs. R. C. GRAUER (Proc. Soc. Exp. Biol. Med., 1932, 30, 57—59). CH. ABS.

Preparation of a blood-calcium-raising substance from placenta. C. BOMSKOV and H. BREMM (Klin. Woch., 1933, 12, 944—946).—Human placentas, treated by Collip's original method of preparing parathormone (I), yield a substance, possibly identical with (I), which increases the Ca content of blood. NUTR. ABS. (*m*)

Thyroxine and tissue oxidation. U. S. VON EULER (Klin. Woch., 1933, 12, 671).—Addition of thyroxine in concns. of 10^{-11} to 10^{-7} to tissue preps. slightly increased the rate of reduction of methylene-

blue in vac. tubes. The rate of O_2 uptake was also slightly increased when the O_2 pressure was sub-optimal. NUTR. ABS. (*b*)

Hormonal regulation of purine metabolism. O. FLOSSNER, F. KUTSCHER, and W. WITTNEBEN (Z. physiol. Chem., 1933, **220**, 13—19).—In athyreotic and hypothyreotic conditions the purines (I), particularly adenine, in the urine are greatly increased. Thyroxine treatment restores (I) almost to normal. *d*-Lysine, which is present before treatment, disappears. J. H. B.

Anti-oxidative action of thyroxine and of substances resembling thyroxine.—See this vol., 1126.

Detoxication of the thyroid hormone. E. HESSE and K. R. JACOBI (Klin. Woch., 1932, **11**, 2117; Chem. Zentr., 1933, i, 2167).—Oral or subcutaneous administration of Cu^{II} compounds or $Fe_2(SO_4)_3$ to dogs protects against the toxic effect of thyroid powder by the formation of insol. and physiologically inactive thyroxine complexes. A. A. E.

Effect of thyroid on fat metabolism. F. SILBERSTEIN, F. GOTTDENKER, and A. GLASER (Klin. Woch., 1933, **12**, 788—789).—Intravenous injection of di-iodotyrosine into cats rendered hyperlipæmic by administration of olive oil increases and prolongs the hyperlipæmia. NUTR. ABS. (*m*)

Transmineralisation and liver damage due to thyroid. E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1933, **12**, 631—632).—After administration of the thyreotropic hormone of the pituitary or of thyroxine, the liver contains little or no glycogen and the Na content of blood and liver is diminished; K and Cl′ are unchanged. NUTR. ABS. (*m*)

Determination of thyroxine in thyroid. N. F. BLAU (J. Biol. Chem., 1933, **102**, 269—278).—The distribution ratios of thyroxine (I), di-iodotyrosine, and KI in presence of Na_2SO_4 and the products of alkaline hydrolysis of muscle-proteins are determined. For the determination of (I) the NaOH-hydrolysate of the gland is cooled and H_2SO_4 added, while shaking, to p_H 3·5. The flask used for hydrolysis is washed with BuOH and the washings are transferred to the separating funnel. The aq. layer is removed and the BuOH layer extracted twice with 4*N*-NaOH containing 5% Na_2CO_3. The BuOH solution is removed and the BuOH distilled off. The residue is ashed and analysed for I. H. D.

Determination of thyroxine-iodine in thyroid gland powder. L. CUNY and J. ROBERT (J. Pharm. Chim., 1933, [viii], **18**, 233—246).—The method of Harington and Randall (A., 1930, 504) is somewhat superior to that of Leland and Foster (A., 1932, 432). F. O. H.

Influence of insulin, adrenaline, and thyroxine on galactose assimilation. L. POLLAK and G. FEHÉR (Arch. exp. Path. Pharm., 1933, **172**, 407—428).—Insulin promotes the assimilation of both orally and intravenously administered galactose (I). Adrenaline and orally or intravenously administered glucose have a similar action with orally but not with intravenously administered (I); the mechanisms of adrenaline and glucose action are therefore probably identical. Thyroxine inhibits the assimilation of orally administered (I); with intravenously administered (I) its action is not apparent. F. O. H.

Plasma-phosphate and -lactic acid in normal and adrenalectomised animals during changes in carbohydrate metabolism. C. F. CORI and G. T. CORI (Arch. exp. Path. Pharm., 1933, **172**, 249—260).—Intravenous injection of sub-convulsive doses of insulin (I) into rabbits lowers the plasma-inorg. PO_4 (II), the effect being considerably diminished by adrenalectomy (III). Subcutaneous injection of adrenaline (IV) also lowers (II) both before and after (III). During (I)-hypoglycæmia in normal rabbits, the blood-lactic acid (V) is approx. doubled, whereas after (III) the level is unchanged. These facts together with the changes in muscle-hexose phosphate (A., 1932, 199) indicate that in normal fasting animals the fall in (II) and the rise in (V) following injection of (I) are secondary effects of (IV) liberated from the adrenals. Intravenous injection of glucose produces only slight changes in (II). After (III), hypoglycæmia is accompanied by a return to normal vals. of (II), whilst with normal animals it produces a further decrease in (II). The probability of a rapid utilisation of sugar leading to the formation of a hitherto unidentified P compound at the expense of (II) is discussed. F. O. H.

Physiology of insulin. G. H. TUTTLE (Lancet, 1933, **225**, 687—690).—A review. The view that wherever carbohydrate metabolism occurs some kind of insulin, either pancreatic or cellular, must be present is advanced, and evidence for the existence of multiple insulins is discussed. L. S. T.

Hypoglycæmic effect of insulin injected into the portal vein of the dog. E. AUBERTIN and E. TRINQUIER (Compt. rend. Soc. Biol., 1933, **112**, 583—584; Chem. Zentr., 1933, i, 2167).—The usual hypoglycæmic effect, and the initial hyperglycæmia, are observed; hence the liver has no "neutralising" action on insulin. A. A. E.

Influence of insulin on reduced glutathione of blood. E. ZUNZ (Ann. Physiol. Physicochim. biol., 1931, **7**, 314—317; Chem. Zentr., 1933, i, 2128).—Insulin produces a slight increase in the glutathione-SH content of arterial blood; the effect is not related to the corpuscle : plasma ratio. A. A. E.

Antagonism between insulin and pituitrin. P. WERMER and J. MONGUIÓ (Klin. Woch., 1933, **12**, 748—751).—Pituitrin (I) (subcutaneously) had no effect on the action of insulin (II) injected intravenously; when (II) was administered subcutaneously, (I) diminished its effect in some cases. Probably (I) inhibits absorption of (II) from the subcutaneous tissue. NUTR. ABS. (*b*)

Exciting action of the vagus on the secretion of insulin studied by anastomosis of pancreatic and jugular veins and by similar methods. R. GAYET and M. GUILLAUMIE (Compt. rend. Soc. Biol., 1933, **112**, 1327—1331, 1331—1336).—When a pancreatic–jugular vein anastomosis is established between two dogs there is no evidence of increased secretion of insulin when the right vagus nerve of the

donor is stimulated, or when its head is perfused with hyperglycæmic blood. NUTR. ABS. (*m*)

Callicrein in the internal and external pancreatic secretions. E. K. FREY and E. WERLE (Klin. Woch., 1933, **12**, 600—601).—The callicrein (I) content of the urine of the dog with pancreatic fistula does not diminish, but does so when the whole gland is removed. Diminution also occurs when the blood supply of the pancreas is shut off. Significant quantities of (I) are found in the pancreatic juice of dogs and in human duodenal juice. (I) is not inactivated by trypsin. NUTR. ABS. (*m*)

Reduction of blood-pressure by vagotonin and other pancreatic extracts not containing insulin. D. SANTENOISE, L. MERKLEN, E. MORELLE, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1932, **111**, 912—916; Chem. Zentr., 1933, i, 2426).—The effect is hormonal; that of other pancreatic extracts is pharmacodynamic. A. A. E.

Effect of the parotid gland on carbohydrate metabolism. M. CAHANE (Compt. rend. Soc. Biol., 1933, **112**, 1438—1441).—The parotid glands (dog) appear to contain an internal secretion which acts antagonistically to insulin. NUTR. ABS. (*m*)

Adrenalinæmia and adrenalinuria. G. VIALE (Rev. sudamer. endocrinol., 1933, **16**, 387—391).—Adrenaline (I) is identified by the production of a red colour after boiling with $HgCl_2$, sulphanilic acid, and KIO_3. (I) is inactivated against this reaction by CH_2O. Dog's blood contains 1 in 4×10^5 and serum 1 in 5×10^5. The blood of adrenalectomised animals is only slightly lower in (I). Healthy individuals excrete (I) in the urine. High vals. are recorded in persons with high blood-pressure. CH. ABS.

Mechanism of adrenaline hyperglycæmia. R. C. FORMIGUERA and E. BIETO (Compt. rend. Soc. Biol., 1933, **113**, 333—336).—In dogs receiving 0·026 mg. of adrenaline (I) per kg. the sugar content of arterial and venous blood is identical after saphenous injection, but is higher in arterial than in venous blood after injection into the mesenteric vein. When (I) acts peripherally it does not cause retention of glucose in the tissues, but when it acts principally, if not exclusively, on the liver, it produces a hyperglycæmia by acting on liver-glycogen, part of the liberated glucose being immediately retained by the tissues. This action on the liver is partly independent of the action of (I) in stimulating the metabolism of sugar in the peripheral tissues. NUTR. ABS. (*m*)

Adrenal cortex. II. Metabolism, circulation, and blood concentration during adrenal insufficiency in the dog. G. A. HARROP, A. WEINSTEIN, L. J. SOFFER, and J. H. TRESCHER. **III. Plasma electrolytes and electrolyte excretion during adrenal insufficiency in the dog.** G. A. HARROP, L. J. SOFFER, R. ELLSWORTH, and J. H. TRESCHER (J. Exp. Med., 1933, **58**, 1—16, 17—38).—II. The assumption that the adrenal cortex or its hormone has a detoxifying action on some product of metabolism is unnecessary.

III. One function of cortical extract injected into the adrenalectomised dog is participation in the regulation of Na and Cl metabolism. CH. ABS.

Anterior pituitary hormone with specific effect on carbohydrate metabolism, antagonistic to that of insulin. H. LUCKE, E. R. HEYDEMANN, and R. HECHLER (Z. ges. exp. Med., 1933, **88**, 65—77).—In pregnant bitches which are excreting prolan there is no disturbance of carbohydrate metabolism (II) despite hypertrophy of the anterior pituitary (I), so that the sex hormone of (I) is apparently not concerned with (II). Injection of praphyson (III) (anterior pituitary extract not containing prolan) produces a rise of blood-sugar in rabbits, dogs, and man. The hypoglycæmic effects of insulin are reduced or abolished by simultaneous administration of (III) in normal dogs and in those with (I) removed. The disturbances in (II), especially the increased reaction to insulin, occurring in dogs in which (I) has been removed, can be greatly reduced by administration of (III). NUTR. ABS. (*m*)

Fat metabolism hormone of the anterior pituitary lobe. H. MAGISTRIS (Endokrinol., 1932, **11**, 176—191; Chem. Zentr., 1933, i, 1464).—A rabbit unit is the smallest quantity of the hormone (I) which, 2 hr. after injection, doubles the total ketonic substances in the blood. The $OH{\cdot}CHEt{\cdot}CO_2H$ is particularly increased. Normal vals. are reattained after 24 hr. The prep. is completely or largely inactivated by *N*-NaOH; hence the active substance is not histamine and it is not identical with known anterior pituitary hormones. The sp. dynamic action and effect on the basal metabolism are described. (I) is found in the urine; only the gonadotropic hormone is adsorbed by animal C. The two hormones are closely similar in properties. (I) is not combined with protein, and probably has a relatively small mol. wt. A solution free from protein (ultrafiltration) gives the biuret reaction, but no turbidity with sulphosalicylic acid. (I) is adsorbed by kieselguhr, but not by bone-C, kaolin, or talc. A. A. E.

Glycosuria in rabbits following injections of saline extract of anterior pituitary. E. J. BAUMANN and D. MARINE (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1202—1223).—Hyperglycæmia, lipæmia, glycosuria, and polyuria were produced by injection of ox pituitary gland extract. "Phyone" caused severe glycosuria in only one of four rabbits. CH. ABS.

Anterior pituitary hormone in saliva. B. OFSTAD (Klin. Woch., 1932, **11**, 1761; Chem. Zentr., 1933, i, 2833).—Saliva of pregnancy, when injected by Aschheim and Zondek's method into mice, did not give a positive pregnancy reaction, but hyperæmia of the ovary and uterus indicated the presence of the anterior pituitary hormone in small concn. A. A. E.

Influence of the gonads on protein metabolism. III. (*a*) Effect of injections of anterior pituitary extracts on urinary creatinine in normal and castrated rabbits. (*b*) Tolerance of normal and castrated animals to injected creatine. I. SCHRIRE and H. ZWARENSTEIN (Biochem. J., 1933, **27**, 1337—1341).—Normal but not castrated rabbits show an increased excretion of creatinine (I) in the urine following the subcutaneous injection of antuitrin or extracts of the anterior lobe (II) of the pituitary. The results support the view that there is

a direct relationship between (II) and (I) metabolism. Normal rabbits excrete less, and thus retain more, creatine than do castrated rabbits when large amounts are injected subcutaneously. A. W.

Melanophore hormone. A. JORES (Klin. Woch., 1932, **11**, 2116; Chem. Zentr., 1933, i, 2425).—Polemical (cf. Zondek and Krohn, A., 1932, 432; this vol., 98, 319). A. A. E.

Oxytocic hormone of the posterior lobe of the pituitary gland. IV. Action of animal proteolytic enzymes: nature of the hormone. J. M. GULLAND and T. F. MACRAE (Biochem. J., 1933, **27**, 1383—1393).—One commercial trypsin (I) prep. rapidly inactivated the oxytocic hormone (optimum inactivation at p_H 8·8), whereas another was only slightly effective. Enzyme preps. of equal (I) activity had different inactivating powers. The inactivating enzyme is probably therefore not (I) and the hormone may not be proteinoid in nature. The hormone was not attacked by a pepsin prep., or by a bone-phosphatase prep. W. O. K.

Œstrogenic hormones. ANON. (Nature, 1933, **132**, 609—610).—A review. L. S. T.

Extraction of folliculin from the urine of pregnant mares. A. LIPSCHÜTZ and E. POCH (Compt. rend. Soc. Biol., 1932, **111**, 856—857; Chem. Zentr., 1933, i, 2265).—The urine is acidified with HCl (10—20%), boiled for 5 min., and extracted with Et_2O. A. A. E.

Does menstrual blood contain growth-hormones or auxins as well as the supposed menotoxins? A. SACK (Münch. med. Woch., 1933, **80**, 10—12; Chem. Zentr., 1933, i, 2126).—The presence of auxin has not been detected. The stimulating action on plant growth is attributed to the presence of follicular hormone. A. A. E.

Relation between ovarian function and calcium metabolism. O. BOKELMANN (Arch. Gyn., 1933, **152**, 492—500; Chem. Zentr., 1933, i, 2833).—The total and ash-Ca of mice receiving injections of folliculin was < those of controls. The total ash was normal. A. A. E.

Inhibitory factors and the mechanism of the action of sex hormones of the opposite sex on the development of sex glands. W. SCHOELLER and M. GEHRKE (Biochem. Z., 1933, **264**, 352—356).—Inhibition of the development of male sex glands on administration to young male animals of œstrin is confirmed and an explanation attempted. P. W. C.

Sexual hormone in the urine of men of various ages. F. BÜHLER (Z. ges. exp. Med., 1933, **86**, 650—658; Chem. Zentr., 1933, i, 2126).—At 20—40 years (male) the daily excretion is 1—2 fowl units; in puberty and old age androkinin could not be detected except after administration of proviron." The thelykinin (I) content is (male): puberty—30 years 25—20, 30—50 years 10—15 mouse units. Before puberty and after 60 years (I) was not detected in the urine. A. A. E.

Male hormone from pigs' testicles. A. OGATA and S. HIRANO (Proc. Imp. Acad. Tokyo, 1933, **9**, 345—346).—An improved method for the isolation of the testicular hormone is described. Saponification with 10% KOH in EtOH almost, oxidation with $KMnO_4$ in $COMe_2$ solution completely, destroyed the gonadotropic activity of the preps. A. L.

Action of the testicular hormone on cockscombs and seminal vesicles. K. MATSUZAKI (Proc. Imp. Acad. Tokyo, 1933, **9**, 342—344).—Hormone preps. from male urine, active in promoting comb growth (I), showed no activity on the vesicles of rats (II). The testicular hormone (III) from pigs, on the other hand, showed activity in respect of both (I) and (II), although on treatment with $KMnO_4$ in $COMe_2$ solution (II) was no longer apparent. (III) is therefore considered to contain two different hormones. A. L.

Vitamins and hormones. J. KÜHNAU and W. STEPP (Münch. med. Woch., 1933, **80**, 87—92; Chem. Zentr., 1933, i, 2126).—Chemical relationships are discussed. A. A. E.

Systematisation of avitaminosis and vitamins. W. KOLLATH (Med. Klinik, 1933, **29**, 143—146; Chem. Zentr., 1933, i, 1470—1471).—A classification based on bodily changes produced in dietary experiments on rats is advanced. A. A. E.

Dietary factor concerned with carbohydrate metabolism. L. G. WESSON and F. C. MURRELL (J. Biol. Chem., 1933, **102**, 303—311; cf. this vol., 527).—A liquid-fat fraction (I), obtained from the mother-liquors from crystals of an EtOH solution of lard after the solid fraction has crystallised out, is ten times as active as the solid fraction in restoring the carbohydrate metabolism of rats, fed on a fat-deficient diet (II), to normal. The feeding of Et stearate in (II) reduces the effectiveness of (I). Saponified (I) is active. The abnormal metabolism is ascribed to the absence of a metabolic factor in fat. H. D.

Vitamin-*A* in fish-liver oils. P. N. CHAKRAVORTY, H. C. MOOKERJEE, and B. C. GUHA (J. Indian Chem. Soc., 1933, **10**, 361—366).—The Carr–Price blue vals. of the liver oils from *Labes rohita* (*Rohit*) (I), *Cirrhina mrigala* (*Mrigal*), *Catla catla* (*Katla*), *Clupea ilisha* (*Hilsha*), and *Lates calcarifer* (*Vetki*) are 227, 174, 109, 59, and 284, respectively. Considerable seasonal variations may occur with (I). The mesenteric fat of (I) contains no vitamin-*A*. The relation between dilution of the oil and the intensity of the colour in the Carr–Price method (A., 1926, 870) is discussed. H. B.

Vitamin-*A* content of milk irradiated by various carbon arcs. R. C. BENDER and G. C. SUPPLEE (Amer. J. Dis. Children, 1933, **45**, 995—998).—The vitamin-*A* content of milk containing 1·2% of fat was not appreciably reduced by irradiation during 8—48 sec. CH. ABS.

Vitamin content of the Indian mango. B. C. GUHA and P. N. CHAKRAVORTY (Indian J. Med. Res., 1933, **20**, 1045—1048).—Three varieties of Indian mangoes were fairly good sources of vitamin-*A*, but were relatively poor in the vitamin-*B* complex and in vitamin-*C*. NUTR. ABS. (*b*)

Vitamin-*C* and -*A* in blueberries. C. R. FELLERS and P. D. ISHAM (J. Agric. Res., 1933, **47**,

163—165).—The vitamin-*C* content of *Vaccinium corymbosum* is high and not appreciably affected by freezing or by certain methods of canning. *V. pennsylvanicum* contains less vitamin-*C* and is practically devoid of -*A*. A. G. P.

Role of fat-soluble vitamin in the nutrition of growing cattle and pigs, with consideration of certain other vitamin problems. H. Isaachsen, O. Ulvesli, M. Husby, and K. Breirem (Foringsforsøk. Norges Landbruksh., 1931, No. 30, 27 pp.; Biod. Zentr., 1933, **A**, **3**, 419—420).—Various typical rations and special supplements are examined as sources of vitamin-*A* and -*D*. A. G. P.

Application of the paired feeding method to the determination of the vitamin-*A* content of foods and artificial concentrates. O. F. Garrett and H. H. Mitchell (Amer. J. Physiol., 1933, **104**, 608—614).—4% of butter-fat from stall-fed cows provided sufficient vitamin-*A* (I) for normal growth of newly-weaned rats, the mothers of which were deprived of (I) during lactation but received 1% of cod-liver oil during gestation. Nutr. Abs. (*b*)

Complement content of sera in avitaminosis-*A* and -*C*. P. E. Simola (Acta Soc. med. Fennicae "Duodecim," 1932, **A**, **16**, No. 1, 12 pp.).—In guinea-pigs (I) suffering from vitamin-*C* deficiency, there is no change in the val. for serum-complement, but it decreases in (I) suffering from vitamin-*A* deficiency. Addition of vitamin-*D* to the diet does not alter the serum complement of (I). Nutr. Abs. (*m*)

Vitamin-*A* deficiency in dogs. A. M. Stimson and O. F. Hedley (Pub. Health Rep., U.S. Treasury Dept., 1933, **48**, 445—449).—The symptoms of the deficiency in dogs are conjunctivitis, corneal opacity, ulceration, perforation (in 6—32 weeks), ophthalmia, nasal hæmorrhage, bronchopneumonia, and malnutrition. Deposit appears on the teeth and deciduous teeth fail to shed. In some cases there is disturbance in locomotion. The spinal cord is also affected. Nutr. Abs. (*m*)

Occurrence of γ-carotene. A. Winterstein (Z. physiol. Chem., 1933, **219**, 249—252).—The new provitamin-*A* found in *Gonocaryum* fruits (I) is a mixture of γ-carotene (II) and *δ-carotene*, absorption bands 526, 490, 457 mμ in CS_2. The rind of (I) is the best source of (II). J. H. B.

Activity of carotene from the suprarenal glands of various animals. L. Randoin and R. Netter (Bull. Soc. Chim. biol., 1933, **15**, 944—953).—The activity of the carotene (I) extracted by the method of Bailly and Netter (A., 1932, 76) from the suprarenal glands (II) of the ox is only slightly < that of purified (I). (I) is also present in the (II) of the horse and the pig, but not in the white rat. A. L.

Biological relation between carotene and vitamin-*A*. J. C. Drummond and R. J. Macwalter (Biochem. J., 1933, **27**, 1342—1347).—The vitamin-*A* (I) content of the liver, determined spectrophotometrically, showed no increase following the injection of carotene (II) into the portal circulation of rabbits until 8 days after the injection. The possibility cannot be excluded that the vitamin produced is utilised or the amounts are too small for determination by this method. Attempts to obtain *in vitro* conversion of (II) into (I) by liver-tissue have failed. A. W.

Metabolism of carotene in different animals. B. Ahmad and K. S. Malik (Indian J. Med. Res., 1933, **20**, 1033—1038).—Rats' livers contained large quantities of vitamin-*A* when carotene had been administered after a vitamin-*A*-deficient diet, but no increase occurred in the case of the cat, whilst the rabbit, pigeon, and chicken showed moderate increases. Nutr. Abs. (*b*)

Influence of the carotenes on growth, xerophthalmia, cornification, and the œstrous cycle. R. Kuhn and H. Brockmann (Klin. Woch., 1933, **12**, 972—973).—For growth promotion and for the cure of xerophthalmia and of persistent vaginal cornification in rats α-, β-, and γ-carotenes were active, but β-carotene, which presumably affords 2 mol. of vitamin-*A* (I), appeared to be twice as active as the α- and γ-forms, which may be supposed to lose half the mol. as inactive material on conversion into (I). For the complete restoration of the œstrous cycle the dose required was 5—8 times the min. dose for growth. Only above this level was (I) stored in the liver, the amount found after β-carotene feeding being double that found after feeding α-carotene. A daily dose of 1·0 mg. of carotene produced no signs of hypervitaminosis-*A*, possibly on account of incomplete absorption. Nutr. Abs. (*b*)

Antirachitic action of β-cholic acid. T. Kikuzawa (Z. physiol. Chem., 1933, **220**, 54—56).—Irradiated Me α-cholate (2 mg. dose) and β-cholate (20 mg. dose) protect rats to a small extent against rickets. J. H. B.

Evaluation of vitamin-*D* preparations. III. M. Schieblich (Biochem. Z., 1933, **265**, 1—4; cf. A., 1931, 531).—When buckwheat (I), which contains less P than wheat (II), is substituted for (II) in McCollum's diet (A., 1921, i, 757) the amount of vitamin-*D* required to prevent rickets in rats receiving the diet is doubled. The modified diet is otherwise as useful as the original. When the vitamin-*D* content of foods is determined, only a half or one third of the (II) should be replaced by (I). W. McC.

Bile in the absorption of vitamin-*D* in the rat. J. D. Greaves and C. L. Schmidt (J. Biol. Chem., 1933, **102**, 101—112).—Bile-fistula rats have negative Ca and P balance. Irradiated ergosterol (I) is absorbed in small amounts only from the intestinal tract, but deoxycholic acid, given orally, can act as a carrier of (I) across the intestinal wall. H. G. R.

Renal lesions in hypervitaminosis-*D*: urinary calcium and phosphorus excretion. J. Gough, J. B. Duguid, and D. R. Davies (Brit. J. Exp. Pathol., 1933, **14**, 137—145).—Calcification and parenchymatous degeneration ("nephrosis"), which frequently coexist in the kidneys of rats in hypervitaminosis-*D*, are largely independent of one another. Whilst calcification could be correlated with a high renal excretion of Ca, no connexion could be established between nephrosis and any urinary disturbances, although it was influenced by administration of NaH_2PO_4 with excess of vitamin-*D*. The urinary Ca was greatest

when the alkaline phosphate was administered with vitamin-*D*, and urinary P when NaH_2PO_4 was given. Calciferol decreased the urinary P when either the acid or alkaline salt was administered. NUTR. ABS. (*b*)

Behaviour of glycogen in the organism in absence of the vitamin-*B* complex (particularly -B_1) from the diet. E. ABDERHALDEN and E. WERTHEIMER (Pfluger's Archiv, 1932, 230, 601—613; Chem. Zentr., 1933, i, 1645).—In pigeons avitaminosis-B_1 is accompanied by marked accumulation of glycogen in the liver and heart muscle; blood-sugar is unchanged. Normal vals. are regained on administration of yeast, but not if the yeast has been heated at 120° for 6 hr. A. A. E.

Application of the paired feeding method to the determination of the relative vitamin-*B* contents of foods and artificial concentrates. H. H. MITCHELL (Amer. J. Physiol., 1933, **104**, 594—607).—The vitamin-B_1 (I) content of a substance was measured by determining the least amount of it which prevented any significant difference in growth between the animal and its paired control on adequate (I) diet. This was 40—45% for maize and 50—55% for wheat, with diets containing 18% of protein. Less (I) appeared to be needed for higher % of protein (caseinogen). 6% of whole dried yeast supplied sufficient of the vitamin-*B* complex for max. growth of young rats. NUTR. ABS. (*b*)

Photochemical activation of adenine. B. C. GUHA and P. N. CHAKRAVORTY (Nature, 1933, 132, 447; cf. A., 1932, 1294).—Further biological experiments indicating the formation of a growth-promoting substance on irradiation of adenine sulphate are described. L. S. T.

Concentration and probable chemical nature of vitamin-B_2. L. E. BOOHER (J. Biol. Chem., 1933, 102, 39—46).—The probable identity of vitamin-B_2 and the fluorescent pigment of whey is suggested. A 2000-fold concn. of fresh milk, of which the lactochrome is the main constituent, active in 1 mg. doses, practically free from vitamin-B_1, is described. H. G. R.

Vitamin-*C*. VI. Identity of ascorbic acid and vitamin-*C*. F. MICHEEL and T. MOLL (Z. physiol. Chem., 1933, 219, 253—256; cf. this vol., 936).—The $COMe_2$ compound of ascorbic acid (I) has less antiscorbutic activity than (I) *per os* and none when parenterally administered. The identity of (I) with vitamin-*C* is thus confirmed. J. H. B.

Potentials of ascorbic acid.—See this vol., 1015.

Vitamosazone. Y. KOTAKE and M. NISHIGAKI (Z. physiol. Chem., 1933, 219, 224—232).—A substance (phenylosazone, m.p. 205—206°; 2 : 4-dinitrophenylosazone, m.p. about 240°) of high reducing power found in many animal organs and fluids and also in a species of orange is probably ascorbic acid. From ox testes and aq. humour a *phenylosazone*, m.p. 158—160°, of a pentose was also obtained. J. H. B.

Ascorbic acid content of corpora lutea. S. HUSZAK (Z. physiol. Chem., 1933, 219, 275—277).—Corpora lutea contain about the same amount (1 mg. per g. of tissue) as the adrenals, much > any other animal organ. J. H. B.

Determination of vitamin-*C* (antiscorbutin) in milk. B. BLEYER (Münch. med. Woch., 1933, 80, 257—258; Chem. Zentr., 1933, i, 2577).—Titrimetric determinations (Tillmans) gave the highest results with human colostrum; vals. become const. after 1 month. Vals. are approx. double those for cow's milk. On keeping in air at room temp. 50% of the vitamin-*C* content is lost in 4 hr.; at 0° only 3% is lost. Heating at a high temp. for a short time has less destructive effect than pasteurisation. Ni, Cr, and Al have no influence; Cu and Ag are injurious. Goat's milk has approx. the same vitamin-*C* content as cow's milk, ewe's milk one sixth thereof, and ass' milk six times as much as cow's milk. A. A. E.

Biochemistry of carotenoids and of vitamin-*C* (ascorbic acid). H. VON EULER and E. KLUSSMANN (Z. physiol. Chem., 1933, 219, 215—223).—NH_2-acids assist the dissolution of carotene (I) by means of bile-acid salts. (I) is liberated when the p_H of the solution becomes > 7—7·5 or when the bile acids or salts are bound by other substances. Egg-yolk contained 9×10^{-6} g. of vitamin-*A* and 40×10^{-6} g. of (I) per g. In determining the vitamin-*C* (II) content of beans, the extraction should be performed in H_2. The O_2 uptake by guinea-pig's liver is less for scorbutic than for normal or *C*-hypervitaminised animals. Fish-roe contains relatively little (II). J. H. B.

Plant growth-substances. VII. Occurrence of auxins in the human and animal organism. VIII. Occurrence of auxins and growth-substances of the "bios" group in carcinomata. F. KÖGL, A. J. HAAGEN-SMIT, and H. ERXLEBEN. F. KÖGL, A. J. HAAGEN-SMIT, and B. TÖNNIS (Z. physiol. Chem., 1933, 220, 137—161, 162—172; cf. this vol., 987).—VII. Excretion of auxin *a* in human urine is independent of age and sex, and is not increased during pregnancy or influenced by menstruation. Carcinomatous and tuberculous patients showed a normal excretion. The max. excretion occurs about 3 hr. after the main meal. The excretion is much increased after ingestion of salad (arachis) oil and butter, but not after hydrogenated coconut oil and other foods devoid of auxin; *i.e.*, foods containing auxin (even although chiefly *b*) increase the output of auxin *a*, no *b* being obtainable from urine. Certain individuals show a high auxin excretion (about four times normal); this is a constitutional idiosyncrasy. Auxin occurs in small amount in many animal organs.

VIII. In human carcinoma plant-growth substances and "bios"-factors occur in higher concn. than in neighbouring normal tissue. Auxin *a* and *b* do not stimulate the growth of heart-fibroblasts in tissue culture, nor of yeast cells. J. H. B.

Presence of growth-promoting substance in animal and plant material. E. MASCHMANN and F. LAIBACH (Naturwiss., 1933, 21, 517).—The growth-promoting substance (cf. A., 1932, 1156) is found in the blood, liver, and kidneys of fasting guinea-pigs and rabbits in smaller quantities than in the case of fed animals. It is also found in rabbit's lung, pig's thyroid, calf's thymus, and ox testicle and pancreas. It exists in various grains, but decreases during ger-

mination; it occurs also in peas, beans, lentils, asparagus, tomatoes, oranges, and lemons. W. O. K.

Growth substance (auxin) in plants. F. A. F. C. WENT (Nature, 1933, **132**, 452).—A summary. L. S. T.

Plant growth hormone. J. BONNER (J. Gen. Physiol., 1933, **17**, 63—76).—Sections of *Avena* coleoptiles (I) immersed in H_2O cease growth after 7—8 hr. Addition of "growth substance" (II) increases the length by 55% in 24 hr. Top sections of (I) grow more rapidly in the presence of (II) than the lower sections. An optimum concn. of (II) exists in the region of 10 units per c.c. Addition of KCN or phenylurethane, or the absence of O_2, inhibits growth. A correlation exists between growth and respiration. H. D.

Increased respiration coefficient of stimulated seeds. M. POPOFF and M. STEFANOWA (Biochem. Z., 1933, **264**, 434—436).—Using millet seeds, stimulated (with 3% KBr) embryos always gave a higher R.Q. than non-stimulated. P. W. C.

Mechanism of the activation of oxygen by irradiated pigments. H. GAFFRON (Biochem. Z., 1933, **264**, 251—271).—In continuation of the author's work on the photochemical reactions during O transport by chlorophyll (I) and porphyrins (A., 1927, 67, 428, 1225) an attempt is made to follow quantitatively the relationship between O_2 concn. and photochemical action. The pigment does not react itself with mol. O_2 and all the autoxidation processes with (I) depend on reactions with peroxides arising by secondary processes. The oxidising action of irradiated pigment in solutions containing pigment, O_2, and oxidisable substance (acceptor) depends on an activation, not of O_2, but of the acceptor. P. W. C.

Assimilation of sulphates by fungi: euthiotrophy and parathiotrophy. M. VOLKONSKY (Compt. rend., 1933, **197**, 712—714).—Cultures of 26 varieties of *Saprolegnia* are parathiotrophic, *i.e.*, unable to grow on the basic nutrient medium (this vol., 752) if K_2SO_4 is the source of S. Growth occurs if S is supplied as cysteine (I). Several euthiotropic species are described which assimilate SO_4'' as well as, or better than, S in the form of (I). A. C.

Effects of starvation on distribution of mineral nutrients in French prune trees grown in culture solutions. H. L. COLBY (Plant Physiol., 1933, **8**, 357—393).—Symptoms of Ca starvation appeared almost entirely in roots, little or no leaf growth occurring. Deficiencies of other elements were apparent primarily in the leaves. Mg starvation resulted in high N and P and low Ca and Mg in leaves, low N and P in the trunk, and high ash contents in all organs except leaves. In the absence of Ca all parts of trees except wood had low N and ash contents. Ca in the trunk prior to starvation was not translocated. K starvation produced leaves high in N, P, Ca, and Mg and low in total ash. Trunk and roots had low N contents. Trees starved of N had low ash contents except in wood and very low N throughout. Young wood had low Ca and Mg and high K. Main roots were very low in N, low in Mg and P, and high in Ca. Leaves of P-starved trees were high in ash and N, very high in Mg and Fe, and low in Ca and P. All other parts were low in N, and roots and trunks were low in Mg. S starvation produced leaves low in N, ash, and SO_4''. Young wood was low and the remainder of the tree high in N. K absorption decreased and that of Ca and Mg increased. The Fe content of young wood and roots was high in trees starved of K, Mg, or S. High Fe in bark occurred only in cases of P and Ca starvation in which young wood and main roots showed low vals. for Fe. Trees grown for 2 years in distilled H_2O made better growth than those in nutrients containing all essential elements except Ca, but were inferior to those in aq. $Ca(OH)_2$ at p_H 7·2. K starvation was more detrimental to growth than complete starvation. Starvation of one element was more effective in changing the p_H of leaf sap than were changes in the p_H of the nutrient solutions. A. G. P.

Bast-sap. H. H. DIXON (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 487—494).—Further evidence is presented for the theory that the bast is the most important channel for the transport of org. substances, which is brought about by a difference in the osmotic pressure between the upper and lower levels. H. G. R.

Factors affecting the electrolytes of starch granules. D. S. EDWARDS and J. C. RIPPERTON (J. Agric. Res., 1933, **47**, 179—191).—In sol. canna- but not in potato-starch lowered viscosity is associated with lower K and increased Ca contents. Electrolytes held by starch *in vivo* are influenced by sap composition and growth conditions, but the variations are small compared with corresponding effects on starch *in vitro*. A. G. P.

Hydrolysis of dipeptides in germinating chlorophyll mutants of barley. H. VON EULER and B. SJOMAN (Biochem. Z., 1933, **264**, 237—245).—A stronger dipeptidase action using *d*-alanylglycine and *l*-leucylglycine is detected both in the scutellum and in the embryo of chlorophyll-defective strains of barley than in chlorophyll-normal mutants. P. W. C.

Apparatus for making autographic records of catalase activity of plant tissues. A. J. HEINICKE (J. Agric. Res., 1933, **46**, 1137—1143).—Apparatus is described whereby the O_2 produced forces H_2O into a burette containing a floating indicator pen. Records of twelve simultaneous determinations may be obtained. A. G. P.

Graphic registration of the transpiration of leaves. K. BORESCH (Planta [Z. wiss. Biol.], 1933, **20**, 448—469).—The movement of a strip of cellophane lightly attached to the leaf is utilised to obtain a record of transpiration activity. A. G. P.

Changes in leaves during the period preceding frost. F. E. DENNY (Contr. Boyce Thompson Inst., 1933, **5**, 297—312).—No important changes occurred in the dry matter or total carbohydrate content of leaves of *Viburnum dentatum* or *Syringa vulgaris* during 3—5-day periods before frost. Considerable migration of N from leaves of *Viburnum* but not from *Syringa* are recorded in this period. A. G. P.

Influence of carbohydrates on the daily course of photosynthesis. A. L. KURSSANOV (Planta [Z.

wiss. Biol.], 1933, **20**, 535—548).—The curve of photosynthesis has two max. with a min. early in the day. Artificially increased carbohydrate in the leaves reduced CO_2 assimilation and *vice versa*. A. G. P.

Seasonal osmotic variations in some evergreen woody plants. M. STEINER (Jahrb. wiss. Bot., 1933, **78**, 564—622).—Variation in the osmotic pressure of the expressed sap of *Ilex aquifolium*, *Hedera helix*, and *Pinus sylvestris* is largely controlled by changes in the sugar content, in *Buxus sempervirens* by changes in total H_2O content. Both factors operate in *Taxus baccata*. A. G. P.

Effect of ethylene chlorohydrin vapour on the chemical composition of gladiolus corms. F. E. DENNY (Contr. Boyce Thompson Inst., 1933, **5**, 435—440).—In comparison with untreated corms, those treated with the $CH_2Cl{\cdot}CH_2{\cdot}OH$ showed marked lowering of reducing sugar and some increase in sucrose contents together with an increase in sol. and a decrease in insol. N constituents. A. G. P.

Effect of potassium thiocyanate and ethylene chlorohydrin on amylase activity. F. E. DENNY (Contr. Boyce Thompson Inst., 1933, **5**, 441—450).—The action of $CH_2Cl{\cdot}CH_2{\cdot}OH$, KCNS, and $CS(NH_2)_2$ in stimulating the growth of dormant buds is in no way related to the direct effect of these substances on amylase activity. A. G. P.

Carbon dioxide narcosis. III. Salt antagonism. IV. Is lack of oxygen a factor in the narcotic effects of carbon dioxide? V. Water and electrolytes in *Nitella* during exposure to carbon dioxide solutions. D. L. FOX (J. Cell. Comp. Physiol., 1933, **3**, 340—354).—The presence of dissolved salts, *e.g.*, KNO_3, in concns. of 0·1—0·4%, with or without traces of $CaSO_4$, $Ca_3(PO_4)_2$, and $FePO_4$, increases the threshold tolerance of *Nitella* (I) for CO_2. Solutions of NaCNS (0·2%) or glucose (0·2%) do not antagonise the effects of CO_2. Dil. salt solutions induce antagonism in (I) towards strong acids, *e.g.*, HCl. Narcotic and lethal effects previously observed are not due to deficiency of O_2 but to sp. action of the CO_2 or H_2CO_3 mol. Excess O_2 is not injurious. A. G. P.

(*a*) Anæsthesia produced by distilled water. (*b*) Anæsthesia in acid and alkaline solutions. (*c*) Reversible loss of potassium effect in distilled water. W. J. V. OSTERHOUT and S. E. HILL (J. Gen. Physiol., 1933, **17**, 87—98, 99—103, 105—108).—(*a*) Cells of *Nitella* fail to respond to electrical stimulation after 2 or 3 days in distilled H_2O; the same anæsthesia (I) is produced on restricted areas of a cell. The sensitivity returns after 1—2 days in their normal environment or in dil. solutions of $CaCl_2$. It is concluded that (I) is due to a loss of substances from the cell which is inhibited by $Ca^{\cdot\cdot}$.

(*b*) Cells of *Nitella* in 0·001*M*-NaOH and 0·0001*M*-HCl lose their irritability. In the case of NaOH they fail to regain it on neutralisation, and only partial recovery occurs on treatment with $CaCl_2$. With HCl complete recovery occurs on treatment with $CaCl_2$.

(*c*) The p.d. between one part of *Nitella* in contact with a mixture of electrolytes and another part in contact with NaCl becomes more negative on replacing the NaCl by KCl. This effect disappears reversibly on exposure of the cell to distilled H_2O. The change appears to be confined to the outer surface of the protoplasm. H. D.

Effects of temperature on metabolism in tomato. G. T. NIGHTINGALE (Bot. Gaz., 1933, **95**, 35—58).—Tomato plants grown in sand cultures for 10-day periods at 13° accumulated relatively large amounts of carbohydrates (I), especially starch. Absorption and translocation of NO_3' was rapid, but protein synthesis was very slow. Reducase activity was small. Leaves were deficient in chlorophyll and stems coloured purple due to the presence of anthocyanins. These conditions were accentuated in N-deficient plants. During exposure to 21° plants having no external N supply showed considerably decreased (I) contents and symptoms of protein deficiency were less marked than at 13°. Added NO_3' was absorbed at once and translocation was more rapid than at 13°. The plants possessed high NO_3'-reducing powers and N assimilation was rapid. (I) accumulation was reduced to a much lower level when N was supplied. At 35° decomp. of (I) was rapid in N-deficient and N-supplied plants and was accompanied by degradation of proteins. The temporarily accelerated growth was quickly followed by the death of the plants. Absorption and translocation of NO_3' was rapid. Reducase activity was high for a short period, but soon declined. At this temp. plants receiving N died sooner than those in N-free media. A. G. P.

Rubber content of various species of goldenrod. L. G. POLHAMUS (J. Agric. Res., 1933, **47**, 149—152).—Of twenty-four species of *Solidago* examined none contained more than traces of rubber in any parts other than leaves. A. G. P.

Aromatic constituent of products from sugar maple [*Acer saccharum*]. J. RISI and E. BOIS (Natural. Canad., 1933, **60**, 181—193).—The aromatic constituent of maple syrup is readily extracted with Et_2O; it contains phenolic and aldehydic functions in a ratio of approx. 1, and differs from the aromatic principle of fenugreek. H. A. P.

Determination of coumarin and melilotic acid in *Melilotis officinalis*. S. J. KANEVSKAJA and A. M. FEDOROVA (Z. anal. Chem., 1933, **93**, 176—180).—The substance is extracted with boiling Na_2CO_3 solution. Coumarin dissolves, with the opening of a lactone ring and formation of a salt of coumaric acid. The salt is extracted with Et_2O, and coumarin is regenerated by adding dil. acid. The org. acid present in the original substance is determined by acidifying the Na_2CO_3 solution and extracting with Et_2O. Results of analysis of *M. officinalis* are given. E. S. H.

Latex of the lac tree of Cambodia. G. BERTRAND and G. BROOKS (Compt. rend., 1933, **197**, 661—665).—Moreac, the lac of *Melanorrhœa laccifera*, yields a H_2O-sol., EtOH-insol. gum (2·5%), and Et_2O-sol. *moreacol* (I) (55—60%), $C_{23}H_{36}O_2$, b.p. 242—250°/0·5 mm., m.p. 28°. Like laccol (this vol., 947), (I) contains two phenolic OH groups (Ac_2 derivative, b.p. 233—240°/0·2—0·3 mm.), and is hydrogenated in presence

of Pt-black to *tetrahydromoreacol*, m.p. 95·3°, b.p. 280—290°/12—14 mm. (Ac_2 derivative, m.p. 70·5°). (I) is either $C_6H_3(OH)_2 \cdot C_{17}H_{31}$, or more probably $C_6H_3Me(OH)_2 \cdot C_{16}H_{29}$. A. C.

Oleoresin of *Pinus monticola*, Dougl. P. A. Foote and N. T. Mirov (J. Amer. Pharm. Assoc., 1933, **22**, 828—834).—The oleoresin contains 60% of *d*-α-pinene, 26% of β-pinene, limonene (uncertainly), indeterminate amounts of sesquiterpenes, and 1—2% of *n*-undecane. The significance of the latter constituent is discussed in relation to a possible origin of petroleum. W. S.

Enzymes of lichens and constitution of umbilicaric acid. G. Koller and G. Pfeiffer (Monatsh., 1933, **62**, 359—372).—The extraction of a depsidase from *Umbilicaria pustulata*, *U. deusta*, and *E. prunastri* is described. This effects enzymolysis of lecanoric, gyrophoric, evernic, and diploschistesic acids into orcinol (I) and its mono-ether. A carboxylase, also present, readily attacks orsellinic and evernic acids, but not atranorin, umbilicaric (II), paraorsellinic, β-resorcylic, quinolcarboxylic, or pyrogallolcarboxylic acids. It is suggested that such H_2O-insol. depsides are reserve materials in the lichen and are broken down by the enzymes into H_2O-sol. orcinol derivatives. Alcoholysis of (II) with MeOH at 140° affords (I), Me orsellmate (III), and a *substance* (IV), $C_{18}H_{18}O_7$, m.p. 163—165°, which is a didepside containing the *iso*evernic residue, obtained by fission of (I) and subsequent esterification of the new CO_2H. With EtOH at 160° (IV) gives (III). Longer alcoholysis of (II) gives Me *iso*evernate (Me 5-hydroxy-3-methoxy-*o*-toluate) in addition to (I) and (III). Of the alternative structures previously suggested (this vol., 714), that given as (I) with a CO_2H added between Me and OH in the right-hand nucleus is preferred for (II) on the basis of these results, and (IV) is $C_6H_3Me(OH)(OMe) \cdot CO \cdot O \cdot C_6H_2Me(OH) \cdot CO_2Me$. J. W. B.

Rotenone. XXVIII. Preparation of dihydrorotenone. H. L. Haller and P. S. Schaffer (Ind. Eng. Chem., 1933, **25**, 983).—Hydrogenation of rotenone (I) with a Ni catalyst in neutral solution at 35—40° and atm. pressure gives about 90% of dihydrorotenone. Plant extracts containing (I) may also be used. F. R. S.

Active constituents of *Urtica dioica* and *U. urens*. E. Starkenstein and T. Wasserstrom (Arch. exp. Path. Pharm., 1933, **172**, 137—148).—The pharmacological properties of 50% EtOH extracts (I) of nettles were investigated. From (I) were isolated the following fractions: (*a*) pptd. by Pb acetate and containing HCO_2H, (*b*) pptd. by $HgCl_2$ and free from N, and (*c*) the filtrate from (*b*) containing small amounts of fructose and glucose. None of these fractions contained any glucoside, alkaloid, or protein. (I) contained 0·003—0·005% of HCO_2H. Analytical data for the ash of (I) and of the plant residue are given. F. O. H.

Arrow grass—chemical and physiological considerations. O. A. Beath, J. H. Draize, and H. F. Eppson (Wyoming Agric. Exp. Sta. Bull., 1933, No. 193, 36 pp.).—The poisonous principle of arrow grass is HCN derived from glucosides present mainly in the leaf, which also contains a high proportion of NaCl. HCN is more readily released from dried than from fresh samples. Extraction with H_2O is the most effective method of removing toxic matter. A. G. P.

Pungent principle from the water-pepper, *Polygonum hydropiper*, L. W. R. Witanowski and H. P. Krynska (Arch. exp. Path. Pharm., 1933, **172**, 463—470).—The Et_2O-extracted substance of the dried plant was steam-distilled and the distillate extracted with Et_2O to yield an oil (n_D^{23} 1·4886, d^{23} 0·932, $[\alpha]_D$ −5·4°, acid val. 39·6, ester val. 81·5, Ac val. 94·5) from which was separated polygonum oil (I) (n_D^{20} 1·5054, d^{20} 0·994) [*thiosemicarbazide*, $C_{20}H_{34}N_6O_2S_2$, m.p. 194—195° (*Ag* derivative)]. Fractional distillation of (I) yielded *polygonone*, $C_{18}H_{26}O_3$, an unsaturated ketone. (I) paralyses the isolated intestine and uterus and, when intravenously injected into cats and rabbits, lowers the blood-pressure. F. O. H.

Indian medicinal plants. I. *Withania somnifera* [winter cherry]. II. *Swertia chireta*. D. N. Majumdar and P. C. Guha (J. Indian Inst. Sci., 1933, **16**, A, 29—33, 34—39).—I. The Bengal variety contains the same constituents as the South African variety, namely, KNO_3, tannin, glucose, phytosterol, hentriacontane, stearic, palmitic, oleic, linoleic, and withanic acids, ipuranol, somnirol, somnitol, and an alkaloid, $C_{12}H_{16}N_2$ (cf. Power and Salway, J.C.S., 1911, **99**, 490), and there are indications of the presence of three other basic constituents.

II. The following have been isolated from an aq.-EtOH extract of the drug: *iso*amyl alcohol, a phenolic *compound* $(C_{13}H_{14}O_5)_x$, m.p. 179—180°, oleic, palmitic, stearic, and (probably) cerotic acids, a *phytosterol*, m.p. 128—130° (*acetate*, m.p. 127—129°), a OH-*acid*, $C_{26}H_{44}(OH) \cdot CO_2H$, m.p. 295° (*Ac* derivative, m.p. 250—251°), a phenolic *compound*, m.p. 256—257°, ophelic acid (*tetrabromide*, m.p. 114—115·5°), and a neutral *compound*, m.p. 197—198°. Chiratin (Hohn, Jahr. Fort. Chem., 1869, 771) is a mixture and has been resolved into two *compounds*, m.p. 118—119° and 179—180°, respectively, and a viscous resin. The drug contains no alkaloids. S. C.

Volatile oil of *Sarothra gentianoides*, L., and detection therein of *n*-nonane. M. T. Bogert and S. J. Marion (J. Amer. Chem. Soc., 1933, **55**, 4187—4194).—The oil (I), obtained in approx. 0·1—0·2% yield by steam-distillation of the whole green plant, contains C 84·03 and H 14·75% and has d_{20}^{20} 0·7665, n_D^{20} 1·4262, $[\alpha]_D$ +6·39°, acid val. 0·58, sap. val. 4·43, ester val. 3·85, and sap. val. after acetylation 17·35; 96% of (I) is localised in the tops of the plants. (I) contains *n*-nonane (< 20%), an optically active olefine (probably an octene), unidentified terpenes and sesquiterpenes, α-terpineol, geraniol, traces of phenols, aldehydes, and ketones, hexoic acid, and an ester of octoic acid. H. B.

Non-pre-existence of azulene in milfoil. K. Graham (J. Amer. Pharm. Assoc., 1933, 22, 819—824). W. S.

Kæmpferol rhamnoside from the leaves of *Pueraria hirsuta*, Matumura. I. T. Ohira (J. Agric. Chem. Soc. Japan, 1933, **9**, 337—342).—Extrac-

tion with 60% EtOH containing 3% NaOH at 60—70°, neutralisation with HCl, evaporation under diminished pressure, acidification, filtration, neutralisation, and concn. afforded kæmpferol in 0·15% yield; the sugar residue was rhamnose. CH. ABS.

Occurrence of dulcitol in *Irideæ laminarioides* (*Rhodophyceæ*). W. Z. HASSID (Plant Physiol., 1933, **8**, 480—483).—Dulcitol, but not mannitol, is present. A. G. P.

Determination of carbohydrates in leaves. R. H. DASTUR and K. M. SAMANT (Indian J. Agric. Sci., 1933, **3**, 460—477).—A modification of the method of Davis, Daish, and Sawyer (B., 1916, 373) is used. Basic Pb acetate is used for clarification of the conc. extract and excess Pb is removed by Na_2HPO_4. Hexoses are determined by a modification of the method of Folin and Wu. For determining sucrose 10% aq. tartaric acid is used in place of citric acid, since Na citrate inhibits the production of the blue colour. Maltose, if present, is determined by measuring the reducing power before and after hydrolysis with H_2SO_4. Starch is determined as glucose after successive hydrolysis with takadiastase and 10% aq. H_2SO_4. Reducing sugars can be determined at a concn. of 1 : 100,000 and sucrose at 1 : 20,000.
NUTR. ABS. (*m*)

Micro-analysis of plant juice for reducing sugars and sucrose. F. S. SCHLENKER (J. Biol. Chem., 1933, **102**, 29—34).—Clarification is effected by neutral $Pb(OAc)_2$, which removes colouring matter and proteins. Folin's Cu method (A., 1929, 714) gives most trustworthy results, discrepancies being due not to NH_2-acids, but to some other type of non-glucose reducing substance. H. G. R.

Alkaloids of *Artabotrys*. I. Artabotrin and suaveolin. A. C. SANTOS and F. R. REYES (Univ. Philippines Nat. Appl. Sci. Bull., 1932, **2**, 407—415).—*A. suaveolens* affords artabotrin, $C_{21}H_{25}O_4N$ (cf. Maranon, A., 1929, 857), m.p. 187°, $[\alpha]^{30}$ +198·7° in $CHCl_3$, and *suaveolin*, $C_{16}H_{10}(OH)(OMe)_3{\cdot}NMe$, m.p. 182°, $[\alpha]^{30}$ +203—206° in $CHCl_3$ (*chloroaurate*, decomp. 167°). CH. ABS.

Proteins of mulberry leaves. I. Kinds of protein-nitrogen in mulberry leaves and a comparison of the quantities of protein-nitrogen in different parts of the mulberry tree. III. Quantitative changes of proteins contained in the mulberry leaves during maturation. Y. KISHI (J. Agric. Chem. Soc. Japan, 1933, **9**, 397—411, 412—415).—I. Of the protein-N 66% is extracted by 60% EtOH containing 0·3% NaOH. Proteins of the root, seed, sap, and stem consist chiefly of globulin. The extracted protein contains very little P.

II. Mulberry leaf-protein decreases with maturation. CH. ABS.

Nitrogenous composition of horse beans and peas. K. YOSHIMURA and T. IWATA (J. Agric. Chem. Soc. Japan, 1933, **9**, 375—378).—Horse beans (5 kg.) afforded arginine (-NO_3) 0·4, betaine (-HCl) 2·7, trigonelline (-HCl) 0·5, and choline (Au salt) 1·8 g. Peas (5 kg.) afforded adenine, trace, trigonelline (-HCl) 0·5, and choline (Au salt) 0·3 g. CH. ABS.

Sterols of rice embryo. II. Ergosterol and vitamin-*D*. K. TANAKA (J. Biochem. Japan, 1933, **18**, 1—13).—The absorption spectra of irradiated (I) and non-irradiated sterols of rice embryo and the antirachitic activity of (I) indicate the presence of ergosterol. F. O. H.

Kernel-fats of the Palmæ: *Acrocomia sclerocarpa*, Mart. (gru-gru palm), *Manicaria saccifera*, Gaertn., *Astrocaryum tucuma*, Mart., *Maximiliana caribæa*, Griseb., *Attalea excelsa*, Mart. (pallia palm), and *Cocos nucifera*, Linn. (coconut). G. COLLIN (Biochem. J., 1933, **27**, 1366—1372).—Analyses are given for these six seed-fats, the first five of which have not previously been examined completely. The composition of the fatty acid mixtures indicates a tendency for the various species within the palm family to synthesise fats of similar composition. Figures are given for the % of the different fatty acids present in each fat, and the content of saturated and unsaturated glycerides.
A. W.

Fat and oil from the seeds of *Actinodaphne Hookeri*, Meissn. Indigenous source of lauric acid. S. V. PUNTAMBEKAR and S. KRISHNA (J. Indian Chem. Soc., 1933, **10**, 395—400).—The fat and oil from the seeds contain glycerides of lauric acid, oleic acid and its isomerides, and sitosterol; the oil also contains a small amount of resin acids.
F. R. S.

Oil from the seeds of *Tectona grandis* (teak). S. V. PUNTAMBEKAR and S. KRISHNA (J. Indian Chem. Soc., 1933, **10**, 401—403).—The oil contains mainly stearic, palmitic, oleic, and linoleic acids. F. R. S.

Constituents of the wax from alkanet root. M. V. BETRABET and G. C. CHAKRAVARTI (J. Indian Inst. Sci., 1933, **16**, A, 52—53).—The wax from alkanet root (m.p. 78°, d^{30} 0·9676, n_D^{80} 1·438, sap. val. 69·16, acid val. 12·92, unsaponifiable 58·56%, I val. 12·2, mol. wt. of mixed acids 380) consists essentially of carnaubyl cerotate. A small amount of an *acid*, m.p. 68°, was also isolated. S. C.

Barium as a normal constituent of brazil nuts. W. M. SEABER (Analyst, 1933, **58**, 575—579).—Ba found in sweets was traced to the Brazil nuts present, and the white kernels of various samples of such nuts were found to contain 0·02—0·31% (Para nuts, 0·02—0·17%); negligible amounts were found in Brazilian oranges and sugars. Solubility determinations indicate that Ba is present as a salt of an org. acid which is insol. in H_2O, slightly sol. in acids of the concn. of those present in the human stomach, and readily sol. in more conc. acids. J. G.

Relation between chlorophyll and iron in green and chlorotic pear leaves. J. OSERKOWSKY (Plant Physiol., 1933, **8**, 449—468).—CaO-induced chlorosis is not necessarily associated with low total Fe contents in leaves. "Active" Fe [*i.e.*, that effective in chlorophyll (I) formation] is determined by extraction with 1% HCl of dried leaves, in which Fe appears in the ionic form or as compounds readily yielding $Fe^{\cdots}$. The (I) content of leaves is proportional to their "active" Fe contents, but the ratio of (I) to "active" Fe differs considerably in different sets of leaves.
A. G. P.

Salicylic acid as a fixative. I. COHEN (Stain Tech., 1933, 8, 153—156).—Two fixatives containing salicylic acid are described; the first is recommended for studying mitosis and chromosomes, and the second for plastids. H. W. D.

Method for staining certain bacteria and antherozoids. W. N. STEIL (Stain Tech., 1933, 8, 139—142).—A modification of Loeffler's method is adopted. It is particularly suitable for the antherozoids of mosses, liverworts, and ferns. H. W. D.

Verification of analytical technique for biological media, by the method of added quantities. H. GRIFFON (J. Pharm. Chim., 1933, [viii], 18, 198—206).—The applicability of the method of added quantities is discussed theoretically. A. C.

Apparatus for study of redox potential in biological systems. J. P. BAUMBERGER (J. Gen. Physiol., 1933, 17, 1—6).—The Thunberg tube is modified, avoiding the use of a greased stopper and being capable of sustaining high vac. The Borsook and Schott tube (A., 1931, 1189) is modified by substituting the evacuation sealing system for ground-glass stoppers by adding a boot (I) at the tip so that satisfactory circulation may be obtained and by introducing the Pt electrode (II) into (I). A simplified reduction burette (Clark, A., 1928, 129) is described. A vac. oxidation–reduction cell adapted to the study of cell suspensions has, besides (I) and (II), a glass electrode, thus dispensing with a salt bridge. H. D.

Liebermann–Burchard colour reaction for cholesterol. I. A. MIRSKY and M. BRUGER (J. Lab. Clin. Med., 1932, 18, 304—306).—Appearance of a brown colour resulting from the action of H_2SO_4 and Ac_2O on $CHCl_3$ extracts containing cholesterol can be avoided by keeping the reaction mixture at 5°. CH. ABS.

Mesobilirubinogen as a standard in the determination of urobilin. M. ROYER (Rev. soc. argentina biol., 1932, 8, 489—490).—Mesobilirubinogen (0·0128 mg.) is dissolved in a little dil. aq. NaOH, a few crystals of $Zn(OAc)_2$ are added, and then a few drops of I solution to effect oxidation to urobilin; the solution is acidified with HCl and diluted to 1 litre. This solution has the same intensity of fluorescence as the trypaflavine solution (0·05 mg. per litre) used for comparison. CH. ABS.

Micro-methods for determining proteins in medicine and biology. A. WASITZKY (Mikrochem., 1933, 14, 85—112).—A review.

Micro-determinations of purine substances in tissues. II. Guanine, adenine, and hydroxypurines. G. SCHMIDT (Z. physiol. Chem., 1933, 219, 191—206; cf. A., 1932, 870).—The acid hydrolysate of 1—3 g. of tissue is pptd. with H_4WO_5 to remove protein degradation products. In one portion of the filtrate (I) aminopurines are pptd. by ammoniacal Ag solution, and the NH_2-N, determined by HNO_2, $\times 5$ gives the total N of aminopurines. Guanine is separately determined by means of guanase, adenine being obtained by difference. The purines in a portion of (I) are pptd. by $CuSO_4$ and $NaHSO_3$. A Kjeldahl determination on the ppt. gives the total purine-N, from which the hydroxypurine-N is found by difference. Other purine derivatives must be absent. J. H. B.

Histochemistry of enzymes. VI. Micro-determination of ammonia. K. LINDERSTRØM-LANG and H. HOLTER (Z. physiol. Chem., 1933, 220, 5—12; cf. this vol., 864).—A micro-technique for NH_3 by distillation at 40° is described. J. H. B.

Gasometric determinations by means of the ureometer. IV. G. D'ESTE (Boll. Chim.-farm., 1933, 72, 601—614).—With the apparatus described (A., 1932, 550), 0·010 g. of urea when treated with alkaline NaOBr yields 3·41 c.c. of N_2 (at 0° and 760 mm.). The greatest accuracy is obtained by parallel determinations with a standard solution of urea. Serum and milk are deproteinised by $CCl_3{\cdot}CO_2H$ before urea determinations; normal cerebrospinal fluid is used directly. With the same method applied to NH_4 salts, 0·010 g. of NH_3-N yields 7·45 c.c. of N_2. For total N, the material is first treated by the Kjeldahl method. Differentiation of NH_3- and urea-N is achieved by xanthhydrol pptn. of urea. The application of the apparatus to the determination of the alkaline reserve of blood (1 c.c.) is described. F. O. H.

Errors in determination of bound water. H. B. BULL (J. Gen. Physiol., 1933, 17, 83—86).—The results of Greenberg and Greenberg (this vol., 523) show that an adsorption of solute on to the substrate can produce large changes in the calc. bound H_2O.

Analysis. XVII. Micro-determination of lead and zinc in organic material. L. PINCUSSEN and E. BRUCK (Biochem. Z., 1933, 265, 58—60).—Pb ($\lessgtr$ 0·1 mg.) is determined by destroying org. matter (I) with H_2SO_4, HNO_3, and H_2O_2, dissolving the pptd. $PbSO_4$ in NH_4OAc, pptg. the Pb with 10% aq. Na_2S in presence of gum arabic, and comparing the colour of the suspension produced with that of a standard. Fe salts, if present, must be removed by boiling after the addition of NH_4OAc. Zn is determined, after destruction of (I) as before, treatment with HCl and H_2S, filtration, and removal of Fe by pptn. with H_2S in dil. AcOH (II), ignition of the ZnS, dissolution of the ash in (II), repptn. with H_2S in presence of HCl, AcOH, and NH_4OAc, and comparison of the turbidity so obtained with that produced in a standard solution. $\lessgtr$ 0·03 mg. in 15 c.c. of solution can be determined. W. McC.

Histochemical detection of gold. F. TIMM (Deut. Z. gerichtl. Med., 1933, 20, 211—214; Chem. Zentr., 1933, i, 2436—2437).—Sanocrysin is decomposed in the body affording Au_2S_3 which is detected ultramicroscopically. A. A. E.

[Determination of uranium] by the magneto-optic method. H. D. JONES and R. GOSLIN (J. Amer. Chem. Soc., 1933, 55, 3500—3501; cf. this vol., 137).—The distribution of U, after injection into the blood of animals, has been determined to within $\pm 10\%$. J. G. A. G.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1933.

General, Physical, and Inorganic Chemistry.

Spectrum of H_2. Bands ending on $2p^3\Pi$ levels. III. O. W. Richardson and P. M. Davidson (Proc. Roy. Soc., 1933, **A**, **142**, 40—62).—The band systems which end on $2p^3\Pi_{ab}$ and come from $4d^3\Sigma_g$, $4d^3\Pi_b$, $4d^3\Pi_a$, and $4d^3\Delta_b$ are described. The properties and consts. of the various levels $2p^3\Pi_{ab}$, $3d^3\Sigma_g$, $3d^3\Pi_b$, $3d^3\Pi_a$, $3d^3\Delta_b$, $3d^3\Delta_a$, $4d^3\Sigma_g$, $4d^3\Pi_b$, $4d^3\Pi_a$, and $4d^3\Delta_b$ are considered. L. L. B.

Spectrum of H_2. The $3d^1\Delta$ and $4d^1$ levels. O. W. Richardson and P. M. Davidson (Proc. Roy. Soc., 1933, **A**, **142**, 63—76).—The bands which go down from $3d^1\Delta_{ab}$ to $2p_1\Sigma_u$ and $2p^1\Pi_{ab}$ are described. These determine the $3d^1\Delta_{ab}$ levels. Analogy with these 3-electronic states enables bands from 4-electronic states to $2p^1\Sigma$ and $2p^1\Pi$ to be extended and interpreted. L. L. B.

Isotope of hydrogen in the atomic spectrum. D. H. Rank (Physical Rev., 1932, [ii], **42**, 446).—The H^2 γ line, wave-length 4339·256 Å., has been photographed. L. S. T.

Continuous absorption spectrum of helium. J. P. Vinti (Physical Rev., 1933, [ii], **44**, 524—528; cf. this vol., 199; Wheeler, *ibid.*, 331).—Mathematical. Intensity distributions, f vals., and series limits are found. The calc. at. absorption coeff. of He for the $K\alpha$ line of C is $3{\cdot}24\times10^{-20}$ cm.$^{-1}$ N. M. B.

Nuclear spin of Li^7 from hyperfine structure data. N. M. Gray (Physical Rev., 1933, [ii], **44**, 570—574).—Mathematical. Theoretical patterns for the λ 5485 line of Li II are calc. N. M. B.

Nuclear moment of beryllium. A. E. Parker (Physical Rev., 1932, [ii], **40**, 1014—1015).—An attempt to find a band system due to Be_2 was unsuccessful. L. S. T.

Hyperfine structure of beryllium lines. P. G. Kruger and R. C. Wagner (Physical Rev., 1932, [ii], **41**, 373).—No positive result for the nuclear moment of Be has yet been obtained. L. S. T.

Zeeman effect of the infra-red arc lines of krypton. B. Pogány (Naturwiss., 1933, **21**, 719).—A photograph showing the effect for field of strength 11,800 gauss is given. A. J. M.

Second spectrum of krypton. T. L. de Bruin, C. J. Humphreys, and W. F. Meggers (Bur. Stand. J. Res., 1933, **11**, 409—440).—By observation of the intensity changes accompanying variations of the capacity and inductance in the electrical circuit, 1050 lines of the Kr spectrum excited in Geissler tubes have been attributed to Kr II. These cover the wave-length range 2080—10,659 Å., and their wave-lengths and relative intensities are tabulated. The majority have been classified. The ionisation potential of Kr^+ is calc. as 24·4 volts. J. W. S.

Fluorescence spectra of cadmium vapour. W. Cram and J. G. Winans (Physical Rev., 1932, [ii], **41**, 388—389).—The 3050—2288 Å. band in the fluorescence of Cd vapour extends to 2212 Å. The spectrum of the electrodeless discharge shows the same band with a different intensity distribution. L. S. T.

Zeeman effect of the spectra of Sb II and Sb III. J. B. Green and R. A. Loring (Physical Rev., 1932, [ii], **42**, 909).—Zeeman patterns of the lines of Sb II and Sb III obtained with fields of 40,000 gauss are in agreement with Lang's classification. L. S. T.

Variations of the absorption and fluorescence spectra of diatomic tellurium vapour with temperature and pressure. M. Migeotte (Bull. Acad. roy. Belg., 1933, [v], **19**, 789—808).—The absorption and fluorescence spectra of Te_2 vapour have been investigated at pressures between its saturated v.p. at 334° and 560° and at temp. of 480—780°. J. W. S.

Perturbations in the barium I spectrum. G. O. Langstroth (Proc. Roy. Soc., 1933, **A**, **142**, 286—308).—It is shown that the departures from the normal intensities which occur in certain Ba multiplets are due to interactions of "overlapping" electron configurations, and the mutually perturbed terms have been identified. The perturbations in the diffuse series are probably of magnetic origin, whilst those in the fundamental series are electrostatic. L. L. B.

Nuclear moment of tantalum. J. H. Gisolf and P. Zeeman (Nature, 1933, **132**, 566).—The nuclear moment of Ta obtained from an examination of hyperfine structure is $(7/2)(h/2\pi)$. L. S. T.

Term system of iridium I. W. Albertson (Physical Rev., 1932, [ii], **42**, 443—445).—Data are tabulated. L. S. T.

First spark spectrum of gold. Au II. B. V. Raghavendra (Proc. Roy. Soc., 1933, **A**, **142**, 118—128).—All the terms of the configuration $5d^96s^2$ have been identified, nearly all the terms of $5d^96d$, and several of those of the configuration $5d^86s7s$. More than 100 lines have been classified. L. L. B.

Quenching of mercury resonance radiation by hydrogen, carbon monoxide, and nitrogen. J. S. Owens and O. S. Duffendack (Physical Rev.,

1932, [ii], **40**, 1042; cf. this vol., 109).—From 200° to 700° the quenching of Hg resonance radiation by H_2 is a two-step process independent of temp., whilst that by CO and by N_2 is a complicated process which decreases with rise in temp. L. S. T.

Radiation originating from a beam of electrons in mercury vapour and the mean life of the 2^3S_1 state. L. R. MAXWELL (Physical Rev., 1932, [ii], **42**, 148—150). L. S. T.

Two vector problem in Pb V and Bi VI. A. T. GOBLE and J. E. MACK (Physical Rev., 1932, [ii], **42**, 909). L. S. T.

***g*-value of the normal state of Bi I.** R. F. BACHER and J. WULFF (Physical Rev., 1932, [ii], **40**, 123).—The *g*-val. of 1·65(4) of the normal state of Bi obtained from an investigation of the hyperfine structure of the Bi arc line 3067 Å. with and without a magnetic field does not agree with the val. 1·45 given by the Stern-Gerlach experiment. L. S. T.

Series in the spark spectrum of radium. Ra II. E. RASMUSSEN (Z. Physik, 1933, **86**, 24—32).—An analysis of 62 lines between 1880 and 11,000 Å. gives the ionisation potential as 10·099 volts. A. B. D. C.

Transition probabilities in the subsidiary series of thallium. A. FILIPPOV and W. PROKOFIEV (Z. Physik, 1933, **85**, 647—660). A. B. D. C.

Paschen-Back effects in the spectra of thallium. A. M. CROOKER (Phil. Mag., 1933, [vii], **16**, 994—1005).—Visible Tl lines were examined. Results agree with Goudsmit and Bacher's theory (A., 1931, 135). H. J. E.

Multiplet separations and perturbed terms. N. G. WHITELAW (Physical Rev., 1933, [ii], **44**, 544—550).—Mathematical. N. M. B.

Identification of a certain number of lines observed in the spectra of the sun and of sunspots. P. SWINGS (Bull. Acad. roy. Belg., 1933, [v], **19**, 925—928).—Some of the lines may be due to Ba^{++}. C. W. G.

Atomic multiplets in stellar spectra. L. M. DONNAY (Bull. Acad. roy. Belg., 1933, [v], **19**, 755—769).—The intensities of the multiplets of normal and ionised Fe, Ti, V, O, and N observed in solar and stellar absorption spectra are compared with the respective calc. intensities. The fact that the observed relative intensities are sometimes > the calc. is attributed to superposition of lines. J. W. S.

Resonance function for collisions of the second kind. W. HANLE and K. LARCHE (Z. Physik, 1933, **85**, 548—554).—Dependence of the efficiency of collisions of the second kind on the sharpness of resonance was determined from the polarisation of resonance radiation of Na vapour in a magnetic field. A. B. D. C.

Intensities in atomic spectra. M. H. JOHNSON, jun. (Proc. Nat. Acad. Sci., 1933, **19**, 916—921).—Mathematical. N. M. B.

Collisions of the second kind involving ionisation and excitation. K. B. THOMSON and O. S. DUFFENDACK (Physical Rev., 1932, [ii], **40**, 1042).—The excitation of spark levels in metallic atoms by collisions of the second kind with rare gas ions has been studied as a function of the energy discrepancy. In general, the probability of excitation of levels increases as the discrepancy between the level, measured from the normal atom, and the ionisation potential of the rare gas atom decreases, but exceptions occur. L. S. T.

High-frequency glow discharge. A. C. VAN DORSTEN (Nature, 1933, **132**, 675—676). L. S. T.

Nature of glow discharges. H. ROTHE and W. KLEEN (Naturwiss., 1933, **21**, 772). A. J. M.

Electronic structure of the *a*–*X* band system of nitrogen. E. T. S. APPLEYARD (Physical Rev., 1932, [ii], **41**, 254—255).—Certain bands belonging to this system, which is ascribed to a $^1\Pi_u$–$^1\Sigma_g^+$ transition, have been measured and are discussed. L. S. T.

Absorption of oxygen in the region of short wave-lengths. R. LADENBURG, C. C. VAN VOORHIS, and J. C. BOYCE (Physical Rev., 1932, [ii], 1018—1020).—The absorption of O_2 down to 300 Å. shows two strong absorption regions from 1750 to 1300 with a max. at 1450 Å., and from below 1100 to 300 Å. L. S. T.

Isotope shift in neon. J. H. BARTLETT, jun., and J. J. GIBBONS, jun. (Physical Rev., 1933, [ii], **44**, 538—543).—Mathematical. The theory of isotopic displacement due to the motion of the nucleus is extended to atoms with any no. of electrons, and applied to the transitions $2p^53s$— in Ne. The shift in singlet is 0·0195 cm.$^{-1}$ > in triplet states. N. M. B.

Neon absorption lines in stellar spectra. D. H. MENZEL and R. K. MARSHALL (Proc. Nat. Acad. Sci., 1933, **19**, 879—881).—The strongest line λ 6402·24 of Ne I was observed in one stellar spectrum. Data and evidence for 20 lines of 6 multiplets of Ne II in certain stellar spectra are tabulated. Equal abundance of O_2 and Ne is indicated. N. M. B.

Polarisation of sodium resonance radiation and nuclear moment of the sodium atom. N. P. HEYDENBURG, L. LARRICK, and A. ELLETT (Physical Rev., 1932, [ii], **40**, 1041).—The polarisation in zero magnetic field of the Na *D* line resonance radiation has been calc. as a function of nuclear moment. The mean val. observed for the polarisation is 16·48± 0·33%, in agreement with the val. calc. for a nuclear moment of 1; band spectra indicate a nuclear moment ≮ 3/2 and present views of nuclear structure, an odd multiple of $\frac{1}{2}(h/2\pi)$. L. S. T.

Transition probabilities in the subsidiary series of Na. L. S. ORNSTEIN and J. KEY (Z. Physik, 1933, **85**, 565—567). A. B. D. C.

Magnetic rotation spectrum of the red bands of sodium. W. R. FREDRICKSON and C. R. STANNARD (Physical Rev., 1933, [ii], **44**, 632—637).—For the region beyond 6800 Å., data for absorption band heads and 28 magnetic rotation doublets are tabulated and discussed. N. M. B.

Luminosity of sodium flames. C. D. CHILD (Physical Rev., 1932, [ii], **42**, 146).—A criticism (cf. A., 1932, 551). L. S. T.

Paschen–Back effect of hyperfine structure and the polarisation of resonance radiation: the *D* lines. L. LARRICK (Physical Rev., 1932, [ii], **40**, 1041).—The polarisation of Na resonance radiation has been calc. Agreement with experimental vals. is good, with certain exceptions. L. S. T.

Plausible explanation of the alkali inverted doublets. H. E. WHITE (Physical Rev., 1932, [ii], **40**, 316). L. S. T.

Inversion of doublets in alkali-like spectra. (MISS) M. PHILLIPS (Physical Rev., 1933, [ii], **44**, 644—650).—Mathematical. The tendency to inversion, attributed to the polarisability of the core, is examined by a study of the energies and wave functions of the excited core configuration states of the levels of the optical doublet for the spectra Na I to S VI. N. M. B.

Theory of quantum defect due to polarisation, with application to multiplet anomalies in Al II. N. G. WHITELAW and J. H. VAN VLECK (Physical Rev., 1932, [ii], **41**, 389—390). L. S. T.

Quantum defect of non-penetrating orbits, with special application to Al II. J. H. VAN VLECK and N. G. WHITELAW (Physical Rev., 1933, [ii], **44**, 551—569).—Mathematical. N. M. B.

Spectra of diatomic sulphur molecules. M. L. HUBIN (Bull. Acad. roy. Belg., 1933, [v], **19**, 770—788).—The resonance spectrum of S_2, excited by a Hg arc, has been investigated. The results are discussed in relation to those of Rosen (A., 1927, 608) and of Christy and Naudé (A., 1931, 779). A general formula is developed for the heads of the S_2 vapour absorption bands and compared with those previously suggested. It is concluded that certain vibration levels in the $^3\Sigma_u^-$ state are perturbed, both odd as well as even levels. J. W. S.

Sulphur arc spectrum. K. W. MEISSNER, O. BARTLET, and L. ECKSTEIN (Z. Physik, 1933, **86**, 54—76). A. B. D. C.

Sulphur spark spectrum S II. O. BARTLET and L. ECKSTEIN (Z. Physik, 1933, **96**, 77—81). A. B. D. C.

Continuous absorption spectrum of chlorine. G. E. GIBSON and N. S. BAYLISS (Physical Rev., 1932, [ii], **41**, 388).—A rise in temp. decreases the absorption coeff. at the max. and broadens the region of continuous absorption. The results agree qualitatively with Gibson and Rice's theory of continuous absorption. L. S. T.

Effect of the anode on the stability of the homogeneous column in argon. W. PUPP (Physikal. Z., 1933, **34**, 756—761).—Experiments are described which show how the anode fall depends on the ions, in this case produced artificially, in the neighbourhood of the anode. In the presence of large ionic concns. it may become negative. A. J. M.

"Flash" in the afterglow of argon with a fixed vacuum. C. T. KNIPP (Physical Rev., 1932, [ii], **39**, 871). L. S. T.

Zeeman effect in the $^2\Pi^2\Sigma$ Ca *H* bands. W. P. CUNNINGHAM (Physical Rev., 1932, [ii], **41**, 389). L. S. T.

Hyperfine structure of the vanadium spectrum. H. WHITE (Physical Rev., 1932, [ii], **40**, 1041).—Preliminary results obtained with V I lines indicate that for the V nucleus $I \leqslant 5/2$ and that the g-factor is small. L. S. T.

Spark spectrum of iron in the extreme ultraviolet. L. BLOCH and E. BLOCH (Compt. rend., 1933, **197**, 679—681; cf. this vol., 2).—171 lines of Fe, λλ 1148·92—364·99, have been measured, showing considerable disagreement from previous results (cf. A., 1921, ii, 609). C. A. S.

Fluorescence of diatomic molecules of arsenic. P. SWINGS and M. MIGEOTTE (Compt. rend., 1933, **197**, 836—838).—A resonance series is excited in the vapour of As at 1100—1150° by each of Hg λλ 2536, 2483, 2654, and 2804; the fundamental frequency is apparently 410 cm.$^{-1}$, which gives as the distance As—As in As_2 1·94 Å., or 77% of the distance in cryst. As; the emission appears to consist only of a Q branch. C. A. S.

Magnetic nuclear moment of rubidium isotopes. D. A. JACKSON (Z. Physik, 1933, **86**, 131).—Published work (this vol., 439) is in agreement with that of Kopfermann (*ibid.*, 880), who gives Rb^{85} as 5/2, and Rb^{87} as 3/2. A. B. D. C.

***X*-Ray emission spectra of gaseous elements: *K* spectrum of xenon (emission and absorption).** H. HULUBEI and (MLLE.) Y. CAUCHOIS (Compt. rend., 1933, **197**, 644—646; cf. this vol., 657).—The method was modified for smaller quantities of gas. With Ce, La, Cs, and I as reference elements $K\alpha_2$, $K\alpha_1$, $K\beta_1$, and $K\beta_2$ are respectively 419·58, 415·12, 367·72, and 359·16 X, and the crit. absorption limit for K is 357·77 X. C. A. S.

***X*-Ray emission spectra of gaseous elements: weak lines in *K*-spectrum of krypton.** (MLLE.) Z. CAUCHOIS and H. HULUBEI (Compt. rend., 1933, **197**, 681—682; cf. this vol., 657).—More detailed examination gives $K\beta_4$ 863·47, $K\beta_2$ 864·34, $K\beta_5$ 869·04, ? 872·71, $K\beta_1$ 876·68, $K\beta_3$ 877·19, $K\beta_0$ 881·40; β_4, β_5 and β_0, are identified with the forbidden transitions KN_{IV-V}, KM_{IV-V}, and KM_I, respectively. C. A. S.

***L*-*X*-Ray spectrum of solid aluminium.** T. H. OSGOOD (Physical Rev., 1933, [ii], **44**, 517—519).—The spectrum consists, not of sharp lines, but of a wide continuous band in the approx. range 170—200 Å., agreeing with the Pauli–Sommerfeld theory of free electrons in metals. N. M. B.

$K\alpha_1\alpha_2$ doublet of phosphorus. O. LUNDQUIST (Nature, 1933, **132**, 518).—The doublet of P emitted from violet P, NaH_2PO_2 (I), and Na phosphate (II) shows displacements, relative to the doublet of P, of 1·7 X for (I), and 2·5 X for (II) towards shorter wave-lengths. L. S. T.

Production of the molybdenum $L\alpha$ satellites by fluorescent absorption of silver $L\alpha$ radiation. F. R. HIRSH, jun., and F. K. RICHTMYER (Physical Rev., 1932, [ii], **40**, 1033). L. S. T.

X-Ray satellites of high atomic number elements. F. K. RICHTMYER and S. KAUFMAN (Physical Rev., 1933, [ii], **44**, 605—609).—Examination in the at. no. range Ta (73) to U (92) gave two satellites for $L\alpha$, one extending from Au (79) to U (92), and the other (shorter wave-length) from Os (76) to Bi (83). $L\beta_2$ has two satellites, extending from Ta to U, and from below Ta to U, respectively. N. M. B.

Soft X-rays from (100) and (111) faces of copper single crystals. M. L. WILLIAMS (Physical Rev., 1933, [ii], **44**, 610—617).—In determining whether a difference exists in the soft *X*-ray crit. potentials for different faces of the same crystal, 14 crit. potentials between 90 and 120 volts were found for both faces, each break being within 1·5 volts for the two targets. The bearing of the results on explanations of theoretical structure and calc. vals. is discussed. N. M. B.

Ionisation potential of radon. H. YAGODA (Physical Rev., 1932, [ii], **40**, 316—317).—From the vals. found by various workers for the ionisation potential of Rn, the best val. is 10·7 volts. Calc. quantum defects and ionisation potentials of the inert gas are compared with observed vals. L. S. T.

Distribution of energies of electrons in gases. J. S. TOWNSEND (Phil. Mag., 1933, [vii], **16**, 729—744; cf. A., 1930, 973).—Theoretical. J. W. S.

Inner potential of metals. J. A. DARBYSHIRE (Phil. Mag., 1933, [vii], **16**, 761—775).—There is definite evidence of refraction due to an inner potential when high-speed electrons are reflected from cleavage faces of Zn and Sb single crystals, but not in the cases of Bi and Te. The vals. calc. for the inner potential are 12+1 and 15·5±1 volts for Sb and Zn, respectively. J. W. S.

Electron diffraction patterns from platinised asbestos. D. A. RICHARDS (Phil. Mag., 1933, [vii], **16**, 778—787).—The electron diffraction patterns of Pt–asbestos show no Pt pattern with the ratio asbestos : Pt 1 : 1·8 (by wt.). The results are in agreement with the view that the platinisation results in a splitting of the fibres, with the result that a fresh surface of asbestos is presented to the electron beam, nullifying the effect of the Pt. J. W. S.

Atomic ionisation by electric fields. R. SCHULZE (Naturwiss., 1933, **21**, 737).—Electrons may be split off atoms of S by application of electric fields. A. J. M.

Diffraction of electrons by metal surfaces. C. J. DAVISSON and L. H. GERMER (Physical Rev., 1932, [ii], **40**, 124; cf. this vol., 657).—Electron beams (13,000—55,000 volts) directed on etched surfaces of Au, W, Mo, and Co give about 20 Debye-Scherrer rings characteristic of the known structures of the metals. Ni gives rings of Ni and NiO; Cr etched in dil. HCl gives hexagonal Cr rings, and after re-etching in warm conc. HCl, a pattern of spots only, with radial distances possibly consistent with the rhombohedral structure of large crystals of $CrCl_3$. A single crystal of W finally gave rings indicating a body-centred cubic structure of const. 7·4 Å. L. S. T.

Theory of diffusion of high-voltage electrons. J. WINTER (Compt. rend., 1933, **197**, 828—829; cf. this vol., 550).—Mathematical; the method is applied to the case of very swift electrons, giving results in agreement with those of Born. C. A. S.

Influence of space charge on measurements of excitation functions. J. M. W. MILATZ (Z. Physik, 1933, **85**, 672—675).—A method for measuring the velocity of electron beams is developed, and is applied to determination of space charge. A. B. D. C.

Inelastic scattering of slow electrons in gases. III. F. H. NICOLL and C. B. O. MOHR (Proc. Roy. Soc., 1933, A, **142**, 320—332; cf. A., 1932, 1185).—The inelastic scattering of electrons in H_2, He, and A has been measured from 80 volts down to about 3 volts above the excitation potential of the gas atom, and over the angular range 10—155°. The curves for A show diffraction max. and min. at large angles similar to those which occur for the elastic scattering; these disappear as the energy of the electrons approaches the excitation potential of the gas. No unusual features are found for low-velocity electrons in H_2 and He. The inelastic scattering curves for small angles (10—30°) agree with those given by the Born formula down to relatively low velocities. L. L. B.

Liberation of electrons from surfaces by ions and atoms. H. KALLMANN and A. ROSTAGNI (Nature, 1933, **132**, 567—568).—Curves obtained for the electron emission of metallic surfaces by H_2, He, Ne, and A are discussed. L. S. T.

Electron affinity of hydrogen. G. GLOCKLER (Physical Rev., 1932, [ii], **41**, 685).—The empirical val. calc. for the electron affinity of hydrogen is +0·66 ev. L. S. T.

Electron interference at mechanically worked surfaces. H. RAETHER (Z. Physik, 1933, **82**, 82—104).—Changes in surfaces were followed by electron interference for ruling with steel points, rubbing with emery, and polishing both on polycryst. metals, on NaCl, $CaCO_3$, CaF_2, FeS_2, and graphite, and for pressing and hammering polycryst. metals. A. B. D. C.

Angular distribution of electrons scattered in mercury vapour. A. L. HUGHES (Physical Rev., 1932, [ii], **42**, 147—148). L. S. T.

Diffraction of slow electrons by graphite crystals. V. E. LASCHKAREV, E. V. BARENGARTEN, and G. A. KUZMIN (Z. Physik, 1933, **85**, 631—646).—The inner potential of graphite is 20 volts. A. B. D. C.

Electron-diffraction investigation of the structure of molecules of methyl azide and carbon suboxide. L. O. BROCKWAY and P. PAULING (Proc. Nat. Acad. Sci., 1933, **19**, 860—867).—The 3 N atoms in MeN_3 are in a line, with 1 triple linking (1·10 Å.) and 1 double linking (1·26 Å.). The Me—N distance is 1·47 Å., and the linking angle is 135±15°. The C_3O_2 mol. is linear, the distances C—O and C—C being 1·20±0·02 and 1·30±0 02 Å. The linkings in C_3O_2 have properties intermediate between those of double and triple linkings. H. J. E.

Electron-diffraction investigation of the molecular structure of cyanogen and diacetylene (with a note on chlorine dioxide). L. O. BROCKWAY (Proc. Nat. Acad. Sci., 1933, **19**, 868—874).—C_2N_2 is a linear mol. with the distances C—N and C—C $1{\cdot}16\pm0{\cdot}02$ and $1{\cdot}43\pm0{\cdot}03$ Å. In diacetylene the distances C—C (at end) and C—C (in centre) are $1{\cdot}21\pm0{\cdot}02$ and $1{\cdot}43\pm0{\cdot}03$ Å. Wierl's results (A., 1932, 670) are criticised. The Cl—O distance in ClO_2 is $1{\cdot}53\pm0$ 03 Å. (cf. this vol., 557). H. J. E.

Electron diffraction and molecular structures: carbonyl compounds. R. W. DORNTE (J. Amer. Chem. Soc., 1933, **55**, 4126—4130).—In general agreement with other structural determinations, COS is linear, whilst the halogen-C linkings of $COCl_2$ and $COBr_2$ subtend an angle of 110°. AcCl and AcBr conform to the tetrahedral model. The C—O interat. distance is const. J. G. A. G.

Possibility of the emission of positive electrons from the nucleus by γ-rays. A. BRAMLEY (J. Franklin Inst., 1933, **216**, 427—428; cf. this vol., 883).—It is concluded that the photo-electric effect of positive electrons should be realisable with γ-rays from radioactive sources. If the nucleus were composed of heavy particles, *e.g.*, protons, however, the effect of the photo-electric emission of protons under the action of *X*-rays would be negligible. J. W. S.

High-speed hydrogen ions. M. S. LIVINGSTON (Physical Rev., 1932, [ii], **42**, 441—442; cf. A., 1932, 554).—An apparatus which produces H ions with energies equiv. to 3,600,000 volt-electrons has been constructed. L. S. T.

Energy levels of the hydrogen molecular ion. C. GILBERT (Phil. Mag., 1933, [vii], **16**, 929—944).—Theoretical. H. J. E.

Limitation in currents of positive alkali ions of homogeneous velocities. P. KECK and L. B. LOEB (Rev. Sci. Instr., 1933, [ii], **4**, 486—490).—When K atoms were ionised by impact with a Pt strip filament at 1000° in high vac. the currents at the higher source temp. were limited by space charge, and the energy distribution was affected by the presence of the vapour. The method could be adapted to the separation of Li isotopes. N. M. B.

Ionisation of inert gases by slow alkali ions. O. BEECK (Ann. Physik, 1933, [v], **18**, 414—416).—A comparison of the results of Beeck (A., 1930, 1083, 1494) with those of Mouzon (A., 1932, 1184) is made. In the case of K^+ in A there is considerable deviation between the results owing to scattering of primary ions through large angles. The best val. for the ionisation function of K^+ in A is Nordmeyer's (this vol., 442). Observations of Beeck and Mouzon (A., 1931, 1206) are corr. A. J. M.

Mobility of cæsium atoms adsorbed on tungsten. I. LANGMUIR and J. B. TAYLOR (Physical Rev., 1932, [ii], **40**, 463—464; cf. A., 1932, 459; this vol., 333). L. S. T.

Passage of positive ions through gases. H. S. W. MASSEY and R. A. SMITH (Proc. Roy. Soc., 1933, **A**, **142**, 142—172).—Elastic and inelastic collisions of slow positive ions with gas atoms are discussed in terms of a quantum-mechanical theory of collisions. Good agreement is found between observed and calc. collision cross-sections. The case of collisions of ions with similar atoms is also considered in detail. L. L. B.

Positive ions of mass 220. L. L. BARNES and R. C. GIBBS (Physical Rev., 1932, [ii], **40**, 318).—A mixture of alkali sulphates heated on Pt between 600° and 700° at $< 10^{-6}$ cm. pressure in a Dempster mass spectrograph gave a steady emission of positive ions corresponding with singly-charged atoms of at. wt. 220 ± 1. L. S. T.

Radiation from moving helium, neon, and argon ions. A. I. MCPHERSON (Physical Rev., 1932, [ii], **41**, 686—687; **42**, 903). L. S. T.

At. wt. of tellurium. II. Synthesis of silver telluride. O. HÖNIGSCHMID (Z. anorg. Chem., 1933, **214**, 281—288; cf. Brauner, J.C.S., 1895, **67**, 540).—Ag_2Te was synthesised by slowly passing Te vapour, carried in N_2, over heated Ag. The product was heated in vac. at 550—600° to const. wt. Vals. found were $Ag_2Te : 2Ag = 1{\cdot}591446$; $Te = 127{\cdot}61$ ($Ag = 107{\cdot}880$). H. J. E.

Isotopes. A. J. G. KAPTEIN (Chem. Weekblad, 1933, **30**, 695—701).—A review.

Possibility of the existence of the chlorine isotope Cl^{39}. M. F. ASHLEY and F. A. JENKINS (Physical Rev., 1932, [ii], **42**, 438—440).—A more complete account of negative evidence previously given (this vol., 204). L. S. T.

Transformation product of potassium. F. ALLISON and R. GOSLIN (Physical Rev., 1932, [ii], **40**, 1015—1016).—Four samples of sylvite each gave a min. of light intensity intermediate between Ca^{40} and Ca^{44} and appropriate to Ca^{41}. The approx. % of Ca^{41} (I) and of ordinary Ca (II) in the samples were 0·2, 0·04; 0·1 and 0·2; 0·1 and 0·005; and 0·02 and 0·005, respectively. The concns. of (I) are $>$ the calc. vals. (A., 1931, 1209). The approx. % of (I) and (II) in (C.P.) K compounds are KCl (Merck) 3×10^{-6} and 2×10^{-3}, K_2SO_4 (Merck) 2×10^{-6} and 4×10^{-4}, KOH (Merck) 1×10^{-6} and 1×10^{-3}, and K_3PO_4 (Baker) 3×10^{-3} and 4×10^{-3}, respectively. Recrystallisation of the KCl reduced the (I) content by 90%. (I) was detected in six out of fourteen Ca reagents (C.P.) and hence the optical min. is not due to a third isotope of (II). It is not possible to assign a mass of 41 rather than 42 or 43 to (I), but its mass lies definitely between 40 and 44. A third isotope of K which might be responsible for the radioactivity and which might be the parent of a Ca atom of mass other than 41 could not be found. No min. corresponding with a Ca isotope of mass 39 associated with sylvite exists, indicating that K^{39} does not take part in the radioactivity of K. The results appear to show that Ca of probable at. mass 41 is the transformation product of K. L. S. T.

Long-range α-rays emitted by active actinium deposit. (MME.) P. CURIE and (MLLE.) W. A. LUB (J. Phys. Radium, 1933, [vii], **4**, 513—516).—Preps. of active Ac-B+C+C'+C'' emitting α-rays of the amount emitted by 5—8 millicuries of Ra-C' appear

to give rise to rays of approx. 10 cm. range in the proportion of 3×10^{-7} per α-ray of Ac-*C*. N. M. B.

Analysis of the long-range α-particles from radium-*C′* by the magnetic focussing method. (Lord) Rutherford, W. B. Lewis, and B. V. Bowden (Proc. Roy. Soc., 1933, **A**, **142**, 347—361).—The velocities of the long-range α-particles from Ra-*C′* have been accurately measured by means of the annular ring magnet (this vol., 443). The α-ray spectrum has been analysed into twelve groups (thus separated for the first time), and the corresponding energy levels of the excited nucleus have been deduced. The observed α-particle levels are correlated with the emission of γ-rays. The relative intensities of the α-ray groups and the γ-rays show variations, which suggests the necessity of dividing the γ-rays into quadripole and dipole. Quantum nos. have been tentatively assigned to the levels. L. L. B.

Application of probabilities to the counting of α-particles. N. I. Adams, jun. (Physical Rev., 1933, [ii], 44, 651—653).—Mathematical. N. M. B.

Theory of β-ray disintegration. G. Beck and K. Sitte (Z. Physik, 1933, **86**, 105—119).—The β-ray is one of a pair of positive and negative electrons arising in the nucleus, the positive electron being absorbed by the nucleus. A. B. D. C.

Emission of γ-rays by actinium and its derivatives. (Mme.) P. Curie and P. Savel (J. Phys. Radium, 1933, [vii], **4**, 457—458).—The absorption in Pb was measured, and mass-absorption coeffs. were obtained, for highly penetrating γ-rays of Ra and of Ac accompanied by its derivatives. The initial intensity per atom transformed for Ac is approx. 0·1 of that for Ra. N. M. B.

Interaction between γ-rays and atomic nuclei. E. Stahel and H. Ketelaar (J. Phys. Radium, 1933, [vii], **4**, 460—485).—The nature of the radiation emitted when screens of Pb, Al, Sn, and Fe were irradiated with γ-rays from Ra was investigated by the ionisation method. The emitted radiation, attributed to interaction with at. nuclei, contains components softer than the primary rays. Data for wave-lengths, intensities, and coeffs. of absorption are given; the relation with the corresponding Compton radiation, divergences from the results of other investigators, and theory of the effect observed are discussed. N. M. B.

Internal conversion of γ-rays. II. H. M. Taylor and N. F. Mott (Proc. Roy. Soc., 1933, **A**, **142**, 215—236).—Mathematical. If a γ-ray escaping from a nucleus be represented by an electromagnetic wave, then the reduction of intensity suffered by it in passing through the *K* ring is not equal to the no. of electrons ejected, but is generally small, even when this no. is comparable with the no. of γ-ray quanta emitted. L. L. B.

Effect of internal conversion. J. Solomon (Compt. rend., 1933, **197**, 670—672).—The author's inferences regarding the electronic transitions accompanying internal conversion (cf. this vol., 995) point to the emission of a γ-ray of energy $2{\cdot}852\times10^6$ ev. in the case of radiation from Ra-*C*+*C′*; the absence of such favours Dirac's theory and the results of Sauter and Hulme (cf. A., 1930, 271; 1931, 1209, 1346). C. A. S.

Gamow's treatment of radioactive disintegration. G. Breit (Physical Rev., 1932, [ii], **40**, 127).—Theoretical. Gamow's method is justified as a means of finding the probable energies and the disintegration const. L. S. T.

Exponential law of radioactive disintegration. A. E. Ruark (Physical Rev., 1933, [ii], **44**, 654—656).—Mathematical. The assumption of const. decay probability is justified. N. M. B.

Half-life of actinouranium and the problem of geologic time. F. Western and A. E. Ruark (Physical Rev., 1933, [ii], **44**, 675—681).—Assuming U^{235} as the only long-lived U isotope, equations are developed for its decay const. These equations also give the decay const. of U^{238} and mineral ages. The half-life of U^{238} is $(4{\cdot}58\pm0{\cdot}09)\times10^9$ years. A quant. study of leaching is initiated, and applied to Katanga pitchblende. N. M. B.

Actinium branching ratio. F. Western and A. Ruark (Physical Rev., 1932, [ii], **42**, 903). L. S. T.

Electrons by "materialisation" and by transmutation. (Mlle.) I. Curie and F. Joliot (J. Phys. Radium, 1933, [vii], **4**, 494—500).—Penetrating radiation excited by α-rays in Be cause the emission of positive electrons from matter which they traverse, the emission being attributed to γ-rays. The effect is interpreted as due to the transformation of a γ-ray, on impact with a nucleus, into a positive and a negative electron (materialisation). Deductions on the complexity of a proton and the mass of a neutron are considered. N. M. B.

The neutron. J. Chadwick (Proc. Roy. Soc., 1933, **A**, **142**, 1—25).—Bakerian lecture. Recent work on the production and properties of the neutron is reviewed. L. L. B.

Neutron in quantum mechanics. B. M. Sen (Nature, 1933, **132**, 518).—Theoretical. L. S. T.

Spin of the neutron. R. F. Bacher and E. U. Condon (Physical Rev., 1932, [ii], **41**, 683—685).—Hypothetical. Various possibilities of spin and nuclear structure are discussed especially in relation to Li^6, Li^7, and N^{14}. It is concluded that the neutron must have a spin and that the proton has a spin of ½ in the nucleus. L. S. T.

Neutrons. J. Perrin (Compt. rend., 1933, **197**, 628—631).—The consequences of the view that the neutron, ω, is simple and the proton, consists of a neutron and a positron, *i.e.*, $\omega\beta^+$, are discussed. It is suggested that the demihelion (or hydron), η, is $\omega_2\beta^+$, and not $-_2\beta^-$, and the helion consequently $\omega_4\beta_2{}^+$, formed with loss of 0·050 of mass, instead of $-_1\beta_2{}^-$, with loss of 0·032. Thus all at. nuclei consist of $n\omega+m\beta^+$ associated as protons, hydrons, or helions, and containing no free electrons, β^-. Radioactive emission of β-rays would result from simultaneous formation of β^+ and β^- by absorption of a penetrating photon, β^- being expelled, β^+ uniting with a neutron. The bearing of these ideas on the conversion of matter

into light (in the stars) and conversely (in space) with production of cosmic rays is considered. C. A. S.

Disintegration of elements by high-speed protons. J. D. Cockcroft (J. Phys. Radium, 1933, [vii], **4**, 421—426).—A lecture. N. M. B.

Artificial production of neutrons. H. R. Crane, C. C. Lauritsen, and A. Soltan (Compt. rend., 1933, **197**, 639—641).—A plate, one side of brass and the other of Be, was bombarded by He ions accelerated by 10 milliamp. at 6—$9{\cdot}75\times10^5$ volts, accompanying electrons being deviated magnetically. The resultant radiation (neutrons and γ-rays) was determined in an ionisation chamber with walls (*a*) covered with paraffin (*b*) uncovered and more sensitive to γ-rays and less so to neutrons. Results indicate a rapid increase of neutrons when the voltage exceeds 7×10^5 volts, whilst a tube working with 30 milliamp. at $9{\cdot}5\times10^5$ volts is a much more intense source of neutrons than Po+Be as usually employed. C. A. S.

Disintegration of the nuclei of nitrogen and other light atoms by neutrons. I. W. D. Harkins, D. M. Gans, and H. W. Newson (Physical Rev., 1933, [ii], **44**, 529—537).—Of 31 disintegrations of N found in 7600 Wilson photographs when neutrons were shot from a Be–MsTh source, 19 were disintegrations in which the neutron was captured according to: $N_0^{14}+n_1' \longrightarrow N_1^{15} \longrightarrow B_1^{11}+He_0^4$. The velocity limits for disintegration were $1{\cdot}9\times10^9$ and $5{\cdot}5\times10^9$ cm. per sec. The conversion of disappearing energy into γ-rays, and disintegration as related to scattering are discussed. In 3200 photographs, 13 disintegrations of Ne nuclei and 2 of C_2H_4 (probably of C nuclei) were found. N. M. B.

Artificial atomic disintegration. F. Kirchner (Physikal. Z., 1933, **34**, 777—786).—A summary of recent work on at. disintegration by protons, H^2, and He, with special reference to the cloud-chamber method of investigation. A. J. M.

Disintegration of lithium by swiftly-moving protons. E. O. Lawrence, M. S. Livingston, and M. G. White (Physical Rev., 1932, [ii], **42**, 150—151).—Preliminary experiments on the disintegration of Li by bombardment of LiF with protons having energies of 360,000, 510,000, and 710,000 volts support, in the main, the results of Cockcroft and Walton (A., 1932, 893). Slight divergencies are discussed. The results agree with Gamow's theory. L. S. T.

Excitation of neutrons in beryllium. G. Bernardini (Z. Physik, 1933, **85**, 555—558).—The intensity of neutrons emitted by Be has been related to the range of the exciting α-rays. A. B. D. C.

Chemical detection of artificial transmutation of elements. W. Sokolov and M. Gurevich (Nature, 1933, **132**, 679).—Examination of the disintegration of Al by α-rays by the method described shows the formation of quantities of H_2 > those formed by the scintillation method. Bombardment of Li and of NaI with β-rays from strong Ra emission preps. forms traces of He and of He and Ne, respectively. KI gave negative results for formation of inert gases. K emits small quantities of H_2 even without the action of β-rays: this suggests that H_2 is a product of the radioactive decomp. of K, which is supported by the fact that only the natural gases from K salt deposits contain H_2. L. S. T.

Atomic transmutation and the temperatures of stars. (Sir) A. S. Eddington (Nature, 1933, **132**, 639). L. S. T.

Ultra-penetrating radiation in the Jungfrau. (Mlle.) I. Curie and F. Joliot (J. Phys. Radium, 1933, [vii], **4**, 492—493).—No evidence of excitation of at. nuclei by cosmic rays at the Jungfrau scientific station was obtained, indicating the absence of neutrons in the cosmic rays. N. M. B.

Absorption of cosmical radiation. I. F. Soddy (Nature, 1933, **132**, 638—639). **II.** H. Booth (*ibid.*, 639). L. S. T.

Absorption of cosmic rays. H. J. Bhabha (Z. Physik, 1933, **86**, 120—130).—The simplest hypothesis consistent with experimental data is that of complete absorption to give the "showers" of Blackett and Occhialini (this vol., 441). A. B. D. C.

Conservation theorem in the theory of metals. F. Bloch (J. Phys. Radium, 1933, [vii], **4**, 486—491).—Mathematical. From the lattice theory of metals a principle of "conservation of wave vectors" is established. N. M. B.

Size of the mercury metastable atom. H. W. Webb and H. A. Messenger (Physical Rev., 1932, [ii], **40**, 466—467).—The distance between the centres of metastable Hg atoms (I) and N_2 mols. at impact has been found to be $3{\cdot}7\times10^{-8}$ cm. The small difference between this and the kinetic theory val. of $3{\cdot}35\times10^{-8}$ cm. indicates that (I) are not very different in size from the normal atom. L. S. T.

Physical system of the elements. C. G. Bedreag (Compt. rend., 1933, **197**, 838—849; cf. A., 1925, ii, 363).—The arrangement of the elements previously deduced has been confirmed by subsequent investigations with slight modifications; revised tables are given. C. A. S.

Quantum mechanics of lithium hydride. M. Muskat and E. Hutchisson (Physical Rev., 1932, [ii], **39**, 859). L. S. T.

Nuclear spin of cæsium by the method of molecular beams. I. I. Rabi (Physical Rev., 1932, [ii], **39**, 864).—The difference in the effect of a weak, inhomogeneous magnetic field on beams of Cs and K atoms shows the presence in Cs of a nuclear spin which can be calc. L. S. T.

Models of the electric field and of the photon. (Sir) J. J. Thomson (Phil. Mag., 1933, [vii], **16**, 809—845).—In the model developed the ether is regarded as a gas of which the mols. (granules) are infinitesimal in comparison with electrons. Electrons and protons are the ends of tubes of force, which latter are represented as vortex filaments in the gas. This theory leads to Maxwell's equations and is in agreement with other known laws. J. W. S.

Streaming processes in gases at low pressures represented by Reynold's numbers. H. Ebert (Z. Physik, 1933, **85**, 561—564). A. B. D. C.

Physics of cold and of the atomic nucleus. H. STUCKLEN (Naturwiss., 1933, **21**, 772—776).—A summary of a conference. A. J. M.

Nature of waves and corpuscles. É. SEVIN (Compt. rend., 1933, **197**, 980—982; cf. *ibid.*, 1929, **188**, 986; 1933, **196**, 1379; this vol., 881).—Mathematical; the conclusion is that in nature there are neither symbolic waves nor photons, but waves and material particles are subject to one and the same dualism, which includes the conceptions of both Fresnel and Maxwell. They may therefore be viewed from both aspects. C. A. S.

Quantisation of the Kramers and Pauli model. P. M. DAVIDSON (Proc. Roy. Soc., 1933, A, **142**, 269—274).—Mathematical. L. L. B.

Structure of atomic nuclei. J. H. BARTLETT, jun. (Physical Rev., 1932, [ii], **41**, 370—371; **42**, 145—146, 737).—Previous views (A., 1932, 894) are extended to nuclei of intermediate wt., which may consist of closed shells of protons and neutrons, an arrangement which would explain the presence of clusters of nuclei discovered by Barton. Certain difficulties can be avoided if it is assumed that electrons have a separate existence in some nuclei, thus making three types of primary particle, the proton, the neutron (a simple unit and not proton+electron), and the electron. Known as well as predicted isotopes are discussed. L. S. T.

Unitary theory, pure number ratios, and the masses of atomic nuclei. E. E. WITMER (Physical Rev., 1932, [ii], **42**, 317).—Numerical formulæ for certain pure no. ratios of the universal dimensional physical consts. and for masses of at. nuclei have been found. L. S. T.

Probable values of e, h, e/m, and α. R. T. BIRGE (Physical Rev., 1932, [ii], **41**, 319—320; cf. A., 1932, 672). L. S. T.

Probable values of e, h, e/m, and α. W. N. BOND (Physical Rev., 1932, [ii], **41**, 368—369; cf. preceding abstract).

Value of e/m. R. T. BIRGE (Physical Rev., 1932, [ii], **42**, 736).—Corr. results (cf. above) are $-h$ $(6{\cdot}5420 \pm 0{\cdot}0083) \times 10^{-27}$ erg. sec., e $(4{\cdot}7668 \pm 0{\cdot}0038) \times 10^{-10}$ e.s. units, e/m $(1{\cdot}7592 \pm 0{\cdot}0011) \times 10^{7}$ e.m. units, and $1/\alpha$ $137{\cdot}374 \pm 0{\cdot}048$. An examination of recent work indicates that $(1{\cdot}759 \pm 0{\cdot}001) \times 10^{7}$ e.m. units is the present most probable direct evaluation of e/m. L. S. T.

Gyromagnetic ratios for nickel and cobalt. S. J. BARNETT (Physical Rev., 1932, [ii], **42**, 147).—Preliminary vals. for the gyromagnetic ratios for Ni and Co are $1{\cdot}06m/e$ and $1{\cdot}07m/e$, respectively, in agreement with previous work. L. S. T.

Law of force between two helium atoms. W. G. PENNEY (Physical Rev., 1932, [ii], **42**, 585).—The law of force obtained by recent quantum considerations is in good agreement with that found from classical considerations of η and the equation of state of He gas (A., 1925, ii, 253). L. S. T.

Perturbation theory of molecules formed from $2p$ atoms. J. R. STEHN (Physical Rev., 1932, [ii], **42**, 582—584).—A comparison of the various methods used to determine the energy levels of diat. mols. for the case of a mol. formed from two similar atoms each containing a single $2p$ electron. L. S. T.

Energy levels of the rare-gas configurations. G. H. SHORTLEY (Physical Rev., 1933, [ii], **44**, 666—674).—Mathematical. N. M. B.

Experimental proof of Einstein's radiation recoil collision. R. FRISCH (Z. Physik, 1933, **86**, 42—48).—A beam of slowly moving Na atoms irradiated with resonance radiation showed recoil at absorption and emission. A. B. D. C.

Magnetic deviation of isotopic hydrogen molecules and the magnetic moment of the "deuton." I. ESTERMANN and O. STERN (Z. Physik, 1933, **86**, 132—134).—The nuclear moment of H^2 is $\gtrless$, and is probably $<$, that of H^1. A. B. D. C.

Optical properties of metallic and crystalline powders. A. H. PFUND (J. Opt. Soc. Amer., 1933, **10**, 375—378).—Au, Ag, Ni, Cu, Zn, Cd, Pb, Bi, Sb, Se, and Te "blacks" have been prepared by distillation of metals at relatively high pressures. The transparency in the infra-red region has been determined. NaCl and TlCl distilled on to radiometer vanes yield a selective receiver for the far infra-red. A new type of transmission band, shown by coarsely powdered quartz and calcite, is described. E. S. H.

Light absorption of metals. A. SMAKULA (Physikal. Z., 1933, **34**, 788—790).—The absorption of Cu, Ag, Au, Al, Sn, Pb, Sb, Bi, Cr, and Mn has been investigated in the range 700—186 mμ. The absorption of Ag does not diminish below 250 mμ. Cu and Au show no new transmission ranges in the ultra-violet. Besides the major absorption max. all the metals investigated show numerous smaller max. and min. over the whole range. The absorption of Cu, Ag, and Au can be explained by considering the behaviour of colloidal layers. The absorption min. are related to the at. conductivity of the metal. A. J. M.

Absorption spectra of solutions of iodine bromide, cyanogen iodide, and cyanogen bromide. A. E. GILLAM (Trans. Faraday Soc., 1933, **29**, 1132—1139).—IBr (and in a limited sense CNI) exhibits dichroism, giving in unsaturated solvents (*e.g.*, EtOH) yellow solutions with an absorption band near 400 mμ and in saturated solvents (*e.g.*, $CHCl_3$) red solutions with a band near 490 mμ. Cl_2, Br, I, BrCl, ICl, and IBr exhibit broad bands in the visible or near ultra-violet, CNI and CNBr exhibit only some end absorption in the ultra-violet. In HCl or HBr, IBr forms the compounds HIBrCl and $HIBr_2$. A. G.

Investigations of the negative group of CO^+. H. BISKAMP (Z. Physik, 1933, **86**, 33—41).—Twenty-two new bands were investigated, and potential–nuclear separation curves are given. A. B. D. C.

Absorption of aqueous solutions of hydrochloric acid in the far ultra-violet. R. TREHIN (J. Phys. Radium, 1933, [vii], **4**, 440—456; cf. this vol., 111).—Full data are tabulated and plotted for optical density and mol. absorption coeffs. in the range 2816—1990 Å. at 20°, 40°, 60°, and 80°, the HCl and H_2O being highly purified. The absorption is

continuous at all concns. and temp. The mol. absorption coeff. increases regularly with decrease of concn. and with rise of temp. N. M. B.

Absorption of NaCl, KCl, and KI in the far ultra-violet. A. SMITH (Physical Rev., 1933, [ii], **44**, 520—523).—Absorption curves for the range 190—1550 Å. are given. Max. are: NaCl, 655, 535, 350, 890; KCl, 705, 530, 320, 1120; KI, 825, 625, 510 Å., at variance with earlier extrapolated vals. N. M. B.

Additive colouring of alkali halide crystals. III. Spectrophotometric results. E. REXER (Z. Physik, 1933, **85**, 1—13).—Spectrophotometric measurements showed that absorption due to amicroscopic particles moves towards the red with rising temp.; that due to colloid particles was uncertain in position for untempered crystals, but tempering gave these bands a position independent of temp. Motion of electrons and additive colouring by foreign vapours were also studied. A. B. D. C.

Absorption spectrum of sulphur dioxide. J. A. DUNCAN (Physical Rev., 1932, [ii], **41**, 388).—The absorption spectrum of SO_2 has been photographed in the region 2165—2410 Å. The bands are partly resolved into rotational band lines and are analysed particularly with regard to rotational structure. L. S. T.

New system of bands in sulphur dioxide. T. C. CHOW (Physical Rev., 1932, [ii], **40**, 1039; cf. this vol., 144).—Approx. 80 bands in the region 2000—2400 Å. have been obtained from a discharge in rapidly flowing SO_2 gas. These bands do not belong to SO, O_2, or O_2^+. SO_2 is the probable emitter. L. S. T.

Spectrum of sulphur dioxide. T. C. CHOW (Physical Rev., 1933, [ii], **44**, 638—643).—From a discharge in flowing SO_2 with comparatively little dissociation, data and analyses are given for emission and absorption bands in the regions 4000—2500 and 2600—2000 Å. N. M. B.

Absorption spectra of burning hydrocarbons. A. EGERTON and L. M. PIDGEON (Proc. Roy. Soc., 1933, **A, 142**, 26—39).—The absorption spectra of various hydrocarbons undergoing combustion show three characteristics: (1) an absorption in the far ultra-violet, proved to be due mainly to the formation of acids; (2) bands identified with those of CH_2O; and (3) in the case of the higher hydrocarbons, a band with a max. at about 2600 Å. During the induction period no absorption is visible. For C_4H_{10} and higher hydrocarbons the band at 2600 Å. is the first to appear, and is followed by the aldehyde bands. The corresponding aldehydes do not give this band on combustion. L. L. B.

Ultra-violet absorption of substances containing two benzene rings. CHAIX (Bull. Soc. chim., 1933, [iv], **53**, 700—711).—Ultra-violet absorption curves of fluorene, CH_2Ph_2, carbazole, $NHPh_2$, fluorenone, $COPh_2$, Ph_2S_2, Ph_2Se_2, diphenylene sulphide, Ph_2S, $(p\text{-}C_6H_4Me)_2S$, Ph_2Se, diphenylene sulphoxide, Ph_2SO, Ph *p*-tolyl sulphoxide, m.p. 73° [the compound, m.p. 124°, described as this by Gilman *et al.* (A., 1926, 1239) is (I) (below)], $(p\text{-}C_6H_4Me)_2SO$, $(p\text{-}C_6H_4Br)_2SO$, Ph_2SeO, diphenylene sulphone, Ph_2SO_2, $p\text{-}C_6H_4Me\cdot SO_2Ph$ (I), and $(p\text{-}C_6H_4Me)_2SO_2$ are given; *M*/2000-solutions in EtOH are used. For the compounds Ph_2X, the chromophoric effect of X decreases in the order Se_2, CO, S_2, Se, S, SO, SeO, SO_2, CH_2. $(C_6H_4)_2X$ are more bathochromic than Ph_2X. Br exerts a bathochromic effect. H. B.

Ultra-violet absorption of alkyl- and allyl-*cyclo*hexanones. (MME.) RAMART-LUCAS and CORNUBERT (Bull. Soc. chim., 1933, [iv], **53**, 744—753).—Comparison of the ultra-violet absorption spectrum of an allyl*cyclo*hexanone (I) with that of the corresponding propyl*cyclo*hexanone (II) shows that the positions of the absorption max. are approx. the same; the coeff. of absorption of the (I) is > that of the (II). Increase in the no. of 2- and 6-substituents causes an increase in the absorption intensity and a displacement of the absorption max. towards the visible. Curves are given for solutions (in EtOH and hexane) of 2-propyl-, 2 : 6-dipropyl-, 2 : 2 : 6 : 6-tetrapropyl-, 2 : 2 : 6 : 6-tetramethyl-, 2-allyl-, diallyl- (containing about 87% of the 2 : 6- and 13% of the 2 : 2-derivatives), 2 : 2 : 6-triallyl-, and 2 : 2 : 6 : 6-tetra-allyl-*cyclo*hexanones. Increase in absorption corresponds with a diminution in chemical reactivity. H. B.

Polyatomic molecules. Structure and activation of benzaldehyde. I. Absorption of ultra-violet light by benzaldehyde vapour. F. ALMASY (J. Chim. phys., 1933, **30**, 528—547).—The positions of the absorption bands have been determined in the regions 3747·3—3162·6, 2963·0—2599·2, and 2428·0—2348·9 Å. E. S. H.

Extinction curves of alkaloids of the quinoline group. I. MANTA (Z. physikal. Chem., 1933, **B, 22**, 465—468).—In the alkaloids of the quinine group it is the substituted quinoline nucleus which is responsible for the two characteristic max. on the absorption curve; the quinuclidine nucleus has no material effect on the form of the curve, and therefore neither has the replacement of a vinyl group of this nucleus by a CO_2H group or addition of IEt. Quinine and its derivatives have the spectrum of *p*-methoxylepidine and cinchonine derivatives the spectrum of lepidine. R. C.

Character of linking in hydrogen halides deduced from absolute intensity measurements on infra-red ground vibration bands. E. BARTHOLOMÉ (Z. physikal. Chem., 1933, **B, 23**, 131—151).—If to the gas under examination is added a foreign gas, X, under sufficient pressure, the fine structure of the band disappears and the extinction coeff., even with the small dispersion of a prism apparatus, becomes approx. const. over the whole slit width, so that a single measurement of the band at this pressure of X gives the abs. intensity. Measurements have been made with the H halides in presence of air/60 atm. The vals. $1{\cdot}93\times10^{15}$, $1{\cdot}67\times10^{15}$, and $0{\cdot}35\times10^{15}$ have been obtained for the probability of transition, B^1_0, and the vals. $0{\cdot}086e$, $0{\cdot}075e$, and $0{\cdot}033e$ for the effective charge, ε, of HCl, HBr, and HI, respectively. These small vals. of ε are reconcilable only with a homopolar linking. R. C.

Infra-red region of the spectrum. IX. Absorption spectrum of chlorine monoxide. C. B. BAILEY and A. B. D. CASSIE (Proc. Roy. Soc., 1933, A, 142, 129—141).—Four bands of Cl_2O have been isolated between 1 and 18 μ. Fundamental frequencies are assigned, and the mol. dimensions calc. The isotopic effect is shown to account for the envelopes of some of the bands. The similarity between the Cl_2O, H_2O, and H_2S mols. is discussed. L. L. B.

Near infra-red bands of ammonia under high dispersion. J. D. HARDY (Physical Rev., 1932, [ii], 40, 1039).—Fine structure has been detected in the NH_3 bands at 1·5 and 2·2 but not at 1·9 μ. L. S. T.

Absorption spectra of benzene derivatives near 1 μ. R. FREYMANN and A. NAHERNIAC (Compt. rend., 1933, 197, 829—831).—Using a modification of the previous method (cf. A., 1932, 6; this vol., 550) new weak complex bands have been measured near 1 μ in C_6H_6 and PhX (X=Cl, Br, I, NO_2, or Me) apparently corresponding with intense bands near 1 μ in the saturated compounds $CHCl_3$, CH_2Cl_2, MeOH, and C_6H_{12} (cf. this vol., 559), probably attributable to C·H. C. A. S.

Infra-red spectra of propane and diacetylene. E. BARTHOLOMÉ (Z. physikal. Chem., 1933, B, 23, 152—157).—The spectra indicate that in C_3H_2 there is a linear arrangement of atoms. R. C.

Near infra-red [spectra]. R. FREYMANN (Ann. Physique, 1933, [x], 20, 243—345).—Data are given for the band spectra in the region 0·84—1·16 μ of many org. liquids, and deductions are discussed on the structure of the bands, and the effects of the length of C chains and corresponding variations in the position and intensity of the bands, isomerism and the introduction of double linkings in the mol. resulting in band displacements, substitution of electro-positive or -negative groups in C_6H_6, infra-red absorption on the rotatory power of optically active substances, and temp. and dilution. The two last-named lead to displacements or intensity variations which can be explained on the hypothesis of mol. associations and intermol. forces. N. M. B.

Theory of the Raman rotation spectra. W. V. HOUSTON (Physical Rev., 1932, [ii], 41, 263—264).—The Raman spectrum can be treated as due to variable polarisability (I). If the tensor of (I) is transformed by means of the Eulerian angles (II) to axes which are fixed with reference to the incident beam of light, then the periodic change of (II) gives the Raman lines (III) of the rotation spectrum. The relative intensities and the polarisation of (III) can thus be evaluated without knowledge of the electronic levels of the mol. This treatment explains why a spherically symmetrical mol. such as CH_4 shows a rotation-vibration spectrum but no rotation spectrum. L. S. T.

Raman effect in nitric acid. L. MÉDARD and H. VOLKRINGER (Compt. rend., 1933, 197, 833—836).—The Raman spectrum of HNO_3 has been determined for ten solutions containing 6·3—99·8% HNO_3; three new bands, at 1048, 1103, and 1537 cm.$^{-1}$, were found in the 99·8% acid (cf. A., 1931, 1111). In the dil. acid both position and intensity change, the line 1048 cm.$^{-1}$ of NO_3' decreasing, whilst all others increase in intensity as % HNO_3 increases from 64 to 99·8; the H_2O line, 3400, appears below 52% HNO_3 (cf. A., 1930, 840; 1931, 1367). In $CHCl_3$ solution the intensity of all HNO_3 lines decreases at the same rate as dilution increases. C. A. S.

Raman effect in crystalline ammonium chloride. F. T. HOLMES (Physical Rev., 1932, [ii], 41, 389).—In addition to the broad Raman lines at 3155 and 3035 cm.$^{-1}$ most of the characteristic frequencies in the infra-red appear in the Raman spectrum as rather broad lines. The line at approx. 1700 cm.$^{-1}$, however, is sharp. Four weak lines near 3155 and 3035 cm.$^{-1}$ may be vibration–rotation lines associated with the 3035 cm.$^{-1}$ vibrational shift. The moment of inertia of the rotating NH_4 is calc., on certain assumptions, to be approx. 2×10^{-40} g.-cm.^{2} L. S. T.

Inner vibrations in molecules from the Raman effect. W. D. HARKINS and H. E. BOWERS (Physical Rev., 1932, [ii], 39, 182; cf. A., 1932, 109; this vol., 7).—The independence of the Raman frequency characteristic of C–halogen linking in normal compounds and the length of chain between two and five C atoms indicates that the characteristic frequency is related to an inner and not to an outer vibration; the CH_2 adjacent to the halogen atom appears to be the vibrating group. The calc. force consts. are 3·0, 2·6, and $2·2\times10^5$ dynes per cm. for chloride, bromide, and iodide, respectively. L. S. T.

Rotational Raman effect of gases. C. M. LEWIS (Physical Rev., 1932, [ii], 41, 389).—The study of the Raman effect of gases has been extended to the pure rotation of the simpler hydrocarbons. C_2H_2 shows the same pattern of alternating intensities found in absorption. C_2H_6 and C_2H_4 show more complicated fine structure, but no evidence of > one moment of inertia. The pure rotation spectrum of CH_4 is either missing or is of a lower order of intensity than the rotation–vibration band already found by Rasetti. L. S. T.

Depolarisation of Raman radiation by liquids. L. S. ORNSTEIN and P. STOUTENBEEK (Z. Physik, 1933, 85, 754—760).—Depolarisation was observed for Raman lines of CCl_4 and $C_2H_4Cl_2$. A. B. D. C.

Raman effect of tetranitromethane. M. MILONE (Gazzetta, 1933, 63, 453—456).—Raman spectrum measurements indicate a true nitro-derivative structure for $C(NO_2)_4$, $CCl_3{\cdot}NO_2$, and $CBr_3{\cdot}NO_2$. O. J. W.

Raman spectrum of some heterocyclic compounds. II. M. MILONE (Gazzetta, 1933, 63, 456—463; cf. this vol., 886).—The differences shown by the Raman spectra of isomeric furazans, azoximes, and oxdiazoles are characteristic of the particular structure of the C_2N_2O ring in the three types of compound. O. J. W.

Raman effect. XXVI. Raman spectrum of methyl and ethyl esters of monobasic fatty acids. K. W. F. KOHLRAUSCH, F. KOPPL, and A. PONGRATZ. **XXVII. Raman spectra of esters of formic and**

chloroformic acids and of acid chlorides. K. W. F. KOHLRAUSCH and A. PONGRATZ (Z. physikal. Chem., 1933, **B**, **22**, 359—372, 373—383; cf. this vol., 661).—XXVI. In the frequency range $\Delta\nu$ 600—1200 there are no differences between the normal acids and their esters which can be ascribed to the entrance of the Me or Et group. In the region $\Delta\nu$ 1000—1450 the acids and esters with a normal side-chain have in common the frequencies 1020, 1070, 1110, 1170, 1300, and 1450. The frequencies 1268, 1410, and 1420 are taken as characteristic of the groups CO_2Et, CO_2H, and CO_2Me, respectively. The frequencies 1410 and 1650 in the acids are tentatively accounted for by the Werner–Hantzsch formulation of the CO_2H group, the angle between the C·O valencies being calc. to be much $<$ the tetrahedral angle. Almost every Me ester, but neither the corresponding acid nor Et ester, exhibits the frequencies 2840 and 3030 approx., which are assumed to be C·H valency frequencies in the special CO_2Me configuration.

XXVII. Characteristic of the formic esters are the CO frequency $\omega=1716$ and the frequency $\omega=1379$, probably belonging to the terminal H atom. In the chloroformic esters the CO frequency has become 1775 and there is a characteristic Cl frequency, 476. The characteristic frequencies of the acid chlorides are 1793 (CO), 433 (Cl), and 1400 (probably arising from a perturbed CH_2 deformation vibration). All these frequencies are in general const. in position within a homologous series. R. C.

Molecular scattering of light in liquids. E. CANALS and P. PEYROT (Bull. Soc. chim., 1933, [iv], **53**, 741—744).—The degree of polarisation, p, of scattered light is an inverse measure of the mol. anisotropy of the liquid. For the compounds examined, p decreased in the order $Pr^{\beta}I > iso C_5H_{12} > n\text{-}C_7H_{16} > CHCl_3 > C_5H_{11}Cl > C_5H_{11}Br > EtBr > Pr^{\alpha}Br = Pr^{\beta}Br > C_6H_6 > C_6H_5Cl$. The abnormally high val. for $Pr^{\beta}I$ is probably due to isotropic particles of colloidal I present as an impurity. D. R. D.

Raman effect and chemistry. α-Ethylene oxides. R. LESPIEAU and (MLLE.) B. GREDY (Bull. Soc. chim., 1933, [iv], **53**, 769—782; cf. this vol., 337).—Detailed measurements on eleven substituted α-ethylene oxides are given. D. R. D.

Raman spectra of two liquid phases of nitrobenzene. A. M. THORNE and P. L. BAYLEY (Physical Rev., 1932, [ii], **41**, 376—377).—No evidence of a modification of the Raman spectrum of $PhNO_2$ at temp. $>$ and $<$ 9·5° could be obtained (cf. this vol., 1232). Additional lines, which may belong to an impurity, are reported. L. S. T.

Raman effect of methylacetylene. G. GLOCKLER and H. M. DAVIS (Physical Rev., 1932, [ii], **41**, 370).—The frequencies of the monosubstituted C:C linking (2128 cm.$^{-1}$) and the :C·H linking (3306 cm.$^{-1}$) found are in agreement with the vals. of other workers. Lines for the aliphatic C·H linking (2928 cm.$^{-1}$) and the C·C linking (618 and 931 cm.$^{-1}$) as well as the unidentified lines 310, 1384, 2871, 3144, and 3207 cm.$^{-1}$ were also found. L. S. T.

Fluorescence of gaseous formaldehyde. S. GRADSTEIN (Z. physikal. Chem., 1933, **B**, **22**, 384—394).—The fluorescence spectrum under 50—100 mm. for monochromatic excitation is independent of which absorption band is utilised for excitation. This is ascribed to collisions during the life of the excited mol. which cause it to pass into the vibrationless state of the excited electronic state. The band of longest wave-length capable of strongly exciting fluorescence is the first principal absorption band, *A*, but the fluorescence spectrum indicates that the fluorescence band of shortest wave-length is α, which is of longer wave-length than *A* (cf. this vol., 766). R. C.

Decay of luminescence and light absorption in phosphorescent materials. D. H. KABAKJIAN (Physical Rev., 1933, [ii], **44**, 618—624; cf. A., 1931, 783).—Curves for the rise and decay of phosphorescence and for the changes in light absorption coeff. of certain materials under continuous irradiation with α-, β-, and γ-rays are given. The coeff. of each sample reaches a saturation val. which is a function of the radiation intensity and the temp. N. M. B.

Electrical conductivity of silicon carbide. R. W. SEARS and J. A. BECKER (Physical Rev., 1932, [ii], **40**, 1055).—Conduction in crystals of Si carbide obeys Ohm's law; sp. resistance of a black, opaque crystal, is 2·13 ohm cm., of a semi-transparent crystal, 0·41 ohm cm. Resistance is independent of direction of current. L. S. T.

Photo-electric emission from cadmium and mercury. D. ROLLER and H. ZENOR (Physical Rev., 1932, [ii], **39**, 866).—The photo-electric properties, the prep. of thin films of pure Cd and Hg on oxidised Fe and on glass, and the effects of contamination on the photo-electric behaviour of Hg in bulk are described. L. S. T.

Prediction of photo-electric power. H. SPINDLER and R. COUSTAL (Compt. rend., 1933, **197**, 982—984).—As shown to be probable by Spindler's classification of the elements (detailed) Cu_2O in a photo-electric cell may be replaced by CuBr, but not by CuCl or CuI. The CuCl cell has a sensitivity of approx. 60% that of Cu_2O, but it soon alters on illumination, and ceases to function. C. A. S.

Measurements on contact potential difference between different faces of copper single crystals. B. A. ROSE (Physical Rev., 1933, [ii], **44**, 585—588).—Contact potential–time curves between the (111) and (100) faces at different stages of outgassing were obtained by the Kelvin null method. N. M. B.

Cuprous oxide photo-cells. Unidirectional layer photo-effect. W. BULIAN (Physikal. Z., 1933, **34**, 745—756).—The application of Cu_2O photo-cells in practical measurement is discussed, with reference to the spectral sensitivity, max. efficiency factor, and dependence of emission on temp. The position of the selective max. is not dependent on the metal of the receiving electrode. In Au sputtered cells the direction of the photo-current is dependent on λ of incident light. The optimum thickness of the Cu_2O layer for max. current efficiency is 0·1 mm. for all λ in the visible. By choosing the correct metal a cell

can be produced which will give const. current over any desired temp. range. A. J. M.

Inner potential of semi-conductors. K. R. DIXIT (Phil. Mag., 1933, [vii], **16**, 980—994).—Visual measurements of electron diffraction gave the inner potentials of natural cryst. ZnS, PbS, FeS_2, and Fe_2O_3 as −4·8, +12·5, +5·1, and +12·6 volts, respectively. H. J. E.

Crystal photo-effect. G. MONCH (Naturwiss., 1933, **21**, 751—752).—A potential was observed between electrodes connected at opposite ends of the axis of symmetry of a crystal (cuprite, Cu_2O, proustite, Ag_3AsS_3, pyrargyrite, Ag_3SbS_3, cinnabar, HgS) when illuminated from both sides, in agreement with Dember (A., 1931, 999). With artificial Cu_2O crystals the effect was not observed, showing that it cannot be explained as due to light pressure or diffusion potentials, but is probably due to impurities. Except cinnabar, all natural crystals showing the photo-effect have negative thermo-potential. A. J. M.

Electrical properties of calcite. S. SHIMIZU (Sci. Rep. Tohoku, 1933, **22**, 570—598).—Electrical properties of Japanese calcite specimens cut parallel and perpendicular to the *c* axis indicate that there is no condensed polarisation such as that observed in Iceland calcite. The electrical conductivity varies remarkably over the range 680—850° for the parallel specimen and over the range 815—840° for the perpendicular specimen. E. S. H.

High-frequency properties of dielectrics. I. Anomalous variation of capacity and resistance of quartz with temperature and frequency. I. K. NAKAMURA (Sci. Rep. Tohoku, 1933, **22**, 614—631).—The capacity of a quartz plate cut parallel to the optical axis increases linearly with rising temp.; the high-frequency resistance also increases with rise of temp. A slight discontinuity is observed at the β transformation point, 573°. With specimens cut perpendicular to the optical axis the capacity increases greatly with rising temp., whilst the resistance decreases up to 490°, when it increases. E. S. H.

Dielectric polarisation. VIII—XI. E. G. COWLEY and J. R. PARTINGTON (J.C.S., 1933, 1252—1259).—VIII [with H. J. MOSS]. The dipole moments of Me, Et, Pr, and Bu nitrates are approx. const. (2·85—2·98), and the same is true of Et and Pr nitrites (2·20 and 2·28, respectively). In the nitrates the moment of the $\cdot NO_2$ group presumably acts at 90° to the chain, in contradistinction to the nitro-compounds, in which induction occurs along the chain. The moments rise, and the solubilities in non-polar solvents fall, in the order nitrite, nitrate, nitro-compound.

IX. The dipole moments of a no. of alkyl- and aryl-nitrosoamines and hydrazo-compounds and of NHPhEt are recorded and discussed.

X. The observed dipole moment of *p*-nitroanisole is in close agreement with the val. calc. on the assumption of complete freedom of rotation of the OMe group, but this is not the case for the *o*- and *m*-compounds owing to interaction between the groups. The order in the nitroanisole and nitrophenol series is not the same, owing probably to the presence of a semi-polar linking in $o\text{-}OH\cdot C_6H_4\cdot NO_2$.

XI. The dipole moment of pyrrole is 1·83, compared with 2·11 and 2·18, respectively, for C_5H_5N and quinoline. H. F. G.

Dielectric constant. XI. Electric moment of substituted amides and carbamides. G. DEVOTO (Gazzetta, 1933, **63**, 495—499; cf. this vol., 777).—Dielectric const. measurements are recorded for C_6H_6 or dioxan solutions of dimethyl-, tetraethyl-, and propyl-carbamides, pyrrolidone, NH_2Ac, NH_2Bz, $NO_2\cdot C_6H_4\cdot CO\cdot NH_2$, $p\text{-}NH_2\cdot C_6H_4\cdot CO\cdot NH_2$, NH_2CN, and $SO_2(NH_2)_2$. The irregular behaviour of the substituent $CO\cdot NH_2$ is discussed. O. J. W.

Polarity of chemical compounds. III. IV. K. HIGASI (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, **12**, 771—779, 780—789).—III. Dielectric const. and density data are given for Et_2O solutions of EtOH, $C_2H_4(OH)_2$, and AcOH over the range −60° to 25°. The equation $P_2=a+b/T$ is valid for solutions of EtOH, but not for those of glycol or AcOH.

IV. Similar data are recorded for cetyl alcohol in C_6H_6, C_6H_{14}, and Et_2O, for $\alpha\text{-}C_{10}H_7\cdot OH$ in C_6H_6 and Et_2O, and for $\beta\text{-}C_{10}H_7\cdot OH$ in Et_2O, at various temp. between 0° and 60°. Dipole moments are calc. The vals. for the naphthols are considerably > those of Puchalik (A., 1932, 560). D. R. D.

Dipole moment and group rotation. I. Moments of the chloro- and nitro-benzyl chlorides and the effect of group separation. J. M. A. DE BRUYNE, R. M. DAVIS, and P. M. GROSS (J. Amer. Chem. Soc., 1933, **55**, 3936—3944).—Dielectric consts., densities, and refractive indices of dil. solutions in C_6H_6, C_7H_{16}, and CCl_4 have been determined at 30°. The average dipole moments, μ, are: *o*-, *m*-, *p*-$C_6H_4Cl\cdot CH_2Cl$ and *o*- and *m*-$CH_2Cl\cdot C_6H_4\cdot NO_2$ 2·31, 2·06, 1·71, 4·00, and 3·86, respectively. Calc. vals. for the *m*- and *p*-compounds accord with the observed vals. The discrepancies found for the *o*-compounds, as well as the variations of μ with solvent, suggest a partial inhibition of free rotation in these cases. J. G. A. G.

Properties of conjugated compounds. XVI. Dipole moments and atomic polarisation of the monomethyl- and dimethyl-butadienes. XVII. Determination of the dipole moments of monomethyl- and dimethyl-butadienes. E. H. FARMER and F. L. WARREN (J.C.S., 1933, 1297—1301, 1302—1304).—XVI. A method of measuring the dielectric consts. is described. The dipole moments of β-methyl-, αα- and βγ-dimethyl-butadienes are, respectively, 0·15, 0·52, and $0\,0\times10^{-18}$ e.s.u. These hydrocarbons cannot show geometrical isomerism. Alkyl substitution at the α-C atom of a butadiene chain appears to cause greater permanent polarisation than at the β-C.

XVII. The dipole moments of α-methyl-, αβ-, αγ-, and αδ-dimethyl-butadienes are, respectively, 0·50, 0·53, 0·59, and 0·36 (high-b.p. fraction), $0·31\times10^{-18}$ e.s.u. (low-b.p. fraction). These hydrocarbons can show geometrical isomerism. H. S. P.

Electric moments of cyclic 1 : 1-dicarboxylic esters in relation to the valency-deflexion hypothesis. E. H. FARMER and N. J. H. WALLIS (J.C.S., 1933, 1304—1309).—Using a highly sensitive appar-

atus, the dipole moments of *cyclo*-propane-, -butane-, -pentane-, and -hexane-1 : 1-dicarboxylic esters have been found to be 2·40, 2·22, 2·14, and $2{\cdot}23\times10^{-18}$ e.s.u., respectively. Assuming the constancy of the effect of the CO_2Et system, the changes in moment do not correspond with those calc. from the valency-deflexion hypothesis of Ingold and Thorpe. H. S. P.

Interpretation of electric polarisation coefficients. F. R. Goss (J.C.S., 1933, 1341—1345).—The errors in deducing dipole moments are considered. Raman and Krishnan's theory of optical and electrical properties is applied to the polarisation of C_6H_6. The dielectric consts. of C_6H_6 and CCl_4 have been measured. H. S. P.

Relations between stereochemistry and physics. P. Debye (J.C.S., 1933, 1366—1371).—Faraday lecture. An historical account is given of the development of the study of dipole moments and the relationship between dipole moment and chemical structure is considered. The application of *X*-rays and cathode rays to the measurement of the spacing of atoms in mols. is described. H. S. P.

Determination of electric moment in solution by the temperature coefficient method. I. Experimental method and the electric moment of some benzyl compounds. F. Fairbrother (Proc. Roy. Soc., 1933, A, 142, 173—197).—*cis*- and *trans*-Decahydronaphthalene have been obtained by fractionating commercial "dekaline" and are non-polar. *p*-$C_6H_4Me_2$ is also non-polar. All these liquids show a slight increase of polarisation with rise of temp. The polarisations of $CH_2Ph{\cdot}OH$ (I) and CH_2PhCl (II) have been measured in decahydronaphthalene solution from 20° to 160°, and of *o*- (III), *m*- (IV), and *p*- (V) -$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$ in *p*-$C_6H_4Me_2$ from 20° to 120°. The estimated electric moments are: (I) 1·6, (II) 1·72, (III) 3·93—3·97, (IV) 3·71—3·80, (V) $3{\cdot}45\times10^{-18}$ e.s.u. The polarisation of (I) except in very dil. solution, rises at first with temp., owing to a decrease of mol. association. The moments of (III) and (IV) increase with rise of temp., whilst that of (V) is const. The results are consistent with a rotation of the CH_2Cl group about its axis. L. L.

Electric polarisation of vapours. Anomalous behaviour of phosphorus trichloride. U. Grassi (Nuovo Cim., 1933, 10, 3—20; Chem. Zentr., 1933, i, 3165).—For PCl_3 vapour vals. of ε are not linearly related to $1/T$. It is assumed that there are two moments corresponding with two levels of internal mol. energy. A. A. E.

Polar structure of molecules and nature of residual valency forces. G. Briegleb (Z. physikal. Chem., 1933, B, 23, 105—130).—It is suggested that residual affinities are qualitatively identical with van der Waals forces, and a scheme for modes of combination in mol. compounds is proposed. Mol. interaction in the gaseous state has been theoretically examined. Adopting Wohl's classification into permanent gases and normal substances on the one hand and associated substances on the other (A., 1928, 827; 1931, 1216), it appears that associated mols. do not differ fundamentally in the nature and mode of action of their intermol. forces from normal substances, but the properties determining orientation effects are prominent. Orientation effects cannot be ascribed solely to di- or quadri-polar forces; orientation may occur owing to interaction with London forces. With NO there is an orientation effect in the gaseous state which has no relation to either dipole or London effects. The relative magnitudes of the induction, polarisation, and dispersion effects with various mols. are represented as attraction potential curves. The effect of dipole moment may be obscured by steric shielding. The theoretical calculation of the second virial coeff. and its relation to the temp. is described and the results are compared with experimental data. If the reduced virial coeffs. of normal substances are plotted against the crit. temp. a continuous curve results. R. C.

Magnetic dipole fields in unsaturated cubic crystals. L. W. McKeehan (Physical Rev., 1933, [ii], 44, 582—584; cf. this vol., 766). N. M. B.

Covalency, co-ordination, and chelation. R. C. Menzies and H. Overton [with E. R. Wiltshire] (J.C.S., 1933, 1290—1294).—The halides of $PtMe_3$, $AuEt_3$, and thallium dialkyl are associated in C_6H_6 solution, but those of HgMe and $PbEt_3$ are not associated. Chelation and association of the halides depend on the effective co-ordination no. being > the no. of covalencies functioning. H. S. P.

Rotatory dispersion of organic compounds. XXIII. Rotatory dispersion and circular dichroism of aldehydic sugars. H. Hudson, M. L. Wolfrom, and T. M. Lowry (J.C.S., 1933, 1179—1192).—The acetates of the open-chain μ-forms of glucose, galactose, and arabinose exhibit the :CO absorption band at 2900 Å. which is optically active and gives rise to *l*-rotation in the visible spectrum. The band is either symmetrical (wave-length scale) or slightly steeper on the longer wave-length side. Whereas the rotatory dispersion of the arabinose derivative is simple, those of the other derivatives involve two terms, viz., a *l*-rotation due to the induced dissymmetry of the ·CO group and a *d*-rotation attributed to the asymmetry of the :CH·OAc groups; the latter has a characteristic frequency in the Schumann region. The observed partial rotation of the ·CHO group is represented more closely by the equation of Lowry and Hudson than by those of Natanson and of Kuhn and Braun. The validity of Hudson's rules of iso-rotation is discussed. H. F. G.

Nature and extension in space of scattering moments of optically active molecules. W. Kuhn and K. Bein (Z. physikal. Chem., 1933, B, 22, 406—422; cf. this vol., 889).—If the scattering moment corresponding with a vibration and consisting of two components localised at points in the mol. separated by a distance d is partly or wholly quadrupolar in character, then the relation $d \gg g\lambda/2\pi$, valid if the scattering moment were essentially dipolar, must be replaced by where g is the anisotropy factor and f the no. of electrons effective in the vibration at either point. This modification removes the difficulty that for very weak absorption bands vals. of d calc. from g are often many times the mol. dia-

meter; acceptable vals. are now obtained. If all the mols. are uniformly oriented relative to the incident light, total circular dichroism may be realised, in the sense that the system has finite absorption coeff. for right-circular light, whilst it does not respond at all to left-circular light. This would explain the behaviour of optically active substances in the liquid-crystal state. R. C.

Forced double refraction. K. F. HERZFELD and R. H. LEE (Physical Rev., 1933, [ii], 44, 625—631).—Mathematical. The forced double refraction induced in rock-salt and KCl by elastic stress, taking account of the Lorentz–Lorenz force and the " potential dip " due to the forced anisotropic arrangement of the ionic charges, is calc. N. M. B.

Dispersion of fused quartz in the short-wave infra-red. C. MÜLLER and A. WEITHAUER (Z. Physik, 1933, 85, 559—560).—The refractive index for fused quartz has been determined from 0·5 to 2·6 μ. A. B. D. C.

Existence of time lags in the Faraday effect. J. S. WEBB (Physical Rev., 1933, [ii], 44, 589—601).—An investigation of the min. produced by surge currents and oscillatory currents in a magneto-optic apparatus indicate that Allison's results (cf. this vol., 204) are not, as he assumes, due to a time lag in the Faraday effect, but to some unknown cause. N. M. B.

Variation in the Kerr electro-optical constant of nitrobenzene with temperature near a transition (9·6°). H. TROTTER, jun. (Physical Rev., 1932, [ii], 40, 1052).—A change in this const. at approx. 9·6 has been observed (cf. A., 1931, 899; 1932, 1190). L. S. T.

Electro-optical Kerr effect in gases. C. W. BRUCE (Physical Rev., 1933, [ii], 44, 682—686).—The Kerr const. B of CO_2 and N_2 measured as a function of density from 0·06 to 0·32 g. per c.c. and of temp. from 7·2° to 34·6° agrees with the Langevin–Born theory. The const. for H_2 was too small to be detected. N. M. B.

Natural classification of chemical compounds. III. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1933, 3, 269—278).—Theoretical. R. T.

Molecular structure. J. C. SLATER (Physical Rev., 1932, [ii], 41, 255—257).—The methods of Hund (A., 1932, 321) and Mulliken (*ibid.*, 902) for considering the structure of polyat. mols. are discussed in relation to those of Pauling (A., 1931, 670) and the author (*ibid.*, 1356). These methods are complementary and not antagonistic. L. S. T.

Theory of co-ordinative linking. III. Identification of absorption bands of complex salts. R. SAMUEL, A. A. H. KHAN, and N. AHMAD (Z. physikal. Chem., 1933, B, 22, 431—443; cf. A., 1927, 921).—Measurements of the absorption bands of various ammines in aq. solution show that all salts with co-ordinated NH_3 or $C_2H_4(NH_2)_2$ are characterised by two bands at about 500 and 350 mμ. If Cl′ or NO_2' enters the ammino complex, bands appear at 260 and 245 mμ. Complex cyanides have three band systems with principal max. at 315, 290, and 255 mμ. The effect of foreign ions on the absorption spectra of complex salts consists of a kind of Stark effect, which modifies the intensities of all the bands, and a polarisation or mol. deformation which affects only some of the bands, altering the frequency of the max. R. C.

Relation between co-ordination number and valency electrons in intermetallic compounds. F. LAVES (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1932, 519—524; Chem. Zentr., 1933, i, 3269—3270).—A discussion. A. A. E.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1933, [v], 19, 881—892). C. W. G.

Magnetism of free radicals. S. SUGDEN (Faraday Soc., Nov., 1933, Advance proof).—χ_μ, the term in the general mol. mass susceptibility equation $\chi_m=\chi_d+\ +\chi_r$, responsible for paramagnetism, should be about 1300 for odd mols. This is so for some inorg. odd mols. *e.g.*, NO, NO_2, ClO_2, and for org. free radicals. The hypophosphates are diamagnetic, and must therefore be derived from $H_4P_2O_6$, not H_2PO_3. The magnetic evidence shows that the K compound of p-$COPh{\cdot}C_6H_4Ph$ exists in Et_2O solution as the free radical. A. J. M.

Electronic structure and the interaction of some simple radicals. J. E. LENNARD-JONES (Faraday Soc., Nov., 1933, Advance proof).—The electronic structures of some related radicals are investigated to find out their mode of interaction with others, or their breakdown into simpler substances. A. J. M.

Three-dimensional models of the potential energy of triatomic systems. C. F. GOODEVE (Faraday Soc., Nov., 1933, Advance proof).—Instructions for the prep. of models representing the potential energy of triat. systems as a function of at. distances are given. The models for 3 H atoms, 1 C and 2 O atoms arranged in a line, and 2 Na and 1 Cl atom are described. A. J. M.

Free radicals in electrical discharges. W. D. HARKINS (Faraday Soc., Nov., 1933, Advance proof).—The apparatus required for the production of the electrodeless and glow discharges, respectively, in org. vapours is described. The characteristics of the discharges in various org. vapours are given. The principal radicals formed by these methods are CH, OH, C_2, NH, and CN. Bands corresponding with radicals more than diat. are absent. The energy of electron impact is probably the chief cause of the breakdown of the mols., although collisions of the second kind also play a part. The free radicals very rapidly recombine to give a substance of high mol. wt. A. J. M.

Determination of the probability of energy transfer during collisions. N. M. SEMENOFF (Faraday Soc., Nov., 1933, Advance proof).—Mathematical. The method described is based on the recombination of free radicals. A. J. M.

Free radicals in the electric discharge. E. J. B. WILLEY (Faraday Soc., Nov., 1933, Advance proof).—CH is formed in the decomp. of CH_4 by the electrical discharge. The presence of OH when the discharge is passed through H_2O vapour is discussed. NH

is probably formed in the discharge through NH_3 and mixtures of N_2 and H_2 under a variety of conditions. Its presence accounts for the Schuster band. A. J. M.

Free radicals and spectroscopy. R. MECKE (Faraday Soc., Nov., 1933, Advance proof).—The use of spectroscopic methods in the study of free radicals is described. A. J. M.

Magnetic susceptibility of argon. Measurements by A. Roth. W. GERLACH (Z. Physik, 1933, **85**, 545—547).—Precision measurements gave the susceptibility as $-19{\cdot}7\times10^{-6}$. A. B. D. C.

Variation of paramagnetic susceptibility with temperature. B. W. BARTLETT (Physical Rev., 1933, [ii], **44**, 687).—Corrections to an earlier paper (cf. A., 1932, 1191). N. M. B.

Diamagnetism of organic compounds and the influence of temperature and constitution. I. Primary alcohols, nitrobenzene, and *m*-cresol. B. CABRERA and H. FAHLENBRACH (Z. Physik, 1933, **85**, 568—591; cf. this vol., 1002).—MeOH, EtOH, hexyl, octyl, and dodecyl alcohols, $PhNO_2$, and *m*-cresol were investigated between $-50°$ and 130°. A. B. D. C.

Susceptibility of paramagnetic solutions. G. FOËX (Compt. rend., 1933, **197**, 749—751).—Recent results (cf. A., 1928, 454; this vol., 22) support the view that C and not χT (cf. this vol., 340, 664) in the equation $\chi(T-\theta)=C$ is to be taken as the Curie const. when calculating the magnetic moment of ions following Weiss' law, and θ is not small. C. A. S.

Paramagnetic Faraday effect with alums. H. KAUFMANN (Ann. Physik, 1933, [v], **18**, 251—264).—The Faraday effects of K Cr, NH_4 Cr, and NH_4 Fe alums have been examined, and by comparison with the isomeric K Al and NH_4 Al alums the paramagnetic components have been calc. The results are not in agreement with theory. J. W. S.

Recent researches on paramagnetism and atomic moments. G. FOEX (J. Phys. Radium, 1933, [vii], **4**, 517—532).—A general survey. N. M. B.

Electric field in paramagnetic crystals. C. J. GORTER (Physical Rev., 1932, [ii], **42**, 437—438).—Van Vleck's theory indicates that the metallic ion is surrounded by 6 mols. of H_2O in the hydrated salts of the Fe group, and by six O atoms in the octahydrated sulphates of Nd and Pr. L. S. T.

Ferromagnetic powders and magnetic susceptibility of rocks. G. GRENET (Compt. rend., 1933, **197**, 746—748; cf. A., 1930, 673; this vol., 1030). C. A. S.

Heavy hydrogen in contact with normal water. M. L. OLIPHANT (Nature, 1933, **132**, 675).—The heavy H content of mixtures of $He+H_2$ (containing heavy H) is greatly reduced by storage over H_2O. The mols. of heavy H probably undergo a process of exchange with the H mols. in the H_2O until concns. of heavy H in the liquid and gas are equal. L. S. T.

Heavy hydrogen and heavy water. ANON. (Nature, 1933, **132**, 536—538).—A summary. L. S. T.

Properties of heavy water. P. W. SELWOOD and A. A. FROST (J. Amer. Chem. Soc., 1933, **55**, 4335—4336).—The proportion of O^{18} is not increased during the production of heavy H_2O by electrolysis. By extrapolation, pure H^2H^2O has n_D^{20} 1·3281, η^{20} 14·2, and surface tension at 20° 67·8 dynes/cm. The magnetic susceptibility of 92% H^2H^2O is $-0{\cdot}65\times10^{-6}$. J. G. A. G.

Dissociation of nitrous oxide by light, and the electronic levels of ozone, nitrous oxide, and nitrogen dioxide. O. R. WULF and E. H. MELVIN (Physical Rev., 1932, [ii], **39**, 180; cf. A., 1932, 474).—The absorption observed from 2000 to 2300 Å. approx. is probably accompanied by the dissociation of N_2O into NO and N. The electronic levels of O_2, O_3, N_2O, and NO_2 are discussed. L. S. T.

Position of the hydrogen ions in the NH_4Cl lattice from electron diffraction. V. E. LASCHKAREV and I. D. USYSKIN (Z. Physik, 1933, **85**, 618—630).—The protons are $0{\cdot}95\pm0{\cdot}07$ Å. from the N atom. A. B. D. C.

Nuclear distances of mercuric chloride, bromide, and iodide. H. BRAUNE and S. KNOKE (Z. physikal. Chem., 1933, **B**, **23**, 163—170).—The distance apart of the nuclei has been determined by the electron diffraction method, the quotient by the sum of Pauling's ionic radii having the same val. for each halide. The frequency of flexional vibration has been calc. R. C.

Mean free paths of gases. J. A. ELDRIDGE (Physical Rev., 1932, [ii], **40**, 1050).—The mean free paths of H_2, He, N_2, and O_2, measured by a mol. beam method, are much $<$ the vals. determined indirectly from the kinetic theory (I). The difference is probably due to the neglect of the persistence of velocity in (I). L. S. T.

Constants of the nitrous oxide molecule. E. F. BARKER (Physical Rev., 1932, [ii], **41**, 369—370).—Revised data (cf. A., 1932, 108) are given. The moment of inertia of the N_2O mol. is now given as $66{\cdot}0\times10^{-40}$. L. S. T.

Dynamic reflexion of *X*-rays at ideal and especially absorbent crystals. M. KOHLER (Ann. Physik, 1933, [v], **18**, 265—298).—Mathematical. J. W. S.

Refraction of *X*-rays by glass. G ORBAN (Z. Physik, 1933, **85**, 741—753).—The dependence of the refractive index on angle of incidence was investigated. A. B. D. C.

Influence of chemical binding on absorption coefficients of light elements for ultra-soft *X*-rays. R. H. MESSNER (Z. Physik, 1933, **85**, 727—740).—The absorption coeff. for 44·5 and 68 Å. with H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, N_2, O_2, CO, and CO_2 varies systematically with chemical binding. The Z^4 and $\lambda^{2\cdot5}$ laws are obeyed in this region. A. B. D. C.

Crystal structure model. G. GLOCKLER (Rev. Sci. Instr., 1933, [ii], **4**, 529).—A new type of model consisting of hinged cellophane sheets carrying black and white dots, and folding flat, is described. N. M. B.

Structure of crystals. I. U. DEHLINGER (Physik regelmässig. Ber., 1933, **1**, 7—14; Chem. Zentr., 1933, i, 3535).—A review. A. A. E.

Molecular rotation in the solid state and the polymorphic relations of the univalent nitrates. F. C. KRACEK, T. F. W. BATH, and C. J. KSANDA (Physical Rev., 1932, [ii], **40**, 1034).—Rotation of the NO_3 group in KNO_3 is discussed. L. S. T.

Lattice geometrical conditions for slip planes in crystals. H. G. SOSSINKA, B. SCHMIDT, and F. SAUERWALD (Z. Physik, 1933, **85**, 761—771).—Plasticity cannot be explained by lattice geometry alone, and must be referred in addition to at. physics. A. B. D. C.

Photographic development of lines of slip in deformed silver chloride crystals. G. TAMMANN and G. BANDEL (Z. anorg. Chem., 1933, **214**, 403—406).—If a thin (cast) plate of AgCl is bent and afterwards floated on a dil. (1 : 7) metol–quinol developer, the lines of slip are more darkened than the remainder. The effect is still observed when the deformed plates are annealed for 2 hr. prior to development, whence it is inferred that the preferential darkening is not due to enhanced reactivity of the AgCl, but to separation of an impurity which catalyses the reduction. The impurity is not Ag, as it is not affected by prolonged treatment with Cl_2. F. L. U.

Isothermal crystallisation or transformation of a given mass as a function of time. G. TAMMANN (Z. anorg. Chem., 1933, **214**, 407—413).—If nuclei are formed only at the surface of a specimen, the bulk rate of crystallisation remains const. until the ingrowing crystals interfere. If nuclei are distributed at random throughout the mass, the curve describing the bulk rate of crystallisation is S-shaped. Examples are given to illustrate the course of the change. F. L. U.

Lattice constants of pure iron and iron–carbon alloys at temperatures up to 1100°. H. ESSER and G. MÜLLER (Arch. Eisenhüttenw., 1933—1934, **7**, 265—268).—The lattice parameter (P) of two specimens of electrolytic Fe and a specimen of carbonyl Fe, all melted in vac., have been determined in vac. at 20—1100°. For the α-phase the val. of P is not a linear function of the temperature (T) and an inflexion occurs in the P–T curve at the magnetic transformation point, the magnitude of which is different with the three specimens. For the γ-phase the P–T graph is a straight line. For Fe–C alloys P in the γ-field is not a linear function of the C content. In hypoeutectoidal steels P at 720° increases linearly with the C content; this fact does not appear to be in accordance with the equilibrium diagram. A. R. P.

Structure and gas content of nickel layers produced by cathodic sputtering. W. BÜSSEM and F. GROSS (Z. Physik, 1933, **86**, 135—136).—Ni layers deposited in H_2 or Ne+He are hexagonal or cubic, and in N_2 tetragonal, hexagonal, or cubic; the first layers could be transformed from one into the other, and also the second. The gas content and influence of temp. were also investigated. A. B. D. C.

Mosaic structure of cobalt crystals. F. BITTER (Physical Rev., 1932, [ii], **40**, 125).—Experimental verification of the existence of a block structure, as predicted by Zwicky, is furnished by the distinct deposits obtained on Co samples. L. S. T.

Does the change in lattice constants on formation of mixed crystals depend on particle size ? A. PHILLIPS and R. M. BRICK (Metallwirt., 1933, **12**, 161—162; Chem. Zentr., 1933, i, 3049).—In Al–Cu the contraction is the greater the smaller is the particle size of polycryst. material of equal Cu content. A. A. E.

Crystal structure of ammonium hydrogen carbonate. R. C. L. MOONEY (Physical Rev., 1932, [ii], 39, 861).—NH_4HCO_3 has a 7·29, b 10·79, and c 8·76 Å., 8 mols. per unit orthorhombic cell; space-group $Pccn$ The axial ratios are 0·676 : 1 : 2 (0·406). Relative intensity considerations indicate that the CO_3 groups lie approx. in planes parallel to the a face, in agreement with optical properties. Their dimensions are practically the same as in normal carbonates. The H atoms not belonging to the NH_4 groups appear to lie between the O atoms of different CO_3 groups. L. S. T.

Iridionitrites of ammonium, potassium, rubidium, cæsium, thallium, and barium. A. FERRARI and C. COLLA (Gazzetta, 1933, **63**, 507—513).—The compounds $M_3Ir(NO_2)_6$ (M=NH_4, K, Rb, Cs, and Tl, respectively) are isomorphous with a structure of the $K_3Co(NO_2)_6$ type. The vals. of a are 10·73, 10·57, 10·77, 11·17, and 10·73 Å., and of $d_{calc.}$ 2·812, 3·297, 3·856, 4·134, and 5·817, respectively. $Ba_3[Ir(NO_2)_6]_2$ has a 10·60 Å. and is also isomorphous with the univalent compounds. O. J. W.

Ferrites. II. Alkali, alkaline-earth, and lead ferrites. S. HILPERT and A. LINDNER [with A. WILLE and R. SCHWEINHAGEN] (Z. physikal. Chem., 1933, **B**, **22**, 395—405; cf. A., 1932, 985).—X-Ray examination shows that in their crystal structure K, Rb, Cs, Ca, Sr, Ba, and Pb ferrites are in many respects analogous, and differ completely from the spinel ferrites. With K, Sr, and Pb there exist in addition to the metaferrites compounds with the formula $MO,2Fe_2O_3$, which are able to take up > 6 mols. of Fe_2O_3 without producing any perceptible effect on the X-ray diagram. Sr metaferrite may be obtained in two different forms according as it is prepared from SrO or $SrCO_3$. The magnetisability–composition curve of Fe_2O_3–PbO mixtures exhibits a max. at $2PbO,3Fe_2O_3$, which, however, apparently represents a mixture. Amorphous *Rb ferrites* have been prepared by heating Rb_2CO_3 with Fe_2O_3. R. C.

Effective radii of hexammine cations $M(NH_3)_6^{\cdot\cdot}$ in crystals of fluorspar type. G. BÖDTKER-NÆSS and O. HASSEL (Z. physikal. Chem., 1933, **B**, **22**, 471—472).—Lattice consts. of chlorides, bromides, iodides, and perchlorates have been determined, M being Mg, Ca, Mn, Fe, Co, Ni, Zn, and Cd, and used to calculate the effective radii of the cations. The results show that the concept of effective radius can be advantageously applied to complex ions. R. C.

Crystal structure of potassium nitrilopentachloro-osmate and of Schlippe's salt. J. VER-

HULST (Bull. Soc. chim. Belg., 1933, 42, 359—375).—K_2OsNCl_5 has orthorhombic pyramidal symmetry and belongs to space-group C_{2v}^{12}. The unit cell has a 13·07, b 9·06, c 7·33 Å. and contains 4 mols.; $d_{calc.}$ 3·53. $Na_3SbS_4,9H_2O$ has a simple cubic lattice Γ_c, space-group T_1; the unit cell has a 12 02. Å. and contains 4 mols. H. S. P.

Crystal forms of carbamide oxalate and nitrate. P. GAUBERT (Bull. Soc. franç. Min., 1932, 55, 235—273; Chem. Zentr., 1933, i, 3308).—Conditions of production of three types of $2CO(NH_2)_2,H_2C_2O_4$ (I) and two types of $CO(NH_2)_2,HNO_3$ (II) are described. (I) is monoclinic, with $a:b:c=0·5642:1:0·4106$, β 97° 50′; n_g 1·6165, n_m 1·6116, n_p 1·3885; d 1·585. (II) is monoclinic, with $a:b:c=1·1556:1:0·9012$, β 123° 55′; n_g 1·654, n_m 1·647, n_p 1·375; d 1·071. A. A. E.

Physical chemistry of alumina–silica refractories. I. Role of silicon and aluminium in complex silicates. B. E. WARREN. **II. Structure of sillimanite and related materials.** W. H. TAYLOR. **III. Bauxites and mullites.** M. E. NAHMIAS (J. Amer. Ceram. Soc., 1933, 16, 412—417, 418—420, 420—421).—I *X*-Ray examination has shown that Si is surrounded tetrahedrally by O and the various structures are composed of these strongly linked SiO_4 groups. Although in some cases Al is surrounded tetrahedrally by O, it is generally associated with 6 O. In the complex silicates, *e.g.*, hornblendes, Al is substituted for part of the Si. The OH is associated with Al, Mg, Ca, etc. and never with Si. Proposed structures for the SiO_2–Al_2O_3 minerals are described. Asbestos, mica, and kaolin have sheet-like structures.

II. See A., 1932, 1079.

III. *X*-Ray examination shows that there is no compound intermediate between Al_2O_3,SiO_2 and $3Al_2O_3,2SiO_2$. SiO_2 in bauxites is present as kaolinite and the excess of Al_2O_3 chiefly as bohmite (Al_2O_3,H_2O). On heating bauxite to < 950° γ-Al_2O_3 and amorphous SiO_2 are formed, but above this temp. mullite appears and no sillimanite was found at 700°. The differences found between the Debye photographs of various mullites may be due to dissolution of TiO_2 and Fe_2O_3. In order to fit in with the unit cell and space-group, either the d or chemical formula of mullite needs adjustment. J. A. S.

***X*-Ray examination of some ceramic raw materials. III, IV.** T. NAKAI and Y. FUKAMI (J. Soc. Chem. Ind. Japan, 1933, 36, 559—562B).—III. Ceramic materials were heated to 1100° and the cryst. structures were examined. The fine grains of felspar (I) melt under this treatment, but not the coarser. There is no change in quartz (II) Clays give mullite (III) and cristobalite (IV).

IV. The same materials were heated for 8 hr. at 1200°, 1300°, and 1400°, respectively, and for 1 hr. at 1500°. (I) melts almost completely at 1200°, attacking any SiO_2 present. (II) changes partly into (IV) at 1200° and the amount changed increases with fineness of particle and time and temp. of heating. Al_2O_3 modifies its cryst. structure several times as the temp. rises, and finally becomes corundum at 1500°. In clays containing much kaolinite (V) the amount of (IV) formed decreases as the temp. rises above 1300° and becomes zero at 1500°. There is no change in the amount of (III) formed. Clays containing the same amounts of (V) and (II), but different amounts of (I), give practically identical *X*-ray photographs before heat-treatment, but different ones after heating at 1200—1500° because of the action of (I) on (II). M. S. B.

Crystal structure of troilite and magnetic pyrites. G. HÄGG and I. SUCKSDORFF (Z. physikal. Chem., 1933, B, 22, 444—452; cf. this vol., 342).—In the system Fe–S there exists at the composition FeS a hexagonal over-structure of the Ni arsenide type formed from this lattice by the longest basal diagonal becoming the a axis and the c axis being at the same time doubled. This over-structure vanishes between 51 and 52 at.-% S, leaving a Ni arsenide structure which persists up to about 55·5 at.-% The increase in S content is accompanied by a lattice contraction, but is shown by the d vals. to occur by filling of empty places in the Fe lattice by S. Such solid solutions are described as "subtractional" (cf. this vol., 1111). The reported transition points of FeS at 138° and 298° could not be confirmed. R. C.

***X*-Ray study of *p*-diphenylbenzene.** (MISS) L. W. PICKETT (Proc. Roy. Soc., 1933, A, 142, 333—345).—p-$C_6H_4Ph_2$ has a 8·08, b 5·60, c 13·59 Å., β 91° 55′, space-group $P2_1/a$, 2 mols. per unit cell. Evidence is adduced to show that the mol. is planar in form, and consists of regular hexagons of C atoms 1·42 Å. apart with a probable distance of 1·48 Å. between the hexagons. This latter distance is intermediate between the lengths of purely aliphatic and purely aromatic linkings. The position of the mol. may be defined by two successive rotations of 34° and 15·3° about the c and b axes from an original position in the (100) plane parallel to the c axis. L. L. B.

***X*-Ray study of konnjakumannan.** I. SAKURADA and K. HUTINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 287—301; cf. this vol., 544).—Konnjakumannan occurs in two modifications, one amorphous, the other cryst. The unit cell contains three hexose residues; the micelles orient themselves on stretching parallel to the direction of stretch. Absorption of H_2O by the cryst. modification causes the lattice to expand transversely to the fibre axis. D. R. D.

Crystal structure of insulin. G. L. CLARK and K. E. CORRIGAN (Physical Rev., 1932, [II], 40, 639).—*X*-Ray diffraction patterns obtained by using the $K\alpha$ radiation of Mg and Al give for insulin spacings of 130, 100, and 80 Å. and thus axial ratios 4/3 : 1 : 4/5. The crystals are positive, monoclinic, frequently becoming pseudo-hexagonal; there are 26 mols. per unit cell. L. S. T.

Structure of cellulose gels. V. Structure of natural cellulose fibre as revealed by *X*-ray analysis. VI. Structure of viscose rayon and cellophane as analysed by *X*-rays. K. ATSUKI and M. ISHIWARA (J. Soc. Chem. Ind. Japan, 1933, 36, 517—521B, 521—524B).—V. Data of *X*-ray photographs of hemp and cotton are given.

VI. *X*-Ray photographs are reproduced and data

given for viscose rayon and for sheet prepared by the spontaneous coagulation of viscose in the laboratory. A. G.

Structure of thin celluloid films. I. E. T. JONES (Phil. Mag., 1933, [vii], **16**, 793—808; cf. A., 1931, 1205).—Electron diffraction photographs have been obtained with thin films of celluloid in which the pattern is composed of two double patterns. It is suggested that each double pattern consists of two forms, having elliptical instead of circular rings. J. W. S.

Structure of thin celluloid films. II. E. T. JONES (Phil. Mag., 1933, [vii], **16**, 953—961; cf. preceding abstract).—Data for three additional patterns, obtained by passing cathode rays through a celluloid film, are recorded, and their origin is discussed. H. J. E.

Comparison of *X*-ray patterns of liquid crystals and the normal liquid phase of the same substance. W. KAST (Naturwiss., 1933, **21**, 737).—The *X*-ray diagrams obtained with the isotropic and the anisotropic melt of *p*-azoxyanisole using monochromatic (Cu $K\alpha$) radiation were compared. The photometer curves show practically no difference. In both cases groups of oriented mols. with approx. the same mol. aggregation must exist. A. J. M.

Cybotactic condition of ethyl ether in the region of the critical point. R. D. SPANGLER (Physical Rev., 1932, [ii], **42**, 907).—At const. pressure and rising temp. and sp. vol., the *X*-ray diffraction curves of Et_2O change from that typical of a liquid, with a pronounced peak (I) signifying cybotactic mol. groups, to that of a polyat. gas with no peak, signifying random mol. arrangement. (I) disappears approx. at the crit. vol. but not at the crit. temp. At intermediate temp. and sp. vols. the curves indicate that some of the mols. are in groups, whilst others are arranged at random. At const. sp. vol. the type of curve does not change with temp. within the pressure range examined, and beyond a certain sp. vol., approx. the crit. vol., no indications of groups occur. L. S. T.

Liquefaction. G. W. STEWART (Physical Rev., 1932, [ii], **42**, 907; cf. preceding abstract).—Although well-defined aggregates are essential to liquefaction, they can exist under other conditions, *e.g.*, at temp. $>$ and sp. vols. $<$ the crit. vals. Liquefaction does not require an increase in the no. of mols. per c.c. in the cybotactic groups; it may occur with the no. of aggregated mols. either const. or decreasing and pressure and temp. decreasing. The extent of the groups depends chiefly on sp. vol. Liquefaction depends on the possible existence of a second fluid phase in equilibrium and not directly on aggregation, as hitherto supposed. L. S. T.

Loss of heat by and temperature distribution in electrically heated wires. A. FARKAS and H. H. ROWLEY (Z. physikal. Chem., 1933, **B**, **22**, 335—343).—The discontinuity in the relation between temp. and heat loss from an electrically heated Ni wire in H_2 (A., 1932, 28, 917) is due, not to an abrupt change in the character of the surface, *e.g.*, by the formation or decomp. of a hydride, but to the temp. distribution becoming uneven; a similar effect is observed with Pt wires under comparable conditions. R. C.

Crystal structure and electrical properties. III. Lattice structure and conductivity of longitudinally magnetised bismuth single crystals. O. STIERSTADT (Z. Physik, 1933, **85**, 697—707; cf. this vol., 1109).—Longitudinal magnetisation gives conductivity dependent on the lattice structure, as was observed with transverse fields. A. B. D. C.

Superconductivity. F. ZWICKY (Proc. Nat. Acad. Sci., 1933, **19**, 818—823).—Theoretical. H. J. E.

Electrical conductivity of single crystals. W. LEHFELDT (Z. Physik, 1933, **85**, 717—726).—The electrical conductivity of Li, Na, and K fluoride, of Li, Na, K, Ag, and Tl chloride, of Na, K, Rb, Ag, and Tl bromide, and of Na and K iodide was investigated for single crystals between $-180°$ and their m.p. Ohm's law is obeyed, and just below m.p. the conductivity appears to be a const. of the material, but at lower temp. it depends on the working and purity of the crystal. A. B. D. C.

Law of discontinuous distribution of ferromagnetic Curie points. III. Applications. IV. Applications to variation of Curie point in metallic solid solutions. R. FORRER (J. Phys. Radium, 1933, [vii], **4**, 427—439, 501—512; cf. this vol., 667).—III. The law of Curie points is applied to a no. of ferromagnetics to give the electronic orientation lattice, and to the transformation of hexagonal Co and the temp. of deformation limit of magnetite, showing that the law can be extended to paramagnetics. The strong binding of the FeO_4 group in magnetite is shown. Application to certain alloys which show an electronic lattice only by temp. anomaly indicates that the lattice can exist in the absence of a magnetic moment of the constituent atoms. In the Heusler alloys the lattice is indicated by the existence of a magnetic moment.

IV. Using the respective methods of atoms considered individually, and electronic distribution among the atoms of the alloys, application of the variation of the function Θ for solid solutions of Fe–Ni, Fe–Co, Fe–Si, Ni–Co, Ni–Pd, and Ni–Cu shows a linear variation of the no. of contacts with the at. proportion, and further supports the proportionality of the no. of contacts to the square of the Curie points. The linear variation allows the determination of the no. of contacts of the dissolved atom with the atoms of the solvent metal, and, in certain cases, the no. of electrons in the electronic orientation lattice. N. M. B.

Change of magnetic susceptibility of platinum, copper, and silver caused by cold-working. K. HONDA and Y. SHIMIZU (Nature, 1933, **132**, 565—566).—Theoretical and observed vals. are in satisfactory agreement, and support the conclusion that the effect of cold-working on the susceptibility is a real one. L. S. T.

Magnetic anisotropy of colloidal crystals of graphite. A. GOETZ, A. FAESSLER, and A. B. FOCKE (Physical Rev., 1932, [ii], **39**, 553).—The large, artificially prepared, single crystals of Ceylon graphite (this vol., 1128) have high magnetic anisotropies,

$\chi_{\parallel}/\chi_{\perp}$ being 1 : 18 as compared with 1 : 4 to 1 : 7 for the natural crystals. L. S. T.

Temperature variation of viscosity and of the piezoelectric constant of quartz. K. S. Van Dyke (Physical Rev., 1932, [ii], 42, 587).—The viscosity of quartz, defined as the ratio of logarithmic decrement to Young's modulus, increases from $0{\cdot}7\times10^{-17}$ at $-80°$ to $2{\cdot}4\times10^{-17}$ at 40°, the increase being approx. twice as rapid at the upper as at the lower temp. At room temp., the variation is of the order of 1% per degree. The piezoelectric const. of quartz decreases from $5{\cdot}57\times10^{4}$ abs. e.s.u. at $-80°$ to $5{\cdot}27\times10^{4}$ at 40°. This variation is ten times as large at 40° as at $-80°$. L. S. T.

Mechanostriction and the ΔE effect. N. Akulov and E. Kondorsky (Z. Physik, 1933, 85, 661—671). A. B. D. C.

Temperature coefficient of the elastic modulus of ferromagnetic substances. M. Kersten (Z. Physik, 1933, 85, 708—716).—An expression is deduced for this coeff., and is applied to the "Elinvar" ferromagnetic alloys. A. B. D. C.

Elastic constants of single crystals of copper. R. Kimura (Sci. Rep. Tohoku, 1933, 22, 553—564).—The results are not in agreement with Cauchy's relation. The modulus along the trigonal axis is about twice that along the tetragonal axis. E. S. H.

Remanence in single crystals of iron. C. J. Gorter (Nature, 1933, 132, 517—518). L. S. T.

Nature of polish layers. J. A. Darbyshire and K. R. Dixit (Phil. Mag., 1933, [vii], 16, 961—974).—Polished surfaces of Bi, Sb, Zn, Te, Cd, Au, Ag, Pb, Mo, Cu, Cr, Se, and Si were shown by the electron diffraction method to be amorphous, resembling a supercooled liquid (cf. French, this vol., 769). Except for Se and Si, the interat. distance in the polished surface was abnormally low compared with the val. in a crystal. PbS and FeS_2 on polishing gave no indication of an amorphous surface; very small surface crystals were produced. H. J. E.

Characteristics of praseodym[ium]. B. Brauner (Coll. Czech. Chem. Comm., 1933, 5, 279—286).—Mainly historical. The mol. wt. of $PrCl_3$, determined ebullioscopically, is normal, indicating that the Pr is tervalent. In PrO_2, however, it is quadrivalent, since PrO_2 behaves analogously to CeO_2 and MnO_2, and not as a true peroxide. Pr_5O_9 is a definite compound. D. R. D.

Effect of a magnetic field and of temperature on the specific heat of gases. T. Okamura (Sci. Rep. Tohoku, 1933, 22, 519—536).—Using a field of 4000 gauss, no influence on the sp. heat of H_2, O_2, N_2, or CO_2 was observed. Determinations of the sp. heat of O_2 and N_2 at 20—180° verify the theory of sp. heat of diat. gases at high temp. E. S. H.

Atomic heats, and the heats of fusion and transformation of gallium, indium, and thallium. W. A. Roth, I. Meyer, and H. Zeumer (Z. anorg. Chem., 1933, 214, 309—320).—Sp. heats from 0° to 24°, 0° to 154°, and 99° to 350°, respectively, and the heats of fusion, were measured. The elements obey Dulong and Petit's law. The heat of transformation of Tl at the transition temp. (232·3°) = 0·36 g.-cal. per g. Tabulated vals. for 25 metals show that the entropy change on fusion is not const. H. J. E.

Heats of dissociation of hydrogen and nitrogen. W. W. Lozier (Physical Rev., 1933, [ii], 44, 575—581).—An improved apparatus of Ta, to eliminate contact potential errors, was employed. Results are: H_2^+ $2{\cdot}59\pm0{\cdot}03$, H_2 $4{\cdot}43\pm0{\cdot}03$, N_2^+ $6{\cdot}73\pm0{\cdot}02$, N_2 $7{\cdot}90\pm0{\cdot}02$ volt. N. M. B.

Heat capacities of *cis*- and *trans*-dichloroethylenes. A. R. Olson and F. W. Brittain (J. Amer. Chem. Soc., 1933, 55, 4063—4068).—From determinations of the velocity of sound in *cis*- and in *trans*-$C_2H_2Cl_2$ at pressures between 112 and 193 mm., the val. of C_v is $12{\cdot}14\pm0{\cdot}26$ g.-cal. per mol., which is independent of temp. between 22° and 244°, thus indicating that nine vibrational degrees of freedom have such high frequencies that they do not contribute to the sp. heat below 250°. J. G. A. G.

M.p. and b.p. of potassium perrhenate. D. Vorländer and G. Dalichau (Ber., 1933, 66, [*B*], 1534—1536).—The true m.p. of $KReO_4$ is probably 2—4° below 552°; it has b.p. 1375°/763 mm., 1359°/752 mm. The Tl salt has m.p. 527° (corr. $\pm3°$) and the Ag salt, m.p. 430° (corr.), decomp. about 455° (corr.). H. W.

Thermal expansion of certain crystals with layer lattices. (Miss) H. D. Megaw (Proc. Roy. Soc., 1933, A, 142, 198—214).—The thermal expansion of brucite, $Ca(OH)_2$, and hydrargillite has been measured from the change in their lattice spacings as determined by *X*-rays. The crystals all possess layer structures. The expansion of phlogopite has also been measured. The hydroxides show marked anisotropy, the expansion coeff. perpendicular to the layer being > those in the layer. L. L. B.

Thermal expansion of quartz by *X*-ray measurements. A. H. Jay (Proc. Roy. Soc., 1933, A, 142, 237—247).—*X*-Ray powder photographs of quartz have been taken for a no. of temp. from 18° to 730°, and the various corresponding lattice dimensions have been found. From the form of the expansion curve above and below the $\alpha\longrightarrow\beta$ change point the transformation is given as 579°, in agreement with the acknowledged temp. 575°. An expansion law is found for each of the directions parallel and perpendicular to the principal axis which is identical with those found by using optical methods of measurement. The results indicate that for Ag and quartz there is no difference between the coeffs. of expansion as measured by *X*-rays and by optical methods. L. L. B.

Thermal expansion of antimony. P. Hidnert and H. S. Krider (Physical Rev., 1932, [ii], 42, 911).—Data for the linear expansion of cast Sb between room temp. and 560° are recorded. L. S. T.

Density of a vapour in equilibrium with a liquid near the critical temperature. J. S. Tapp, E. W. R. Steacie, and O. Maass (Canad. J. Res., 1933, 9, 217—239).—An apparatus is described for determining the density of both the liquid and gaseous phase almost simultaneously up to and past

the point where the meniscus vanishes, special precautions being taken to eliminate errors due to temp. gradients, which, it is shown, greatly alter the results. Measurements with Me_2O cast considerable doubt on van der Waals' classical theory of the continuity of state. O. J. W.

Vapour pressure of sulphur at 50°. R. R. H. Brown and J. J. Muir (Physical Rev., 1932, [ii], **41**, 111).—Assuming the S to be present as S_8 the v.p. at 50° is 0·000155 mm. L. S. T.

***i*–*s*-Diagram for water up to 400 atm. between 0° and 370°.** E. Schlegel (Z. tech. Physik, 1933, **14**, 105—107; Chem. Zentr., 1933, i, 2790).

Table and diagrams for mercury vapour. H. Eck (Forsch. Ingenieurwes., 1933, **A**, **4**, 21—25; Chem. Zentr., 1933, i, 2790).

Viscosity of vapours of organic compounds. III. T. Titani (Bull. Chem. Soc. Japan, 1933, **8**, 255—276).—Measurements have been made of η of a no. of org. vapours at temp. between 120° and 300°. Collision diameters are calc. in good agreement with those derived from vals. of b in van der Waals' equation. A. S. C. L.

Viscosity of various refrigerants in liquid and vapour state in relation to pressure and temperature. H. Stakelbeck (Z. ges. Kalte-Ind., 1933, **40**, 33—40; Chem. Zentr., 1933, i, 2986).—Vals., determined with a Lawaczek viscosimeter, are tabulated for CO_2 (5—120 atm.), NH_3 (1—26 atm.), SO_2, (0·5—8 atm.), and MeCl (0·5—7 atm.) between −20° and 40° (NH_3 to 80°). A. A. E.

Thermal expansion of copper alloys. P. Hidnert (Physical Rev., 1932, [ii], **39**, 551).—Data for Cu alloys containing Sn and Pb, and Sn, Zn, and Pb are recorded for 20—700°. The substitution of 5% Zn and 5% Pb for 10% Sn has little, if any, effect on the coeff. of expansion. L. S. T.

Nickel–chromium alloys. Y. Matsunaga (Japan Nickel Rev., 1933, **1**, 347—363).—Thermal, magnetic, and microscopical observations show that Ni and Cr are completely miscible in the liquid state, but form two solid solutions which have a eutectic at 1346°, containing 51% Cr. Determinations of rate of oxidation, hardness, and electrical resistance show that the best heat-resisting alloys contain 15—35% Cr. E. S. H.

Transformation and properties of gold–copper alloys. E. Schuch (Metallwirt., 1933, **12**, 145—147; Chem. Zentr., 1933, i, 2742—2743).—The tetragonal phase stable at low temp. is little harder than the cubic mixed crystals, whilst the intermediate form obtained by slow transformation is characterised by great strength and hardness. The cause of the phenomenon is discussed. A. A. E.

***X*-Ray studies of antimony–lead and tin–lead alloys.** I. Obinata and E. Schmid (Metallwirt., 1933, **12**, 101—103; Chem. Zentr., 1933, i, 2602—2603).—Pure Pb has a 4·9389 Å.; mixed-crystal formation with Sb or Sn is accompanied by a diminution in the lattice const., approx. proportional to the at.-% of addendum, and amounting to 0·010% and 0·034%, respectively, for 1 at.-%. A. A. E.

***X*-Ray study of the plastic working of magnesium alloys.** L. G. Morell and J. D. Hanawalt (Physical Rev., 1932, [ii], **40**, 1035).—*X*-Ray photographs of Mg alloys (I) produced at various temp. show that rolling, forging, or extruding results in characteristic fibre structures. Forged (I) possess a [001] fibre axis lying in the direction of forging, whilst extruded (I) show a [210] fibre axis lying in the direction of extrusion. Dependence of grain size and distortion of the micro-crystals on the temp. and degree of working is also revealed. L. S. T.

Influence of rate of cooling on the structure of eutectics. G. Tammann and G. Moritz (Z. anorg. Chem., 1933, **214**, 414—426; cf. A., 1929, 388).—The structure of binary, ternary, and quaternary eutectics of Bi, Cd, Pb, Sn, and Zn has been studied microscopically in relation to the rate of cooling. In general, the structure is granular when cooling is slow, and fibrous when it is rapid. With sufficiently rapid cooling the fibres are not always resolvable. The hardness of Sn–Zn eutectics decreases with thickening of the cryst. fibres caused by heating at 182°. The tensile strength of wires of Cd–Pb–Sn eutectics in which the fibres are parallel to the axis is twice that of wires in which the directions have a random distribution, but even in the latter case the strength is > that calc. by the mixture rule. F. L. U.

***X*-Ray diffraction patterns of mixtures.** M. Y. Colby (Physical Rev., 1932, [ii], **39**, 861).—Powder photographs of mixtures of freshly-prepared Zn and Cu filings are identical with the composite photographs of the components (cf. A., 1931, 671). Mixtures of freshly-prepared Cu and old Zn dust show eight new lines which correspond with the eight strong lines of ZnO. L. S. T.

New orientations forming in a crystal of silver–copper during precipitation. C. S. Barrett and H. F. Kaiser (Physical Rev., 1932, [ii], **40**, 1035).—Changes in the orientation of individual grains of a solid solution of Cu (4%) in Ag produced by annealing at 300° have been followed by means of *X*-rays. L. S. T.

Magnetic susceptibility of electrolytically charged palladium–hydrogen alloys. B. Svensson (Ann. Physik, 1933, [v], **18**, 299—304).—The magnetic susceptibility of Pd decreases with increasing H concn., the χ–H/Pd curve consisting of two straight lines with a sharp inflexion point at a H/Pd ratio 0·66. The slight paramagnetism found for Pd saturated with H_2 is attributed to impurity. By regarding the constituents of the alloys as Pd and PdH, comparison can be made with similar data for Pd–Ag and Pd–Au alloys. J. W. S.

Influence of strong magnetic fields on the hardening of metals and alloys. H. Esser and H. Cornelius (Metallwirt., 1933, **12**, 210—213; Chem. Zentr., 1933, i, 3492).—No effect on steels containing 1·18% C was detected. A. A. E.

System iron–nickel–aluminium. W. Köster (Arch. Eisenhüttenw., 1933—1934, **7**, 257—262).—The space model for the Ni–Al–Fe system up to 30% Al and equilibrium diagrams for const. Ni contents of 10, 20, 30, 40, 50, 60, and 80% have been constructed.

NiAl forms an uninterrupted series of solid solutions with α-Fe so that the system consists solely of α- and γ-phases with a restricted α+γ field. The peritectic reaction liquid+α⇌γ in the Fe–Ni merges gradually into the eutectic equilibrium liquid⇌α+γ in the Ni–Al system, reaching a min. at 1320° and 60—70% Ni. In alloys with > 15% Ni there are two α+γ fields, the first being very narrow and corresponding with that in the Fe–Al system and the second extending from room temp. up to about 1000° with 4—12% Al for the 10% Ni alloy. In alloys with a high Ni content these two fields merge into one which is narrower at the eutectic than at room temp. The magnetic transformation point of Fe–Al alloys is raised at first with increasing addition of Ni, then reduced with > 50% Ni. The α-phase is ferromagnetic up to 20% Al and 70% Ni. Microstructures of characteristic alloys after various heat-treatments are illustrated. A. R. P.

System iron–cobalt–aluminium. W. Koster (Arch. Eisenhuttenw., 1933—1934, **7**, 263—264).—This system is similar to the corresponding Ni system (preceding abstract) except that the α+γ field is much narrower and with > 25% Fe no longer extends to room temp.; the transition from peritectic to eutectic equilibrium occurs at about 50% Co. With const. Al content the magnetic transformation point (I) is raised by increasing the Co content; with 10% Al the curve shows a max. at 50% Co (980°). For the saturated α-solid solution with 10% Al (I) is 890° and for the saturated γ-solid solution (I) rises with decreasing Al content from 640° in the Co–Al system to 940° with 80% Co in the Co–Fe system. A. R. P.

α–γ-Transformation in ternary systems of iron. W. Koster and W. Tonn (Arch. Eisenhuttenw., 1933—1934, **7**, 193—200).—From a review of published equilibrium diagrams of ternary systems of Fe it is shown that the space models of these systems can be divided into three basic types according to whether the two binary Fe systems in the ternary system have an expanded or a constricted α+γ field. The three basic models are illustrated and their characteristics are discussed, together with the numerous special modifications of these types caused by limited solid solubility or by the appearance of a new phase. A. R. P.

Hall effect and resistance of hydrogen-charged palladium–silver and palladium–gold alloys. J. Wortmann (Ann. Physik, 1933, [v], **18**, 233—250; cf. A., 1932, 789).—The Hall effect (I), unlike the photo- (II) and thermo-electric (III) effects, of Pd–Ag and Pd–Au alloys is decreased by adsorbed H_2. The (I)–concn. curve shows a max. at 60% Ag and a subsidiary max. at 20%. The adsorbed H_2 has a max. influence on (I) at 40% Ag; the same concn. is characteristic of the max. shown by (II) and (III). (I) of Pd–Au alloys is a max. at 65% Au, whether adsorbed H_2 is present or not, but max. reduction in this and the other effects is observed at 40% Au. H_2 lowers the conductivity of Pt–Ag alloys of high Pd content, but the lowering diminishes with increasing Ag concn. and vanishes at 70% Ag. H_2 also lowers the conductivity of Pd–Au alloys containing < 30% Au, raises it for 30—80% Au, and has no influence at higher Au concn. The subject is discussed from the viewpoint of the Sommerfeld electron theory. J. W. S.

Superconductivity of alloys from a phase theory viewpoint. C. Benedicks (Z. Metallk., 1933, **25**, 197—202).—The relations between the five types of binary alloys of Roozeboom and the superconductivity diagrams (concn. [*C*]–transition to superconductivity [*S*]) are discussed. The *C*–*S* curve in all cases shows inflexions corresponding with phase-field boundaries in the ordinary equilibrium diagrams and is particularly useful in indicating heterogeneity in solid solutions. All the known facts of superconductivity phenomena are in accordance with Weber's phoretic theory of metallic conductance. A. R. P.

Superconductivity of alloy systems. J. F. Allen (Phil. Mag., 1933, [vii], **16**, 1005—1044; cf. A., 1932, 800).—The superconductivity (I) of the systems Au–Sn, Au–Pb, Ag–Sn, Ag–Pb, Cu–Sn, Cu–Pb, and Tl–Sn has been examined, and the characteristics for each of three structural types have been determined. In all types of structure (I) varies continuously with concn. H. J. E.

Use of the radioactive lead isotope, thorium-*B*, in the solution of metallographic problems. G. Tammann and G. Bandel (Z. Metallk., 1933, **25**, 153—156, 207—209).—When Th-*Em* is allowed to impinge on a strip of metal for 24—48 hr. the surface becomes covered with Th-*B*. If the metal is melted the Th-*B* becomes distributed throughout the liquid and on solidification produces a characteristic pattern when a section of the metal is placed on a photographic plate. This pattern consists of more or less regularly distributed black spots in the case of Pb, Tl, Mg, and Cd, indicating that the Th-*B* is sol. in the metal. In Bi, Sb, Sn, Ni, Ag, Au, and Zn the grain boundaries are thrown into sharp relief, indicating complete segregation of the Th-*B* along these, *i.e.*, the solubility of Th-*B* in these metals is $< 1\times10^{-6}$%, which is much < the accepted solid solubility of its isotope, ordinary Pb. Alloying with Th-*B* serves to reveal the presence of slag inclusions in Fe and steel and of Al_2O_3 in Al, since the Th-*B* collects in these impurities. When molten Al or Zn containing Th-*B* is shaken with Pb, Bi, or Tl all the Th-*B* passes into the heavy metal. The changes which take place in the crystal structure of a metal during cold-work and annealing can be followed by adding Th-*B* and taking radiograms at the various stages. A. R. P.

Densities of mixtures of benzene with phenylethyl alcohol and with methyl salicylate [at 25°]. R. C. Glowaski and C. C. Lynch, jun. (J. Amer. Chem. Soc., 1933, **55**, 4051—4052).—Data for the complete range of binary mixtures are recorded. J. G. A. G.

Azeotropic mixture of *sec.*-butyl alcohol and *sec.*-butyl bromide. D. F. Houston (J. Amer. Chem. Soc., 1933, **55**, 4131—4132).—The azeotropic mixture, b.p. 87·2°/749 mm., n_D^{20} 1·4256, contains 71·0±0·4 mol.-% *sec.*-BuBr. Vals. of for the complete range of mixtures are recorded. J. G. A. G.

Thermal expansion of the binary liquid system $Na_2B_4O_7$–B_2O_3. M. P. Volarovitsch (Bull. Acad. Sci. U.R.S.S., 1933, **7**, 663—674).—The sp. vol. (v)–temp. curves of the system $Na_2B_4O_7$–B_2O_3 have been determined at 500—1300° by a dilatometric method. The coeff. of expansion of B_2O_3 is greatest at the m.p. The val. of v for mixtures is < for the pure components. Batschinski's formula $\eta = c/(v-\omega)$ (A., 1913, ii, 928), where ω and c are consts., applies at temp. > 820° for the pure components, and > 820° to 950° for mixtures. R. T.

Dielectric constants: ethyl alcohol–diethyl ether and carbamide–water solutions between 0° and 50°. J. Wyman, jun. (J. Amer. Chem. Soc., 1933, **55**, 4116—4121).—The data obtained by a resonance method (λ=3·6—20 m.) cover the entire concn. range of EtOH–Et_2O mixtures and mixtures containing 0—42·5 wt.-% $CO(NH_2)_2$. The latter data lead to heats of dilution which are consistent with the observed vals. for KCl solutions in aq. $CO(NH_2)_2$ (cf. A., 1931, 42). J. G. A. G.

Dielectric constant and electric polarisation of mixtures in the neighbourhood of the critical point. A. Piekara (Physical Rev., 1932, [ii], **42**, 448—449).—Data for the system C_6H_{14}–$PhNO_2$ are recorded. L. S. T.

Existence of a complex in racemising solutions. A. N. Campbell and A. J. R. Campbell (Trans. Faraday Soc., 1933, **29**, 1240—1247).—Determinations of d, viscosity, n, and heat of dissolution of K Na tartrate (I) and of mandelic acid in different conc. solutions of NaOH show that complex formation in the (I) solution is probable. The complex is believed to have been isolated in an impure state, and probably contains 20—40% NaOH. Viscosity determinations give evidence of complex formation with mandelic acid. E. S. H.

Solubility of gases. II. Solubility of argon. B. Sisskind and I. Kasarnovski (Z. anorg. Chem., 1933, **214**, 385—395; cf. A., 1931, 1365).—Absorption coeffs. of A in 22 org. liquids, including homologous series of alcohols and ketones, have been measured at pressures of 20—125 atm. The solubilities are determined largely by the polarisability, and are scarcely affected by the dipole moment of the solvents. The results are discussed from the viewpoint of London's theory of van der Waals forces. F. L. U.

Solubility of salts in H^2H^2O. H. S. Taylor, E. R. Caley, and H. Eyring (J. Amer. Chem. Soc., 1933, **55**, 4334—4335).—1 g. of H_2O containing 92% H^2H^2O dissolves only 0·305 g. of NaCl at 25° and 0·289 g. of anhyd. $BaCl_2$ at 20°. J. G. A. G.

Solubility of potassium and sodium ferrocyanides in aqueous solutions of ammonia. A. Tettamanzi (Gazzetta, 1933, **63**, 575—579).—$K_4Fe(CN)_6$ and $Na_4Fe(CN)_6$ are pptd. unaltered from aq. solution by NH_3. The solubilities of the two salts in various aq. NH_3 solutions at 18° have been determined. O. J. W.

Molasses formation. IV. Equilibrium of the system sucrose–water–sodium or potassium sulphate at 30° and the viscosity of the liquid phase. K. Nishizawa and M. Amagasa (J. Soc. Chem. Ind. Japan, 1933, **36**, 535—537B).—The influence of the sulphates on the solubility of sucrose and of the latter on the solubility of the former has been examined. The relative viscosity of the saturated solution of sucrose is increased by the addition of Na_2SO_4, whilst the relative saturation decreases, but no marked effect is produced by K_2SO_4. The influence of the sulphates on viscosity appears to be much < that of the carbonates and acetates. Similar investigations with $CaSO_4$ and $CaCO_3$ indicate that these have no appreciable influence on molasses formation. M. S. B.

Solubilities of salts in liquid ammonia. I. Solubility of sodium chloride and the saturated vapour pressure of the solution. S. Abe and R. Hara (J. Soc. Chem. Ind. Japan, 1933, **36**, 557—559B).—Determinations have been made between −23° and 30°. Both solubility and v.-p. depression curves show an increase with rise of temp. up to −9·7°, and then a fall; this is the transition point between $NaCl,5NH_3$ and NaCl. M. S. B.

Acetamide as a solvent. O. F. Stafford (J. Amer. Chem. Soc., 1933, **55**, 3987—3988).—In general, there is a close correspondence between the solubilities of inorg. compounds in NH_2Ac at 100° (approx.) and in H_2O. Of 400 org. substances tested, only cellulose is quite insol. The wide range of solvent action of NH_2Ac is related to its constitution. J. G. A. G.

Heat of sorption of water vapour by massive gold. E. P. Barrett (J. Amer. Chem. Soc., 1933, **55**, 4006—4009; cf. this vol., 1014).—The integral heat of sorption, H millical. per sq. cm., for W g. of H_2O vapour is $H=13{\cdot}3W^{0\cdot310}$, according to which it is probably impossible to remove the last mols. of H_2O from a Au surface. J. G. A. G.

Analysis of hydrogen absorption phenomena. M. C. Johnson (Trans. Faraday Soc., 1933, **29**, 1139—1155).—When H_1 strikes a surface from a gas phase it may be reflected, re-evaporated as H_1 or H_2, or it may form a layer in static or kinetic equilibrium. H_2 may be re-evaporated as H_1, as H_2, or as H_2 with transformation into the spin-isomeride, or it may form a stable layer, or diffuse into the solid as H_1. The conditions for the formation of unimol. structures in static or kinetic equilibrium are considered, and the experimental data classified according to the type of equilibrium. A. G.

Statistical derivation of adsorption isotherm for a binary gas mixture. G. Damkohler (Z. physikal. Chem., 1933, **B**, **23**, 58—68).—The isotherm has been derived for unimol. adsorption disregarding intermol. forces in the film, but making no assumption as to the nature of the motion of the gas mols. in either phase. In the adsorption on a homogeneous surface one component must be preferentially adsorbed over the whole concn. range and the composition of the adsorbed phase must remain const. for a given composition of the gas phase independent of the pressure. If the difference in adsorption potentials of the gases greatly exceeds RT, the selectivity of the adsorption must decrease as T rises, but if it is

commensurable with RT no general principle as to the effect of variation in T can be laid down. R. C.

Adsorption of mixtures of nitrogen and argon. G. DAMKOHLER (Z. physikal. Chem., 1933, **B**, **23**, 69—88).—Data for N_2, A, and mixtures on SiO_2 gel at 90—163° abs. and under 100—700 mm. and for mixtures on norit (charged with CO_2 and gas-free) at 111° abs. and 250 mm. are recorded. The results indicate that at first N_2 is preferentially adsorbed; this is ascribed to the operation of the valency forces of the adsorbent. The adsorption potential on SiO_2 gel exceeds that of A by some 200 g.-cal. When the adsorbed film becomes thicker these forces become ineffective, and A is then adsorbed preferentially. The saturation of the most active centres on norit with CO_2 reduces the adsorption of N_2. It is suggested that in multimol. adsorption the principal effect of fall in pressure or rise in temp. is to disperse the outer parts of the adsorbed film. In this region the adsorption of the various components is parallel with their condensabilities (cf. preceding abstract). R. C.

Study of the adsorptive power of active charcoals by the polarographic method. B. A. GOSMAN (Chim. et Ind., 1933, **29**, Spec. no., 199—203).—The dropping Hg cathode method has been applied to the determination of the adsorption of methylene-blue on various forms of active charcoal, and also to the adsorption of $H^{\cdot}$ from HCl solutions. The activity of active C can be characterised by its effect on the max. of polarographic curves. J. W. S.

Discontinuity in the adsorption of gases, vapours, and liquids on solid surfaces at the critical temperature under critical pressure: system propylene–alumina. H. E. MORRIS and O. MAASS (Canad. J. Res., 1933, **9**, 240—251).—An apparatus for studying the adsorption of gases, vapours, and liquids on solid surfaces in the region of the crit. temp. and pressure is described. In the system C_3H_6–Al_2O_3 adsorption from the gas and vapour phases indicates the formation of a surface complex unstable at low pressure and high temp. The density of the adsorbed phase is $>$ that of the bulk phase. There is no discontinuity in the adsorption process with a change from vapour to gaseous state, but there is a marked discontinuity with a change from liquid to gaseous state, there being no adsorption from the liquid state. O. J. W.

Adsorption of mercury vapour by certain adsorbents and catalysts, and manganese dioxide amalgam. E. V. ALEXEEVSKI [with F. J. RATSCHINSKI] (J. Gen. Chem. Russ., 1933, **3**, 360—366).—Various active charcoals, $Al(OH)_3$, kaolin, and Zn dust absorb negligible quantities of Hg vapour. Hopcalite and CoO are feeble absorbents, whilst activated MnO_2, pptd. from aq. $KMnO_4$ by $MnSO_4$, absorbs 42% of its wt. after 5 years of exposure to Hg vapour. The action of MnO_2 is ascribed to its capacity for forming amalgams, which vary in appearance from a black powder (MnO_2 : Hg 1 : 1) to a mobile, silvery liquid (1 : 7). The liquid amalgams form adherent films on glass, porcelain, leather, and other surfaces. R. T.

Dependence of Richardson's law and Traube's rule on the optimum adsorption range of aliphatic homologues (aldehydes). E. MICULICICH (Arch. exp. Path. Pharm., 1933, **172**, 373—383).—The adsorption (I) of CH_2O, MeCHO, EtCHO, $Pr^{\alpha}CHO$, and $Pr^{\beta}CHO$ on charcoal in dil. aq. HCl with various concns. of aldehyde has been examined in relation to Traube's rule. (I) varies with the no. of C atoms, especially under optimum conditions. For the corresponding homologous alcohols, the toxicities found by Dold (A., 1906, ii, 558) yield a curve which is the mirror-image of that representing the (I)-activities of the aldehydes when the activities are expressed in a reversed form. This is in accord with Richardson's law. F. O. H.

Ionic exchange and sorption of gases by chabazite. E. RABINOWITSCH and W. C. WOOD (Nature, 1933, **132**, 640; cf. A., 1932, 458).—The relation between the sorptive power of chabazite (I) and its ionic content has been studied in experiments on the sorption of H_2 and of N_2 at —190° by samples of natural (I) from Rübendorfel, Czechoslovakia, which had been boiled for 200 hr. in solutions containing $K^{\cdot}$, $Na^{\cdot}$, $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, or $La^{\cdot\cdot\cdot}$. The sorption by such samples is different from that of natural (I) containing mainly $Ca^{\cdot\cdot}$, especially in the case of Na, K, and Cd. The exchange of $Ca^{\cdot\cdot}$ for $Na^{\cdot}$ alters the sorptive power for H_2 only slightly (small increase) compared with a large decrease for N_2. The sorption of N_2 by K-(I) is decreased still further, practically to zero. The change in sorptive power is reversible, since the sorption isotherms for Ca-(I), prepared by the reconversion of K-(I), are practically identical with that of the original Ca-(I). Replacement of one $Ca^{\cdot\cdot}$ (r 1·06 Å.) by two $Na^{\cdot}$ (r 0·98 Å.) thus decreases the sorption space of the crystals for N_2 but not for H_2, whilst replacement by two $K^{\cdot}$ (r 1·33 Å.) closes the sorption space even for H_2. Experiments with the bivalent ions $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, and $Ba^{\cdot\cdot}$ (r 1·06—1·43 Å.) show differences in sorption from that of the original (I) $\not>$ 10%. L. S. T.

Influence of varying the relative concentrations of reagents on the activity of aluminium hydroxide. V. K. MARKOV (Ukrain. Chem. J., 1933, **8**, 34—35).—The adsorptive capacity for C_6H_6 vapour of $Al(OH)_3$ pptd. from $Al_2(SO_4)_3$ exhibits abrupt and considerable variations when the concn. of the added aq. NH_3 is increased. R. T.

Corrections for thermo-molecular flow. F. C. TOMPKINS and D. E. WHEELER (Trans. Faraday Soc., 1933, **29**, 1248—1254).—The magnitude of the Knudsen effect is discussed and the rapidity with which it varies with pressure in the case of fairly wide tubing is emphasised. Results of calibrations made on an apparatus used for studying adsorption at low temp. and pressures are given. E. S. H.

Absorption of dyes by cellulose. I. Kinetics of the absorption of sky-blue FF on viscose sheet, in the presence of various amounts of sodium chloride. S. M. NEALE and W. A. STRINGFELLOW (Trans. Faraday Soc., 1933, **29**, 1167—1180).—The absorption of purified sky-blue FF by small discs of sheet viscose has been followed colorimetrically.

Absorption is negligible in the absence of NaCl. When NaCl is present the kinetics of absorption agree with the assumption that the process is controlled by diffusion of the dye through the viscose. The diffusion const. is 10^{-7} (cm.^{2} per min.) at 100°, and passes through a max. at a concn. of NaCl of 10 g. per litre. A. G.

Sorption of vapours by nitrocotton. J. W. McBain, S. J. Good, A. M. Bakr, D. P. Davies, H. J. Willavoys, and R. Buckingham (Trans. Faraday Soc., 1933, **29**, 1086—1100).—Sorption isotherms with the sorption balance have been determined for nitrocotton (12·27% N) in a no. of solvents. From the best to the poorest solvents the range of sorption is 100-fold. At lower relative pressures the laws of sorption are followed, but at higher pressures the structure is opened up and sorption increases; liquid condenses in the pores which are thereby produced. The predominating factor is persorption, but the data do not agree with any one of the various hypotheses (solution, heterogeneous chemical equilibrium, capillary condensation, compressed film) which have been put forward. When nitrocotton containing sorbed vapour is heated for 4 days at 60° a change termed "consolidation" occurs and the sorption falls. A. G.

Adsorptive power of silica gels precipitated together with salts of metals. V. K. Markov (Ukrain. Chem. J., 1933, **8**, 16—20).—The adsorptive power of SiO_2 gel (I) for C_6H_6 vapour is diminished by pptg. (I) together with salts of Al, $Cr^{...}$, $Fe^{...}$, Ni, Co, $Cu^{..}$, $Sn^{..}$, or $Sb^{...}$; except in the case of Ni and Co the inactivation is proportional to the metal oxide content. R. T.

Adsorption of benzene vapour from air on alkaline, neutral, and acid silica gels. M. O. Charmandarian and E. L. Kopeliovitsch (Ukrain. Chem. J., 1933, **8**, 21—33).—The mechanical strength and transparency of SiO_2 gels increase, whilst the adsorptive capacity C for C_6H_6 vapour diminishes, with increasing $[H^{\cdot}]$ of the medium at the moment of pptn. For alkaline gels (I) C is diminished, and for neutral (II) and acid (III) gels increased, by drying before washing. (I) may be activated by washing with aq. HCl, and (II) by washing with aq. NH_3, whilst the C of (III) is unaffected by acids or alkalis. R. T.

Evaporation and diffusion of volatile materials into an inert gas stream. E. Preston (Trans. Faraday Soc., 1933, **29**, 1188—1198).—Experiments with glasses containing PbO, Na_2O, and K_2O (cf. B., 1932, 982) suggest that evaporation at normal pressures is essentially a process by which a thin vapour or "supersurface" layer, in equilibrium with the liquid phase, diffuses into the passing gas. The vapours of PbO, Na_2O, and K_2O are assumed to be unimol. E. S. H.

Ratio of molecular heat of vaporisation to molecular surface energy for crystals and liquids. R. Kaischev and L. Krastanov (Z. physikal. Chem., 1933, **B**, **23**, 158—162).—From the work of separation of an idealised homopolar crystal it is deduced that the ratio is always > 2; the same conclusion is extended to liquids. R. C.

Exchange of hydrogen between water and hydrogen compounds dissolved in it. K. F. Bonhoeffer and G. W. Brown (Z. physikal. Chem., 1933, **B**, **23**, 171—174).—Observations on solutions in "heavy" H_2O have shown that in solutions of NH_3 and NH_4 salts there is continual exchange of H atoms between solvent and solute, and that in sucrose solutions there is exchange of H atoms of the OH groups with H atoms of the solvent. R. C.

Chemical action of electrolytes in changing surface energy at the boundaries: metal–mineral oil–aqueous salt solution. II. M. S. Golombik, J. S. Lev, and N. N. Petin (J. Gen. Chem. Russ., 1933, **3**, 279—290).—Mineral oil is removed from forged Fe surfaces by immersion in a solution containing 1% NaOH and 1% Na_3PO_4 at 15—17°, and passing a current (c.d. 0·01—0·02 amp. per sq. cm.) during 20—30 min., reversing the direction of the current every 5—10 min.; a.c. is not applicable. The degreasing effect is unaffected by varying the concn. of Na_3PO_4, and adversely affected by increasing or diminishing that of NaOH. The velocity of degreasing increases rapidly with rising temp. The temp. coeff. per 10° is 1·2 for both chemical and electrolytic degreasing. R. T.

Formation of oxide films on gold and iron. W. J. Shutt and A. Walton (Trans. Faraday Soc., 1932, **29**, 1209—1216).—The passivity induced in Au on treatment with alkalis is traced to the formation of a film of Au_2O_3 and simultaneous production of H_2, which is adsorbed by the Au. Subsequent anodic treatment renders the Au completely passive. The oxide film is removed easily by dil. HCl, but the adsorbed H_2 prevents the further action of alkalis. Conc. HNO_3 and acid $KMnO_4$ do not produce a detectable film on Au. The presence of adsorbed H_2 in the metal is shown by the more negative potential acquired. E. S. H.

Electrical properties of surface layers. K. Lark-Horovitz and J. E. Ferguson (Physical Rev., 1932, [ii], **42**, 907).—Using a Po electrode as sounding device, the potential at the interface air–liquid has been investigated for H_2O, electrolyte solutions (I), and unimol. layers of stearic and oleic acids (II) spread on the surface of (I). The surface of (I) does not consist of a pure H_2O layer, for ions diffuse into it. The surface layers (II) act like solid electrolytes, and when the p_H changes their behaviour resembles that of a H_2 electrode on the acid side and that of a Na electrode on the alkaline side. The surface of pure H_2O which has not been cleaned as for surface tension experiments appears to be covered with a film of org. substance acting like the fatty acids above. The phenomena observed with these layers are closely analogous to those observed with glass, quartz, and paraffin films. L. S. T.

Surface charge of large particles in liquids. H. A. Abramson (Physical Rev., 1932, [ii], **41**, 386—387).—For negatively-charged surfaces of graphite, glass, cellulose, collodion, and paraffin oil and ions which do not reverse the sign of charge, the surface charge density–concn. curves are simple and represent typical adsorption with an initial steep slope (I) and

saturation at 0·01*M* concn. of salt. (I) varies markedly with the nature and valency of the anion, *e.g.*, for glass I>Br>Cl, but the differences diminish as saturation is approached. L. S. T.

Interaction between soot films and oil. S. C. Blacktin (Nature, 1933, **132**, 515—516).—A criticism (cf. this vol., 1010). L. S. T.

***In vitro* experiments on the osmosis of aluminium through various artificial and animal membranes.** H. Kowalzyk (Mendel Bull., 1933, 5, 68—73).—Observations have been made with aq. $Al_2(SO_4)_3$ (0·1 mg. Al per c.c.) on one side of the membranes and H_2O on the other. Ch. Abs.

Electro-osmosis. I. Electrokinetic potential difference at the interface in acid electrolytes of varying concentration. H. Isobe and S. Imai (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, **12**, 790—813).—Data are given for HCl, H_3PO_4, AcOH, $CH_2Cl{\cdot}CO_2H$, HCO_2H, $H_2C_2O_4$, maleic, fumaric, succinic, and citric acids. D. R. D.

Viscosity of aqueous solutions as a function of the concentration. II. Potassium bromide and potassium chloride. G. Jones and S. K. Talley (J. Amer. Chem. Soc., 1933, **55**, 4124—4125; cf. this vol., 347).—The viscosities, η, at 25° of 0·001—3·75*N*-KBr and 0·5—3*N*-KCl are recorded. For 0·01—3·75*N*-KBr η is <, but for 0·001—0·005*N*-KBr is >, that of H_2O as predicted by Jones and Dole (A., 1929, 1385). J. G. A. G.

Accuracy of Einstein's viscosity law for strong electrolytes. H. Tollert (Naturwiss., 1933, **21**, 693).—Theoretical. A. J. M.

Amphoteric oxyhydrates, their high molecular compounds and solutions. XX. *iso*- and Heteropolytungstic acids and the optical absorption of 1-tellurium-1-hexatungstic acid. G. Jander and H. Witzmann (Z. anorg. Chem., 1933, **214**, 275—280; cf. this vol., 1118).—The addition of $HClO_4$ or H_2TeO_4 to aq. Na_2WO_4 shifts the light-absorption curve from approx. 2500 Å. to 4000—2800 Å. The change is attributed to complex ion formation, and the results are compared with those on adding H_3AsO_4, H_3PO_4, or HIO_4. H. J. E.

Dielectric constants of aqueous solutions at very high frequencies. E. Plötze (Ann. Physik, 1933, [v], **18**, 288—298).—The electrolyte effect for aq. solutions of $CuSO_4$, $La(NO_3)_3$, and $K_4Fe(CN)_6$ of concn. up to $2\times10^{-3}M$ has been investigated by Drude's first method with a wave-length of 60 cm. No change of dielectric const. with concn. could be detected. The results are in agreement with the Debye–Onsager–Falkenhagen theory. J. W. S.

Theory of non-stationary phenomena in electrolytes and some problems relating to electrolytes. H. Falkenhagen and W. Fischer (Physikal. Z., 1933, **34**, 786—788).—The dispersion effect in liquids, and some unsolved problems relating to the behaviour of electrolytes, are discussed. A. J. M.

Influence of convection on Brownian motion. I. M. Satô (Z. Physik, 1933, **85**, 676).—A reply to Sitte (this vol., 901). A. B. D. C.

[Influence of convection on Brownian motion.] K. Sitte (Z. Physik, 1933, **85**, 677—678).—A reply to Sato (this vol., 460). A. B. D. C.

Demonstration of the Brownian movement. M. Satô (Sci. Rep. Tohoku, 1933, **22**, 598—613).—An apparatus is described and the theory worked out. E. S. H.

Colloid correlation principle. S. C. Blacktin (Chem. and Ind., 1933, 781; cf. this vol., 777).—Examples of the operation of this principle in the transformation of certain natural colloid systems into their successors are given. A. R. P.

Effect of hydrogen-ion concentration on the flocculation values of [ferric,] chromic, and aluminium oxide sols. M. H. Bedford, W. H. Keller, and J. L. Gabbard (J. Amer. Chem. Soc., 1933, **55**, 3953—3956).—The stability of Cr^{III} and Al oxide sols towards added electrolytes increases with fall of p_H from 5·7 to 3·5, but the pptn. vals. of $FeCl_3$ and $AlCl_3$ are const. within certain ranges of p_H. The constancy is probably due to the buffer action of the hydrolysed salts (cf. A., 1931, 304). J. G. A. G.

Clarifying action of fuller's earth. M. E. Fogle and H. L. Olin (Ind. Eng. Chem., 1933, **25**, 1069—1073).—A fuller's earth containing 1·2% of zeolitic Ca was found to flocculate $Fe(OH)_3$–H_2O sol by adsorptive action, HgS–EtOH sol and HgS–$COMe_2$ sol by a combination of adsorptive and zeolitic action, the latter being regarded as the replacement of univalent peptising ions in the sol by $Ca^{\cdot\cdot}$ ions from the earth. The relative effects of these factors vary considerably with the zeolitic Ca content of the earth. D. K. M.

Condition of cellulose compounds in solution. I. Optical rotation of cellulose acetate. J. Duclaux and (Mme.) A. Dobry (Bull. Soc. chim., 1933, [iv], **53**, 724—728).—[α] is independent of concn. in thirteen solvents, and bears no obvious relation to the nature of the solvent. [α] is a linear function of λ, the lines for all the solvents being concurrent. A theoretical explanation is offered. D. R. D.

Structure of cellulose gel. VII. *X*-Ray study of cellulose nitrate gel. K. Atsuki and M. Ishiwara (J. Soc. Chem. Ind. Japan, 1933, **36**, 540—544B).—The structure of the film of cellulose nitrate (I) containing 11·2—11·4% N is nearly amorphous, although the *X*-ray diagram indicates a tendency to form mol. cryst. aggregates. The viscosity of (I) prepared at a higher nitration temp. is < when prepared at a lower temp., indicating that depolymerisation occurs at the higher temp. At the same time the *X*-ray pattern becomes more diffuse, suggesting that the film is more cryst. and has less internal distortion and weaker mechanical properties. A film prepared from an $COMe_2$ solution has a more uniform structure than one prepared from an Et_2O–EtOH solution, which forms a network with internal distortion. In the presence of glyceryl nitrate a mol. compound of this with (I) is obtained. M. S. B.

Viscosity of silk solution. I. Effect of nickel and copper in the ammoniacal solution. H. Sobue and S. Manago (J. Soc. Chem. Ind. Japan,

1933, **36**, 576—579B).—η is determined for solutions of silk in NH_3–H_2O containing Cu and Ni. J. L. D.

Action of alkaline copper solutions on silk fibroin. II, III. Y. TAKAMATSU (J. Soc. Chem. Ind. Japan, 1933, **36**, 566—568B; cf. B., 1932, 415).—II. In Schweitzer's solution 90% solubility of fibroin (I) is reached in ½ hr. and dissolution is complete in 4 hr. The solubility of (I) in Cu–amine solution increases with the amount of (I) present up to a max., after which it decreases. This is comparable with the behaviour of colloidal solutions. The mol. ratio of (I) at its max. solubility to the Cu content of the solution is 1, and from such a CuO–$C_2H_4(NH_2)_2$ solution a compound can be isolated in which the mol. ratio of (I) : Cu : amine is 1 : 1 : 1. The smallest amount of Cu and amine necessary to dissolve a definite amount of (I) can also be expressed by this ratio.

III. A solid phase of definite mol. composition, undissolved (I) : Cu : amine = 2 : 1 : 1, may exist in contact with the solution of max. solubility previously described. This suggests that there is probably definite chemical reaction taking place and not simply adsorption. M. S. B.

Calcium acetate gels. H. HENSTOCK (Trans. Faraday Soc., 1933, **29**, 1101—1107).—Gels formed by the addition of various liquids to a solution of $Ca(OAc)_2$ in MeOH are described. A. G.

Bound water of gelatin gels. D. J. LLOYD and T. MORAN (Nature, 1933, **132**, 515).—H_2O can be squeezed out of gelatin (I) in a collodion–canvas ultra-filter. The equilibrium concn. of the gel at different pressures increases with a rise in pressure up to approx. 2000 lb. per sq. in. The concn. of (I) in the gel at this pressure is 60%, in fair agreement with the val. obtained at −20° by the freezing method (A., 1932, 466). The view that H_2O in (I) exists as (i) firmly bound or "combined" H_2O and (ii) loosely bound or "free" H_2O is thus confirmed. 1 g. of (I) combines with approx. 0·5 g. of H_2O. L. S. T.

Discontinuous diffusion in gelatin. (MLLE.) S. VEIL (Compt. rend., 1933, **197**, 756—758; cf. this vol., 224).—A drop of solution of Na_2S, $Pb(OAc)_2$, $Pb(NO_3)_2$, or $HgNO_3$ on moist gelatin gives a zoned aureole (the last with reduction); tartaric acid, or Na, K, or NH_4 tartrate gives an aureole composed of spots, and Na, K, or NH_4 phosphate an intermediate aureole, the inner ring being cryst. C. A. S.

Influence of the reaction of the medium during coagulation on the structure of silica gel. I. M. O. CHARMANDARIAN and V. K. MARKOV (Ukrain. Chem. J., 1933, **8**, 1—15).—The mean diameter of the pores of SiO_2 gel, and its sp. gravity, diminish with increasing [H·] at the moment of flocculation. *X*-Ray spectra indicate that this transition is associated with increasing irregularity in the microcryst. structure of the gels. R. T.

Ageing of fresh aluminium hydroxide gels. R. FRICKE and K. MEYRING (Z. anorg. Chem., 1933, **214**, 269—274).—Freshly pptd. $Al(OH)_3$ in contact with aq. NaOH is transformed successively into the less sol. bohmite (Al_2O_3,H_2O) and bayerite (Al_2O_3,$3H_2O$). The changes are correlated with p_H measurements. H. J. E.

Elastic properties of glycerol-gelatin gels and of gelatin gels hardened with formaldehyde. E. HATSCHEK (Trans. Faraday Soc., 1933, **29**, 1108—1131).—Methods are described for determining Young's modulus for gelatin in compression, data being reproducible to 3%. Gels containing 8—12% of gelatin have well-defined moduli for stresses > 45 g. per sq. cm. The modulus is increased by addition of sucrose or glycerol (I), but the increase bears no simple relation to the concn.; the modulus of (I) gels increases with time. The time required for an imposed compression to become irreversible increases with increasing (I) content. A. G.

Gels. IV. Swelling of silica gel. V. Effect of neutral electrolytes on the syneresis of silica gels. D. G. R. BONNELL (Trans. Faraday Soc., 1933, **29**, 1217—1220, 1221—1226; cf. A., 1932, 123, 572).—IV. Electrolyte-free SiO_2 gel, stored in distilled H_2O at 70°, takes up large quantities of H_2O, swells, and is gradually peptised. The process is reversible. The swelling pressure is low.

V. The effect of NaCl, KCl, Na_2SO_4, or K_2SO_4 on the syneresis of SiO_2 gel is slight. The initial velocity of exudation and the total amount of liquid exuded increase with increasing concn. of electrolyte up to a certain concn., after which added electrolyte causes a decrease in the amount of exuded liquid. The setting time and the period of induction decrease rapidly with increasing concn. of electrolyte. E. S. H.

Electrophoresis of lecithin in the presence of neutral salt; the dual nature of the charge. C. W. PRICE and W. C. M. LEWIS (Trans. Faraday Soc., 1933, **29**, 1181—1188).—A lecithin sol containing a small amount of $BaCl_2$ may be regarded as a dispersion of a simple amphoteric substance, free from adsorption effects, the isoelectric charge of which is found to agree with the val. previously calc. (this vol., 778). The effect of varying the concn. of $BaCl_2$ is in agreement with theory. The total charge of the particles in 0·01*N*-citrate is due in part to ionisation of the amphoteric groups and in part to adsorption of negative ions at the fatty surfaces. The adsorption charge passes through a min. at the isoelectric point of the amphoteric groups. E. S. H.

Law of force between the molecules in a liquid or gaseous mixture. R. D. KLEEMAN (Physical Rev., 1932, [ii], **39**, 871).—Theoretical. L. S. T.

Displacement of equilibrium at constant volume. R. ÉTIENNE (Compt. rend., 1933, **197**, 986—988; cf. this vol., 783). C. A. S.

Law of displacement of chemical equilibrium. J. E. VERSCHAFFELT (Compt. rend., 1933, **197**, 753—754; cf. this vol., 783).—Mathematical. C. A. S.

Displacement of chemical equilibrium by mass changes. J. E. VERSCHAFFELT (Natuurwetensch. Tijds., 1933, **15**, 146—148).—Theoretical. Le Chatelier's law is not necessarily applicable to gaseous mixtures unless the vol. remains const. H. F. G.

Spectral physics and thermodynamics. Calculation of free energies, entropies, specific

heats, and equilibria from spectroscopic data and the validity of the third law. H. ZEISE (Z. Elektrochem., 1933, **39**, 758—773, 895—909).—A review.

Determination of the ionisation constant of slightly volatile weak acids by fractional distillation. P. JAULMES (J. Chim. phys., 1933, **30**, 556—559).—A method is devised whereby the ionisation const. of a non-volatile or slightly volatile weak acid is determined by distilling its Na salt in dil. solution with an acid of low volatility (such as AcOH) of which the ionisation const. is known. Results are given for salicylic and lactic acids. E. S. H.

Solubility of naphthenic acids in water and determination of their dissociation constants. A. B. MALYATSKI and L. Y. MARGOLIS (Azerbaid. Neft. Choz., 1933, No. 3, 75—81).—Baku naphthenic acids from naphtha, kerosene, and gas oil have, respectively, acid val. 316·5, 259·9, 195·2; mol. wt. 176·8, 216, 287; dissociation const. ($\times 10^{-7}$) 8·84, 8·21, 6·02; solubility in H_2O (mg. per litre) 37, 22, 7; hydrolysis const. of Na salt ($\times 10^{-8}$) 1·13, 1·21, 1·66. CH. ABS.

Activity coefficients of hydrochloric acid in aqueous solutions containing either sodium or potassium perchlorate. S. J. BATES and J. W. URMSTON (J. Amer. Chem. Soc., 1933, **55**, 4068—4073).—The activity coeffs. have been calc. from the e.m.f. of the cell Pt,H_2|0·046—0·25M-HCl+0·0—089M-$NaClO_4$ (or -$KClO_4$)|AgCl,Ag at 25°. $NaClO_4$ has the same influence on the activity coeff., α, of HCl as NaCl. There is thus no difference between the effects of salts with and without a common ion. $KClO_4$ and KCl produce equal changes in α, but in general, the effects are sp. J. G. A. G.

Activity coefficients of hydrochloric acid in aqueous solutions containing either sodium dithionate or perchloric acid. P. G. MURDOCH and R. C. BARTON (J. Amer. Chem. Soc., 1933, **55**, 4074—4079).—The activity coeffs., α, have been calc. from the e.m.f. of the cell Pt,H_2|0·01—0·5M-HCl+0·0—0·5M-$Na_2S_2O_6$ (or 0·025—0·9M-$HClO_4$)|AgCl,Ag at 25°. With increasing ionic strength, α at first decreases and then increases, and in the case of $HClO_4$ rises to vals. > that (α_0) for pure HCl at the same ionic strength, μ. The results conform to the equation $\log \alpha = \log \alpha_0 + k(\mu - m)$, where m is the concn. of HCl and k is a const. characteristic of both electrolytes (cf. preceding abstract). J. G. A. G.

Activity of potassium in dilute potassium amalgams. H. E. BENT and E. S. GILFILLAN (J. Amer. Chem. Soc., 1933, **55**, 3989—4001).—From the e.m.f. of K–Hg concn. cells between 0° and 50° the partial molal free energy, heat content, and entropy of K and Hg have been calc. The solubility of K in Hg has been determined. The deviations from Raoult's law are consistent with the existence of slightly dissociated compounds in the liquid phase. The free energy of formation of KHg_{12} (s) is −23,430 g.-cal. per mol. and the heat of formation in solution is −25,705; the heat of dissolution in saturated solution is 8114. J. G. A. G.

Volatilisation of silica and copper in steam. J. GILLIS (Natuurwetensch. Tijds., 1933, **15**, 153—154).—Amorphous SiO_2 is more volatile in steam than quartz; this is shown by the quantities of willemite formed on the surface of ZnO placed at a distance of 5 cm. from the SiO_2 in a H_2O atm. at 300 atm. pressure. Cu cylinders weighing 20 g. lost about 50 mg. in steam at 300 atm. after 3 days, but cassiterite and rutile showed no change. H. F. G.

Iron–nitrogen system. S. NISHIGÔRI (Tech. Rep. Tohoku, 1933, **11**, 68—92).—Magnetic and X-ray analysis, electric resistance measurements, and micrographic examination of thin wires of electrolytic Fe heated in NH_3, and then in N_2 at 650° for 40 days, have confirmed the equilibrium diagram of the Fe–N system proposed by Lehrer (A., 1930, 996, 1121). Fe_6N does not exist and the non-variant reactions at 605° and 650° are eutectoidal. A. R. P.

M.-p. diagram of refractory oxide [mixtures] with lime. H. J. REUSCH and H. VON WARTENBERG (Heraeus Vacuumschmelze [10th Anniv. Vol.], 1933, 349—355).—CaO forms eutectics with Cu_2O (28% CaO, 1140°), BeO (50% CaO, 1470°), ThO_2 (24% CaO, 2300°), Mn_3O_4 (15% CaO, 1450°), NiO (36% CaO, 1750°), and CoO (36% CaO, 1420°). The m.-p. diagram of mixtures of CaO and TiO_2 shows max. at CaO,TiO_2, $2CaO,TiO_2$, and $3CaO,TiO_2$ and eutectics at 12% CaO, 1420° and 52% CaO, 1780°. A. R. P.

Thermal analysis of system HCl–BCl_3. W. GRAFF (Compt. rend., 1933, **197**, 754—755; cf. this vol., 676).—The simple diagram shows a eutectic at −134·5°±1·0 and 44±1% BCl_3. The transition point of HCl (cf. A., 1924, ii, 820) is −176° and is perceptible in mixtures containing > 48% BCl_3. C. A. S.

Binary system lead iodide–potassium iodide. H. S. VAN KLOOSTER and E. I. STEARNS (J. Amer. Chem. Soc., 1933, **55**, 4121—4123).—Significant points are PbI_2, m.p. 412°±1, $KPbI_3$, m.p. 349°, KI, m.p. 686°, and the eutectics with 69 and 47·5 mol.-% of PbI_2 at 321° and 346°, respectively. J. G. A. G.

Active oxides. LXVII. Aluminium oxide and its additive products with water (thermodynamics of the equilibrium in systems with two solid phases). G. F. HUTTIG and F. KOLBL (Z. anorg. Chem., 1933, **214**, 289—306; cf. this vol., 1111).—The processes of dehydration, and of the addition of H_2O to the dehydrated product at 20°, have been studied for pptd. $Al(OH)_3$ gel, bohmite, bayerite, and diaspore. The results are discussed in relation to the thermodynamic equilibrium. H. J. E.

System cadmium nitrate–nitric acid–water. A. SIEVERTS and W. PETZOLD (Z. anorg. Chem., 1933, **214**, 396—402; cf. this vol., 1013).—Isotherms have been determined for 0°, 15°, 25°, 35°, 45°, and 50°. No Cd H nitrates exist. F. L. U.

Solubilities of complex metal thiocyanates. III. System $Ba(CNS)_2$–$Co(CNS)_2$–H_2O. V. CUVELIER (Natuurwetensch. Tijds., 1933, **15**, 177—180).—The 25° isotherms are recorded. The compound $BaCo(CNS)_4,8H_2O$ has a large range of

stability and separates when the saturated solution contains > 5% of $Co(CNS)_2$ or >20% of $Ba(CNS)_2$. H. F. G.

Systems (*a*) ammonium *d*-tartrate–lithium *d*-tartrate–water, and (*b*) ammonium lithium *d*-tartrate–ammonium lithium *l*-tartrate–water. A. N. CAMPBELL and L. SLOTIN (J. Amer. Chem. Soc., 1933, 55, 3961—3970).—The solubility data refer to 0°, 30°, and 60°. The transition point $Li_2T,2H_2O \longrightarrow Li_2T+2H_2O$ is 21·67° (T=$C_4H_4O_6$). The stability of the *double salt* $(NH_4)_2Li_2T_2$ increases with rise of temp., and the *racemate* $(NH_4)_2Li_2T_2,H_2O$ exists at all temp. J. G. A. G.

Absorption of carbon dioxide in aqueous sodium carbonate–hydrogen carbonate solutions. II. Rate of absorption. C. R. HARTE and E. M. BAKER (Ind. Eng. Chem., 1933, 25, 1128—1132).—In solutions which are 1—2*N* with respect to Na, the absorption coeff. in the temp. interval 25—63° is independent of the [Na'], and decreases with increase of the [HCO_3'] from 0·2 to 0·6*N*. At const. [HCO_3'] the coeff. doubles with a temp. rise of 22°. The selection of the optimum [HCO_3'] for CO_2 absorption and removal by boiling is discussed. H. F. G.

System ammonium carbamate–carbamide–water. K. G. CLARK, V. L. GADDY, and C. E. RIST (Ind. Eng. Chem., 1933, 25, 1092—1096).—The equilibrium has been approached from both sides and at temp. between 135° and 200°. The % of $CO(NH_2)_2$ at equilibrium rises from 42·0 at 135° to 49·5 at 190° in " Rezistal " vessels and at a wt. : vol. ratio of 0·9 g. per c.c., and from 42·7 to 52·1 in Pyrex glass vessels at a ratio of 1·0. The yield of $CO(NH_2)_2$ is inversely proportional to the wt. : vol. ratio, and is a max. at 190°. H. F. G.

Hydrolytic decomposition of tricalcium silicate. B. TAVASCI (Annali Chim. Appl., 1933, 23, 413—427).—In the system $CaO–SiO_2–H_2O$ at ordinary temp. and pressure, the solid phase in equilibrium with cryst. $Ca(OH)_2$ and liquid has sensibly the composition $5CaO,3SiO_2$,aq., so that the hydrolysis of Ca_3 silicate may be expressed by: $3(3CaO,SiO_2)+aq.=5CaO,3SiO_2,aq.+4Ca(OH)_2$. The hydrosilicate formed resembles zeolite in its behaviour. When the solid $Ca(OH)_2$ disappears, the concn. of CaO in the liquid falls rapidly to vals. below that corresponding with the decomp. of Ca_2 aluminate. When this condition is established, puzzuolana and slag cements should have greater chemical stability than fused cement. T. H. P.

Cause of molasses formation. II. Equilibrium of the ternary system sucrose–water–sodium (or potassium) carbonate at 30° and the viscosity of the liquid phases. III. Equilibrium in the ternary system sucrose–water–sodium (or potassium) acetate at 30° and the viscosity of the liquid phases. K. NISHIZAWA and M. AMAGASA (J. Soc. Chem. Ind. Japan, 1933, 36, 497—501B, 501—504B; cf. A., 1931, 1005).—II. Triangular and solubility diagrams are given. The solubility of sucrose (I) in H_2O is raised by the addition (unless very small) of Na_2CO_3 or K_2CO_3, and the solubility of the carbonates is raised by (I), the chief solid phases being $Na_2CO_3,7H_2O$ and $K_2CO_3,1·5H_2O$. The *compound* $C_{12}H_{22}O_{11},Na_2CO_3$ is found. Addition of Na_2CO_3 or K_2CO_3 to aq. (I) raises the viscosity > corresponds with the increased concn. of (I).

III. Triangular and solubility diagrams are given. Moderate amounts of NaOAc or KOAc increase the solubility of (I) and (I) increases that of the acetates, the chief solid phases being $NaOAc,3H_2O$ and $2KOAc,H_2O$. Acetates also increase largely the viscosity of the liquid phase. A. G.

Decomposition pressures of nitrates and sulphates. II. Vanadyl sulphate and lead nitrate. B. NEUMANN and A. SONNTAG (Z. Elektrochem., 1933, 39, 799—806).—The reaction $2VOSO_4 \rightleftharpoons V_2O_5+SO_3+SO_2$ begins at 410° and is completely reversible. The solid product, unlike the commercial substance, is readily sol. in warm H_2SO_4. The decomp. pressure over the range 704—826° abs. is affected very considerably by small changes of temp. The SO_3 pressure reaches 1 atm. at 610° C. (by extrapolation). The calc. heat of formation of $VOSO_4$ is 31,420 g.-cal. Similar determinations have been carried out with $Pb(NO_3)_2$ between 539° and 809° abs. Decomp. is detectable at 250—260°. The heats of formation of some basic Pb nitrates are calc. E. S. H.

Equilibrium in the reduction of silver chloride by hydrogen. F. ISHIKAWA and M. WATANABE (Sci. Rep. Tohoku, 1933, 22, 393—406).—The reaction has been followed by a static method over the range 380—700°, above which reduction is practically complete. The vals. of the equilibrium const. show a linear relation between log K_p and $1/T$. E. S. H.

Equilibrium in the reduction of cuprous chloride by hydrogen. M. WATANABE (Sci. Rep. Tohoku, 1933, 22, 423—435).—A static method has been used over the range 304—726°. The relation $\log K_p=-2303/T+3·1880$ holds for liquid CuCl and $\log \quad 4069/T+5·7510$ for solid CuCl. Combining the results with existing data, the calc. entropy of CuCl (solid) is 20·66 g.-cal. per degree. E. S. H.

Equilibrium in the reduction of antimony trioxide by carbon monoxide. M. WATANABE (Sci. Rep. Tohoku, 1933, 22, 407—413).—Results obtained by the static method show that reduction is complete at 500° and that at 600° about 0·2% of CO is present in the equilibrium gas. The results agree well with those derived from thermodynamic data. E. S. H.

Equilibrium in the reduction of nickelous oxide by carbon monoxide. M. WATANABE (Sci. Rep. Tohoku, 1933, 22, 436—447).—The static data from 663° to 852° show a linear relation between log K_p and $1/T$. Vals. for the reaction $Ni+0·5O_2=NiO$ have been calc. as follows: ΔH_{298} −57,112 g.-cal., ΔF°_{298} −50,333 g.-cal., entropy of NiO at 25° 8·97 g.-cal. per degree. E. S. H.

Double decomposition in the absence of a solvent. XVI. N. S. DOMBROVSKAJA (J. Gen. Chem. Russ., 1933, 3, 291—308).—Compound formation is absent in the systems $AgBr–Ag_2SO_4$ and $Tl_2SO_4–TlBr$, whilst the fusion diagram of the system TlBr–AgBr indicates the formation of a *compound*, 2TlBr,AgBr, transition point 298° at 60 mol.-% TlBr. Owing to the positive heat effect (+9·55 kg.-cal.), the

equilibrium in the reaction $Ag_2SO_4+2TlBr \rightleftharpoons 2AgBr+Tl_2SO_4$ is displaced to the right. The fusion diagrams for the systems Tl_2SO_4–AgBr–TlBr and Tl_2SO_4–AgBr–Ag_2SO_4, and for the quaternary system Ag_2SO_4–TlBr–AgBr–Tl_2SO_4 have been determined. R. T.

Equilibria in saturated solutions of H_2O–KNO_3–KCl–K_2SO_4 at 25°. I. Kritschevski and E. Goldmann (Z. anorg. Chem., 1933, **214**, 307—308).—Solubility data are recorded. H. J. E.

Dilatometric study of some silica–soda–beryllia glasses. E. Rencker (Compt. rend., 1933, **197**, 840—843).—The temp. at which the coeff. of expansion changes rapidly (*a*), and the coeff. itself (*b*), have been determined for glasses containing $>$ 14% BeO and $<$ 50% SiO_2. Replacement of SiO_2 or Na_2O by BeO raises (*a*), whereas (*b*) remains unaltered in the former case and diminishes in the latter. C. A. S.

Melting region of silicon dioxide–glass oxide systems and conclusions reached therefrom. H. Hollenweger and H. Rumpett (Angew. Chem., 1933, **46**, 662—667).—Systems with 55—87·5% SiO_2 consist after melting of a true physical solution; *X*-ray examination shows it to be amorphous. Systems with $>$ 87·5% SiO_2 consist of mixed crystals in which foreign mols. occupy spaces in the SiO_2 lattice; *X*-ray examination shows these substances to be cryst. Three phases (solid cryst., solid amorphous, and liquid) exist in equilibrium only at the m.p. of the mixture containing 87·5% SiO_2 (1472°). In the melting regions of the mixtures only two states coexist. At lower temp. apparently pure SiO_2 may crystallise out, the temp. of separation falling with decreasing content of SiO_2. E. S. H.

Thermodynamic studies of lithium hydroxide and lithium chloride. Y. Ueda (Sci. Rep. Tohoku, 1933, **22**, 448—474).—From electrode potential, tensimetric, and calorimetric data, the following thermodynamic vals. have been derived: for $Li+0·5O_2+0·5H_2=LiOH$, ΔF_{298}° -105,128 g.-cal., ΔH_{298} -115,253 g.-cal., entropy 13·7 g.-cal. per degree; for $Li+0·5Cl_2=LiCl$, ΔF_{298} −91,612 g.-cal., entropy 14·8 g.-cal. per degree. E. S. H.

Thermodynamic data relating to lead sulphide, and the standard electrode potential of sulphur. M. Watanabe (Sci. Rep. Tôhoku, 1933, **22**, 414—422).—Theoretical. The calc. data are based on experimental vals. recorded by Jellinek and Deubel (A., 1929, 1012). The entropy of PbS is 21·01 g.-cal.; the standard electrode potential of S is 0·48 volt. E. S. H.

Heat of synthesis of ammonia as a function of temperature and pressure. L. Kowalczyk (Przemysł Chem., 1933, **17**, 199—218).—Calc. vals. for the intervals 0—1200° abs. and 1—3000 atm. indicate that, except for low temp. and pressures of 200—300 atm., the heat of formation of NH_3 rises with increasing pressure. R. T.

Calorimetric researches. XXI. Heats of combustion of methyl-, ethyl-, and phenyl-substituted succinic acids and of their anhydrides. P. E. Verkade and H. Hartman (Rec. trav. chim., 1933, **52**, 945—968; cf. this vol., 935).—Heats of combustion of thirty-two acids and anhydrides are recorded. F. L. U.

Electrolytic transport of water in 0·1*N*-lithium, -sodium, and -potassium bromide. O. Viktorin (Chem. Listy, 1933, **27**, 364—367).—The electrolytic transport of H_2O is 8·15, 6·00, and 4·32, respectively, for 0·1*N*-LiBr, -NaBr, and -KBr, and the transport nos. of the cations are respectively 0·401, 0·486, and 0·582. R. T.

Electro-osmotic transport, and the electrokinetic potential of aqueous lithium, sodium, and potassium chlorides, and of potassium bromide and iodide. J. Velísek and A. Vasícek (Chem. Listy, 1933, **27**, 361—364).—Electro-osmotic transport vals. in 0·002*N*-LiCl, -NaCl, -KCl, -KBr, and -KI are nearly identical; in more conc. solutions the vals. are in the order NaCl=LiCl>KCl>KBr>KI. Max. vals. for electrokinetic potential are shown with increasing dilution by LiCl, NaCl, and KCl, but not by KBr and KI. R. T.

Distribution of current in electrolytes. M. A. Rabinovitsch and S. J. Pasetschnik (Ukrain. Chem. J., 1933, **8**, 127—131).—Differences in the increase in wt. of cathodes immersed in the same electrolyte at different distances from the anode become less marked as the concn. of the electrolyte and its conductivity diminish. R. T.

New electrolytic element. A. Thielemann (Z. Elektrochem., 1933, **39**, 783—791).—The properties of the MnO_2–Pb electrode have been examined. With a continuous discharge of 100 milliamp. the best performance is given using 2*N*-HNO_3 as electrolyte. Pyrolusite gives better results than artificial MnO_2, but increased surface of the Pb has no influence. The dissolution of Pb in the electrolyte is almost completely prevented by adding rodinal, glycine, or NH_4HS. E. S. H.

Effect of internal resistance of the galvanic cell on the measurement of e.m.f. by the capillary electrometer, and the method of correction. II. Method of correction. T. Ishino and H. Imagawa (J. Soc. Chem. Ind. Japan, 1933, **36**, 571B).—The position of balance on the bridge (cf. this vol., 786) is corr. by taking the mean of the two bridge readings, one when the standard cell (I) is connected in the same direction as the cell to be tested and the other when reversed. Then the true e.m.f. $e=E(n_1-n_m)/n$, where E is the e.m.f. of (I), n the bridge reading for (I) only, n_1 the bridge reading with the cells in the same direction, and n_m the mean val. of the bridge readings. M. S. B.

Electrochemical properties of the ternary system iodine–water–sodium iodide. A. N. Strelnikov (Bull. Acad. Sci. U.R.S.S., 1933, **7**, 715—728).—Solubility and conductivity have been measured at 25°. The e.m.f. of the cells Pt–Cu, Sn, Ni, Fe, Pb, Ag, Al, Cd, Zn, and Mg in an electrolyte containing H_2O 12·90, I 63·28, and NaI 23·82% increases in the order given. R. T.

Single potential of aluminium. H. Endô and S. Kanazawa (Sci. Rep. Tohoku, 1933, **22**, 537—

552).—The potential of Al in *N*-KCl is not affected by the presence of H_2, N_2, or CO_2, but the abs. val. is lowered considerably by O_2, probably as the result of the formation of an oxide film. The val. depends on the purity of the Al; Si has no influence, but addition of Fe steadily lowers the potential. The most probable val. for pure Al is −1·29 volts. E. S. H.

Phenomena occurring on moving one electrode in the electrolyte, and the electrokinetic potential. M. O. CHARMANDARIAN and B. I. PERVUSCHIN (Ukrain. Chem. J., 1933, **8**, 44—48; cf. A., 1930, 707).—If two Pt electrodes, one of which is in motion, are immersed in aq. acid containing dissolved H_2, a negative charge is observed on the moving electrode; with time, the charge becomes positive in solutions of high $[H_2]$, whilst with low $[H_2]$ it remains negative. This phenomenon is ascribed to the same factors as those which give rise to the inversion of sign of colloidal particles. H_2 in acid solutions exhibits a certain polarity. R. T.

Theory of electrocapillarity. I. Capillarity. S. R. CRAXFORD, O. GATTY, and J. ST. L. PHILPOT (Phil. Mag., 1933, [vii], **16**, 849—864).—Theoretical. H. J. E.

Electrometric titration of creatine ester hydrochloride and some related compounds. C. F. FAILEY and E. BRAND (J. Biol. Chem., 1933, **102**, 767—771).—Dissociation consts. at 25° are: creatine (I) 2·67, *iso*creatine 2·88, guanidoacetic acid (II), 2·86, creatinine 4·84, glycocyamidine (III) 4·80. No val. could be obtained for the hydrochlorides of Me esters of (I) and (II), owing to an irreversible change to the anhydride; on adding HCl to the alkaline solution, p_H vals. are obtained which agree with those for (I) and (III). H. G. R.

Oxidation-reduction potential of ascorbic acid (vitamin-*C*). H. BORSOOK and G. KEIGHLEY (Proc. Nat. Acad. Sci., 1933, **19**, 875—878; cf. A., 1931, 1189).—At 35·6°, and at any given p_H between 2·0 and 5·75, the potential is proportional to the ratio of the concn. of reduced and oxidised forms. At p_H >5·75 the rate of decomp. of the oxidised form is too rapid for accurate measurements. H. J. E.

Oxidation-reduction. XX. Adrenaline and related compounds. E. G. BALL and T. T. CHEN (J. Biol. Chem., 1933, **102**, 691—719).—An apparatus for use with unstable systems is described. With pyrocatechol, quinol, and derivatives as stable reductants, the slope of the p_H—E_0' (potential of the half-reduced solution) curve is 0·06 in acid solution. The instability of the oxidants did not allow a study above p_H 8·0. When the reductants are the isomerides of adrenaline, the systems have the same normal potential. Substitution in the side-chain increases the instability of quinones and the oxidants become more unstable as p_H increases. Potentials of naturally-occurring systems are so positive that they occur in a completely reduced state in living tissues. H. G. R.

Oxidation-reduction. XIX. *apo*Safranines. R. D. STIEHLER and W. M. CLARK (J. Amer. Chem. Soc., 1933, **55**, 4097—4109; cf. this vol., 464).—Data are recorded for six dyes in the p_H range 3—10·7 at 30°. The potential of $3\times10^{-5}M$-sulphonated rosindone (I) (90% reduced) at p_H 7·0 is equal to that of the H_2 electrode at 1 atm. Potentiometric, spectrophotometric, and distribution data are consistent with (I) existing in aq. solutions as an equilibrium of uni- and bi-mol. species. Induline-scarlet and (I) are approx. supplementary as oxidation–reduction indicators with potentials near that of the H_2 electrode (1 atm.) in the p_H ranges 3—5 and 6—10, respectively. The application to biochemical problems is discussed. J. G. A. G.

Limiting currents in the anodic polarisation of metals in aqueous solutions. III. K. SCHWABE (Z. Elektrochem., 1933, **39**, 791—799; cf. this vol., 785).—Periodic fluctuations in current strength, with an amplitude of 6—20 milliamp., have been observed with anodes of Zn in aq. $ZnCl_2$ or $Zn(ClO_4)_2$ at 20°, but not in aq. $ZnSO_4$ or $Zn(NO_3)_2$. Periodic phenomena have also been observed with a Ag anode in $AgClO_4$ dissolved in Pr^{n}OH, although not when an aq. solution is used. The nature of the films appearing at the surface of the electrode is discussed. E. S. H.

Photovoltaic properties of Cu–Cu_2O | $Pb(NO_3)_2$ solution | Cu–Cu_2O photocells. W. E. MESERVE (Physical Rev., 1932, [ii], **41**, 396). L. S. T.

Dependence of the minimum potential of electrolytic valve action on significant variables. O. MOHR (Z. Physik, 1933, **85**, 679—692).—The dependence of the electrolytic valve action of Ta and Al on current, formation potential, electrolyte, and temp. was investigated. In aq. electrolytes, except those with $Na^{\cdot}$ and $K^{\cdot}$, a linear relation exists between formation potential and min. potential, and this is independent of the concn. of the electrolyte, but diminishes rapidly with rising temp. A. B. D. C.

Mechanism of chemical reactions. C. N. HINSHELWOOD (J.C.S., 1933, 1357—1360).—Reactions fall into two classes according to whether the rate is equal to or considerably < the rate of activation. In the first class the predominating factor in promoting reaction is mol. energy; in the latter, the probability of occurrence of a suitable energy redistribution within the mol., which is favoured by local perturbing forces. D. R. D.

Gaseous reactions. M. POLANYI (Nature, 1933, **132**, 747—748).—A principle for measuring the velocity of reaction between two gases is developed. L. S. T.

Upper pressure limit of ignition. N. N. SEMENOFF (Nature, 1933, **132**, 566—567).—Polemical (cf. this vol., 909). L. S. T.

Upper pressure limit of ignition. C. N. HINSHELWOOD (Nature, 1933, **132**, 567).—A reply (cf. preceding abstract). L. S. T.

Kinetics of gas explosions. IV. Ozone explosions induced by hydrogen. B. LEWIS (J. Amer. Chem. Soc., 1933, **55**, 4001—4006; cf. A., 1927, 114; 1932, 1001).—The rate of decomp. of 50 mm. of O_3 at 85° is directly proportional to the pressure of H_2 < 50 mm. With 80 mm. of H_2, explosion occurs, and all of the H_2 is converted into H_2O; this is not so in the slow decomp. Without prolonged evacu-

ation between each experiment, the reaction vessel becomes progressively more active until, for a given mixture, a const. max. reaction rate is obtained. The activity is attributed to the formation, during the reaction, of H atoms which are adsorbed on the walls. The enhanced decomp. of O_3 is attributed to a chain reaction involving: $H+O_3 \longrightarrow OH^*+O_2^*$, $OH^*+O_3 \longrightarrow 2O_2+H$. J. G. A. G.

Explosion of CS_2–N_2O and of CS_2–N_2O–NO mixtures. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1933, 52, 862—868).—Explosion limits have been determined for both systems. The light emitted by the binary mixture during explosion is a max. for $CS_2 : N_2O = 1 : 3{\cdot}5$ independently of the pressure, and for a given composition $\propto p^2$ between 10 and 25 cm. The duration and colour of the flash and rate of emission of light are approx. the same as for CS_2–NO mixtures (cf. this vol., 910). The ignition temp. is 1800—1900°. Explosion limits and quantity of light emitted, the latter of which is a max. in the binary region CS_2–NO, have also been determined for the ternary mixture. F. L. U.

Carbonyl chloride-sensitised oxidation of carbon monoxide. G. K. ROLLEFSON and C. W. MONTGOMERY (J. Amer. Chem. Soc., 1933, 55, 4036—4043; cf. this vol., 237).—At low pressures of O_2 in the system $COCl_2$–CO–O_2, the rate of oxidation of CO is given by $d[CO_2]/dt = kI_0^{1/2}[COCl_2]^{1/2}[CO]^{1/2}[O_2]^{1\cdot2}$, whilst at higher $[O_2]$ the rate becomes $d[CO_2]/dt = kI_0^{1/2}[COCl_2]^{1/2}[CO]^{1\cdot2}$. From the similarities between this reaction and the Cl_2-sensitised oxidation of CO it is inferred that the processes have similar mechanisms. J. G. A. G.

Slow combustion of benzene: velocity of the reaction. J. AMIEL (Compt. rend., 1933, 197, 984—986; cf. this vol., 600, 815).—Using the same method the mixture ($C_6H_6+7{\cdot}5O_2$) has been heated for 0·25—8 hr. at 380—565° with similar results. The velocity, V, of the reaction at temp. (T) from 420° to 500° is given by $\log V = -12{,}300/T + 18{\cdot}21$, but is probably influenced by the extent of surface of the the Pyrex container (cf. A., 1931, 1372). C. A. S.

Explosive properties of dioxan-air mixtures. G. W. JONES, H. SEAMAN, and R. E. KENNEDY (Ind. Eng. Chem., 1933, 25, 1283—1286).—The lower limit of inflammability of dioxan and air dried with $CaCl_2$ is 1·97% by vol. at room temp. and pressure; the upper limit is 22·25% at atm. pressure and 100—110°. The ignition temp. in an 88-c.c. quartz bulb falls from 476° at 2·15% to 438° at 4·03%; the min. temp. by the drop method is 266°. Measurements with MeOAc, C_5H_{10}, HCO_2Me, etc. show that if the ignition temp. determined by the bulb method fall with rise of concn., the drop method may yield lower results than the bulb method, whereas in the contrary case the former method yields results as high as those given by the latter. Combustion in a closed vessel of air saturated with dioxan (3·54%) at 24—26° and 721—741 mm. produces an excess pressure of 80 lb. per sq. in. H. F. G.

Effect on velocity of evaporation of a liquid of admixtures of other vapours. A. G. ALFIMOV, S. SAMOILOV, and S. SOLTUISH (Azerbaid. Neft. Choz., 1933, No. 3, 80—81).—C_6H_6, PhMe, gasoline (b.p. 100—105°), $COMe_2$, and EtOH were blown with air containing these substances. The energy expended in the evaporation of the liquid decreases with air admixed with any of the other liquids to an extent depending on the dielectric const. of the liquid the vapour of which is present in the air. CH. ABS.

Homogeneous thermal polymerisation of isoprene. W. E. VAUGHAN (J. Amer. Chem. Soc., 1933, 55, 4109—4116; cf. A., 1932, 1209).—The polymerisation of isoprene at pressures between 212 and 739 mm. in the range 286—371° is a homogeneous bimol. association reaction of which the velocity coeff. is $k = 2{\cdot}192 \times 10^{10} T^{1/2} e^{-28{,}900/RT}$, but the dimeric polymeride decomposes slowly into volatile products. 1 mol. of dimeride is obtained for every 530 binary collisions of suitably activated mols., thus supporting the views of Kassel that such a polymerisation process can proceed with a fairly high efficiency. J. G. A. G.

Kinetics of the rearrangement of α-methoxystyrene. F. H. MACDOUGALL, W. M. LAUER, and M. A. SPIELMAN (J. Amer. Chem. Soc., 1933, 55, 4089—4097).—The liquid phase rearrangement, between 223° and 260°, of α-methoxystyrene (I) to propiophenone (II), is accompanied by the interaction of (I) and (II) to form $CH_2Bz{\cdot}CHBzMe$ and CH_4. Both reactions are of the second order and have energies of activation of 34,000 g.-cal. (approx.). J. G. A. G.

Autoxidation of aldehydes. M. T. BOGERT and E. G. MCDONOUGH (Drug and Cosmetic Ind., 1933, 32, 312, 332—338, 514, 533—540).—A study has been made of the initial and max. rates of autoxidation of the following: the C_7, C_8, C_{10}, and C_{11} aldehydes, citral, citronellal, hydroxycitronellal, benz-, *p*-tolu-, *p*-anis-, phenylacet-, cinnam- (I), *n*-α-amylcinnam- (II), β-phenylprop-, and salicyl-aldehyde (III), piperonal, and vanillin, and the effects have been determined of daylight, temp., and admixture with other aldehydes and numerous other org. substances, particularly those used in perfumery. Autoxidation takes place in every case with the exception of (III) and the daylight rate is considerably > that in the dark except with the (I) types, where light has practically no effect. Certain groups in the aldehyde mol., like OH and OMe, act as inhibitors, whilst the C:C linking in the (I) accelerates oxidation. The temp. coeffs. vary from 1·3 to 4 and are identical for reactions carried out in light or darkness. The addition of small amounts of one aldehyde to another sometimes increases, and in other cases decreases, the rate of oxidation, the catalytic effect of (II) being particularly marked. NH_2-compounds, especially $NHPh_2$, NHPhAlk, and $NHPh{\cdot}C_2H_4{\cdot}OH$, are the most powerful inhibitors; phenols are more effective than alcohols. Results obtained with the butyl alcohols indicate that the tendency to oxidation determines the inhibiting power. In most cases the addition of perfumery chemicals decreased the rate of autoxidation. Peracids are initially formed, which react further with the aldehyde, the amount of acid formed in binary mixtures being proportional to the concn. of the aldehyde. In all cases but the substituted benzaldehydes, CO_2 is produced. The decrease in the

rate of the O_2 absorption with time is not due to surface poisoning. S. C.

Kinetics of the reduction, in acid solution, of hydrogen peroxide by iodide ion. H. A. Liebhafsky and A. Mohammad (J. Amer. Chem., Soc., 1933, **55**, 3977—3986).—The rate of the reaction $H_2O_2+2H^{\cdot}+3I'=2H_2O+I_3'$ is given by $d[I_3']/dt=k_1[I'][H_2O_2]+k_2[H^{\cdot}][I'][H_2O_2]$, where $k_1=4{\cdot}91\times10^9e^{-13,400/RT}$ and $k_2=4{\cdot}58\times10^8e^{-10,450/RT}$ between 0° and 50°. The rate-determining steps $H_2O_2+I'\longrightarrow H_2O+IO'$ and $H_2O_2+H^{\cdot}+I'=H_2O+HIO$ (I) proceed simultaneously and independently, and in the range of ionic strength investigated, $\mu=0{\cdot}05$—$0{\cdot}5$, (I) has negligible kinetic salt effect. Magnanini's data (A., 1892, 110) are consistent with these results. J. G. A. G.

Kinetics of action of iodine water on silver nitrate. (Mlle.) M. L. Josien (Compt. rend., 1933, **197**, 988—990).—Excess of aq. $AgNO_3$ appears to act on aq. I as on aq. Cl_2 (cf. this vol., 1017), with pptn. of AgI and $AgIO_3$. Aq. I to which starch paste has been added is decolorised when $AgNO_3$ has been added ($I_2+H_2O+AgNO_3=AgI+HNO_3+HOI$); the stage $3HOI=2HI+HIO_3$, although more rapid than the corresponding stage in the case of Cl_2, still has a measurable velocity, accelerated by increased concn. of $AgNO_3$ and temp., but retarded by dilution. It thus appears that in conc., although not in more dil., solutions the presence of I' is necessary for the blue colour with starch paste (cf. A., 1887, 331; 1905, ii, 508). C. A. S.

Reactions between hydrogen iodide and cyanogen halides. R. B. Mooney and H. G. Reid (J.C.S., 1933, 1318—1323).—The reactions (1) $2HI+ClCN=HCl+HCN+I_2$, (2) $2HI+BrCN=HBr+HCN+I_2$, and (3) $HI+ICN=HCN+I_2$ occur with high but measurable velocity in CCl_4 solution, the velocity decreasing in the order (3)>(2)>(1). The gaseous reactions are still more rapid, only (1) being sufficiently slow for experimental determination. In this case, formimide chloride (?) is formed simultaneously. Bimol. velocity coeffs. and heats of activation and reaction are deduced. D. R. D.

Reaction between hydrogen iodide and chlorine. R. B. Mooney and H. G. Reid (J.C.S., 1933, 1315—1318).—The reaction is rapid and homogeneous in CCl_4 and in the gas phase. Heats of activation calc. for bimol. reaction are $<5{\cdot}5$ kg.-cal., which is $<$ that predicted from several theories considered. D. R. D.

Kinetics of the oxidation of picric acid by potassium permanganate in aqueous solution. F. F. Musgrave and E. A. Moelwyn-Hughes (Trans. Faraday Soc., 1933, **29**, 1162—1167).—In aq. solution picric acid is oxidised to HNO_3 and CO_2 by $KMnO_4$, which is reduced to MnO_2. The reaction is bimol., and the velocity is little affected by the p_H or by addition of electrolytes. The velocity corresponds with one fruitful collision in 10,000 between $KMnO_4$ and picric acid, or to 1 in 30 of ternary collisions involving H_2O. A. G.

Effect of solvent on reaction velocity. G. Buthmann (Z. physikal. Chem., 1933, B, **23**, 100—104).—The reaction of $CCl_3{\cdot}CHO$ with EtOH in various solvents at 21° has been studied. Reaction is most rapid in solvents which have no permanent dipole moment and are not readily polarised, and is appreciably slower in polar solvents. No relation between the reaction velocity and the change in activation energy could be detected. R. C.

Kinetics of the thermal and photochemical reaction between iodine and diazoacetic ester in carbon tetrachloride solution. W. B. S. Newling, L. A. K. Staveley, and E. A. Moelwyn-Hughes (Trans. Faraday Soc., 1933, **29**, 1155—1162).—The velocity of the reaction $I_2+CHN_2{\cdot}CO_2Et\longrightarrow N_2+CHI_2{\cdot}CO_2Et$ in CCl_4 solution is extremely sensitive to the presence of impurities, especially H_2O. There are two or three consecutive reactions, the first of which is bimol. The velocity of the first reaction is equal to or 1/60 of that predicted by the simple collision theory according to whether the regeneration of I_2 is assumed to be slow or fast. The reaction is accelerated by light, the max. quantum efficiency being two. A. G.

Kinetics of diazotisation. I. Aliphatic series. E. Abel, H. Schmid, and W. Sidon (Z. Elektrochem., 1933, **39**, 863—871; cf. A., 1931, 1244).—The velocities of reaction of glycine H sulphate and nitrite with HNO_2, measured by evolution of N_2, are given by $k_1[H_2Gl^{\cdot}][HNO_2]^2/[H^{\cdot}]$ and by $k_2[HGl^{\cdot\cdot}][HNO_2]^2$, respectively, where $H_2Gl^{\cdot}$ denotes $NH_3{\cdot}CH_2{\cdot}CO_2H$. Deviations occur in presence of much NO_2' in strongly acid solution. The reaction resembles the decomp. of NH_4NO_2, an intermediate diazo-product being formed. H. J. E.

Velocity of decomposition of diazo-compounds in water. XI. E. Yamamoto, R. Goshima, and T. Hashima (J. Soc. Chem. Ind. Japan, 1933, **36**, 490—495B).—Data are given for the decomp. of aq. solutions of α- (I) and β- (II) $-C_{10}H_7{\cdot}N_2Cl$ at 0—40°. The concn. of (I) decreases nearly linearly with time, whilst that of (II) decreases at first rapidly and then at a slower, const. velocity. A. G.

Decomposition of acetylsalicylic acid in aqueous solution. C. Morton (Quart. J. Pharm., 1933, 6, 492—495).—The rate of decomp. in presence of K citrate, NaOAc, and NH_4OAc is measured. k for the unimol. reaction is 0·0043 at room temp. and is greatly increased by rise in temp. R. S. C.

Reaction velocities of 1-chloro-2 : 4-dinitrobenzene and 1-chloro-2 : 4-dinitronaphthalene with aromatic amines. H. J. van Opstall (Rec. trav. chim., 1933, 52, 901—911).—Reaction velocities with various aromatic amines in EtOH have been measured at 25° and 100°. The effect of different nuclear substituents is recorded. o-*Tolyl*-, m.p. 125° and 137°, dimorphous, m-*tolyl*-, m.p. 269°, p-*anisyl*-, m.p. 203—204°, p-*phenetyl*-, m.p. 160°, and p-*chlorophenyl*-2 : 4-*dinitro*-α-*naphthylamine*, m.p. 209°, are described. F. L. U.

Determination of velocity of hydrolysis of acid anhydrides by the aniline-water method. I. S. E. Vles (Rec. trav. chim., 1933, **52**, 809—826).—Velocity coeffs. of hydrolysis of Ac_2O, $(EtCO)_2O$, $(Pr^{\alpha}CO)_2O$, succinic and glutaric anhydrides have been

measured at 0° and 25°, and of Bz_2O and phthalic anhydride at 25°. The temp. coeffs. for 10° lie between 1·92 and 2·05. F. L. U.

Interaction of benzoyl chloride and aniline in carbon tetrachloride and hexane solution. G. H. GRANT and C. N. HINSHELWOOD (J.C.S., 1933, 1351—1357).—The reaction is bimol. in CCl_4 and gives abnormally low activation energy. The velocity coeff. falls with dilution and the effect is greater in C_6H_{14}. It is shown to be due to catalysis of solid NH_2Ph,HCl. Thus, low activation energies may not be due only to inefficient activating collisions, although in CCl_4 in this case there may be an inefficient homogeneous reaction as well. D. R. D.

Rate of addition of methyl esters to trimethylamine. L. P. HAMMETT and H. L. PFLUGER (J. Amer. Chem. Soc., 1933, **55**, 4079—4089).—The rate of methylation, velocity coeff. k, of NMe_3 to $NMe_4^{\cdot}$ by the Me esters of nine aliphatic and aromatic carboxylic acids in MeOH at 100° is related to the ionisation const., K_A, of the acid in H_2O thus: $\log k=a+b\log K_A$ (I). The absence of steric hindrance effects compared with their predominance in ester hydrolysis shows that the mechanisms of the two types of reaction are different. The methylation proceeds by the simultaneous addition of NMe_3 to the Me of the ester and the elimination of the acid ion, whereas the ester hydrolysis is an acylation of the OH′. The formal identity of (I) with the relation between acid strength and the rate of general acid catalysis (II) (Bronsted) indicates that the rate-determining step in (II) is the transfer of $H^{\cdot}$ from acid catalyst to weakly basic substrate. J. G. A. G.

Initial absorption rates of carbon dioxide by water and by dilute sodium carbonate solutions. H. S. DAVIS (Ind. Eng. Chem., 1933, 25, 1023—1025).—Previous work (A., 1930, 1512) has been confirmed (cf. A., 1932, 916). E. S. H.

Fluorine. II. Reactions of fluorine oxide with water and with sodium hydroxide solutions. F. ISHIKAWA, T. MUROOKA, and H. HAGISAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, **12**, 742—754).—Henry's law is valid for the solubility of F_2O in H_2O at 20° and various partial pressures. The velocity of reaction in the liquid phase is small compared with the velocity of dissolution, and the temp. coeff. of the velocity of the whole process is about 3 per 10° (20—35°). The velocity of the reaction between F_2O and dil. NaOH solutions is relatively great, and has a temp. coeff. of about 1·5 between 0° and 30°. H. F. G.

Thermal decomposition of solids. W. E. GARNER, A. S. GOMM, and H. R. HAILES (J.C.S., 1933, 1393—1398).—Thermal decomp. of crystals of PbN_6, Hg fulminate, Pb styphnate, and BaN_6 proceeds in three stages: (1) quiescent stage, (2) period of uniform acceleration, (3) unimol. reaction. It is suggested that as the lattice is not continuous throughout the crystal, the internal boundaries hinder the propagation of the reaction. D. R. D.

Effect of hydrogen-ion concentration on the corrosion of iron. J. M. BRYAN (Trans. Faraday Soc., 1933, **29**, 1198—1209).—In absence of air the corrosion of Fe in citric acid (containing varying amounts of Na citrate) is increased by adding $Fe^{\cdot\cdot\cdot}$ to the more acid solutions, but inhibited when $Fe^{\cdot\cdot\cdot}$ is added to the less acid solutions. In presence of $Fe^{\cdot\cdot\cdot}$ access of O_2 causes a pronounced acceleration of corrosion over the whole range of p_H studied; O_2 has a max. effect at about p_H 4. Most of the H_2 is removed by depolarisation in presence of $Fe^{\cdot\cdot\cdot}$, irrespective of p_H or the presence or absence of O_2. Part of the depolarisation of H_2 by O_2 is brought about by $Fe^{\cdot\cdot\cdot}$ acting as an O_2 carrier. E. S. H.

Salt effect in corrosion of metals. R. PODHORSKY (Arh. Hemiju, 1933, 7, 97—114).—The velocity of corrosion of Zn and Fe in aq. NaCl is at a max. in 0·2% and 0·5% NaCl, respectively. Qualitatively similar results are obtained for the currents produced by the cells Fe|aq. NaCl|Pt. R. T.

Corrosion of magnesium alloys.—See B., 1933, 791.

Development of the theory of catalysis during the 19th century. A. MITTASCH (Naturwiss., 1933, **21**, 729—732, 745—749).—A lecture.

Homogeneous catalysis of para-ortho-hydrogen transformation under influence of paramagnetic molecules. I. L. FARKAS and H. SACHSSE (Z. physikal. Chem., 1933, **B**, **23**, 1—18; cf. this vol., 574).—The velocity of transformation, which occurs according to $p\text{-}H_2+X \rightarrow o\text{-}H_2+X$ (X=paramagnetic mol.), has been measured over a wide range of temp., T, in presence of O_2, NO, and NO_2. The collision yield, W, varies only slightly with T. The abs. velocities and relation between T and W agree with Wigner's theory (this vol., 1256). Diamagnetic gases have no catalytic action. The same transformation occurs in solution in H_2O, MeOH, NH_2Ph, C_6H_6, and *cyclo*hexanol, X being the solvent, but the velocity coeff. is about 10^{-6} of that for the gas reaction. The reaction is ascribed to the action of the nuclear moment of the H atoms in the solvent mols. R. C.

Homogeneous catalysis of para-ortho-hydrogen transformation under influence of paramagnetic ions. II. L. FARKAS and H. SACHSSE (Z. physikal. Chem., 1933, **B**, **23**, 19—27).—The reaction velocity, k, in solution in presence of ions of the Fe group increases with the dilution, v, but in presence of rare-earth ions is independent of v, and is proportional to the magnetic moment of the ion. The H_2O does not materially affect the collision no. and yield. For the transformation catalysed by O_2 k is approx. the same for reaction in aq. solution as in the gaseous phase. R. C

Homogeneous catalysis of gaseous reactions by iodine. Decomposition of propaldehyde, and a general discussion. S. BAIRSTOW and C. N. HINSHELWOOD (Proc. Roy. Soc., 1933, **A**, **142**, 77—88).—The kinetics of the thermal decomp. $EtCHO \rightarrow C_2H_6+CO$, catalysed by I (the rate being proportional to the I concn.), can be quantitatively explained on the hypothesis that the active complex involved is deactivated by the aldehyde. Consideration of the types of reaction catalysed by I shows that they involve the movement of an H atom and the breaking of a linking. The energy of activation of the catalysed

reaction is much < that of the uncatalysed, and this energy appears to be placed in a part of the mol. where it is efficiently used in breaking the linking. The existence of a dipole moment in or near the linking broken is considered. L. L. B.

Catalysis of gaseous reactions by chlorine. S. BAIRSTOW (Trans. Faraday Soc., 1933, **29**, 1227—1228).—Cl_2 is about one sixth as effective as I in catalysing the decomp. of Et_2O at 463°. Comparison of the kinetics of the reactions shows that a purely chemical theory is untenable. E. S. H.

Soils containing carbamide. VI. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1933, **15**, 192—198).—K and Na nitrates and chlorides accelerate the hydrolysis of $CO(NH_2)_2$ by urease and by heat (100°), Na being more active than K. NH_4Cl and NH_4NO_3 retard the process. For the chlorides, 5% solutions have a greater influence than 10% solutions, but for the nitrates the reverse is the case. The action of neutral salts is not influenced by the presence of PO_4''', which itself accelerates the hydrolysis. H. F. G.

Induced oxidation of lactic acid by ascorbic acid and the cancer problem. W. P. JORISSEN and A. H. BELINFANTE (Chem. and Ind., 1933, 896).—The oxidation of lactic acid (I) is induced by Na_2SO_3 or P (in castor oil) when these substances themselves are being oxidised. At suitable [H·], aq. (I) is also oxidised by oxidising glycuronic or ascorbic acid (II). The use of (II) for the removal of (I) from cancer tissue is proposed. F. O. H.

Induced oxidation of anthracene in the autoxidation of benzaldehyde. G. E. K. BRANCH, H. J. ALMQUIST, and E. C. GOLDSWORTHY (J. Amer. Chem. Soc., 1933, **55**, 4052—4062).—The rate of absorption of O_2 by PhCHO (I) in the presence of BzOH (II) and small concns. of inhibitors is not in accord with the view that the induced oxidation of the inhibitor occurs only in the act of inhibition. Anthracene (III) is oxidised by peroxides more active than BzO_2H formed during the autoxidation of (I) and the rate of oxidation is of first order with respect to each reactant. That (II) decreases the rate of the induced oxidations of (III) and KI, increases that of quinol, but does not affect that of phenanthrene, is attributed to competitive reductions of the peroxides by the inhibitor and (I) after preliminary combination with (II) (cf. A., 1932, 818). From the variation of O_2 absorption with initial concn. of (III) and (II), it is inferred that the induced oxidation of (III) is due to a mixture of peroxides or a peroxide in different energy states having sp. reactivities towards (I), (II), and (III). J. G. A. G.

Successive reactions on the surface of a single catalyst. II. Hydration of ethyl ether, and its subsequent conversion into acetone. M. J. KAGAN, I. M. ROSINSKAJA, and S. M. TSCHERNTZOV (J. Gen. Chem. Russ., 1933, **3**, 337—344).—50% yields of $COMe_2$ are obtained by passing 5 : 1 mixtures of Et_2O and H_2O vapours over an Al_2O_3–Fe_2O_3–MgO catalyst (I) at 495°; at the same time 10% of the Et_2O is converted into EtOH and 18% into C_2H_4. (I) is prepared by dissolving 1000 g. Al in aq. NaOH, pptg. $Al(OH)_3$ by neutralisation with HNO_3, adding 100 g. Fe_2O_3 and 12 g. MgO to the washed ppt., and drying at 125°; variations in the composition of (I) or in the method of pptn. of $Al(OH)_3$ adversely affect the yields of $COMe_2$. The process consists of the reactions $Et_2O \longrightarrow 2EtOH \longrightarrow 2MeCHO \longrightarrow EtOAc \longrightarrow EtOH + AcOH$; $2AcOH \longrightarrow COMe_2 + CO_2 + H_2O$. R. T.

Hydrolysis of ethyl ether. A. VANSCHEIDT and M. LOZOVSKI (J. Gen. Chem. Russ., 1933, **3**, 329—336).—Activated C at 300° and SiO_2 gel at 400° do not catalyse hydrolysis of Et_2O at atm. pressure. ThO_2 has a feeble action at 300°, and Al_2O_3 catalyses the reactions $Et_2O + H_2O \longrightarrow 2EtOH$ and $Et_2O \longrightarrow C_2H_4 + EtOH$; the reactions commence at 215°, and max. yields of EtOH (15%) are obtained at 280°. 5—10% hydrolysis is obtained by passing moist Et_2O through 70% H_2SO_4 at 170°, whilst with 5—25% H_2SO_4 at 200° 70% hydrolysis is attained after 2—4 hr. The yield of EtOH is considerably reduced if more conc. H_2SO_4 is used, or if the temp. is > 230°. H_3PO_4 has no hydrolytic action under similar conditions. R. T.

Heterogeneous catalysis of decomposition of aliphatic ethers. W. MARX (Z. physikal. Chem., 1933, **B**, **23**, 33—57).—The decomp. of Et_2O, Pr^{α}_2O, and Pr^{β}_2O vapour into olefine and H_2O on bauxite at 150—300° has been examined in a closed apparatus with continuous circulation of gas. If, the initial pressure of ether being comparatively high and the amount of catalyst small, the catalyst is highly charged with adsorbed ether the reaction is retarded by the H_2O formed, but this retardation may be eliminated by the presence of BaO. The unretarded reaction consists of a brief initial stage during which ether is being adsorbed, followed by the principal stage in which ether is being continually supplied to the catalyst from the gas phase as reaction proceeds and the order of reaction is 0·35, and a final stage of order 3 which represents the reaction of ether adsorbed at the active centres. If the amount of catalyst is large and the initial pressure of ether is small, the concn. of ether on the catalyst is small and the reaction then exhibits the above initial and final phases, but there are now two intermediate steps. The first corresponds with diffusion from the gas phase and is of zero order, and is followed by a stage in which the order of reaction is 1—2 and ether is supplied by the inactive surface. The no. of active centres is estimated at 10^{19} to 10^{20} per g. of catalyst. Both retarded and unretarded reactions have the same heat of activation. R. C.

Simultaneous preparation of sulphuric and hydrochloric acids. G. V. PRICHODKO (Ukrain. Chem. J., 1933, **8**, 66—67).—A no. of metal oxides (not specified), pptd. on SiO_2 gel, catalyse the reaction $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$. R. T.

Catalysis and transformation of alkaline-earth cyanides into cyanamides. A. PERRET and R. PERROT (Compt. rend., 1933, **197**, 764—766; cf. this vol., 229).—The reaction $CaCl_2 + 2NaCN \longrightarrow CaCN_2 + C + 2NaCl$ at 570° proceeds to the extent of 21·3% in 30 hr. in absence of catalyst. With addition of 20% of finely-divided Fe, Co, or Ni 82%, of 20% of Mn or Pt 60%, of the theoretical yield of $CaCN_2$ is obtained in 3 hr.; Ag, Ca, Li, V, Mo, W, Cr, Mg,

Al, Be, C, and Si are without effect. In presence of Fe rise of temp. beyond 670°, or increase of concn. of NaCN beyond equiv. mols. (except for a slight increase at 760°) decreases the yield. The reaction takes place in two stages, first (reversible) $CaCl_2+2NaCN \rightleftharpoons Ca(CN)_2+2NaCl$, the $Ca(CN)_2$ then decomposing irreversibly in presence of the catalyst. C. A. S.

Catalytic influences in spontaneous ignition processes. C. ZERBE, F. ECKERT, and H. JENTZSCH (Angew. Chem., 1933, **46**, 659—662).—The ignition temp. of the vapours of C_6H_6 and C_5H_{12} have been determined in presence of Pd and the oxides of Co, U, Cd, Mn, Ni, Mg, Zn, Sn, Pb, Cr, Ca, Fe, Bi, V, Al, and Cu. With C_6H_6 the temp. is reduced considerably by the presence of the solid, excepting Al_2O_3, PbO (yellow), and CuO. With C_5H_{12} the temp. is in general raised. E. S. H.

Relations between structure of catalyst and chemical change. III. J. ECKELL (Z. Elektrochem., 1933, **39**, 807—815; cf. this vol., 790).—A kinetic investigation of the oxidation of CO by O_2 in presence of Fe_2O_3, Al_2O_3, or solid solutions of Fe_2O_3 and Al_2O_3 indicates that the catalyst suffers intermediate reduction. The reduction process is considerably slower than the subsequent re-oxidation. The heats of activation are calc. for the different catalysts. E. S. H.

Relation between structure of catalyst and chemical change. III (cont.). J. ECKELL (Z. Elektrochem., 1933, **39**, 855—863; cf. preceding abstract).—In an Fe_2O_3–Al_2O_3 catalyst for the CO–O_2 reaction the energy of activation decreases linearly with increasing Al_2O_3 concn. up to the miscibility gap (25% Al_2O_3), above which it is const. This is correlated with a parallel decrease in the lattice const. of Fe_2O_3 with additions of up to 25% Al_2O_3, and with changes in particle size, deduced from *X*-ray and electron diffraction measurements. H. J. E.

Platinum catalyst. M. TAUBER (Magyar Chem. Fol., 1932, **38**, 150—156; Chem. Zentr., 1933, i, 3044).—The relation between catalytic activity and Volta p.d. of platinised Pt and Ni catalysts in the hydrogenation of C_2H_4 has been studied. The p.d. is caused by the electrolytic formation of H_2 and O_2 at the protruding end of the wire. With platinised Ni wire the reaction velocity depends chiefly on the p_H of the polarisation solution; polarisation itself has little effect. The catalytic activity of platinised Pt is independent of the p_H. In completely dried gas mixtures the catalytic activity is low. The inactive catalytic surface can be reactivated by electrolytic evolution of O_2. The film of H_2O on the surface of the catalyst plays an important part. A. A. E.

Incomplete oxidation of methane with oxygen and air. C. PADOVANI and P. FRANCHETTI (Giorn. Chim. Ind. Appl., 1933, **15**, 429—432).—As foreseen theoretically, the incomplete oxidation of CH_4 by O_2 or air, expressed by $CH_4+0{\cdot}5O_2=CO+2H_2$—8 kg.-cal., is favoured by the same catalytic influences and conditions as the reaction of CH_4 with mixtures of H_2O vapour and CO_2. With a suitable Ni catalyst and a val. 500 for the ratio velocity : space, results nearly corresponding with the equilibrium are obtained at 850—950°; at 900°, the final gases contain < 1% CH_4. Experiments were made also with ordinary town gas and with a dehydrogenated coke-oven gas, others with a vertical furnace containing 650 c.c. of catalyst, and others at 1200° with 10 litres of refractory material without catalyst. The catalytic oxidation of natural CH_4 by O_2 is used to prepare mixtures of CO and H_2 for the synthesis of benzine at the ordinary pressure. If pure or highly conc. O_2 were available at a low price, these transformations would be of industrial val. for making H_2, NH_3, alcohols, or benzine from hydrocarbons, especially from natural gases containing CH_4. T. H. P.

Present position of the theory of ammonia catalysis. W. FRANKENBURGER (Z. Elektrochem., 1933, **39**, 818—820).—Polemical (cf. this vol., 1018). E. S. H.

Reduction by hydrogen and the thermal decomposition of nitrides made by the reaction of ammonia with various promoted and unpromoted iron synthetic ammonia catalysts. P. H. EMMETT and K. S. LOVE (J. Amer. Chem. Soc., 1933, **55**, 4043—4050).—In general, the rate of evolution of N_2 from Fe_4N at 430—520° is autocatalytic, but under special conditions, with doubly promoted catalysts, the process becomes of zero order. The energy of activation of the reaction $Fe_4N \longrightarrow 4Fe+0{\cdot}5N_2$ is 50,000 g.-cal. (approx.). The rate of decomp. of Fe_2N to Fe_3N decreases rapidly with evolution of N_2, but initially is that of Fe_3N that of Fe_4N. The rate of reduction of Fe_2N by H_2 at 180° is > that of Fe_4N, and in both cases passes through max. vals. The former process takes place in the stages : $3/2H_2+3Fe_2N \longrightarrow 2Fe_3N+NH_3$ and $3/2H_2+Fe_3N \longrightarrow 3Fe+NH_3$. J. G. A. G.

Platinum catalyst on silica gel. M. O. CHARMANDARIAN and G. D. DACHNIUK (Ukrain. Chem. J., 1933, **8**, 36—43).—Satisfactory catalysis of oxidation of SO_2 is given by SiO_2 gel containing 0·1—0·5% Pt. R. T.

Vanadium and manganese catalysts in sulphuric acid manufacture.—See B., 1933, 962.

Promoter action in catalytic decomposition of sodium hypochlorite solutions. IV. J. R. LEWIS and F. SEEGMILLER (J. Physical Chem., 1933, **37**, 917—921; cf. A., 1931, 576).—A study of the promoter effect of various metal oxides and insol. salts on the catalytic activity of hydrated CuO in the decomp. of NaOCl solutions discloses no simple relation between activity and crystal structure. F. L. U.

Removal of thiophen from benzene.—See B., 1933, 953.

Catalytic production of camphene from turpentine.—See B., 1933, 953.

Catalyst for production of butyl alcohol from ethyl alcohol.—See B., 1933, 953.

Separation of the isotopes of hydrogen. C. H. COLLIE (Nature, 1933, **132**, 568—569).—With Ni electrodes in alkaline solution, the efficiency of separation depends on c.d. and the concn. of the electrolyte. The condition necessary for separation

appears to be that $H^{\cdot}$ itself should be discharged at the electrode. Data for Pb electrodes in 5—10% H_2SO_4 show that separation occurs when $H^{\cdot}$ is discharged. L. S. T.

Oxidation of graphite. V. SIHVONEN (Suomen Kem., 1933, **6 B**, 68—70).—A graphite anode with a low c.d. in conc. H_2SO_4 affords a brown graphite oxide (cf. A., 1931, 796) and some carboxylic acid. An explanation is advanced in the light of previous work (cf. this vol., 1021, 1020). J. L. D.

Electrochemical reduction of acid perrhenate solutions. Complex chloride of quinquevalent rhenium. W. F. JAKÓB and B. JEŻOWSKA (Z. anorg. Chem., 1933, **214**, 337—353).—Reduction of $KReO_4$ in 9*N*-HCl at Pt (bright or platinised) and Pd gives green solutions containing Re^{V}. The same stage of reduction is reached by treatment of $KReO_4$ solution with 2 equivs. of HI. On removing I with CS_2 and evaporation in a vac. after addition of KCl, yellowish-green crystals of the *compound* $K_2[Re(OH)_2Cl_5]$ are obtained. F. L. U.

Electrochemical oxidation of tervalent chromium to chromic acid. N. S. DROZDOV (J. Gen. Chem. Russ., 1933, **3**, 345—350).—Müller and Soller's findings for the anodic oxidation of Cr^{III} to CrO_4'' (A., 1906, ii, 66) have been confirmed. The yield of CrO_4'' per unit of current using pure and impure Pb anodes is identical. R. T.

Chromium plating.—See B., 1933, 923.

Anodic films of aluminium and their applications. S. SETÔH and A. MIYATA (J. Electrochem. Assoc., Japan, 1933, **1**, 15—24).—Thick, tough films were obtained with an $H_2C_2O_4$ bath. The thickness of the active layer is proportional to the voltage. Superposition of a.c. on d.c. prevents pitting. Thick, porous films are treated with high-pressure steam for a few min. to make them waterproof and more corrosion-resistant than by ordinary impregnating or painting. CH. ABS.

Electrodeposition of magnesium.—See B., 1933, 923.

Electrodeposition of lead.—See B., 1933, 923.

Electrodeposition of bismuth.—See B., 1933, 923.

Electrodeposition of iron-copper-nickel alloys. —See B., 1933, 922.

Electrolytic refining of mercury.—See B., 1933, 923.

Deposition of beryllium on copper and other metals by electrolysis of fused substances. H. FISCHER and W. SCHWAN (Metallwirt., 1933, **12**, 187—189; Chem. Zentr., 1933, i, 3124).—Electrolysis of fused BeF_2–NaF mixtures at 700—800° affords Be–Cu alloys; compact Be cannot be obtained. Be diffuses very readily into Cu, but only slightly into Be–Cu alloys rich in Be. Very thin layers of Be could be deposited on Cu, Ni, Fe, Al, Sn bronze, and brass. A. A. E.

Electrodeposition of nickel and chromium.—See B., 1933, 872.

Effect of metallic impurities on technical zinc electrolysis.—See B., 1933, 872.

Electrodeposition of silver on metal containing phosphorus.—See B., 1933, 872.

Corrosion and residual current.—See B., 1933, 870.

Electrochemical reduction of pyridine. N. S. DROZDOV (J. Gen. Chem. Russ., 1933, **3**, 351—359).—The yields of piperidine (I) increase, and of polypiperidines (II) diminish, as the concn. of C_5H_5N (III) diminishes, when the H_2SO_4 concn. is maintained const.; the ratio of (I) to (II) is const. when that of (III) to H_2SO_4 is const., and is unaffected by varying the c.d. or temp. R. T.

Hydrogen atoms, oxygen atoms, and the hydroxyl radical. P. HARTECK (Faraday Soc., Nov., 1933, Advance proof).—The production of H atoms by the electric discharge is discussed. The re-formation of H_2 from H is probably a three-body process. H_2O, N_2, and NH_3 do not react with H at room temp. CO and CO_2 will yield small amounts of CH_2O on prolonged action of H. Cl_2 and Br_2 react very quickly with H; in the case of Br_2 there is some back reaction between HBr and H. H reacts with hydrocarbons in three ways: (1) addition to radicals or unsaturated hydrocarbons, (2) dehydrogenation, possible with all hydrocarbons, $C_nH_m+H\longrightarrow C_nH_{m-1}+H_2$, (3) rupture of the C·C linking, *e.g.*, $C_2H_6+H\longrightarrow CH_4+CH_3$. Monohalogenomethanes react spontaneously with H. H_2S reacts giving H_2 and S. O atoms can be produced in a similar way. They do not react with H_2O vapour, but react readily with H halides. O also combines with NH_3, the course of the reaction being uncertain. The life period of the OH radical is much < that of O or H atoms. A. J. M.

Chemical action in the glow discharge. XI. Decomposition of nitrogen dioxide and the nitrogen dioxide equilibrium. A. K. BREWER and P. D. KUECK. **XII. Dissociation of ammonia.** J. W. WESTHAVER (J. Physical Chem., 1933, **37**, 889—896, 897—906; cf. A., 1932, 1097).—XI. The decomp. of NO_2 in the glow discharge is effected by NO_2^+, N_2^+, O_2^+, and He^+ ions. The no. of mols. decomposed per ion lies between 1·55 and 3 at 170°, and is three times as large at room temp. as at 225°. The equilibrium concn. of NO_2 at room temp. is 1·6%. NO is not formed as an intermediate product.

XII. The rate of decomp. of NH_3 is $\propto$ current and is independent of pressure. The no. of NH_3 mols. decomposed per ion is < 1. Decomp. is not appreciably retarded by N_2, O_2, He, A, or Hg. The equilibrium concn. of NH_3 in presence of N_2+3H_2 is 6%. F. L. U.

Physico-chemical reaction modified by electrical connexion with the earth. F. VLÈS and (MLLE.) M. GEX (Compt. rend., 1933, **197**, 777—779; cf. A., 1912, ii, 914).—Colloidal Ag, p_H 6·5, prepared by Bredig's method, in presence of plates of Zn, Al, Cu, Fe, or Pt changes colour and finally flocculates. The reaction proceeds more rapidly as the p_H decreases, becoming instantaneous for p_H 1, but with

$p_H > 6·5$ it is slower and there is no preliminary colour change. A colloidal Ag sol of p_H 3·5 with the metallic electrode insulated changes more quickly (and still more so if in a covered vessel) than one connected to earth. The velocity also varies with the capacity if a condenser is inserted in the earth connexion. C. A. S.

Free radicals and the photochemistry of solutions. E. RABINOWITSCH (Faraday Soc., Nov., 1933, Advance proof).—The mechanism of photochemical reactions in liquids is considered. The probability of reactions proceeding through activated mols. must be >, and rate of formation of free atoms and radicals generally <, in gases in the first step of photochemical reactions. The propagation of reaction chains can take place only by the help of free radicals. A. J. M.

Quantum yields of the photochemical reactions of carbonyl chloride. [Reaction of carbonyl chloride with hydrogen.] C. W. MONTGOMERY and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1933, **55**, 4025—4035; cf. this vol., 237).—The quantum efficiency, γ, of the oxidation of $COCl_2$ by O_2 is 1·80 in light of λ 2537 Å. γ is 90 (approx.) in the $COCl_2$-sensitised oxidation of CO when $P_{COCl_2}=P_{CO}=P_{O_2}=$ 30 cm. H_2SO_4, whilst γ decreases from 4 to 2·5 (approx.) during the course of the reaction $COCl_2+H_2 \longrightarrow CO+2HCl$. The initial rate of the latter increases slightly with increase of P_H, and is directly proportional to the first power of the light absorbed. The velocity equation, $d[CO]/dt=kI_0[COCl_2](1+k_2[H_2]/[CO][M])$ (where M is the sum of effects of the reactants and added CO_2 or N_2), derived from the proposed reaction mechanism, accords with the data. The non-formation of CH_2O is probably due to the inactivity of COCl towards H_2, and this permits an increase of [COCl], so that $2COCl \longrightarrow COCl_2+CO$ becomes the chain-terminating process. J. G. A. G.

Photochemical reactions in solution. L. FARKAS (Z. physikal. Chem., 1933, **B**, **23**, 89—99).—An arrangement is described whereby by measurement of the amount of reaction in a photochemical reaction of known quantum yield, ϕ, with and without filtration of the incident light through a photochemically active gas or solution, ϕ for the latter can be determined. The hydrolysis $CH_2Cl{\cdot}CO_2H(H_2O)+h\nu \longrightarrow HCl+OH{\cdot}CH_2{\cdot}CO_2H$ occurs in a single act and ϕ is independent of the p_H and below 2300 Å. has the val. 0·9. The decomp. of OAc′, leading in the primary process to $AcO'(H_2O)+h\nu \longrightarrow OAc+HO'+H$ ($\phi=1$), gives rise to the concurrent reactions $OAc+H \longrightarrow OAc'+H$ ($\phi=0·95$) and $H+OAc \longrightarrow CH_4+CO_2$ ($=0·05$ at p_H 8·5), the former of which is placed at a disadvantage if the H atoms produced in the primary process in AgOAc may react with Ag^*, $H+Ag^* \longrightarrow H^*+Ag$. For the decomp. of AcOH, $EtCO_2H$, and $C_2H_4(CO_2H)_2$ at 1850—2300 Å. ϕ has the vals. 0·45, 1·0, and 0·4, respectively. Irradiation of NH_3 in solution in C_6H_{14} results in sensitised decomp. of the solvent; the NH_3 is not attacked. R. C.

Formation of the hydroxyl radical from the photolysis of water and the generation of formaldehyde. N. R. DHAR (Faraday Soc., Nov., 1933, Advance proof).—The energy required in the formation of 1 g.-mol. of CH_2O from CO_2 and H_2O is practically the same as that required for breaking the H–OH linking in H_2O. The chief chemical change in photosynthesis (I) is the photolysis (II) of H_2O into H and OH, the H atoms then reducing CO_2 to CH_2O. The mechanism of the formation of CH_2O in the atm. is the same as for (I) in plants. The H_2 of the upper atm. may be due to the (II) of CH_2O according to the equation $CH_2O \quad CO+H_2$. The origin of CH_2O in dew and the ease of formation of this compound in the photo-oxidation of org. compounds are explained by assuming that freshly-formed CO_2 and H_2O, obtained from the oxidation of org. substances, are energy-rich, and undergo (I) to CH_2O even in ordinary light. (I) in plants may be aided by the energy derived from plant respiration. (II) of activated H_2O mols. into H and OH on the leaf surface by light absorbed by chlorophyll resembles the photo-sensitised decomp. of H_2O *in vitro*. H atoms reduce CO_2 to CH_2O, and the OH forms H_2O and O_2. A. J. M.

Latent [photographic] image. C. WINTHER (Z. wiss. Phot., 1933, **32**, 157—181).—The formation of a latent image in a photographic emulsion on exposure to the vapours from a mixture of $HgCl_2$ and $SnCl_2$ is attributed to the reduction of $HgCl_2$ by Hg on the surface exposed; a series of reactions is postulated: $HgCl_2+SnCl_2=Hg+SnCl_4$; hydrolysis of $SnCl_4$, giving HCl; $Hg+2HCl+O=HgCl_2+H_2O$; the $HgCl_2$ is deposited on the plate, where it is reduced: $Hg+HgCl_2=2HgCl$. The destruction of a latent image by exposure of a plate over $HgCl_2$ (cf. Kof and Haehn, B., 1907, 990) is also studied. The theory of the latent image is treated mathematically. J. L.

Highly disperse [photographic] emulsions. II. LUPPO-CRAMER (Z. wiss. Phot., 1933, **32**, 182—184; A., 1931, 1250).—The greater turbidity of highly disperse AgCl emulsions compared with similar AgBr emulsions is not related to the greater sensitivity. The sensitivities of "grainless" AgBr emulsions, ripened with addition of various dyes, are recorded, for both blue and yellow light. J. L.

Influence of pressure on the formation of the latent photographic image, particularly its effect on reversal in the region of solarisation. K. A. MARING (Physical Rev., 1932, [ii], **42**, 911).—Photographic materials exposed under pressure show a reduction (I) in density compared with those without pressure. (I) decreases with an increase in exposure and increases with an increase in pressure, but not linearly. In the region of solarisation, a marked acceleration of reversal occurs in the pressure region. L. S. T.

Intermittency effect in photographic exposure. J. M. BLAIR and M. C. HYLAN (J. Opt. Soc. Amer., 1933, **10**, 353—358).—The intermittency effects are explained on the basis of the equation formerly developed (A., 1932, 1006) and the hypothesis of a photochemical lag. E. S. H.

Time lag in the formation of the latent (photographic) image. L. I. ZIMMERMAN (J. Opt. Soc. Amer., 1933, **10**, 342—352).—By means of rotating

mirrors, emulsions were illuminated for periods of 10^{-5} to $5{\cdot}5\times10^{-8}$ sec. As the duration of the flash decreases the image density decreases gradually until a crit. flash interval is reached, after which the density–flash period curve falls rapidly with small decreases in the flash period. The crit. point is about 10^{-7} sec. for high light intensities, but for lower light intensities the duration is longer. It is concluded that the quantum theory applied to light in this particular field fails, and that the formation of the latent image can probably be explained as a resonance process. E. S. H.

The DIN degree. M. Biltz (Naturwiss., 1933, 21, 734—736).—A method of determining the photographic sensitivity of emulsions is described. A. J. M.

Energy transformations at surfaces. VII. Photo-sensitised oxidation as effect of an active, metastable condition of the oxygen molecule. H. Kautsky, H. de Bruijn, R. Neuwirth, and W. Baumeister (Ber., 1933, 66, [*B*], 1588—1600; cf. A., 1932, 213).—The sensitiser (I) and acceptor (II) adsorbates are made of trypaflavin and leuco-malachite green on SiO_2 gel. In spite of separation of (I) and (II), the oxidation of the (II) when the system is exposed to light is established by the production of a blue colour. The presence of O_2 is necessary and the phenomenon is obvious only during a very restricted region of low pressure. If (I) and (II) are separated by > a few mm., oxidation does not occur. Evidence is adduced that the possibility of meeting of (I) and (II) is excluded under the experimental conditions and that decomp. products of (I) are not the cause of the photo-sensitised oxidation. The light reaction is assumed to consist in the activation of the O_2 mols. by transference to O_2 of the light energy absorbed by (I); this is followed by oxidation of (II), for which light is not essential. The amount of absorbed energy is small, so that the possibility of production of O atoms or O_3 is excluded and a metastable activated condition of the O_2 mol. is postulated (cf. Childs *et al.*, A., 1931, 539). H. W.

Photosynthesis of nitrogenous compounds. L. N. Bhargava and N. R. Dhar (J. Indian Chem. Soc., 1933, 10, 453—458).—When a 2% CH_2O solution containing a small quantity of NH_3 is exposed to sunlight for < 80 hr., in presence of Cu carbonate, TiO_2, ZnO, etc., NH_2Me and nicotine are formed. Hg-vapour lamp radiation produces the same result (25 hr.) without the use of a catalyst. The nicotine may be separated from the $(CH_2)_6N_4$ simultaneously formed by extracting the $HgCl_2$ ppt. with AcOH. In absence of light no nicotine is formed. It is probable that the mechanism of the reaction involves the condensation of 3-aminopyridine and mucic acid. H. F. G.

Organic photochemistry. IV. Influence of solvent and temperature on the light absorption of colour-sensitisers. V. Tautomerides of the "Illuminol R" series. S. Sakurai (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, 12, 699—703, 704—708).—IV. The colour tone of certain colour-sensitisers is dependent on temp. and the nature of the solvent. The change of colour or of the solvent does not influence the photochemical behaviour of the material.

V. The spectral and photochemical properties of the members of each of the four pairs of tautomerides of the colour-sensitisers of the "Illuminol R" series are identical. H. F. G.

Light-sensitivity of 2-benzylpyridine. H. Freytag and A. Muller (Naturwiss., 1933, 21, 720—721).—Pure colourless 2-benzylpyridine, when kept in diffuse daylight, becomes reddish-brown and shows a weak green fluorescence. The behaviour of this compound on exposure to ultra-violet light of short λ has been investigated. It rapidly becomes yellowish-brown and finally brownish-green. A. J. M.

Primary photochemical production of some free radicals. R. G. W. Norrish (Faraday Soc., Nov., 1933, Advance proof).—The action of light on a large no. of org. compounds gives rise to the primary production of free radicals. The absorption of light quanta by a polyat. mol. is not localised in the chromophoric group, and there is frequently a movement of large quantities of energy from one group in the mol. to another. Free Me or Et can be produced by irradiation of simple ketones by light of about 2800 Å.; $RR'CO\longrightarrow\cdot R+R'CO\cdot$. The R'CO decomposes spontaneously. CH_2N_2 and keten give CH_2 primarily. The decomp. is studied from the viewpoint of energy. The CH_2 group is remarkably stable, and perhaps may not be a true free radical at all, but a compound of C^{II}. CH may be formed by direct photo-dissociation of C_2H_2. A new mechanism of photochemical decomp. in the case of the fluorescence of $COMe_2$, which involves also a primary splitting of the mol., is discussed, and is likely to be found in other cases, giving rise to free radicals. It occurs when the mol. falls from a stable excited state to an unstable lower level. A. J. M.

Action of ultra-violet light on pyridine. IV. —See this vol., 1304.

Changes in acid solutions of adrenaline. L. A. Haddock (Quart. J. Pharm., 1933, 6, 496—501).—Racemisation of *l*-adrenaline is rapid at p_H 0·1, but very slow at p_H 1·4—3·7, is catalysed more by visible than by ultra-violet or pure red light, and is not appreciably affected by sterilisation at 80° for 1 hr. Ultra-violet light causes racemisation of dil., but not of conc., solutions. R. S. C.

Reduction by *X*-rays of aqueous chromic acid solutions and the influence of added organic substances. H. Fricke and M. Washburn (Physical Rev., 1932, [ii], 40, 1033; cf. this vol., 793).—The effect of the *n*-fatty acids in increasing the reducing action of *X*-rays on very dil. H_2CrO_4 increases rapidly with the length of the chain; valeric acid is > 100 times as active as AcOH. L. S. T.

Acceleration of decomposition of solids by emission from radium. W. E. Garner and C. H. Moon (J.C.S., 1933, 1398—1400).—Ra rays accelerate thermal decomp. of BaN_6, but not of Hg fulminate. D. R. D.

Paramagnetic transformation of para-ortho-hydrogen. III. E. Wigner (Z. physikal. Chem.,

1933, **B**, 23, 28—32).—Theoretical. In the transformation of para- into ortho-hydrogen and the reverse on collision with a paramagnetic mol. the collision efficiency of collisions with sufficient energy for transformation is inversely proportional to the abs. temp. and to the sixth power of the min. distance apart at collision, and proportional to the square of the magnetic moment of the paramagnetic mol. R. C.

Reaction of hydrogen atoms with oxygen molecules, and life of HO_2. J. R. BATES (Z. physikal. Chem., 1933, **B**, 22, 469—470).—The life is estimated with the aid of the mechanism of reaction of HI with O_2 (this vol., 237). R. C.

Additive reactions of hydrogen and oxygen atoms at low temperatures. K. H. GEIB and P. HARTECK (Faraday Soc., Nov., 1933, Advance proof).—The production of additive products of H and O atoms at low temp. is described. H_2O_2 can be obtained in 100% yield, although it was not the normal form, into which it changed at −80°. With HCN at low temp. a substance CH_3N, which decomposes on slow heating to NH_2Me, NH_3, HCN, and condensation products, was produced. NH_3 and NH_2Me do not react with H atoms under these conditions. SO_2 gave H_2SO_2; C_6H_6 was hydrogenated. With O atoms C_2H_2 gave a product undergoing mol. rearrangement at −110°. C_2H_2 gave largely $(\cdot CHO)_2$. C_6H_6 gave $C_6H_6O_{3\cdot5}$. A. J. M.

Thermal analysis of picrates. I. T. TUCHOLSKI (Rocz. Chem., 1933, **13**, 435—447).—Anhyd. Li picrate has m.p. 301·5°, and the temp. initiating and immediately preceding explosion are respectively 321° and 342°. The corresponding vals. for other salts are: Na 270·4°, 313°, and 322°; K 250·1°, 331°, and 333°, Rb 233·1°, 335°, and 336°; Cs 276·3°, 301°, and 302°; Cu 305°, 290°, and 298°; Ag 296°, 332°, and 339°. The following cryst. hydrates exist: Li, 1 and $4H_2O$; Na, $1H_2O$; Cu picrate, 3, 5, 8, and $11H_2O$. R. T.

[Preparation of] copper selenate tetrammine dihydrate [crystals]. W. LANGE and G. VON KRUEGER (J. Amer. Chem. Soc., 1933, **55**, 4132—4133).—Two new and trustworthy methods are described (cf. *ibid.*, 1931, **53**, 4013). J. G. A. G.

Hydrides of boron. II. Preparation of B_5H_{11}; its thermal decomposition and reaction with hydrogen. III. Dimethoxyborine. A. B. BURG and H. I. SCHLESINGER (J. Amer. Chem. Soc., 1933, **55**, 4009—4020, 4020—4025).—II. Good yields of B_5H_{11}, m.p. −123·3°, are obtained by passing B_2H_6 through a tube at 115° and fractionating the products. The v.p. in the range −44° to 9° is given by $\log_{10} p_{(mm)} = 7{\cdot}901 - 1690{\cdot}3/T$. B_5H_{11} at 100° gives H_2, B_2H_6, B_4H_{10}, and small quantities of an octaborane (?); continued heating affords non-volatile solids, B_5H_9 and $B_{10}H_{14}$. If, however, a large excess of H_2 is present initially, an equilibrium between B_5H_{11}, B_4H_{10}, B_2H_6, and H_2 is established and by suitable adjustment of conditions any component can be obtained in quantity. The prep. of B_5H_9 from B_2H_6 has been improved.

III. The production of *dimethoxyborine*, m.p. −130·6°, by the reaction $4MeOH + B_2H_6 \longrightarrow 2BH(OMe)_2 + 4H_2$ is accompanied by that of an unstable *by-product*, possibly a polymeride of $BH_2 \cdot OMe$. The v.p. of $BH(OMe)_2$ in the range −96° to 14° is given by $\log_{10} p_{(mm.)} = -1849{\cdot}0/T + 175 \log_{10} T - 0{\cdot}008221T + 7{\cdot}1895$, from which the b.p. is 25·9°. The reaction $BH(OMe)_2 + 3H_2O \longrightarrow B(OH)_3 + 2MeOH + H_2$ is rapid, and the gas-phase decomp. $6BH(OMe)_2 \longrightarrow B_2H_6 + 4B(OMe)_3$ is reversible. J. G. A. G.

Thermal and hydrothermal syntheses of mullite. T. AO (J. Soc. Chem. Ind. Japan, 1933, **36**, 546B).—By hydrothermal action on various clays at 1000—1400° a larger proportion of mullite is formed than by any thermal process. When the clays are mixed with Kahlbaum's Al_2O_3 in suitable proportions and then heated at 1600° for 2 hr. they are completely converted into amorphous mullite. A marked lowering of the m.p. of silicates is observed on heating hydrothermally at 1000—1300°, and Seger cones show an increased degree of vitrification after similar treatment. M. S. B.

Burning and colouring of gem stones. EPPLER (Deut. Goldschmiede-Ztg., 1933, **36**, 46—48; Chem. Zentr., 1933, i, 2664).—The coloration of agate and chalcedony by heating after treatment with $FeCl_3$, sugar, or H_2CrO_4 solution is described. A. A. E.

Behaviour of metals, particularly lead and bismuth, in atomic hydrogen, and attempts to prepare atomic hydrogen from hydrides. T. G. PEARSON, P. L. ROBINSON, and E. M. STODDART (Proc. Roy. Soc., 1933, **A**, **142**, 275—285).—The isolation of free Et from $PbEt_4$, described by Paneth and Hofeditz (A., 1929, 788), has been confirmed. Unsuccessful attempts have been made to prepare at. H by the thermal dissociation of hydrides of S, Se, Te, As, Sb, and Sn in a stream of H_2 moving with a velocity of about 10 m. per sec. and at a pressure of 0·1—3 mm. The formation of Bi hydride, described in the lit., has been confirmed, but not that of Pb hydride. Ge, Sn, As, Sb, and Te, which do not react with mol. H_2, yield hydrides with at. H, but neither Pb nor Bi shows this behaviour. L. L. B.

Constitution of hyponitrous acid and nitroamide. A. HANTZSCH (Ber., 1933, **66**, [*B*], 1566—1568).—A reply to Hunter *et al.* (this vol., 555). The inability of nitroamide to be hydrolysed by alkali to NO_3' and NH_3, its non-formation from $AlkNO_3$ and NH_3, and its weak but distinct acidic character are in harmony with the structure $NH{:}N(:O)\cdot OH$. Hyponitrous acid is a weak dibasic acid, the mono- and di-metallic salts of which are respectively neutral and alkaline in H_2O. Its alkyl salts are *O*-esters. Comparison of its properties with those of N compounds leads to the *anti*-structure N·OH / H. W.

Nitrogen phosphide. P. RENAUD (Bull. Soc. chim., 1933, [iv], **53**, 692—697).—$PNCl_2$ reacts with Na at 120° to form a grey compound (I) (NP ?) containing some Cl and insol. in common solvents. PCl_3 and NH_3 react to give a white solid turning yellow when heated in vac. After washing with H_2O and drying, the product (II) may be an isomeric PN contaminated with NH_4Cl. Further heating of (II) in vac. gives (I) in a purer state with loss of NH_3, PH_3, and a solid m.p. > 100°, phosphorescent in air. D. R. D.

Interaction of phosphorus bromides and chlorides. II. A RENC (Rocz. Chem., 1933, **13**, 509—519).—The red crystals (I) obtained on mixing PCl_5 with PBr- (cf. this vol. 1130) have composition $PX_{5\cdot89}$—$PX_{8\cdot52}$ (X=Cl+Br), the yellow crystals (II) are $PX_{5\cdot02}$, the deep red liquid (III) is $PX_{6\cdot70}$—$PX_{8\cdot77}$, and the light red liquid (IV) is $PX_{3\cdot01}$—$PX_{3\cdot19}$. (IV) on freezing partly crystallises, and the liquid phase then has the composition PX_3 ($PCl_{0\cdot99}Br_{2\cdot00}$—$PCl_{2\cdot87}Br_{0\cdot17}$). The formation of P^{III} is ascribed to elimination of Br from PBr_5, to form the chloropolybromides (I) and (III). Attempts to prepare PCl_4Br by adding mixtures of PCl_3 and PBr_3 in various proportions to (II) or to PCl_5 were unsuccessful, the ratio P : Br of the cryst. products being in all cases < 1. The liquid phases of the systems PCl_5–PBr_3 and PBr_5–PCl_3 approximate to (IV), and the solid phases to (I) and (III); in particular, the compound $PClBr_4$ is described. R. T.

Complex chloro- and bromo-compounds of tervalent arsenic. W. PETZOLD (Z. anorg. Chem., 1933, **214**, 355—364).—The following *compounds* are described: $(NH_3Et)_2AsCl_5$, $R_3As_2Cl_9$ (NH_3Me, guanidinium), $RAsCl_4$ (NH_2Me_2, NH_2Et_2, m.p. 112°, C_5H_6N), $R_2As_3Cl_{11}$ ($NHMe_3$, quinolinium with $1H_2O$), $R_3As_2Br_9$ (NH_4, NH_3Et), $RAsBr_4$ (NH_2Et_2, $NHMe_3$, C_5H_6N), $NMe_4As_2Br_7$. F. L. U.

Complex bromo-compounds of formally quadrivalent arsenic. W. PETZOLD (Z. anorg. Chem., 1933, **214**, 365—368; cf. preceding abstract).—Red cryst. *compounds* $R_3As_2Br_{11}$ ($NHMe_3$, NMe_4, C_5H_6N) are obtained by adding Br to solutions of the appropriate bromides in conc. HBr. When dissolved in H_2O the compounds lose their colour and form a mixture of As^{III} and As^{V} compounds. F. L. U.

Rhombohedral and a second monoclinic modification of sulphur. O. VON DEINES (Z. anorg. Chem., 1933, **214**, 330—336).—The slow decomp. of $Na_2S_2O_3$, H_2S_x, or $(NH_4)_2S_x$ under varied conditions gave only normal monoclinic or rhombic crystals of S. Similar results were found on crystallising S from solutions (cf. Muthmann, Z. Krist., 1890, **17**, 338). H. J. E.

"Blue acid." E. BERL, K. WINNACKER, and H. H. SAENGER (Z. anorg. Chem., 1933, **214**, 354; cf. this vol., 580).—A rejoinder to Manchot (this vol., 919). F. L. U.

Lead chamber process. V. Mechanism of transference of oxygen to sulphur dioxide through nitrosylsulphuric acid. E. BERL, H. HILLEBRANDT, and K. WINNACKER (Z. anorg. Chem., 1933, **214**, 369—379; cf. this vol., 684).—The amount and rate of absorption of SO_2 and of $(2SO_2+O_2)$ by aq. H_2SO_4 containing 0·1 mol. per litre of SO_5NH have been measured with reference to temp. and to the content of H_2O. The solubility of SO_2 in aq. H_2SO_4 increases with the H_2O content and is depressed by the presence of SO_5NH. The theoretical furnace gas mixture $(2SO_2+O_2)$ is absorbed with max. velocity by acid with 42·5% of H_2O. With larger proportions of H_2O the SO_5NH is too extensively hydrolysed, whereas in more conc. acid it is too stable to act as an efficient catalyst. The mechanism of O_2 transference is represented by (1) $2SO_5NH+2H_2O+SO_2=2SO_5NH_2$ ("violet acid") $+H_2SO_4$, (2) $2SO_5NH_2+0{\cdot}5O_2=2SO_5NH+H_2O$. Rise of temp. diminishes the rate of transference by promoting decomp. of SO_5NH. If HNO_3 is substituted for SO_5NH the transference is not appreciably catalysed. F. L. U.

Surface actions of organic sulphur compounds on finely-ground sulphide minerals. A. M. GAUDIN and W. D. WILKINSON (J. Physical Chem., 1933, **37**, 833—845).—The action of Na Et and Na *iso*amyl xanthate on galena, ground wet in presence of air, consists primarily in simple metathesis between the xanthate and a surface layer of $PbSO_4$ or basic sulphate produced by oxidation. Subsequent oxidation of the Pb xanthate produces S and org. S compounds. If the mineral is ground and afterwards handled in N_2 much less xanthate is removed from solution by it. When a dixanthogen is used in place of a xanthate it becomes attached to the surface and is there oxidised to S and org. S compounds. The S involved is the singly-bound disulphide-S, since amyl formate disulphide behaves similarly. Similar observations have been made with other sulphide minerals. F. L. U.

Ammines of chromous chloride. H. I. SCHLESINGER and E. S. HAMMOND (J. Amer. Chem. Soc., 1933, **55**, 3971—3976).—Previous data are not trustworthy owing to the use of impure $CrCl_2$ and the slowness with which the equilibria are attained. The dissociation pressures at 35·5° are: hexammine (blue) 23·25 cm., *pentammine* (violet) 3·5, triammine (light blue) 0·85, and *diammine* (sage-green) very small. With high pressures of NH_3, and especially at high temp., $CrCl_2,6NH_3$ turns green, and finally grey, probably owing to ammonolysis. At >250°, Cl_2 oxidises the NH_3 of these compounds, but not the $Cr^{\cdot\cdot}$. J. G. A. G.

Preparation and properties of the permolybdates Na_2MoO_6 and Na_2MoO_8. N. J. KOBOSEV and N. N. SOKOLOV (Z. anorg. Chem., 1933, **214**, 321—329).—The *compound* Na_2MoO_8,nH_2O was prepared by adding 30% H_2O_2 and EtOH to conc. aq. Na_2MoO_4 at 0° to 10°, the red ppt. being washed with cold EtOH and Et_2O and air-dried. It decomposed slowly at room temp., and rapidly at 70—80°. When kept for 2—3 days at 20° it affords the yellow *compound* Na_2MoO_6,nH_2O. From the heats of their decomp. by acid $KMnO_4$, the heats of formation of the compounds were calc. H. J. E.

$(ClO_4)_x$ radical. M. GOMBERG and H. R. GAMRATH (Faraday Soc., Nov., 1933, Advance proof).—By the action of I on $AgClO_4$ in Et_2O solution two reactions take place, (i) iodination of the Et_2O, and formation of $HClO_4$, (ii) $2AgClO_4+I_2=2AgI+(ClO_4)_2$. The relative extent to which these reactions take place was determined, the $(ClO_4)_x$ present being determined by titrating the I liberated when the Et_2O solution was acted on by MgI_2 in abs. Et_2O, and the $HClO_4$ by determining the MeCHO produced on hydrolysis of the perchlorate–Et_2O compound. The addition of $(ClO_4)_x$ to CPh_3 was carried out. The perchlorate of the radical was produced at once, whereas when CPh_3 was treated with $HClO_4$ the amount of perchlorate formed was much less, and

there was considerable polymerisation. From 25 to 50% of the $AgClO_4$ enters into reaction (ii). A. J. M.

Chlorine hexoxide and chlorine trioxide. C. F. Goodeve and F. A. Todd (Nature, 1933, **132**, 514—515).—The ratio 1 : 3 of Cl : O has been confirmed for chlorine hexoxide (I) prepared by the thermal reaction between O_3 and ClO_2 at 0°. (I) exists as ClO_3 in the gaseous phase and is assumed to be associated to Cl_2O_6 in the liquid phase. The name "chlorine trioxide" should be reserved for ClO_3 and not for Cl_2O_3, for which "chlorous oxide" is suggested. L. S. T.

Recovery of iodine from residues. I. Naray-Szabó and Z. Szabó (Magyar chem. Fol., 1932, **38**, 95—98; Chem. Zentr., 1933, i, 2927).—The residues are treated with 5 c.c. of cold saturated aq. $NaNO_2$ and 5 c.c. of conc. H_2SO_4 per litre; the separated I is extracted with 100 c.c. CCl_4, which is then shaken with 10% NaOH. When the latter no longer extracts the I from solution in CCl_4 it is acidified and the I collected and sublimed. For the production of KI, KOH is used and is treated with H_2O_2 after use. A. A. E.

Action of hydriodic acid on the sparingly soluble sulphates. E. R. Caley (J. Amer. Chem. Soc., 1933, **55**, 3947—3952; cf. A., 1932, 1219).—The rates of dissolution in boiling 7·6*N*-HI are $BaSO_4 < Cr_4H_2(SO_4)_7 \ll SrSO_4 < CaSO_4$. For complete dissolution of $BaSO_4$, successive portions of HI are necessary. The HI interacts with the SO_4'' continuously furnished by the salts, forming H_2S, H_2O, and I, and leaving the metallic iodides in solution. $PbSO_4$ is sol. in conc. HI at room temp., and the above reaction ensues at higher temp. The applications of these results to analysis are indicated. J. G. A. G.

Rhenium trioxide and rhenium dioxide. W. Biltz (Z. anorg. Chem., 1933, **214**, 225—238).—ReO_3 was prepared by heating ReO_2 and Re_2O_7 for 7 days at 300°. ReO_2 was prepared (1) by heating Re_2O_7 and Re first at 300° and then at 600—650°, (2) by hydrolysis of K_2ReCl_6, followed by heating of the pptd. hydrated oxide at 650—680° in vac. ReO_2 is feebly paramagnetic. Its *d*, electrical conductivity, and crystal structure were examined. At 1000° the decomp. is $7ReO_2 = 3Re + 2Re_2O_7$. No lower oxides were detected. Fusion of ReO_2 with NaOH gave Na_2ReO_3. Prolonged fusion gave $NaReO_4$ and Re. Fusion of ReO_3 with NaOH gave $NaReO_4$ and Na_2ReO_5. H. J. E.

Rhenium sesquioxide, Re_2O_3. W. Geilmann and F. W. Wrigge (Z. anorg Chem., 1933, **214**, 239—243).—In the hydrolysis of $ReCl_3$ with aq. NaOH small amounts of H_2 are formed, due to reaction of Re_2O_3 with H_2O. H_2 is also formed by hydrolysing $ReCl_3$ in dil., but not in conc., acid solution. Re_2O_3 pptd. by hydrolysis could not be washed free from Cl. It is very easily oxidised. H. J. E.

Reactions of rhenium chlorides. W. Geilmann and F. W. Wrigge (Z. anorg. Chem., 1933, **214**, 248—259).—Hydrolysis of $ReCl_3$ (studied conductometrically) yields Re_2O_3,xH_2O and HCl. H_2 reduces $ReCl_3$ at 250—300° to Re. Oxidation of $ReCl_3$ at 400° gave $ReOCl_4$, ReO_3Cl, and Cl_2. No ReO_2Cl_3 was formed (cf. A., 1932, 585). $ReCl_3$ in 0·5*N*-H_2SO_4 is not oxidised by O_2. The thermal decomp. of $ReCl_5$ gives $ReCl_3$ and Cl_2. When heated in O_2, $ReCl_5$ forms $ReOCl_4$, ReO_3Cl, and Cl_2. $ReCl_5$ and KCl at approx. 500° form K_2ReCl_6 and Cl_2. Aq. NaOH reacts with $ReCl_5$, forming ReO_2,xH_2O and $NaReO_4$; aq. HCl forms $HReO_4$, H_2ReCl_6, and Cl_2. The thermal decomp. of Ag_2ReCl_6 at 300—400° yields $ReCl_5$ and $ReCl_3$; no $ReCl_4$ was isolated. H. J. E.

Rhenium pentachloride. W. Geilmann, F. W. Wrigge, and W. Biltz (Z. anorg. Chem., 1933, **214**, 244—247).—$ReCl_5$ was prepared by heating Re at 500° in Cl_2, and was purified by fractional sublimation in vac. No ReCl. was isolated (cf. A., 1931, 1255). H. J. E.

Evolution of gases from ferrosilicon in presence of water. H. Delomenie (J. Pharm. Chim., 1933, [viii], **18**, 289—292).—Fe–Si containing 20—30% Si evolves H_2 alone, whilst those containing > 30% Si evolve H_2, PH_3, and AsH_3 when treated with H_2O in vac. H_2 is evolved in consequence of the decomp. of $CaSi_2$ and the action of $Ca(OH)_2$ on free Si. Al phosphides and arsenides are responsible for the evolution of PH_3 and AsH_3. H. D.

Ortho-ferric hydroxide with a side-chain. A. Krause and I. Garbaczówna (Rocz. Chem., 1933, **13**, 501—508).—Aq. $FeSO_4$ and H_2O_2 yield a sol of ortho-ferric hydroxide, which flocculates spontaneously to give *iso*ortho-ferric hydroxide (I) sulphate from which brick-red (I) is obtained by adding aq. NH_3. (I) undergoes polymerisation, yielding a series of intermediate products, with α-FeO_2H as the final product. The mol. of (I) contains 8 Fe atoms, with a branched-chain structure; chains of 12 Fe atoms, with one main and two side-chains, probably also exist. Branched-chain compounds are formed only in presence of SO_4'', as the product obtained from $FeCl_2$ and H_2O_2 consists of long, straight chains of poly-ortho-ferric hydroxide. R. T.

Oxidation of ferrous hydroxide. A. Quartaroli (Gazzetta, 1933, **63**, 669—678).—Partial oxidation of freshly pptd. $Fe(OH)_2$ by air yields a voluminous, black, scarcely magnetic substance which is convertible into $Fe(OH)_3$ by H_2O_2. The magnetic susceptibility of the black compound increases autocatalytically with time, and ultimately, after 1—2 hr. at 20°, attains a steady val. of about 30 times the initial val.; the resulting material is black and compact and is not convertible into $Fe(OH)_3$. The transformation is retarded by traces of Mg or Ni. Equimol. mixtures of $Fe(OH)_2$ and $Fe(OH)_3$ change rapidly, but not instantaneously, into the magnetic substance. $Fe(OH)_3$ prepared by oxidation of $Fe(OH)_2$ by H_2O_2 is more compact and magnetic than is pptd. $Fe(OH)_3$. H. F. G.

Emission spectrum analysis and its practical application. H. Lucas (Zeiss-Nachr., 1932, No. 1, 19—25, No. 2, 20—29; Chem. Zentr., 1933, i, 3106).

Sensitiveness of the Debye–Scherrer method, and the possibility of its application to quantitative analysis. M. Paić (Arh. Hemiju, 1933, 7, 143—146).—The composition of mixtures may be calc. from the theoretical equation $A/B = A_1a_1b/B_1ab_1$,

where A and B and A_1 and B_1 represent the mol.-% of two substances, A and B, respectively, in a mixture of unknown and known composition, and a, b, a_1, and b_1 are the intensities of corresponding lines of the X-ray spectra. R. T.

Quantitative mineral micro-analysis. F. HECHT (Mikrochem., 1933, **14**, 81—83; cf. B., 1932, 145).—A claim for priority over Thurnwald and Benedetti-Pichler. F. L. U.

Quantitative mineral micro-analysis. A. A. BENEDETTI-PICHLER (Mikrochem., 1933, **14**, 84; cf. A., 1932, 1011).—A reply to Hecht (preceding abstract). F. L. U.

Vacuum fusion method for determination of gases in metals.—See B., 1933, 872.

Qualitative analysis of anions. A. BIRULIA (J. Gen. Chem. Russ., 1933, **3**, 544—548).—A scheme for the systematic analysis of anions is given. R. T.

Micro-determination of concentration of mixtures of ortho- and para-hydrogen. A. FARKAS (Z. physikal. Chem., 1933, B, **22**, 344—349).—A modification of the ordinary method, by which determinations can be made on a few cu. mm., is described. R. C.

Determination of moisture in mercuric oxide. G. J. W. FERREY (Quart. J. Pharm., 1933, **6**, 406—410).—HgO is dried by heating for 1 hr. at 70°. At 150° decomp. occurs. Hg_2O decomposes at 100°, particularly if impure. R. S. C.

Determination of chloride ion in presence of bromide and iodide ions. M. SCHTSCHIGOL (J. Gen. Chem. Russ., 1933, **3**, 540—543).—I′ is determined by the ordinary methods in 10 c.c. of a 2% solution of the substance, total halides are determined in a second 10-c.c. portion, and Cl′ is determined in a third portion by adding 35—40 c.c. of 2% aq. NH_3 and sufficient $AgNO_3$ to ppt. total halides, when AgBr and AgI are pptd. Ag is pptd. from the filtrate as Ag_3AsO_3, from which Ag is separated by the action of aq. Na_2CO_3, the Ag is dissolved in HNO_3, and determined by Volhard's method. R. T.

Diphenylcarbazide as mercurometric indicator. J. TRTÍLEK (Coll. Czech. Chem. Comm., 1933, **5**, 302—309).—Alcoholic diphenylcarbazide can be used as internal indicator in the titration of chlorides by $Hg(NO_3)_2$, since in slightly acid solution it gives a bluish-violet colour with $Hg^{\cdot\cdot}$ ions but not with the feebly ionised $HgCl_2$. Co, Cu, Pb, Mn, and Cd do not interfere. D. R. D.

Microscopical determination of perchlorate. O. S. FEDOROVA (J. Gen. Chem. Russ., 1933, **3**, 377—384).—Krüger and Tschirch's drop method (B., 1931, 1134) can be applied to the detection of $< 0{\cdot}017 \times 10^{-6}$ g. of ClO_4', at a max. dilution of $1 : 2{\cdot}35 \times 10^6$. The method cannot be applied to determination of ClO_4' in KNO_3 or $KClO_3$. R. T.

Micro-determination of iodine [in organic substances] and a micro-desiccator. W. MÜNSTER (Mikrochem., 1933, **14**, 23—26).—A modification of Leipert's method (A., 1929, 1323) is described. F. L. U.

Detection of traces of iodides in presence of bromides and chlorides. A. VASSILIOU (Praktika, 1932, **7**, 349—351; Chem. Zentr., 1933, i, 2982).—5 c.c. of the solution are treated with 2 drops of 1% starch solution, 3 drops of 3·5% HCl, and 1 c.c. of I solution (0·1 g. I in 10 c.c. NaOH, and dilution of 1 c.c. to 100 c.c.). $1 : 10^6$ of I′ is detected by the blue coloration of starch by I in presence of I′. Tap-H_2O is treated with Na_2CO_3, evaporated to 50%, and filtered. A. A. E.

Detection of iodides with silver nitrate paper. A. J. VELCULESCU and J. CORNEA (Z. anal. Chem., 1933, **94**, 255—257).—Filter-paper soaked in 0·1M-$AgNO_3$ and dried gives a yellow colour with I′ (1 part in 10,000). The test works in presence of Cl′ and Br′, the three halides forming concentric zones, which become visible on exposure to light. H. J. E.

Titration of iodine in presence of iodide and iodate. E. CHIRNOAGA (Z. anal. Chem., 1933, **94**, 252—255).—Total I+iodide is determined by adding aq. Na_2SO_3 until the solution is just yellow, adding starch solution, and titrating with $AgNO_3$. Free I is then determined separately with $Na_2S_2O_3$. After this titration the liquid is acidified with H_2SO_4. Any HIO_3 present reacts with HI, liberating I, which is determined by $Na_2S_2O_3$. H. J. E.

Determination of fluorine in insoluble fluorides. P. URECH (Chem.-Ztg., 1933, **57**, 855—856). The Berzelius–Rose method has been critically examined. The determinations of K and Na in cryolite yield concordant vals. for the F content. Greef's titration method yields results about 0·7% higher, owing to its sensitivity to the [H·]. H. F. G.

Determination of oxygen in gases and waters.—See B., 1933, 962.

Determination of elemental sulphur. N. L. ALLPORT (Quart. J. Pharm., 1933, **6**, 431—435).—S, pure or in pharmaceutical products, with KCN in boiling aq. $N(C_2H_4{\cdot}OH)_3$, gives quantitatively in 1 hr. KCNS, which, after filtration, is determined by $AgNO_3$. R. S. C.

Determination of sulphur in sphalerite etc.—See B., 1933, 913.

Colorimetric determination of hydrogen sulphide, sulphides, and thiosulphates. A. GIBERTON (Compt. rend., 1933, **197**, 646—648).—$Na_2S_2O_3$ and $AgNO_3$ interact thus: $Na_2S_2O_3+2AgNO_3=Ag_2S_2O_3+2NaNO_3$, and $Ag_2S_2O_3+H_2O=H_2SO_4+Ag_2S$, half the S appearing as Ag_2S; this is separated and dissolved in aq. KCN or NaCN, from which the S″ is pptd. as colloidal PbS by aq. Na plumbite in presence of gelatin. The amount is determined colorimetrically by comparison with a similar solution, from a known amount of $Na_2S_2O_3$. The method is applicable whenever S can be separated entirely, or in known proportion, as Ag_2S. C. A. S.

Electrometric titration of sulphurous, selenious, and α-hydroxyalkylsulphonic acids. P. RUMPF (Compt. rend., 1933, **197**, 686—689).—Using the triode method of electrometric titration (cf. A., 1930, 545) the neutralisation curve of H_2SeO_3

agrees with previous results (cf. A., 1925, ii, 867). Addition of form-, acet-, but-, hept-, or benz-aldehyde gave no indication of formation of any "biselenite" compound. A solution of SO_2 similarly examined showed the presence of much SO_2 in solution as well as H_2SO_3. Addition of the above aldehydes indicated production of a strong monobasic acid by interaction of equal mols. Interaction is slow, and the p_H depends on the concn.; the acids are too strong to allow determination of their dissociation consts. by this method (cf. this vol., 31). The activity coeff. is > that of H_2SO_4 (cf. A., 1907, i, 1010). C. A. S.

Potentiometric determination of selenocyanates. R. RIPAN (Z. anal. Chem., 1933, **94**, 331—334).—$SeCN'$ may be accurately determined by potentiometric titration with $AgNO_3$ in neutral solution, down to a concn. 0·0007*N*. J. S. A.

Argentometric determination of selenocyanates with Fajans' adsorption indicators. R. RIPAN (Z. anal. Chem., 1933, **94**, 335—337).—Fluorescein may be used as an adsorption indicator in the titration of $SeCN'$ with $AgNO_3$. J. S. A.

Micro-determination of phosphorus with the Pulfrich photometer. M. GIANI (Giorn. Chim. Ind. Appl., 1933, **15**, 432—435).—Fiske and Subbarow's colour reaction for determining the various P fractions in body fluids and tissues (A., 1926, 443) yields quant. results, between 2 and 64×10^{-6} g. in 10 c.c., when measured by Pulfrich's photometric method. T. H. P.

Colorimetric determination of phosphate in presence of arsenate. Induced reactions. H. K. BARRENSCHEEN, J. BANGA, and K. BRAUN (Biochem. Z., 1933, **265**, 148—153).—The method of Braunstein (A., 1932, 1273), which exemplifies Skrabal's rule (A., 1905, ii, 805) for induced reactions, is impracticable, as is also that of Tschopp and Tschopp (A., 1932, 825). W. McC.

Determination of inorganic phosphate in the presence of arsenic. L. B. PETT (Biochem. J., 1933, **27**, 1672—1676).—The AsO_4''' is reduced to AsO_3''' by the addition to 25 c.c. of the $CCl_3{\cdot}CO_2H$ filtrate of 0·5 c.c. of $3N$-H_2SO_4 and about 0·4 g. of $NaHSO_3$, followed by heating for 1 hr. at 50°. The PO_4''' is then determined colorimetrically. W. O. K.

Colorimetric and nephelometric determination of phosphoric acid. F. ALTEN, H. WEILAND, and H. LOOFMANN (Z. Pflanz. Dung., 1933, **32**, **A**, 33—50).—A no. of existing methods are compared and limits of accuracy for varying ranges of $[PO_4'''']$ are determined. The influence of other substances present on the validity of results is examined. The colorimetric method of Teroda and the strychnine-molybdate nephelometric method (Rauterberg, A., 1932, 1102) proved the most satisfactory. A. G. P.

Detection of very small amounts of arsenic by the Gutzeit test. G. LOCKEMANN and B. F. VON BULOW (Z. anal. Chem., 1933, **94**, 322—330).—By the use of 66% $AgNO_3$ solution, the sensitivity of the test is increased to $0{\cdot}1\times10^{-6}$ g. As. J. S. A.

Sensitive test for boric acid suitable for biochemical investigations. F. HAHN (Compt. rend., 1933, **197**, 762—764).—(i) Enough 0·01*N*-NaOH and phenolphthalein are added to boiling aq. glycerol (1 : 1) to give a slight colour; a similar addition is made to the solution under examination, and the two solutions are mixed; if the latter contains $< 5\times10^{-7}$ g. B per c.c. the colour disappears. (ii) To the solution under examination are added bromothymol-blue and aq. NaOH or HCl to produce a green colour; mannitol is added to one half the mixture, and a drop of each placed on a porcelain plate. If 10^{-9} g. B per c.c. is present the solution containing mannitol will change in colour. The change is due to formation of a complex boro-polyhydroxy-compound of increased (cf. A., 1932, 78; this vol., 105). C. A. S.

Determination of boric and citric acids in nickel-plating baths.—See B., 1933, 872.

Determination of graphitic silicon in a siliceous residue. L. H. CALLENDAR (Analyst, 1933, **58**, 580—594).—The H_2 evolved on boiling the sample with 40 c.c. of 40% NaOH is measured in a modified Hempel gas-volumeter fitted with a pressure–temp. compensator (0·0001 g. Si = 0·16 c.c. H_2 at s.t.p.). The method gave satisfactory results when tested against Al or Si of known purity; against O_2 in the oxidation of pure Si or of Si from a Si–Al alloy; and against the gravimetric soda method (B., 1932, 844), the error being of the order of $\pm$0·3%. The usual empirical gravimetric methods give abnormal results, which increase with a rise in the temp. at which the residue is dried. J. G.

Analysis of glass.—See B., 1933, 915.

Spectroscopic determination of alkali metals in mica with the aid of the air–acetylene flame. A. K. RUSANOV (Min. Suir., 1933, **8**, No. 4, 21—26).—A modification of the Lundegardh burner and a specially designed atomiser were used. CH. ABS.

Separation and determination of the alkali metals using perchloric acid. V. Perchloric acid and chloroplatinic acid in the determination of small amounts of potassium in the presence of large amounts of sodium. G. F. SMITH and J. L. GRING (J. Amer. Chem. Soc., 1933, **55**, 3957—3961).—The method previously described (A., 1932, 711) is extended to the determination of 0·15% KCl in NaCl to within 0·01. The neutral anhyd. perchlorates from 1·48—1·63 g. of NaCl containing KCl are dissolved in 95 c.c. of hot 95% aq. EtOH and 0·2 g. of $H_2PtCl_6{,}6H_2O$ in 5 c.c. of 95% EtOH is added. After digestion, the liquid is cooled at 0° for 1 hr. The K is determined as K_2PtCl_6 or Pt. J. G. A. G.

Conductometric method of titrating potassium. J. H. BOULAD (J.S.C.I., 1933, **52**, 270—272T).—K is pptd. from a 36% EtOH solution as $K_2CaFe(CN)_6$ (I), by titrating with standard $Ca_2Fe(CN)_6$ solution. "Seeds" of (I) are added to initiate pptn. $Na^{\cdot}$, $Ca^{\cdot\cdot}$, or $Mg^{\cdot\cdot}$ (in presence of excess Ca) does not interfere; SO_4'' may be removed by addition of $Ca(OAc)_2$, as also may PO_4''' from alkaline solutions. For K concns. $< 0{\cdot}01N$, 50% EtOH should be employed. J. S. A.

Determination of potassium as perchlorate. M. LENGLEN and MILHIET (Ann. Falsif., 1933, **26**, 469—470).—The vol. of EtOH usually used for washing the ppt. of perchlorates is insufficient to remove $NaClO_4$ completely. It is proposed to double the vol., using EtOH saturated with $KClO_4$ ($1{\cdot}70\times10^{-4}$ g. per litre) to avoid loss. E. C. S.

Spectroscopic determination of lithium. A. K. RUSANOV (Min. Suir., 1933, **8**, No. 4, 27—32).—Lundegärdh's method was applied to solutions obtained by decomposing mica with H_2SO_4–HF and diluting with H_2O. $8{\cdot}5\times10^{-4}$ mg. of Li could be determined. CH. ABS.

Detection of cæsium, rubidium, and thallium. P. ROBIN (J. Pharm. Chim., 1933, [viii], **18**, 384—387).—Small amounts of Rb, Cs, and Tl (*e.g.*, in mineral waters) are detected by removal of NH_3 (if present), pptn. with $Na_3Co(NO_2)_6$, ignition of the ppt., extraction of the sol. nitrites, and conversion of these into chlorides; from these the bulk of Na and K are separated by the HCl–EtOH method, the residue is converted into nitrates, and the Cs, Rb, and Tl present are pptd. as Ag bismuthinitrites and identified spectroscopically. H. A. P.

Colorimetric determination of calcium as picrolonate. F. ALTEN, H. WEILAND, and E. KNIPPENBERG (Biochem. Z., 1933, **265**, 85—89).—The methods of Rona and Kleinmann (A., 1923, ii, 433) and of Feigl and Pavelka (A., 1924, ii, 784) are untrustworthy. By means of a modification of the method of Dvorzak and Reich-Rohrwig (A., 1931, 1259) 0·02—0·15 mg. of Ca can be determined in presence of $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, and $PO_4^{\prime\prime\prime}$. The solution of Ca picrolonate, after treatment with aq. Br, is made alkaline with NaOH and the red colour produced compared with that of a standard. W. McC.

Quantitative drop analysis. I. Apparatus and technique. P. L. KIRK. II. Determination of calcium. R. P. MILLER and P. L. KIRK (Mikrochem., 1933, **14**, 1—14, 15—22).—I. Micro-burettes, pipettes, titration vessels, filter, stirrer, water-bath, and other apparatus for the volumetric analysis of small quantities (about 0·04 c.c.) of liquid, and the technique of the operations involved, are described.

II. Ca has been determined by the oxalate–$KMnO_4$ method in 0·025—0·1 c.c. of $CaCl_2$ solution with a max. error of 1% by means of the apparatus described above. Results obtained with serum are of the same order of accuracy. F. L. U.

Conductometric determination of alkalis in lime and lime-water.—See B., 1933, 962.

Microchemical contributions. IX. L. ROSENTHALER (Mikrochem., 1933, **13**, 317—320; cf. this vol., 583).—With aconitine, alypine, berberine, brucine, quinidine, diocain, heroin, hydrastinine, pantocain, and strychnine, $KReO_4$ yields characteristic cryst. ppts. (cf. A., 1931, 448). Ca gives ppts. with alkaline hydroxyquinoline solution at much higher dilution than Sr or Ba; Cu and Pb also have very low limit concns. Ni and Cd, also Tl and Cr alum initially, give amorphous ppts. Oxidation of $CNS^{\prime}$ by acid $KMnO_4$ yields HCN, recognised by pptn. from $AgNO_3$+methylene-blue (cf. A., 1929, 337). NH_2Me, $NHMe_2$, and NMe_3 give the same drop reactions as NH_3 (cf. this vol., 798) except the Nessler test. J. S. A.

Rhodizonic acid as indicator in determination of barium. A. FRIEDRICH [with S. RAPOPORT] (Mikrochem., 1933, **14**, 41—48).—The results of titration of $SO_4^{\prime\prime}$ with $Ba^{\cdot\cdot}$ in acid solution, with Na rhodizonate as indicator, vary with the speed of titration. In neutral solution the colour of the comparison solution is not permanent. Addition of gelatin keeps the Ba rhodizonate in stable colloidal suspension, the colour of which is, however, rapidly destroyed by dil. HCl. Better, but not satisfactory, results are obtained by the use of gelatin in neutral solution. F. L. U.

Separation of beryllium from allied elements of the third group. P. ADAMI (Annali Chim. Appl., 1933, **23**, 428—432).—The volatility of $(HCO_2)_2Be$ serves for the quant. separation of Be from Fe and Al, but when Ti is present appreciable proportions of Be remain in the residue. T. H. P.

Electrometric determination of magnesium by means of the antimony electrode. A. ITANO and Y. TSUJI (J. Sci. Soil Manure, 1933, **7**, No. 1: Proc. Internat. Soc. Soil Sci., 1933, **8**, 165).—Accurate determinations of Mg may be made by the use of 0·1265*N*-KOH. In presence of Ca (> 4 times amount of Mg) the error is > 5%. A. G. P.

Colorimetric determination of magnesium. F. ALTEN, H. WEILAND, and B. KURMIES (Angew. Chem., 1933, **46**, 697—698).—To the slightly acid NH_3-free solution NaOAc is added, and Fe and Al are removed by 8-hydroxyquinoline (I). Ca is pptd. by NH_4 oxalate, Na tartrate is added to keep any remaining Al in solution, and the Mg is pptd. by adding more (I) and NaOH. The ppt. ($25—50\times10^{-6}$ g.) is dissolved in *N*-HCl, 1 c.c. of sulphanilic acid solution (8·6 g. in 1 litre of 30% AcOH) and 1 c.c. of $NaNO_2$ solution (2·85 g. per litre) are added, and the colour is compared with a standard. Owing to side reactions, including probably oxidation of the reagent, (I) solutions cannot be used for comparison. $10—500\times10^{-6}$ g. of Mg in 1 c.c. may be determined to ±6%. H. F. G.

Determination of small quantities of zinc in aluminium.—See B., 1933, 970.

Analysis of lead alloys.—See B., 1933, 871.

Gas-volumetric determination of lead dioxide.—See B., 1933, 864.

Electrolytic micro-determination of lead. H. BRANTNER and F. HECHT (Mikrochem., 1933, **14**, 30—40).—On account of the difficulty of maintaining the conditions necessary for the deposition of PbO_2 in a suitable form the micro-electrolytic method is not recommended. F. L. U.

Determination of lead dioxide.—See B., 1933, 962.

Oxidation of thallous salts to thallic, and reduction of thallic salts by sodium arsenite. F. ČUTA (Coll. Czech. Chem. Comm., 1933, **5**, 287—301).—$Tl^{\cdot\cdot\cdot}$ is reduced quantitatively to $Tl^{\cdot\cdot}$ by Na_3AsO_3 in acid, neutral, or alkaline solution. As an analytical method, accurate to 0·2%, $Tl^{\cdot\cdot}$ salts may be oxidised

to $Tl^{'''}$ by Br in presence of HCl or HBr (but not H_2SO_4, H_3PO_4, or $HClO_4$), excess of Br boiled off, the solution neutralised by $NaHCO_3$, added to excess of aq. Na_3AsO_3, the $Tl^{''}$ pptd. by KI, and the excess of $AsO_3^{'''}$ determined iodometrically. D. R. D.

Colour reactions of cuprous salts. G. Tartarini (Gazzetta, 1933, **63**, 597—600).—When a $Cu^{''}$ salt solution is reduced with N_2H_4 and a 0·7% solution of 2 : 2′-dipyridyl is added, a brownish-red coloration is produced, and if KI or KCNS is then added a yellow amorphous ppt. is produced in the cold or an orange ppt. if the solution is heated. Phenanthroline added to a $Cu^{'}$ salt solution yields first a brownish-red coloration, and, with an excess of reagent, a violet colour; the red solution yields a yellow ppt. with KI, whilst the violet solution yields a violet-blue ppt. A blue cryst. ppt. is formed if an excess of $NaClO_4$ is added to the violet solution; this reaction serves for the detection of 0·03 mg. of Cu in 1 c.c. The dipyridyl *compounds*, $CuI,C_{10}H_8N_2$, orange-red, $CuCNS,C_{10}H_8N_2$, orange-yellow, and the phenanthroline *compounds*, $CuCNS,C_{12}H_8N_2$, yellow-orange, $CuI,2C_{12}H_8N_2$, violet-blue, are described. H. F. G.

Determination of copper in ferrum reductum and ferrum pulveratum.—See B., 1933, 891.

Electrocapillary method of quantitative analysis. S. I. Dijatschkovski, V. Ustinskaja, and Mitropolski (J. Gen. Chem. Russ., 1933, **3**, 478—480).—If a current is passed through filter-paper wetted with aq. NH_3, and a barrier of Hg_2Cl_2 is placed on the paper between the electrodes, $NH_4^{'}$ moving to the cathode is retained by the Hg_2Cl_2, forming black $HgNH_2Cl$; if aq. NH_4Cl is similarly electrolysed, $NH_4^{'}$ is also retained, but without blackening of the Hg_2Cl_2. $K^{'}$ is identified at the cathode by the yellow, sharply-defined spot given by a drop of aq. $Na_2PbCo(NO_2)_6$, and Na by extracting the paper at the cathode, and adding $UO_2(OAc)_2$ to the extract. The rate of transport of group V ions diminishes in the order $Pb^{''}>Ag^{'}>Hg^{'}$. Crystals of KI and of K_2CrO_4 are placed between the electrodes, when an orange-yellow coloration, insol. in aq. NH_3, in the vicinity of the KI indicates Pb^{II}, a brick-red halo around the K_2CrO_4 (insol. in aq. NH_3) indicates Ag, and a rose-yellow coloration in the same location indicates Hg (Hg^{I} if it blackens with aq. NH_3, and Hg^{II} if it becomes pure yellow). R. T.

Colorimetric determination of aluminium. F. Alten, H. Weiland, and H. Loofman (Angew. Chem. 1933, **46**, 668—669).—The pptn. of Al by hydroxyquinoline is adapted to colorimetric determination. Ca, Mg, and Fe are first removed. E. S. H.

Analytical chemistry of rhenium. X. Determination of rhenium as dioxide. W. Geilmann and L. C. Hurd (Z. anorg. Chem., 1933, **214**, 260—268).—Pptn. of ReO_2 is unsatisfactory for determining Re^{IV}, owing to its ready oxidation, and the difficulty of washing out adsorbed material (cf. A., 1931, 583, 584). H. J. E.

Determination of iron. C. T. Bennett and N. R. Campbell (Quart. J. Pharm., 1933, **6**, 436—442).—Org. matter is destroyed by $KMnO_4$ (excess) and dil. H_2SO_4 before determination of Fe by $SnCl_2$–$HgCl_2$. R. S. C.

Detection and determination of nickel in commercial cobalt salts.—See B., 1933, 963.

Determination of molybdenum in manganese minerals. H. Hauptmann and M. Balconi (Z. anorg. Chem., 1933, **214**, 380—384).—The colorimetric determination of Mo by means of KCNS and $SnCl_2$ (A., 1932, 244) and $NHPh{\cdot}NH_2$ (A., 1930, 313) has been used in the examination of deep-sea Mn–Fe nodules collected by the Challenger Expedition. Mo was found in all the specimens examined. F. L. U.

Determination of molybdenum and lead by Fajans' method. II. C. Rajchinschtein and N. Korobov (J. Gen. Chem. Russ., 1933, **3**, 531—533).—The accuracy obtained by the method previously described (this vol., 246) for determination of Pb is > that given by other analogous methods. The titre of standard aq. $(NH_4)_2MoO_4$ can be determined with an accuracy of 0·3% by evaporating the solution, igniting the residue, and weighing the MoO_3 produced. R. T.

Microchemical reactions for detecting molybdenum and tungsten. G. Tartarini (Annali Chim. Appl., 1933, **23**, 367—372).—The formulæ ascribed by Martini (A., 1928, 387; 1932, 1104) to his Mo and W NH_2Ph–pyrocatechol complexes are disputed. The former has the formula $[MoO_2(C_6H_4O_2)_2]H_2,(NH_2Ph)_2,3H_2O$ and is of known type, and the latter, $[WO_2(C_6H_4O_2)_2]H_2,(NH_2Ph)_2,H_2O$, has been described by Weinland (A., 1920, i, 40; 1926, 397). T. H. P.

Potentiometric determination of molybdenum [in iron].—See B., 1933, 870.

Determination of tin as stannous sulphide. B. Linke and H. Preissecker (Z. anal. Chem., 1933, **94**, 238—239).—The Sn is dissolved in HCl (*d* 1·19), reduced to Sn^{II} by Mg, and pptd. as SnS by H_2S after dilution with hot H_2O. The ppt. is ignited and weighed as SnO_2. H. J. E.

Phenylarsinic acid as a reagent for determining tin. J. S. Knapper, K. A. Craig, and G. C. Chandler (J. Amer. Chem. Soc., 1933, **55**, 3945—3947).—0·1—0·3 g. of Sn in 150—200 c.c. of hot 2·5—5% HCl or < 7·5 vol.-% H_2SO_4 is pptd. rapidly and quantitatively by 35 c.c. of saturated aq. $PhAsO_3H_2$. The Sn is weighed as SnO_2 after ignition at 1100°. By this method Sn is separated quantitatively from Cu, Zn, Pb, Sb, Ni, Cd, and Fe (repptn. necessary), but Zr and Th are not separable and Bi requires special treatment. J. G. A. G.

Titration of bivalent tin with potassium chlorate. E. Azzarello and F. Abramo (Annali Chim. Appl., 1933, **23**, 438—450).—Contrary to Kulvarskaja's statement (A., 1932, 1012) the volumetric determination of $Sn^{''}$ by means of $KClO_3$ in boiling liquids is possible only in an atm. of CO_2 and with moderate concns. of HCl, and even then is not always trustworthy. When $As^{'''}$ is present, precautions must be taken to prevent Bettendorff's reaction occurring during the heating of the solution. Much Fe or little

Cu renders the method inapplicable, but $Sb^{'''}$ is, if anything, beneficial to the titration. T. H. P.

Behaviour of zirconium, thorium, and certain rare earths with 1 : 2 : 5 : 8-tetrahydroxyanthraquinone. A. S. KOMAROVSKI and I. M. KORENMANN (Z. anal. Chem., 1933, **94**, 247—249).—The reagent was used either in alkaline solution (0·05% in 0·5*N*-NaOH), or in EtOH solution (0·005%). A blue colour or ppt. formed with salts of Nd, Pr, Ce, La, Zr, and Th, the limiting concn. being 1 in 2, 0·94, 0·87, 0·50, 0·16, $0{\cdot}15\times10^6$, respectively. The test could also be applied with drops on filter-paper. H. J. E.

Determination of zirconium in iron, steel, and ferro-alloys.—See B., 1933, 920.

Colorimetric determination of vanadium. M. B. ZAPADINSKI and V. M. ZHOGINA (Tzvet. Met., 1932, 513).—The NH_4 molybdate–H_3PO_4 method of Razumnikov and of Zilbermintz and Rozhkova is criticised; colorimetric comparison is difficult, and the acidity must be maintained within narrow limits. CH. ABS.

Colour reaction for bismuth. A. D. POWELL (Quart. J. Pharm., 1933, **6**, 464—466).—0·005 mg. of Bi with dil. HCl, KI, and EtOH or $COMe_2$ imparts a red colour to EtOAc. The test can be adapted for colorimetric determination of Bi, in absence of Pb and certain other metals. R. S. C.

Volumetric determination of bismuth as oxychloride. E. VON MIGRAY (Chem.-Ztg., 1933, **57**, 774).—The Bi is pptd. as BiOCl from a slightly acid solution containing tartaric acid, the washed ppt. is dissolved in HNO_3, $AgNO_3$ is added to ppt. AgCl, and the excess of $AgNO_3$ is titrated with NH.CNS. A. R. P.

Detection of bismuth in presence of lead and mercury. A. I. SHEINKMAN (Farm. Zhur., 1933, No. 1—2, 22).—Dil. aq. NH_3 is added to a solution of the sample in HCl; the ppt. is washed with NH_4OAc and the filtrate tested for Pb ($K_2Cr_2O_7$ and H_2SO_4) and Hg ($SnCl_2$). The residue is dissolved in 2*N*-HNO_3 and tested for Bi (Na_2HPO_4; $K_2Cr_2O_7$ and NaOAc). CH. ABS.

Constant-temperature control circuit. H. CLARKE (J. Sci. Instr., 1933, **10**, 329—330).—The contacts of a thermometer control the grid bias potential of a valve directly coupled to the control grid of a gas relay, in the anode circuit of which are the heater coils. C. W. G.

Simple apparatus for thermal gas reactions, particularly for the thermal dissociation of water vapour. H. RHEINBOLDT (Z. physikal. Chem. Unterr., 1933, **46**, 58—64; Chem. Zentr., 1933, i, 3037).

Adiabatic, non-isothermal micro-calorimeter for the study of the thermal effects of radioactive substances. A. SANIELEVICI (J. Chim. phys., 1933, **30**, 513—527).—Apparatus and technique are described. E. S. H.

Apparatus for facilitating the reading of m.p. G. SPERONI (Annali Chim. Appl., 1933, **23**, 432—434).—An arrangement of mirrors brings together the image of the end of the thermometer thread and that of the m.-p. tube. T. H. P.

Hydrogen ultra-violet lamp. O. DARBYSHIRE (J. Sci. Instr., 1933, **10**, 322—325).—The construction of a robust tube for giving radiation of 3300—1850 Å. is described. C. W. G.

Dark-ground illumination in ultra-violet microscopy. J. SMILES (J. Roy. Microscop. Soc., 1933, [iii], **53**, 203—212).—A condenser suitable for work on virus is described. C. W. G.

Development, and scientific and technical uses, of *X*-ray tubes. W. GERLACH (Chem. Fabr., 1933, **6**, 419—426).—A lecture. H. J. E.

Estimating match-points in divided beam spectrophotometry. R. J. MACWALTER and S. BARRATT (J. Sci. Instr., 1933, **10**, 312—314).—Interference fringes are used instead of the lines of a discontinuous source. C. W. G.

Electrode material for spark spectroscopy. L. DEDE (Heræus Vacuumschmelze, [10th Anniv. Vol.], 1933, 84—85).—For absorption spectra in the region above 2200 Å., electrodes of "contracid B7M" (Cr 15, Ni 60, Fe 16, Mn 2, Mo 7%) give a uniformly bright spectrum with a regular line distribution. A. R. P.

Recording photodensitometer for *X*-ray powder photographs. W. O. MILLIGAN (Rev. Sci. Instr., 1933, [ii], 4, 496).—A simplified instrument for measuring the standard *X*-ray patterns obtained with the ordinary *X*-ray diffraction apparatus is described. N. M. B.

Experimental determination of mean effective wave-lengths and their application in heterochromatic photometry. H. BUCKLEY (J. Sci. Instr., 1933, **10**, 351—357).—The application of the spectrophotometer is described. C. W. G.

Intensity filter for the mercury line at 252·7 mμ. H. W. MELVILLE and H. J. WALLS (Trans. Faraday Soc., 1933, **29**, 1255—1259).—A mixture of S-free CCl_4 and *n*- or *cyclo*-hexane is used as the absorbing liquid. The extinction coeffs. of a no. of solutions were found to obey Beer's law. The applicability of the filter is illustrated by experiments on the photochemical chain reaction between H_2 and N_2O. E. S. H.

Registering photo-cell pyrometer. G. MULLER and H. J. ZETZMANN (Z. tech. Physik, 1933, **14**, 90—94; Chem. Zentr., 1933, i, 3971).

Elimination of errors due to absorption in the prism, and other causes, in infra-red absorption measurements. D. G. DRUMMOND (Proc. Durham Phil. Soc., 1933, **9**, 55—60).—Errors due to differential absorption of two beams in a prism and to the external optical system are considered. C. W. G.

Interferometer with polarised beams. A. DUFOUR (Compt. rend., 1933, **197**, 831—833).—The arrangement is such that the retardation changes monochromatic vibrations from rectilinear to elliptical; a suitable compensator then measures the retardation by a null method, converting the elliptical back to rectilinear vibrations. C. A. S.

Adaptation of the interferometer for hyperfine structure. G. S. MONK (Rev. Sci. Instr., 1933, [ii], 4, 527—528).—Faint secondary fringes due to reflexions from two uncoated surfaces in the ordinary Fabry-Perot interferometer are eliminated by two 30° prisms with their inner surfaces metallically coated and placed parallel. N. M. B.

New method of colorimetry. R. A. HOUSTOUN (Phil. Mag., 1933, [vii], 16, 945—953).—A colour-mixing spectrometer for matching and specifying colours is described. H. J. E.

1931 I.C.I. standard observer and co-ordinate system for colorimetry. D. B. JUDD (J. Opt. Soc. Amer., 1933, 10, 359—374).—The properties of the standard observer recommended by the International Commission on Illumination are given. Formulæ are given for calculating trichromatic coeffs., dominant wave-length, colorimetric purity, and luminous transmission from spectrophotometric data. E. S. H.

Filter for the study of the Raman effect. A. H. PFUND (Physical Rev., 1932, [ii], 42, 581—582).—A saturated solution of $NaNO_2$ is as effective as the quinine sulphate–Noviol glass combination for transmitting the 4358 Hg line and eliminating 4047. L. S. T.

Colorimetry in sugar manufacture.—See B., 1933, 887.

Immersion objective of the geometrical electron microscope. H. JOHANNSON (Ann. Physik, 1933, [v], 18, 385—413).—An apparatus serving as an immersion objective in the electron microscope (A., 1932, 209) is described, and its errors (astigmatism, chromatic and spherical aberrations, etc.) are discussed. A. J. M.

Proportional amplifier for indicating single corpuscular particles. B. ZIPPRICH (Z. Physik, 1933, 85, 592—617).—A "counter" has been developed using collision ionisation below the discharge limit to give amplification by 10^4, and this factor can be maintained const. A. B. D. C.

Thermocouple potentiometer. A. EGERTON and A. R. UBBELOHDE (J. Sci. Instr., 1933, 10, 310—311).—The e.m.f. to be measured is opposed by one nearly equal, produced by thermocouples inserted in thermostats, and the difference is measured directly with a millivoltmeter. C. W. G.

Simple high resistance. P. W. BURBIDGE (Nature, 1933, 132, 677—678).—Details of high resistances, suitable for carrying small currents, made by smoking a rod of silky quartz, are described. L. S. T.

Application of graphite as anode material to high-vacuum transmitting valves. E. E. SPITZER (Proc. Inst. Radio Eng., 1933, 21, 1075—1081). CH. ABS.

Apparatus for the determination of the resonance potential of mercury vapour for practice purposes. G. MÖNCH (Physikal. Z., 1933, 34, 765—766). A. J. M.

Apparatus for separating *iso*hydrogen (deuterium) oxide by electrolysis. W. D. HARKINS and C. DOEDE (J. Amer. Chem. Soc., 1933, 55, 4330—4331).—The apparatus contains 3·5 litres and operates at 400 amp. J. G. A. G.

Diffusion technique for the separation of the isotopes of hydrogen. R. M. LANGER (Physical Rev., 1932, [ii], 40, 1047—1048). L. S. T.

Apparatus for micro-electrolysis. H. BRANTNER and F. HECHT (Mikrochem., 1933, 14, 27—29). F. L. U.

Measurement of electrolytic conductivities at high frequencies, without electrodes. E. DENINA (Gazzetta, 1933, 63, 634—654).—Existing methods are reviewed in detail, and three new methods are described in which (*a*) the current is carried by capacity from electrodes placed against the outer walls of the vessel containing the electrolyte; (*b*) the electrolyte functions as the core of a transformer; and (*c*) the high-frequency current is used to heat the filaments of two diodes connected in a network with the unknown and a known resistance, and the anode currents are compared. The first method has been developed for abs. measurements. H. F. G.

Scale readings of isomeric esters on the magneto-optic apparatus. J. L. MCGHEE and M. LAWRENZ (J. Amer. Chem. Soc., 1933, 55, 4333—4334; cf. this vol., 889).—For corresponding *iso*- and *n*-alkyl acetates, where there is no change in the wts. of the positive and negative radicals, the scale readings are identical, but for isomerides where there is a change in the wt. of both positive and negative radicals, *e.g.*, MeOAc and HCO_2Et, different scale readings for the two compounds are obtained. J. G. A. G.

Accuracy of the Curie–Cheneveau magnetic balance. F. E. HOARE (Nature, 1933, 132, 514).—Measurements of the magnetic susceptibilities of inorg. salts by means of this balance are largely affected by the relative positions of specimen tube and magnetic poles. L. S. T.

Measuring syringe for analytical purposes. G. LJUNGGREN (Z. anal. Chem., 1933, 94, 240—247).—The syringe is controlled by a micrometer screw, and can be adapted as an automatic pipette, as a burette, for handling poisonous liquids, or for filling ampoules. With 1—3 g. of liquid an accuracy of 0·2—0·02% is attained. H. J. E.

Semi-micro-analysis. M. CHAIX (Bull. Soc. chim., 1933, [iv], 53, 697—700).—A simple apparatus for org. elementary analysis using 0·06—0·10 g. is described. D. R. D.

Distilling flask to prevent bumping. S. UCHIDA (J. Soc. Chem. Ind. Japan, 1933, 36, 551—552B).—Four or five hollow pockets are blown into the lower part of the neck of a Claisen flask. They are situated on a helical line around the neck and extend upward and outward so that the bumping liquid rises harmlessly into them and then falls back into the flask. M. S. B.

Laboratory ozoniser. L. I. SMITH and G. E. ULLYOT (J. Amer. Chem. Soc., 1933, 55, 4327—4328).—The apparatus previously described (A., 1925, ii, 896) has been simplified. H. B.

Micro-burette for carbon dioxide determination. S. WEHRLI (Arch. Gewerbepath. Gewerbehyg., 1933, **4**, 665—673). A. G. P.

Constant-pressure gasholder. J. LINDNER (Mikrochem., 1933, **13**, 313—316).—A simple form is described. J. S. A.

Standard and precision weights of molybdenum-chromium-nickel alloy. L. DEDE (Heraeus Vacuumschmelze [10th Anniv. Vol.], 1933, 81—83).—Contracid B7M (Cr 15, Ni 60, Fe 16, Mn 2, Mo 7%) has *d* 8·4, does not adsorb moisture from the air, and is unattacked in the ordinary laboratory atm. Standard wts. of this alloy give satisfactory service and the same tables may be used for reduction to vac. as are used with brass wts. A. R. P.

Micro-Meyer method of vapour density determination. P. DE CEUSTER (Natuurwetensch. Tijds., 1933, **15**, 189—191).—The apparatus is essentially the same as that used in the ordinary Victor Meyer method, although smaller, but the method of heating is slightly modified and the sample ($\not>$ 15 mg.) is weighed into a small capillary tube which need be sealed at one end only. The error is $\not>$ 1·5%, and a complete determination requires $<$ 2 hr. H. F. G.

Soluble anhydrite as a desiccating agent. II. Drying of organic liquids. W. A. HAMMOND and J. R. WITHROW (Ind. Eng. Chem., 1933, **25**, 1112—1115).—The material has the advantages of high affinity for H_2O, insolubility in, and inactivity towards, most org. liquids, stability, and economy, and is regarded as being of more general applicability than any other known drying agent. It should not be used at temp. $>107°$. Regeneration is effected by heating for 2 hr. at 230—250°, and no loss of efficiency occurs. H. F. G.

Improved method of orienting minute specimens for section cutting. D. P. WILSON (J. Roy. Microscop. Soc., 1933, [iii], **53**, 220—226).—A modification of Newth's second method is described. C. W. G.

New type of expansion apparatus. C. T. R. WILSON (Proc. Roy. Soc., 1933, A, **142**, 88—91).—In the apparatus described the expansion is made by suddenly reducing the pressure from one definite val. to another; the pressure thereafter remains const. while the gas expands as a result of the rising temp. This type of apparatus is less restricted as to the size and shape and position of the cloud-chamber than the usual form. L. L. B.

Optical proof of super-oscillations of a quartz crystal by the method of Debye and Sears, and its application to the determination of the velocity of sound in liquids. L. BERGMANN (Physikal. Z., 1933, **34**, 761—764).—The velocity of sound in a liquid can be determined by making use of the super-oscillations of a quartz crystal for the production of the waves, and obtaining the diffraction pattern by the method of Debye and Sears. A. J. M.

Vacuum-technical aid for chemists. W. VON MEYEREN (Chem. Fabr., 1933, 6, 449).—A small rotating oil pump and pressure gauge, capable of measuring to 0·01 mm. pressure, are described. E. S. H.

Vacuum measurements by means of heated wires. H. MURMANN (Z. Physik, 1933, **86**, 14—20).—The dependence of sensitivity of Pirani gauges on the various significant parameters is discussed. A. B. D. C.

Hoppler viscosimeter.—See B., 1933, 944.

Measurement of surface tension of liquids by the parallel-plate method. N. SATA and K. KURANO (Kolloid-Z., 1933, **65**, 191—195).—Tests of the method, using several org. liquids, indicate that it is suitable when plates of sufficient breadth are used. E. S. H.

Determination of size and charge of mist droplets. N. FUCHS and I. PETRIANOV (Kolloid-Z., 1933, **65**, 171—174).—Apparatus and technique are described whereby the size, charge, and concn. of liquid particles of radius $>$ 0·3 μ are determined by photography in an electric field. E. S. H.

New form of dew-point hygrometer. S. R. WILLIAMS (Rev. Sci. Instr., 1933, [ii], **4**, 549—550).—An improved Alluard hygrometer has a dew-forming surface of small heat capacity and concave form, the temp. of dew formation being measured by a thermocouple. N. M. B.

Paper hygrometers. J. GRANT (Nature, 1933, **132**, 677).—The relation between H_2O content and change in length (I) of paper is not linear between vals. of (I) which vary from 5 to 10% according to the kind of paper. There appears to be a crit. point at which there is a sudden loss of power to expand. The curves obtained by plotting H_2O content against expansion on wetting or contraction on drying do not quite coincide; the rate of shrinkage is always less for a given H_2O content. L. S. T.

Hygrometer for use in small spaces. K. MELLANBY (J. Sci. Instr., 1933, **10**, 349—351).—The change in wt. of 10 mg. of paper is measured by means of a torsion balance with sufficient accuracy to enable the R.H. of the air to be determined to 2%. C. W. G.

Measurement of radioactivity by a large plate condenser. (MME.) P. CURIE (J. Phys. Radium, 1933, [vii], **4**, 459).—A standard apparatus of the type described by Piccard (cf. this vol., 481) is described. N. M. B.

Euchlorine. W. LEFEVRE (Nature, 1933, **132**, 714).—Evidence showing that Davy knew the product of the action of HCl on $KClO_3$ to be a mixture of Cl_2 and an oxide of Cl and not a compound is quoted. L. S. T.

Euchlorine. J. R. PARTINGTON (Nature, 1933, **132**, 714; cf. preceding abstract).—There is no reason for supposing that Davy separated Cl_2 from the ClO_2 in "euchlorine" or that he gave the latter name to pure ClO_2. L. S. T.

Twenty-fifth anniversary of Brandt's introduction of iron oxide as a volumetric standard. O. GOEKE (Z. anal. Chem., 1933, **94**, 232—237).—Historical. H. J. E.

Geochemistry.

Theory of the ozone of the lower atmosphere and its relation to the general problem of atmospheric ozone. O. R. WULF (Physical Rev., 1932, [ii], **41**, 375—376).—The absorption of light by the mol. O_4 (I) in the earth's atm. accounts for the main part of the observed failure of radiation between 2200 and 2000 Å. to penetrate this atm. (I) also accounts for at least part of the O_3 in the lower atm. L. S. T.

Occurrence of water containing alum. T. GEDEON (Banyas. Kohas. Lapok, 1933, **66**, 155—157; Chem. Zentr., 1933, i, 3696).—H_2SO_4 formed by oxidation of sulphide rocks by dissolved O_2 attacks rocks forming Ca, then K, Na, and Mg, and finally Al sulphates. Hence H_2O contains $Al_2(SO_4)_3$ only when no K, Na, and Mg compounds are present in the rock, or when H_2SO_4 is present in excess of the quantity necessary to combine with these elements. A. A. E.

Alkali-alkaline underground water from the chalk formation. O. LUNING and K. BROHM (Z. Unters. Lebensm., 1933, **66**, 365—368).—The hardness of two samples of H_2O from test borings 6—7 m. deep in the upper chalk near Brunswick was largely due to $NaHCO_3$. The H_2O had a high I content (0·02 mg. per litre). E. C. S.

Dynamics of salt equilibrium in brine, ooze, and ice of the Doroninsky soda lake. B. P. PENTEGOV, A. A. KOSTROMINA, L. I. TONKONOGOV, and V. V. SIMANOV (Bull. Far Eastern Branch Acad. Sci. U.S.S.R., 1932, No. 3—4, 6—21).—The freezing of the lake on the surface and bottom decreases salt concn. in upper and lower layers; the concn. of salt solution above the ooze increases with depth, and that of the ooze decreases with depth. Separation of natural carbonates above the ice as cryohydrate is due to the fact that it has a higher m.p. than other salt components of the solid phase. Similar separation takes place in the layer over the ooze. The difference in composition of natural deposits, poor in HCO_3', and deposits prepared artificially, rich in HCO_3', is attributed to the fact that in the first case freezing starts from the surface and in the second case from the bottom. The lake contains Na_2CO_3, $NaHCO_3$, NaCl, Na_2SO_4, and KCl. CH. ABS.

Radioactivity of natural salines of the Ural region, Gorki district, and Bashkir Republic. B. A. NIKITIN and P. V. MIATELKIN (Bull. Acad. Sci. U.R.S.S., 1933, **7**, 675—681).—The composition and radioactivity of the H_2O of a no. of salt lakes are given. R. T.

Insolation hypothesis of rock weathering. H. DE TERRA (Amer. J. Sci., 1933, [v], **26**, 523—524).—Evidence in favour of insolation is given (cf. this vol., 928). C. W. G.

Volcanic history of Glass Mountain, Northern California. C. A. ANDERSON (Amer. J. Sci., 1933, [v], **26**, 485—506).—Analyses and petrological details are given. C. W. G.

Tourmaline-bearing gold-quartz veins of the Michipicoten district, Ontario. M. H. FROHBERG (Tsch. Min. Petr. Mitt., 1933, **44**, 349—409).—Lenticular veins of quartz with some tourmaline and carbonates occur in pre-Cambrian grano-dioritic rocks. They carry free Au, and Au is also present in the sulphide minerals. Near the veins the surrounding rocks are extensively altered by hydrothermal action. Analyses are given of fresh and altered porphyrite. L. J. S.

Composition and structure of sedimentary strata as dependent on organic equilibria. J. P. AREND (Compt. rend., 1933, **197**, 995—997).—The derivation by sedimentary rocks of H_2O and dissolved salts from the underlying igneous magma, and the influence thereof on such rocks and their elevation, are discussed. C. A. S.

Formation of oolitic deposits and terrestrial movements. J. P. AREND (Compt. rend., 1933, **197**, 847—850; cf. A., 1932, 829).—These deposits consist of 1—20% of marly sediments and 99—80% chemical ppts., the latter made up of two varieties, one calcareous, the other ferruginous containing micelles of compounds of Fe, Al, Mn, Si, P, V, and As; the composition of these three main constituents is almost const. throughout the deposit, only the relative amounts varying by reason of variation in the p_{H}. The method of formation of oolites is discussed. C. A. S.

Measurement of resistance of rocks. (MME.) BAYARD-DUCLAUX (Compt. rend. 1933, **196**, 1331—1333).—To secure good contact with the polished surface of specimens of rock ($2\times1\times1$ cm.) electrodes consisting of two leaves of beaten Ag or Au, one of Sn (0·4 mm. thick), and one of rubber (0·1 mm.) were used. C. A. S.

Influence of absorbed water on electrical conductivity of rocks. (MME.) E. BAYARD-DUCLAUX (Compt. rend., 1933, **197**, 854—856; cf. preceding abstract).—The conductivity of fourteen varieties of rocks has been examined by the author's method, using samples cut from specimens kept in a glass case for several months, (*a*) as cut, and (*b*) after drying for 3 days at 190° (when 0·02—1·5% H_2O was lost). (*a*) gave conductivities of from 5×10^{-11} mho (obsidian) to $2·5\times10^{-6}$ (schist); (*b*) were all non-conducting ($<8\times10^{-12}$ mho). The conductivity–time curves for the dried rocks when exposed to the atm. indicate that at first absorbed H_2O combines without producing mobile ions; these are later produced, causing electrolytic conductivity, and showing that conductivity is not a surface phenomenon. C. A. S.

Genesis of the manganese deposits of Chinhsien, Kwangtung. L. TIENCHEN (Bull. Geol. Soc. China, 1931, **11**, 307—313).—The material contains H_2O 0·35—1·39, Mn 33·1—46·61, Fe 6·43—27·52, Al 1·09—3·32, Si 0·83—3·59, Ni 0·69—2·13, Co 0·43—1·69, Sb 0·02—0·20, As 0·06—0·21, P 0·021—0·024, S trace—0·36%. CH. ABS.

Origin of gold at Kivu. G. GOFFART (Bull. Acad. roy. Belg., 1933, [v], **19**, 961—966).—The Au is derived from basic rocks. C. W. G.

Gold deposits of Morro Velho, Minas Geraes, Brazil. E. DE OLIVEIRA (Ann. Acad. Brasil. Sci., 1933, 5, 21—40).—An historical account is given of the working of the deposits, and their nature and mode of formation are described. H. F. G.

Ferrous manganous phosphate (zwieselite) found in Sao Gonçalo, Rio de Janeiro. O. BARBOSA (Ann. Acad. Brasil. Sci., 1933, 5, 17—19).—The mineral, *d* 3·9, contains FeO 37·28, MnO 21·44, P_2O_5 31·52, F 6·93%, with CaO (2%), MgO (1%), Fe_2O_3 (1·6%), etc. The crystallographic characteristics are described. H. F. G.

Potassic eruptive rocks of western Tonkin, with and without leucite. A. LACROIX (Compt. rend., 1933, **197**, 625—627).—In the north-west of Tonkin between Lao-kai and the Black river is a series of eruptive rocks in which K predominates (elsewhere in Tonkin Na predominates in such). They include nordmarkite, a melanite-diopside-syenite, and the K analogue of kvellite, traversed by diopside-minette dykes; also rocks deficient in SiO_2—shonkinite and tinguaite (the only rock of the series in which Na>K), traversed by dykes of cocite, a black rock containing olivine, diopside, biotite, and leucite, and somewhat analogous to jumillite but containing less SiO_2 and very little mica; it is the K analogue of murite. In places leucite is absent, giving a rock somewhat similar to absarokite. There is also an intrusion of a doleritic ankaramite. C. A. S.

Differential thermal analysis of montmorillionite clays (bentonites). J. ORCEL and (MLLE.) S. CAILLÈRE (Compt. rend., 1933, **197**, 774—777).—Temp.-time curves (cf. A., 1887, 785; B., 1933, 802) of the clays noted, and of mixtures in known proportions of montmorillionite (I) and kaolin (II) (the presence of 3% of which the method can detect), indicate that bentonite, otaylite, and amargosite are identical, and that confolensite, steargillite, and beidellite are mixtures in varying proportions of (I) and (II). (I) and (II) seem to be formed under the same conditions (cf. A., 1926, 143, 361; 1932, 1228). C. A. S.

The Kramer borax deposit in California and development of other borate ores. R. G. MEAD (Min. & Met., 1933, **14**, 405—409).—The Kramer deposit consists of beds of tincal and kernite between layers of shale containing colemanite and ulexite. A brief account is given of the origin, geology, and working of the deposit and of various other sources of boron minerals. A. R. P.

Great sulphur vein of Alston Moor. L. M. THOMPSON (Proc. Durham. Phil. Soc., 1933, **9**, 91—98).—Mineralogical details are given. C. W. G.

Accessory constituents of Hungarian bauxite. T. GEDEON (Magyar Chem. Fol., 1932, **38**, 134—140; Chem. Zentr., 1933, i, 2930).—Gant bauxite contains, besides Al_2O_3 40·02—73·00, Fe_2O_3 4·42—37·90, TiO_2 0·90—7·50, SiO_2 (0·34—7·10 quartz) 1·08—40·36%, also Mn_2O_3 0·2, Cr_2O_3 0·07, V_2O_5 0·07, NiO 0·0001—0·001, CaO 0·5, MgO 0·2, P_2O_5 0·5%, together with Zr and Be, but not K, Na, or S compounds. A. A. E.

Mineral analyses. G. VAVRINECZ (Magyar chem. Fol., 1932, **38**, 140—144; Chem. Zentr., 1933, i, 2930).—Analyses of various Hungarian and other minerals are recorded. A. A. E.

Hydrothermal metamorphosis of an ultrabasic intrusive at Schuyler, Virginia. H. H. HESS (Amer. J. Sci., 1933, [v], **26**, 377—408).—Petrological details and analyses are given. C. W. G.

Origin of tektites. C. FENNER (Nature, 1933, **132**, 571).—A criticism (cf. this vol., 252). L. S. T.

Origin of tektites. L. J. SPENCER (Nature, 1933, **132**, 571).—A reply to criticism (cf. preceding abstract). L. S. T.

Origin of tektites. J. B. SCRIVENOR (Nature, 1933, **132**, 678).—Spencer's view (this vol., 252) is the best yet proposed for the origin of tektites. L. S. T.

Origin of tektites. V. S. DUBEY (Nature, 1933, **132**, 678; cf. this vol., 802).—The Ra content (I) of eight tektites (II) varies from 0·9 to $1·00\times10^{-12}$ g. per g. The (I) of Darwin glass ($0·5\times10^{-12}$) is < that of (II) and agrees more closely with the (I) of several kinds of glass. The constancy of the val. found for (II) of such widely-distributed origin suggests some kind of genetic relationship, whilst its magnitude suggests an origin from some mass which has the same radioactivity and chemical composition as the granitic layers of the earth. L. S. T.

Roman copper from Wigtownshire and North Wales. G. C. WHITTICK and J. A. SMYTHE (Proc. Durham. Phil. Soc., 1933, **9**, 99—104).—Analyses and a photomicrograph are given. C. W. G.

Occurrence of anthraquinone dyes in mineral kingdom (graebeite). A. TREIBS and H. STEINMETZ (Annalen, 1933, **506**, 171—195).—Three specimens of shale containing a red org. mineral (termed graebeite) (I) have been found [at Ölsnitz (Saxony)] at a fault boundary of the "Rotliegende" and Carboniferous at a depth of 291 metres. (I) is in the interior of the shale and is localised at the fracture surfaces; it is removed mechanically. (I) is considered to be not of recent origin; it is improbable that it arises from the residual products of explosives, or by the action of micro-organisms introduced by wood, used during mining. (I) consists of a mixture of graebeites *a* (main) and *b* (below), and resembles (spectra; dyeing properties; reactions) the polyhydroxyanthraquinones. Dissolution of one sample of (I) in $CHCl_3$ and addition of light petroleum to the conc. extract gave 2 mg. of a substance [*i.e.*, (I)], m.p. 245° (not sharp), containing C 58·02 and H 5·38%. Extraction of a $CHCl_3$ solution of a second specimen with aq. NaOH and pptn. with AcOH afforded non-homogeneous (I), m.p. 250° (after sublimation in a high vac.) (C 56·81, H 3·85%). Similar isolation of (I) from a third specimen and repeated crystallisation from aq. $COMe_2$ gave *graebeite* a (II), $C_{18(17)}H_{14}O_8$, and graebeite *b* (III), separable mechanically. (III) shows absorption spectra different from that of (II). Sublimation of (II) at 165°/high vac. gives a *compound* (IV), $C_{14}H_8O_8$, m.p. 245°, which [like (II)] dyes mordanted wool and gives a Ag salt; (IV) is probably formed from (III) by loss of an

alkyl group. Distillation of (IV) with Zn dust affords a hydrocarbon, m.p. > 140°. Crystallographic data for (I), (II), and (IV), and absorption and fluorescence spectra for (I), (II), (III), (IV), and 1 : 2 : 4 : 5 : 8-penta- and 1 : 2 : 4 : 5 : 6 : 8-, 1 : 2 : 4 : 5 : 7 : 8-, and 1 : 2 : 3 : 5 : 6 : 7-hexa-hydroxyanthraquinones are given. H. B.

Peat formation. G. A. Fester (Anal. Asoc. Quím. Argentina, 1933, **21**, 47—52).—Formation of peat in absence of air, but under dry conditions, is exemplified by a rhizome of *Prosopanche Bonacinai*, Speg., found in calcareous sand in Buenos Aires, which consisted almost entirely of Ca humate. R. K. C.

Microstructures of some Chinese anthracites. C. Y. Hsieh (Bull. Geol. Soc. China, 1933, **12**, 153—171).—Clastoxylon, metadurain, euvitrain, and fusain were recognised. Chinese anthracite is of three types: lignocellulosic (high or low C), cutinic (high volatile matter), and powdered. The initial composition of vegetal matter plays no important part in anthracite formation. Ch. Abs.

Preservation of plant tissues in coal. H. G. A. Hickling and C. E. Marshall (Proc. Durham Phil. Soc., 1933, **9**, 105—116).—Descriptions of vitrain are given. C. W. G.

Radon content of soil gas. H. G. Botset (Physical Rev., 1932, [ii], **40**, 1027).—Determinations of the Rn content (I) of soil gases over extensive areas and under varying conditions show (i) no correlation between (I) and depth from which the sample is taken, (ii) (I) is higher during wet weather, (iii) certain soil formations appear to have more or less characteristic vals. for (I), (iv) large local variations in (I), and (v) a definite correlation between (I) and the heavy mineral content of the eroded edge of a known salt dome. L. S. T.

Zonal sequence of soil profiles in Saskatchewan, Canada. A. H. Joel (Soil Sci., 1933, **36**, 173—187).—The general orientation of profiles is described and their formation discussed. A. G. P.

Red Mediterranean soils of France and their origin. V. Agafonoff (Compt. rend., 1933, **197**, 693—695).—These soils are derived from the underlying limestones or dolomites, and consist, together with some $CaCO_3$ and $MgCO_3$, of the 1—1·5% of these rocks, insol. in aq. HCl, that has penetrated downwards from overlying strata into the limestone etc. in a colloidal condition, and has remained when the carbonates have been mainly removed; some part also is probably due to hot solutions that have risen from below. The exact character depends largely on the climate, as in the case of tropical laterites, from which, however, they differ. C. A. S.

Weathering and soil formation in Spitzbergen granite. E. Blanck and F. Giesecke (Geol. Rundschau, Salamon-Calvi-Festschr., 1932, **23A**; Proc. Internat. Soc. Soil Sci., 1933, **8**, 132).—The hydrolytic action of H_2O on granite in Arctic areas differs from that in more temperate zones. In Spitzbergen physical disintegration predominates over chemical decomp. A. G. P.

Organic Chemistry.

Electrochemical theory of the mechanism of organic reactions. R. Robinson (Inst. int. Chim. Solvay, Conseil Chim., 1931, **4**, 423—501; Chem. Zentr., 1933, i, 207—209).

Free methylene radical. F. O. Rice and A. L. Glasebrook (J. Amer. Chem. Soc., 1933, **55**, 4329—4330).—Decomp. of CH_2N_2 (in a current of Et_2O) at 700° and combination of the fragments produced with Hg (cf. A., 1932, 1108) gives $HgMe_2$ (since treatment with I affords HgMeI). It is inferred that if the CH_2 radical is produced it does not combine with Hg to give Hg:CH_2 (since addition of I should produce CH_2I·HgI), but probably removes a H atom. from a mol. of Et_2O to form free Me. Decomp. at 500° does not give Me, but Sb and Te mirrors are removed; Zn, Cd, Pb, and Hg are not attacked. H. B.

Isolation of free methyl and ethyl by reaction between sodium vapour and methyl and ethyl bromides. E. Horn, M. Polanyi, and D. W. G. Style (Faraday Soc., Nov., 1933, Advance proof, and Z. physikal. Chem., 1933, **B**, **23**, 291—304).—The formation of Me and Et from Na vapour and the alkyl halide at 200—300° is investigated by their initiation in a separate chamber of the chain reaction between H_2 and Cl_2, and by their combination with I to alkyl iodides. The yields deduced by the two methods were comparable and depended, as did the temp., on the partial pressure of Na. The fall in yield with increase in partial pressure of Na appears to be due at < 250° to a bimol. reaction (? dimerisation) between the radicals, although at higher temp. secondary reactions occur. The greatest observed distance of travel of the radicals is 8 cm. H. A. P.

Creation of free radicals in highly diluted gas reactions. H. von Hartel (Faraday Soc., Nov., 1933, Advance proof).—The production of free Et by bringing the vapour of EtBr at low pressure into contact with Na is described. The method can also be used for the demonstration of the formation of CH_2Ph and CN. A. J. M.

Thermal decomposition of organic compounds from the viewpoint of free radicals. IV. Dehydrogenation of paraffin hydrocarbons and strength of the C·C linking. F. O. Rice and M. D. Dooley (J. Amer. Chem. Soc., 1933, **55**, 4245—4247; cf. A., 1932, 1108; this vol., 930).—When C_2H_6 is heated at 850—950°, free Me radicals are formed (as shown by the removal of metallic mirrors). The activation energy of the change $C_2H_6 \longrightarrow 2Me$ is 79,500±3000 g.-cal. (which is the upper limit for the strength of the C·C linking) and is very close to the activation energy of C_2H_6. The formation of C_2H_4

and H_2 from C_2H_6 proceeds by way of free radicals or by this mechanism and simultaneous separation of H (cf. A., 1931, 819). H. B.

Decomposition of organic compounds into free radicals. F. O. RICE (Faraday Soc., Nov., 1933, Advance proof).—From the activation energies of dissociation the strength of C linkings is in the order C·C<C·H<C:C, and consequently preferential rupture of the C·C linking will occur in pyrolysis of org. compounds. Me and Et are shown by experiment to be the only free radicals, and the products of thermal decomp. of saturated hydrocarbons, ketones, and ethers are explained on the basis of chain reactions initiated by these. Free radicals are conveniently identified by combination with Hg and interaction of the Hg dialkyls thus formed with Hg halides. No indication of the formation of Pr or Bu by this means, or of Ac (sought as Ac_2 in absence of Hg); was obtained. The activation energies of dissociation into free radicals are determined by decomp. in a tube at two or more known temp. (T_1, T_2 abs.) and low pressures, and measuring the concn. of free radicals at the end of the tube by the times of disappearance of standard mirrors (t_1, t_2); then $\log \frac{t_1}{t_2} = -1/T_2$). H. A. P.

Thermal catalytic decomposition of methane. L. BELCHETZ (Faraday Soc., Nov., 1933, Advance proof).—Decomp. of CH_4 by a hot Pt wire at 900—1000° gives CH_2, identified by formation of CH_2I_2 with I; at higher temp. at. H (identified as HI) is also formed. CH_2 forms a compound with Te which with Br gives CH_2Br_2 and $TeBr_4$, and at a cooled glass surface (−65°) dimerises to C_2H_4. H. A. P.

Decomposition of hexane, *cyclo*hexane, and benzene in the positive-ray tube. R. CONRAD (Faraday Soc., Nov., 1933, Advance proof; cf. A., 1930, 1305).—The mass spectrograms indicate the existence of members of each group from C_1 to C_6. Under the conditions of the discharge a free radical tends to pass into a stable compound by extrusion of a H atom with formation of a double linking. H. A. P.

***iso*Paraffins of high mol. wt.** H. SUIDA and R. PLANCKH (Ber., 1933, 66, [*B*], 1445—1454).—Hentriacontan-—-ol (I) (palmitol) is converted by red P and I at 100—120° into *π-iodohentriacontane* (II), m.p. 33—35°, which does not react with Na, K, Mg, or Na–K in N_2 at 150°, gives a little hentriacontane (III) in presence of Et_2O, and with MgMeBr yields a little (II) and (III). Palmitone and Mg alkyl halide yield the corresponding carbinol, transformed by red P and I into the iodide, which is reduced to the hydrocarbon (Zn–HCl). Thus are obtained: *methyldipentadecylcarbinol*, m.p. 40—41°, and *π-methylhentriacontane* (IV); *ethyldipentadecylcarbinol*, m.p. 37—38°, and *π-ethylhentriacontane* (V), *butyldipentadecylcarbinol*, m.p. 46—47 or m.p. 47—48° after long preservation, and —-n-*butylhentriacontane* (VI); *dipentadecylcetylcarbinol*, m.p. 46—47°, and —-cetylhentriacontane (VII). The m.p. of (V), (VI), and (VII) vary greatly with age and pretreatment of the samples. Distillation of (IV) or (VI) under atm. pressure causes partial decomp. without darkening; the m.p. of the cryst. products (68—69° and 62—63°, respectively) indicates a partial elimination of the side-chain and maintenance of the main chain. $ClSO_3H$ causes complete decomp. of (VI) at 80°, whereas n-$C_{31}H_{64}$ is unaffected. (VI) reacts vigorously with $SbCl_5$. *iso*Paraffins with terminal branchings have uniformly smaller refractive indices and almost universally lower d than n-paraffins of similar mol. wt., whereas those with simple median branching show uniform higher vals. and those with multiple branching behave irregularly. Mol. refraction and mol. vol. are unsatisfactory criteria for elucidating the constitution of purely aliphatic, saturated hydrocarbons. Mol. refractive index is more helpful, but the vals. of Eisenlohr and Wohlisch are inapplicable to complex compounds for which the data CH_2: +20·455, H_2: −7·06 agree, to within ±0·1, with the observed vals. in the series $C_{16}H_{34}$—$C_{30}H_{62}$. H. W.

Unexpected reactions of ethylene compounds. A. BERTHOUD (Bull. Soc. Neuchatel. Sci. nat., 1931, **56**, 413—424; Chem. Zentr., 1933, i, 2931).—A discussion involving geometrical isomerism. A. A. E.

Position of fission of chemical linkings in unsaturated compounds. R. ODA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **22**, 47—58).—Examples show that the alternate strengthening and weakening of the linkings according to position along a chain from a double linking (A., 1932, 716) is general for non-metallic elements. The effect is discussed in terms of residual affinity, and the rule is extended to substances containing > one double linking, and is used to explain the formation of mol. compounds and other phenomena. CH_2Ph·OEt and CH_2Ph·OPr with EtOH at 200° give a little Et_2O and EtOPr, respectively. A. A. L.

Quantitative hydrogenation at 100—300 atmospheres. H. ADKINS (J. Amer. Chem. Soc., 1933, **55**, 4272—4275).—A modified form of the apparatus previously used (A., 1932, 925) is described. Procedures are outlined. H. B.

Preparation of butinene. T. Y. LAI (Bull. Soc. chim., 1933, [iv], **53**, 687—692).—Lebeau and Picon's method (A., 1913, i, 438) is modified; full details are given. H. B.

Cyclisation of substituted divinylacetylenes. D. T. MITCHELL and C. S. MARVEL (J. Amer. Chem. Soc., 1933, **55**, 4276—4279).—γζ-Dimethylocta-diene-Δ^{δ}-inene, conc. H_2SO_4, and AcOH at 0° (cf. this vol., 591) give 2 : 3 : 4 : 5-*tetramethyl*-Δ^4-cyclo*hexenone*, b.p. 84—86°/5 mm. (2 : 4-dinitrophenylhydrazone, m.p. 158—159°), oxidised (O_3) to AcOH and γ-keto-αβ-dimethylvaleric acid, dehydrogenated (Se at 400°) to 2 : 3 : 4 : 5-C_6HMe_4·OH, and reduced (H_2, Pt-black) to 1 : 2 : 3 : 4-*tetramethyl*cyclo*hexane*, b.p. 84°/5 mm. (dehydrogenated to prehnitene). *γζ-Diethylocta-$\Delta^{\beta\zeta}$-diene-Δ^{δ}-inene*, b.p. 80—81°/5 mm., prepared from OH·CEt_2·C:C·CEt_2·OH by Dupont's method (A., 1914, i, 134), is similarly converted into 3 : 4-*dimethyl*-2 : 5-*diethyl*-Δ^4-cyclo*hexenone*, b.p. 104—107°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 138—139°), which is reduced to 1 : 2-*dimethyl*-3 : 4-*diethyl*-cyclo*hexane*, b.p. 91—92°/4 mm. βε-Dimethylhexa-$\Delta^{\alpha\epsilon}$-diene-Δ^{γ}-inene (modified prep. given) could not

be cyclised. Cyclisation cannot be accomplished when the dieneinene polymerises rapidly. H. B.

Bromination of saturated aliphatic hydrocarbon gases. W. J. PERELIS (Ind. Eng. Chem., 1933, 25, 1160—1161).—CH_4, C_2H_6, n-C_3H_8, and n-C_4H_{10} are passed with Br over Fe at 290—375°. Pure monobromides are formed in every case with a sufficiently low Br concn., and the conversion, although small, is not appreciably < with more Br. In the case of C_2H_6 use of dry reagents considerably increases conversion. H. A. P.

Preparation and properties of neopentyl chloride in relation to molecular rearrangements. F. C. WHITMORE and G. H. FLEMING (J. Amer. Chem. Soc., 1933, 55, 4161—4162).—Cl_2 passed over neopentane at 0° in diffused daylight gives neopentyl chloride (I), b.p. 84·4°/760 mm., f.p. −20±1°, which is stable at 200° and forms a Grignard reagent (treatment with PhNCO affords $CMe_3{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, thus showing the absence of any rearrangement). Contrary to Tissier (A., 1893, i, 542), (I) does not react with AgOAc in Et_2O. (I) does not react with Mg alone, EtOH–KOH CuCN, EtOH–KOAc, or $HgPh_2$. The unreactivity of (I) indicates that the neopentyl group holds its electrons tenaciously. H. B.

Action of concentrated aqueous sodium hydroxide on nitromethane. H. S. FRY and J. F. TREON (Rec. trav. chim., 1933, 52, 827—832).—$MeNO_2$ reacts with 5—15N-NaOH at 130—140° (bath) in accordance with the theory previously developed (this vol., 370), viz., $MeNO_2+2NaOH \longrightarrow Na_2CO_3+NH_3+H_2O$. Reaction probably proceeds: $MeNO_2+3NaOH \longrightarrow 3H_2+NO_2{\cdot}C(ONa)_3 \longrightarrow 2H_2O+NH_2{\cdot}C(ONa)_3$; $NH_2{\cdot}C(ONa)_3+NaOH \longrightarrow NH_3+C(ONa)_4$; $C(ONa)_4+H_2O \longrightarrow Na_2CO_3+2NaOH$. H. B.

Micro-determination of ethyl alcohol and glycerol by means of a selenium photo-electric cell colorimeter. R. FONTEYNE and P. DE SMET (Mikrochem., 1933, 13, 289—304).—10 c.c. of aq. EtOH are treated with excess of $K_2Cr_2O_7$ (about 0·2N), in a pressure flask at 100° for 10 min. The excess of $K_2Cr_2O_7$ is determined from the extinction coeff. for light of 435—443 mμ, using a monochromator and a Se cell photometer. Application to glycerol is less accurate on account of incomplete oxidation. J. S. A.

Ethylene chlorohydrin. D. RADULESCU and P. L. MURESANU (Bul. Soc. Stiinte Cluj, 1932, 7, 129—153; Chem. Zentr., 1933, i, 3156).—Hydrolysis of $C_2H_4Cl{\cdot}OH$ (I) at 56° and 99° in 0·25—2N solution is unimol., the coeff. being 0·0000036 and 0·00029 at 56° and 99°, respectively. Velocity coeffs. calc. from a bimol. equation are also const. 0·2N- and N-$CaCl_2$, NaCl, and HCl have no effect. The formation of (I) from $C_2H_4(OH)_2$ and HCl at 99° in 0·2—2N solutions of equiv. quantities of reactants takes place extremely slowly. A. A. E.

Detection and determination of tribromoethyl alcohol. H. COLLATZ (Biochem. Z., 1933, 265, 199—202).—The alcohol (avertin), in aq. solution, is converted into the bis-p-nitrophenylhydrazone (I) (yield 93%) or the bis-2 : 4-dinitrophenylhydrazone (II) (yield 74%) of AcCHO by heating in a sealed vessel with 2N-HCl [for (II)] or 30% aq. AcOH and NaOAc [for (I)] for several hr. at 110—150° in presence of the appropriate hydrazine. W. McC.

Preparation and storage of tribromoethyl alcohol. W. H. BUTCHERS, K. BULLOCK, and G. R. PRIDDEY (Quart. J. Pharm., 1933, 6, 533—539).—Incipient decomp. of $CBr_3{\cdot}CH_2{\cdot}OH$ is best detected by the B.D.H. universal indicator. Appreciable decomp. occurs overnight at 38°. R. S. C.

Influence of branched chains on optical activity. Configuration of methyl*tert.*-butylcarbinol. P. G. STEVENS (J. Amer. Chem. Soc., 1933, 55, 4237—4240).—According to Freudenberg's displacement rule, $CHMePr^{\beta}{\cdot}OH$, $CHMeBu^{\alpha}{\cdot}OH$, and $CHMeBu^{\gamma}{\cdot}OH$ are configuratively related when they have the same sign of rotation. The order of lowering of optical rotation by various groups is Pr^{β} > *cyclo*hexyl > Bu^{γ}; Bu^{β} causes an exaltation. d-*Methylisopropylcarbinyl acetate*, b.p. 128·5—129°/758 mm., and *benzoate*, b.p. 83—84°/2 mm., and d-*methyltert.-butylcarbinyl acetate*, b.p. 140·5—141°/756 mm., and *benzoate*, b.p. 105—106°/5 mm., appear to be new. H. B.

Preparation and dehydration of δδ-dimethylpentan-β-ol (methylneopentylcarbinol). F. C. WHITMORE and A. H. HOMEYER (J. Amer. Chem. Soc., 1933, 55, 4194—4196).—δδ-Dimethylpentan-β-one is reduced (Na, moist C_6H_6) to 72% of δδ-dimethylpentan-β-ol (I), b.p. 137—137·5°/736 mm. (*carbamate*, m.p. 71°, obtained by the successive action of $COCl_2$ and aq. NH_3; α-naphthylurethane, m.p. 86·5—87°; 3 : 5-dinitrobenzoate, m.p. 95·2—95·7°; acetate, b.p. 92—92·5°/90 mm.; ββ-dimethylbutyrate, b.p. 92—94°/7—8 mm.), and 23% of ββδεηη-*hexamethyloctane-δε-diol*, b.p. 98—100°/2—3 mm., m.p. 34—36°. Dehydration of (I) with conc. H_2SO_4 gives (unexpectedly) an 82% yield of a mixture of δδ-dimethyl-Δ^{β}- (82%) and -Δ^{α}-pentenes (18%). H. B.

Common basis of intramolecular rearrangements. II. Dehydration of di*tert.*-butylcarbinol and conversion of the resulting nonenes into trimethylethylene and *iso*butene. F. C. WHITMORE and E. E. STAHLY (J. Amer. Chem. Soc., 1933, 55, 4153—4157).—$CHBu^{\gamma}_2{\cdot}OH$, b.p. 117—118°/166 mm., m.p. 50—51°, prepared by reduction of $COBu^{\gamma}_2$, is dehydrated by 1 : 4-$C_{10}H_6Cl{\cdot}SO_3H$ (I) at 180° (bath) to $CMe_2{:}CHMe$ (II) (77%), *iso*butene (III) (4%), and a complex mixture of nonenes, dipentenes, and di-, tri-, and tetra-*iso*butenes. Dehydration at < 155° gives 71% of nonenes, b.p. 123—140°/733 mm., converted by (I) at 145—205° into (II), (III), and polymeric material. The various reactions are interpreted by the theory previously developed (A., 1932, 1016). H. B.

Aliphatic compounds. V. Systems with heptadecyl alcohol and heptadecane. Polymorphism of octadecane. (MISS) P. C. CAREY and J. C. SMITH (J.C.S., 1933, 1348—1351; cf. this vol., 782).—F.p. of mixtures of heptadecyl (I), m.p. 53·83°, or hexadecyl with octadecyl alcohol show a medial change in direction in the liquidus curve at the "50–50" composition (cf. A., 1931, 684). Hepta-

decane (II) (this vol., 590) crystallises in transparent plates, m.p. 21·97° (α-form), which become opaque at about 10° (β-form). Octadecane (III) exists in two isomeric forms, m.p. 27·9—28·0° (β-form) and about 27·1° (α-form), the latter being unstable in the absence of impurity. Hexadecane–(II) mixtures crystallise in the α-form up to 95% hexadecane. In (II)–(III) mixtures [below 90% (III)], the α-form crystallises; above 90% (III) the α-form slowly changes into the β-form. J. L. D.

Preparation of primary acetylenic alcohols. T. Y. Lai (Bull. Soc. chim., 1933, [iv], **53**, 682—687).—Mg Δ^{α}-butinyl bromide (from MgEtBr and Δ^{α}-butinene) and CH_2O (gas) in Et_2O give 70% of *Δ^{β}-pentinen-α-ol* (*ethylpropargyl alcohol*), b.p. 81—82°/54 mm. Mg undecinyl and dodecinyl bromides similarly afford *Δ^{β}-dodecinen-α-ol* (90% yield), m.p. 29·5—30°, and *Δ^{β}-tridecinen-α-ol*, m.p. 34—35°, respectively. Δ^{β}-Octinen-α-ol, b.p. 98—99°/15 mm., Δ^{β}-noninen-α-ol, b.p. 118—120°/16 mm., and phenylpropargyl alcohol, b.p. 137—138°/15 mm., are similarly prepared in 70—80% yield. Propargyl alcohol could not be prepared from CH:CNa and CH_2O or by the action of $NaNH_2$, KOH, or soda-lime on $CHCl(CH_2Cl)_2$; a trace is obtained from CH:C·MgBr and CH_2O. H. B.

Ferric complex salts of aliphatic polyhydroxy-compounds. W. Traube, F. Kuhbier, and H. Harting (Ber., 1933, **66**, [*B*], 1545—1556).—Polyhydric alcohols and other polyhydroxy-compouuds yield Fe^{III} complexes in which Fe^{III} replaces 3 H in vicinal OH groups. The complexes of the simple sugars are derived from the aldehydic or ketonic form. In the sparingly sol. Ba–Fe^{III} complexes of normal constitution (Ba : Fe^{III} : compound = 1 : 1 : 1) Ba replaces H in 2 OH placed as nearly as possible together, whereby the OH of sugar oximes is considered vicinal to the neighbouring alcoholic OH. Complex salts of "normal" type are formed only by compounds with at least 5 OH. "Normal" Fe^{III} complexes are very stable and can be boiled without change in alkaline suspension or solution; those derived from reducing sugars are stable when dry, but in contact with H_2O gradually decompose with conversion of Fe^{III} into Fe^{II}. They are all subject to autoxidation. Introduction of Fe^{III} into an optically active polyhydroxy-compound causes an increase of [α]. In the production of the Fe^{III} complexes the use of a large excess of polyhydroxy-compound is frequently advisable. In the cases of glucose (I) or mannitol (II) at most 3—5% of (I) or (II) remains in solution after removal of the Ba–Fe^{III} complex. The polyhydroxy-compounds can be recovered from the complexes. Ba–Fe^{III} *compounds* of normal composition are obtained from the following: glucose ($+4H_2O$); mannose ($+3H_2O$); maltose, $C_{12}H_{18}O_{12}BaFe,2H_2O$; lactose ($+4H_2O$); sucrose glucoseoxime ($+H_2O$); fructoseoxime ($+3H_2O$); mannoseoxime ($+3H_2O$); mannoseoxime Me ether ($+3H_2O$); gluconic acid ($+4H_2O$), whence by means of Na_2SO_4 or $NaHSO_4$, *$C_6H_8O\ NaFe,2H_2O$*; amygdalin; arabitol ($+2H_2O$). Non-normal Ba–Fe^{III} *complexes* are derived from the following: galactose, $C_{24}H_{33}O_{24}Fe_3Ba_3,8H_2O$; arabinose, $C_{20}H_{26}O_{20}Fe_3Ba_3,8H_2O$; glycerol, $C_9H_{17}O_8FeBa_2,5H_2$; erythritol, $C_{20}H_{36}O_{20}Fe_2Ba_4,10H_2O$. Mannitol yields the *compounds* $C_6H_9O_6AlBa,2H_2O$ and $C_6H_9O_6BaCr,5H_2O$. Me ethers of sugar oximes are obtained by action on the sugars of NH_2·OMe prepared by methylation and subsequent hydrolysis of $OH·N(SO_3K)_2$. The *Me ethers* of mannoseoxime, galactoseoxime, and arabinoseoxime have m.p. 117—118°, 153°, and 120—121°, respectively. H. W.

Glycol fission, its mechanism and application. R. Criegee, L. Kraft, and B. Rank (Annalen, 1933, **507**, 159—197; cf. A., 1931, 461; 1932, 722; this vol., 62).—$Pb(OAc)_4$ (I) and MeOH containing about 0·1% of H_2O give the *compound* $Pb(OAc)_2(OMe)·OH$, which is stable in dry air but decomposes in MeOH (CH_2O is produced). The *compounds* $Pb(O·COOt)_2(OMe)·OH$ and $Pb(O·COPr)_2(OMe)·OH$ are similarly prepared. The *compounds*, $Tl(OAc)_2Me$, $Tl(OAc)_2Et$, and $Tl(OAc)_2Pr^{\beta}$ are obtained from $Tl(OAc)_3$ and ROH, whilst the *compound* $Mn(OMe)_2·OAc$ is prepared from $Mn(OAc)_3$ and MeOH. All the above compounds regenerate the original metal acetate when treated with AcOH. Prolonged interaction of (I) and MeOH gives ≮ 81% of CH_2O; EtOH similarly gives MeCHO (89%); $Pr^{\beta}OH$ reacts rapidly and yields $COMe_2$ (96%); $CH_2Ph·OH$ (in C_6H_6) also reacts rapidly and affords PhCHO (66%).

The reaction between (I) and αβ-glycols in AcOH is bimol. The velocity coeffs. (k_{20}; time in min.) for the following compounds are quoted in parentheses; the constitutions are assigned from the data obtained: *cis*-, m.p. 209—210° (all m.p. are corr.) (~120,000) (iso*propylidene* derivative, m.p. 75·6—76·2°), and *trans*-, m.p. 158·5—159·5° (0·03), -7 : 8-dihydroxyacenaphthenes, both oxidised to naphthalene-1 : 8-dialdehyde (*hydrate*, m.p. 130—130·4°; *di*-p-*nitrophenylhydrazone*, decomp. 229°); *cis*-, m.p. 187—189° (lit. 184°) (28,600), and *trans*-, m.p. 182—183° (lit. 158°) (0·06), -7 : 8-dihydroxy-7 : 8-dimethylacenaphthenes, which are converted into 1 : 8-*diacetylnaphthalene*, m.p. 171—172° (this is transformed by hot piperidine into 3-*methyl*-1′ : 8′-*naphthindenone*, m.p. 156°); *cis*-, m.p. 176—177° (lit. 171—173°) (33, 100), and *trans*-, m.p. 155·5—156·5° (284), -7 : 8-dihydroxy-7 : 8-diphenylacenaphthenes (II), which undergo fission to 1 : 8-dibenzoylnaphthalene, m.p. 188—190°; *cis*-, m.p. 201—202·5° (286), and *trans*-, m.p. 181·5—182·5° (24·7), -9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydrophenanthrenes, which are converted into 2 : 2′-dibenzoyldiphenyl. Previously published data are summarised. The ratio $k_{cis} : k_{trans}$ for a five-membered ring glycol is usually very much > that for a six-membered ring glycol; the low val. for (II) is ascribed to the large steric hindrance in the *cis*-isomeride. The half-change vals. (in sec.) for the velocity of fission of *trans-cyclo*hexane-1 : 2-diol in AcOH, C_6H_6, $PhNO_2$, $C_6H_4Cl_2$, and $C_2H_2Cl_4$ are 4340, 1·8, 1·6, 1·1, and 0·9, respectively. The mechanism of the reaction is now considered to be: $OH·C·C·OH + Pb(OAc)_4 \rightleftharpoons OH·C·C·O·Pb(OAc)_3 + AcOH$; $OH·C·C·O·Pb(OAc)_3 \longrightarrow AcOH +$ $\begin{matrix}·C·O\\·C·\end{matrix}>Pb(OAc)_2 \longrightarrow 2>CO + Pb(OAc)_2$. The relation

between reaction velocity and mol. structure is discussed in detail. H. B.

Addition of hydrogen to acetylene derivatives. XIX. J. S. Salkind, V. K. Teterin, and A. Ivanova (J. Gen. Chem. Russ., 1933, 3, 373—376).—Acetylenic *as*-γ-glycols were hydrogenated (colloidal Pd). OH·CPh$_2$·C:C·CMe$_2$·OH behaves very similarly to the *s*-γ-glycols; *i.e.*, after adding 2 H the rate of reaction is greatly diminished. The rate, in general, is > for the *s*-compound. The product has b.p. 91·5—92·5°. With OH·CPh$_2$·C:C·CMe·OH, also, the rate of hydrogenation is, as expected, between that of the two corresponding *s*-glycols, tetraphenyl- and dimethyl-butinediol. The final product is the saturated glycol, OH·CPh$_2$·CH$_2$·CH$_2$·CHMe·OH, m.p. 73°. The existence of an ethylenic glycol as intermediate was proved by the prep. of the corresponding γ-oxide, 2 : 2-diphenyl-5-methyl-2 : 5-dihydrofuran, m.p. 68°, by heating with a little conc. H_2SO_4 in AcOH. M. Z.

Hydrolysis of ethyl ether.—See this vol., 1252.

***n*-Butyl α-substituted-ethyl ethers.** H. R. Henze and J. T. Murchison (J. Amer. Chem. Soc., 1933, 55, 4255—4259).—CHMeCl·OBu (I) and CuCN in C_6H_6 give *Bu*^{a} *α-cyanoethyl ether* (α-n-*butoxypropionitrile*) (II), b.p. 170—172°/750 mm. (all b.p. are corr.), which with excess of the appropriate alcohol, a little H_2O, and dry HCl affords *Me*, b.p. 168—169°/750 mm., *Et*, b.p. 117—118°/52 mm., *Pr*^{a}, b.p. 204—205°/750 mm., *Bu*^{a}, b.p. 219—221°/750 mm., and n-*amyl*, b.p. 132—134°/38 mm., α-n-*butoxypropionates*. (II), Pr^{a}OH, and Et$_2$O–HCl give α-n-*butoxypropionamide*, b.p. 140—141°/35 mm., m.p. 24—26°. α-n-*Butoxypropionic acid*, b.p. 129—130°/38 mm., is prepared by hydrolysis [aq. Ba(OH)$_2$] of (II). (II) and the appropriate MgRX give *Me*, b.p. 164—166°/750 mm., *Et*, b.p. 80—82°/35 mm., *Pr*^{a}, b.p. 195—197°/750 mm., *Bu*^{a}, b.p. 114—116°/35 mm., and n-*amyl*, b.p. 129—130°/35 mm., α-n-*butoxyethyl ketones*; these give oily products with NHPh·NH$_2$, *p*-NO$_2$·C$_6$H$_4$·NH·NH$_2$, and semicarbazide. (I) and NaOAc in C_6H_6 afford α-n-*butoxyethyl acetate*, b.p. 54—54·5°/19 mm.; with NaOBu at 100°, *acetaldehyde di*-n-*butylacetal*, b.p. 51°/12 mm., results. The v.p. of many of the above compounds are determined at 50—200° and the corresponding latent heats of vaporisation calc. Other physical data are given. H. B.

Reaction between aliphatic orthoformates and acetone. H. W. Post (J. Amer. Chem. Soc., 1933, 55, 4176—4177).—CMe$_2$(OEt)$_2$ is obtained in 13—30% yield from equimol. amounts of COMe$_2$, CH(OEt)$_3$, and EtOH in presence of conc. H_2SO_4, conc. HCl, or NH_4Cl; none is produced if EtOH or CH(OEt)$_3$ is omitted, or when *iso*amyl alcohol is used instead of EtOH. Replacement of EtOH by Et$_2$O with H_2SO_4 as catalyst gives the same amount (13%). Equimol. quantities of COMe$_2$, PrOH, and CH(OPr)$_3$ in presence of NH_4Cl (0·15 g. per 0·01 mol. of COMe$_2$) afford 25—30% of CMe$_2$(OPr)$_2$; CMe$_2$(OR)$_2$ was not produced similarly from BuOH, Bu^{s}OH, and amyl and *iso*amyl alcohols with the corresponding CH(OR)$_3$. Illumination of a mixture of CMe$_2$(OEt)$_2$ (1 mol.) and BuOH (2 mols.) at room temp. for 1 week gives CMe$_2$(OEt)·OBu (16%) and CMe$_2$(OBu)$_2$ (10%). H. B.

Esters of nitric acid. A. Majrick (Chim. et Ind., 1933, 29, Spec. no., 727—735).—Hydrolysis of nitric esters with NaHSO$_3$ gives SO_4'', S_2O_6'', and NO_2', whilst Na$_2$S gives S_2O_3'', S_3'', and NO_2', no aldehydes being formed in either case. Approx. methods of analysis of the resulting mixtures are described. CH$_2$Cl·CH$_2$·NO$_3$ with Na$_2$S also gives (OH·C$_2$H$_4$)$_2$S. Hydrolysis with EtOH–H_2SO_4 gives EtNO$_3$, EtNO$_2$, and MeCHO, the speed of hydrolysis of the nitrates being in the order glycol>glycerol>pentaerythritol. Starch nitrate also gives HCO$_2$Et. Tartaric acid dinitrate at room temp. gives dihydroxytartaric acid, whilst more conc. H_2SO_4 and higher temp. gives mainly tartaric acid. The mechanism of hydrolysis with these and other reagents is discussed, the results being considered to favour the peroxide formula, RO·O·N:O, for nitric esters. A. A. L.

Ring–chain tautomerism of partly acylated polyhydric alcohols. II. H. Meerwein and H. Sonke (J. pr. Chem., 1933, [ii], 137, 295—321; cf. A., 1931, 1395).—The position of equilibrium between the open-chain and cyclic forms of the β-hydroxyethyl chloroacetates may be determined by measurement of $M[\alpha]$, the former having the calc. val. or a slight exaltation, and the latter a slight depression. Although the trichloroacetate gives the cyclic ether (78% of theory) only with CH$_2$N$_2$, the equilibrium in the ester itself is in favour of the open-chain form. Attempts to separate the two forms by vac.-distillation failed. The chloroacetates are better prepared from the acid chloride and (·CH$_2$·OH)$_2$, the alternative route from the acid and C$_2$H$_4$O tending to give mono-esters of the polyethylene glycols, complete separation from which is difficult. *Et*, b.p. 119—120°/10 mm., m.p. 76·4°, Pr^a, b.p. 99°/2·1 mm. (*loc. cit.*), and *Bu*^{a}, b.p. 126·5°/5·85 mm., *methylene trichloro-orthoacetates* are prepared by alcoholysis of the Me ester in presence of HCl. *β-Hydroxyethyl dichloroacetate*, b.p. 81—82°/0·5 mm., undergoes disproportionation when treated with CH$_2$N$_2$, and in addition to small amounts of *Me methylene dichloro-orthoacetate*, b.p. 91—92·5°/9 mm. (*Bu*^{a} *methylene* ester, b.p. 117—119°/10 mm.), and *β-methoxyethyl dichloroacetate*, b.p. 58°/0·85 mm. (also prepared from OMe·CH$_2$·CH$_2$·OH and CHCl$_2$·COCl), (·CH$_2$·OH)$_2$, OMe·CH$_2$·CH$_2$·OH, (·CH$_2$·OMe)$_2$, and (·CH$_2$O·CO·CHCl$_2$)$_2$ are also formed. The open-chain and cyclic ethers are separated by hydrolysis of the former. *β-Hydroxyethyl chloroacetate*, b.p. 84°/0·95 mm., gives with CH$_2$N$_2$ only disproportionation products and *β-methoxyethyl chloroacetate*, b.p. 60°/1·3 mm., no cyclic ether being detected. Refractometric measurements show the original ester to be almost entirely acyclic. *Ethylene glycol chloroacetate*, m.p. 45—46·5°, b.p. 142—144°/2 mm., and *diethylene glycol*, b.p. 130—142°/0·2 mm., and *triethylene glycol hemichloroacetate*, b.p. 180—195°, are also described. *γ-Hydroxy*-n-*propyl*, b.p. 101—102·5°/1·4 mm., and *β-methyl-β-hydroxymethylpropyl trichloroacetate*, b.p. 133·5—134°/9 mm., 99°/0·45 mm., react abnormally with CH$_2$N$_2$, giving CHCl$_3$ and

carbonates of high mol. wt. of the corresponding glycols. The former shows the same behaviour with NEt_3, and it is possible that basic impurities in the CH_2N_2 are responsible. H. A. P.

β-Chloroethyl esters of sulphurous acid. J. F. KOMISSAROV (J. Gen. Chem. Russ., 1933, 3, 309—312).—Excess of $CH_2Cl{\cdot}CH_2{\cdot}OH$ (I) and hot $SOCl_2$ give β-chloroethyl sulphite (II), b.p. 117·5—118°/4 mm., whereas a slight excess of cold $SOCl_2$ gives β-chloroethyl chlorosulphinate (III), b.p. 84—85°/20 mm. (III) is an intermediate product in the first reaction, since it gives (II) on heating with more (I) and, conversely, is formed on treatment of (II) with excess of $SOCl_2$, a similar result being also obtained by adding PCl_5. Instead of (I) β-chloroethyl nitrite can be employed. M. Z.

Esters of chlorosulphonic and sulphuric acids. R. LEVAILLANT (Compt. rend., 1933, 197, 648—651; cf. A., 1929, 1269; this vol., 48).—Chlorination of the corresponding sulphite in a freezing mixture yields Bu^{α} (I) (96%) and βγ-dichloropropyl chlorosulphonates (90%). *β-Bromoethyl chlorosulphonate*, b.p. 103—106°/20 mm., is obtained (81%) from the sulphite and SO_2Cl_2. $CH(OPr^{\alpha})_3$, b.p. 82—84°/12 mm. (1 mol.), and $ClSO_2{\cdot}OPr^{\alpha}$ (II; 1 mol.) at 85—105° yield $Pr^{\alpha}{}_2SO_4$, b.p. 110°/13 mm. (65—70%), also obtained (55—60%) from (II) and $Pr^{\alpha}{}_2SO_3$ at 80—100° in presence of a little $ZnCl_2$. *CH(OBu$^{\alpha}$)$_3$*, b.p. 121—122°/12—13 mm., and (I) at 70—80°, or (I) and $Bu^{\alpha}{}_2SO_3$ ($ZnCl_2$) give *Bu_2SO_4*, b.p. 103—105°/1·5 mm. γ-Chloropropyl sulphite and chlorosulphonate at 110—150° yield $CH_2(CH_2Cl)_2$ and *γ-chloropropyl sulphate*, b.p. 163—165°/4 mm. (81%). A. C.

Aliphatic esters of tetrathio-orthocarbonic acid. H. J. BACKER and P. L. STEDEHOUDER (Rec. trav. chim., 1933, 52, 923—934).—Arndt's method (A., 1911, i, 918; 1913, i, 396) of prep. of $C(SAr)_4$ is applicable to the prep. of $C(SAlk)_4$. Thus, *S*-methyl*iso*thiocarbamide sulphate (I) and $NaNO_2$ in 2*N*-HCl give the S-*methyliso*thiocarbamide salt (II), explodes about 85°, of dinitrosomethyl*iso*thiocarbamide, $OH{\cdot}N{:}N{\cdot}C(:N{\cdot}NO){\cdot}SMe$ [*K* salt, explodes violently at about 120°, obtained from (II) and aq. KOAc]. (II) and aq. NH_3 at 50° afford *Me tetrathio-orthocarbonate* (III), b.p. 126—127°/12 mm., m.p. 65° (*compound* with 4 mols. of $HgCl_2$), which is oxidised by HNO_3 or H_2O_2–AcOH to $MeSO_3H$ and by $KMnO_4$ to $MeSO_3H$ and $CH_2(SO_2Me)_2$, reacts with Br in $CHCl_3$ to give a *tetrabromide*, $C(SMe)_2(SBr_2Me)_2$, decomp. about 122°, and with I in CS_2 affords *tetra-*, m.p. 102—103°, *hexa-*, m.p. about 73·5—75° (decomp.), and *dodeca-*, m.p. 67—68·5° (decomp.), *-iodides*. During the treatment of (II) with aq. NH_3, prior addition of a further quantity of (I) is recommended. (III) can be obtained without isolating (II). The S-*ethyliso*thiocarbamide salt, explodes about 95°, of dinitrosoethyl*iso*thiocarbamide is similarly converted into *Et tetrathio-orthocarbonate*, m.p. 33—33·5° (cf. Claesson, A., 1877, 294) (*tetrabromide*, m.p. 67—67·5°), which is oxidised ($KMnO_4$) to $EtSO_3H$. *Pr$^{\beta}$ tetrathio-orthocarbonate*, m.p. 61·4° (crystallographic data given) (*compound* with 4 mols. of $HgCl_2$, decomp. slowly > 100° without melting), is similarly prepared. The S-tert.-*butyliso*thiocarbamide salt, explodes at fairly high temp., of dinitroso*tert.*-butyl*iso*thiocarbamide is unaffected by aq. NH_3; with aq. NaOH, $Bu^{\gamma}SH$ is formed. Other attempts to prepare $C(SR)_4$ are summarised (cf. this vol., 696). H. B.

"Radial" tetrathio-orthosilicic esters. II. H. J. BACKER and F. STIENSTRA (Rec. trav. chim., 1933, 52, 912—915).—*Bu$^{\alpha}$*, b.p. 200°/2·5 mm., 210°/4 mm., sec.-*Bu*, b.p. 182°/4 mm., *Bu$^{\beta}$*, b.p. 183°/4 mm., *Ph*, m.p. 114·5—115°, and p-*tolyl*, m.p. 128·5—129°, *tetrathio-orthosilicates* are prepared from $SiCl_4$ and the appropriate RSNa in C_6H_6 (cf. this vol., 144). $Bu^{\gamma}SNa$ similarly gives *Bu$^{\gamma}$ chlorotrithio-orthosilicoformate*, $ClSi(SBu^{\gamma})_3$, m.p. 71—71·5°. H. B.

"Radial" tetrathio-orthostannic esters. H. J. BACKER and J. KRAMER (Rec. trav. chim., 1933, 52, 916—922).—$SnCl_4$ and the appropriate Alk·SNa in C_6H_6 give the following alkyl tetrathio-orthostannates, $Sn(SAlk)_4$: *Me*, b.p. 81°/0·001 mm., m.p. 31°; *Et*, b.p. 105°/0·001 mm.; *Pr$^{\alpha}$*, b.p. 123°/0·001 mm., *Pr$^{\beta}$*, b.p. 92°/0·001 mm.; *Bu$^{\alpha}$*, b.p. 136°/0·001 mm.; sec.-*Bu*, b.p. 111°/0·001 mm.; *Bu$^{\beta}$*, b.p. 126°/0·0005 mm.; *Bu$^{\gamma}$*, m.p. 188° (crystallographic data given); tert.-*amyl* (I), m.p. 44°. tert.-*Amyl chlorotrithio-orthostanniformate*, $ClSn(S{\cdot}CMe_2Et)_3$, is obtained using an excess of $SnCl_4$; it reacts with $CMe_2Et{\cdot}SNa$ to give (I). $CMe_2Et{\cdot}SH$, b.p. 95°, is prepared from CMe_2EtBr and $CS(NH_2)_2$ in H_2O and subsequent decomp. with 5*N*-NaOH. EtSH and $SnCl_4$ in H_2O give Et_2S_2. H. B.

Walden inversion. I. Dependence of reaction direction on number of free carboxyl groups. A. RAO and P. C. GUHA (J. pr. Chem., 1933, [ii], 138, 167—183).—A general survey of reactions accompanied by inversion shows numerous exceptions to Horton's rule (A., 1913, ii, 743). PCl_5 is not a "const. reagent," and KOH or NaOH and Ag_2O do not always behave differently; successive action of $SOCl_2$ and Ag_2O always converts a OH-acid into its antipode, but this is not the case with NH_2-acids and NOBr–NH_3 or PCl_5–NH_3. H. A. P.

Ester syntheses. I. Rational preparation of esters. E. THIELEPAPE [with A. FULDE] (Ber., 1933, 66, [*B*], 1454—1460).—CaC_2 is recommended for the removal of H_2O formed during esterification, and two forms of apparatus are depicted, whereby immediate contact of CaC_2 with the boiling mixture is avoided. The addition of C_2HCl_3, C_6H_6, PhMe, $CHCl_3$, CCl_4, or Et_2O is advocated, whereas $C_2H_2Cl_4$, $C_6H_4Me_2$, or PhOMe affords little advantage. The prep. of $(\cdot CO_2Et)_2$, EtOBz, $CH_2(CO_2Et)_2$, $(\cdot CH_2{\cdot}CO_2Et)_2$, and EtOAc is detailed. H. W.

Preparation of *tert.*-butylacetic [ββ-dimethylbutyric] acid and derivatives. A. H. HOMEYER [with F. C. WHITMORE and V. H. WALLINGFORD] (J. Amer. Chem. Soc., 1933, 55, 4209—4214).—δδ-Dimethylpentan-β-one is oxidised (NaOBr) to 80—90% of ββ-dimethylbutyric acid (I) [*Na* and *Ca* salts; chloride (II), b.p. 79—81°/150 mm.; Me, b.p. 126·5°/739 mm., Et, b.p. 144·5—144·7°/739 mm., Pr$^{\alpha}$, b.p. 92°/65 mm., Bu$^{\alpha}$, b.p. 91°/30 mm., benzyl, b.p. 146—148°/26 mm., bornyl, b.p. 115—117°/5 mm., and menthyl, b.p. 114—115°/4—4·5 mm.,

esters; amide (III), m.p. 132°; diethylamide, b.p. 69°/3 mm.; anilide, m.p. 131°; nitrile, b.p. 135—136·4°/737 mm., m.p. 32·5°, obtained by dehydration ($POCl_3$ in C_6H_6) of (III)]. Vinyldiacetonealkamine ββ-dimethylbutyrate hydrochloride, m.p. about 210° (decomp.), is prepared from vinyldiacetonealkamine hydrochloride and (II) at 100—160°. (I), Br, and PCl_3 at 60—100° give *α-bromo-ββ-dimethylbutyric acid*, m.p. 72—73° [bromide, b.p. 82°/18 mm.; *amide*, m.p. 138°, reduced (Zn, aq. AcOH) to (III); *diethylamide*, b.p. 106—109°/5 mm., m.p. 35—37°; *Et*, b.p. 93°/23 mm., benzyl, b.p. 145—147°/4·5 mm., *menthyl*, b.p. 148—150°/4 mm., and bornyl, b.p. 148—153°/4—5 mm., esters], the chloride, b.p. 93—97°/37 mm. [by bromination of (II)], of which with $CO(NH_2)_2$ affords *α-bromo-ββ-dimethylbutyrylcarbamide*, m.p. 188·5°. H. B.

Nonadecoic acid. S. Shiina (J. Soc. Chem. Ind. Japan, 1933, **36**, 569B).—Et stearate is converted successively (A., 1924, i, 827) into octadecyl alcohol, m.p. 57·8—58·0°, the iodide, m.p. 32·2—33·3°, and nonadecoic acid, m.p. 68·2—68·4° (Et, m.p. 36·1—36·2°, and Me, m.p. 38·9—39·0°, ester). J. L. D.

Dehalogenation of aliphatic bromo-acids. Bromo- and dibromo-olefines. G. B. Bachman (J. Amer. Chem. Soc., 1933, **55**, 4279—4284).—CHAlk:CH·CO_2H [from Alk·CHO and $CH_2(CO_2H)_2$ in C_5H_5N] and Br in CS_2 at 5° give CHAlkBr·CHBr·CO_2H, which when heated with C_5H_5N (3 mols.) give CHAlk:CHBr (26—35% yield) and CHAlk:CBr·CO_2H; similar decomp. occurs when the Na, K, NH_4, Ag, and C_5H_5N salts are heated in H_2O. CHAlkBr·CBr_2·CO_2H in boiling aq. Na_2CO_3 (slight excess) give CHAlk:CBr_2 (70—80% yield). The following compounds are new: Δ^{α}-*octenoic acid*, b.p. 154° (corr.)/22 mm. (p-*bromophenacyl* ester, m.p. 92·5°); αβ-*dibromoheptoic*, m.p. 74·5°, and *-octoic acids*; *α-bromo-*Δ^{α}-*pentenoic*, b.p. 122—124°/15 mm., m.p. 49—50°, *-hexenoic*, b.p. 143—145°/15 mm., m.p. 37—38°, *-heptenoic*, b.p. 153—156°/15 mm., *-octenoic*, b.p. 165—167°/15 mm., and *-nonenoic*, b.p. 176—179°/15 mm., *acids*; *ααβ-tribromo-valeric*, m.p. 90·5—91°, *-hexoic*, m.p. 102·5°, *-heptoic*, m.p. 72°, *-octoic*, and *-nonoic acids*; *αα-dibromo-*Δ^{α}-*butene*, b.p. 53—55°/22 mm., *-pentene*, b.p. 72—74°/22 mm., *-hexene*, b.p. 90—92°/22 mm., *-heptene*, b.p. 105—107°/22 mm., and *-octene*, b.p. 120—122°/22 mm. The following data are reported: αβ-dibromononoic acid, m.p. 44° (lit. 35°); α-bromo-Δ^{α}-propene, b.p. 58—60° (corr.)/747 mm., -butene, b.p. 87—89° (corr.)/747 mm., -pentene, b.p. 113—115°(corr.)/747 mm., -hexene, b.p. 138—140°(corr.)/747 mm., -heptene, b.p. 161—163°(corr.)/747 mm., and -octene, b.p. 178—180°(corr.)/747 mm.; αα-dibromo-Δ^{α}-propene, b.p. 127·4°/750 mm. H. B.

Addition of hydrogen bromide to olefinic acids. R. P. Linstead and H. N. Rydon (Nature, 1933, **132**, 643).—The peroxide effect (cf. this vol., 1141) is of secondary importance in the addition of HBr to Δ^{γ}-pentenoic acid (I). In C_6H_{14}, addition to (I) normally yields pure δ-bromovaleric acid (II); this is not reversed in presence of H_2, $NHPh_2$, or quinol. In absence of solvent, freshly-prepared (I) and an old sample giving a strong peroxide reaction both yield (II), but a reversal of addition can be induced by addition of Bz_2O_2 and the δ-Br-acid is formed. The importance of the peroxide effect appears to vary with different unsaturated acids, and does not account for the influence of the solvent on the addition of HBr to (I). L. S. T.

α-Chlorovinylacetic derivatives. R. Rambaud (Compt. rend., 1933, **197**, 767—770).—With $SOCl_2$ the appropriate ester CH_2:CH·CH(OH)·CO_2R affords *Me* (I), b.p. 55°/20 mm., and *Pr*, b.p. 75°/17 mm., *α-chloro-*Δ^{β}-*butenoate*, the *nitrile* (II), b.p. 133—134°, being similarly obtained. With HCl–MeOH (II) gives (I), but the corresponding acid cannot be similarly obtained, since with alkali (II) gives α-chlorocrotonic acid, NH_3 giving α-chlorocrotonamide. Similar prototropic change occurs on alkaline hydrolysis of (I), but with dil. HCl *α-chloro-*Δ^{β}-*butenoic acid*, b.p. 103—104°/19 mm., can be obtained, accompanied by traces of γ-chlorocrotonic acid. AgOH converts (I) into cryst. products containing two double linkings: $2AgOH+2CH_2$:CH·CHCl·$CO_2R \longrightarrow (C_6H_6Cl_2)(CO_2R)_2+2Ag+2H_2O$. J. W. B.

Ester-interchange. VII. Interaction of castor oil with mono- and tri-chloroacetic acid. VIII. Interaction of castor oil and polycarboxylic acids. R. Oda (J. Soc. Chem. Ind. Japan, 1933, **36**, 496—497B, 571—574B; cf. this vol., 933).—VII. Interaction of castor oil (I) with $CH_2Cl·CO_2H$ or $CCl_3·CO_2H$ at 170—180° results in esterification (II) and ester-interchange, but at 100—110° only (II) proceeds. (I) reacts fairly easily with $H_2C_2O_4$, but only with difficulty with many other acids.

VIII. Interaction of (I) with $H_2C_2O_4$ in CO_2 at 140—150°/15 mm. during 1 hr. affords an ester as well as a condensation product of 2 mols. of (I) and 1 mol. of $H_2C_2O_4$. (I) also reacts with $CH_2(CO_2H)_2$ and citric acid very easily to give products formed from 1 mol. each of (I) and acid. (I) reacts less easily with $(·CH_2·CO_2H)_2$ and tartaric acid. J. L. D.

Systemisation [definition] of the lipins. W. Halden (Fettchem. Umschau, 1933, **40**, 189—194). E. L.

Synthesis of *d*- and *l*-ascorbic acid and of analogous substances. R. G. Ault, D. K. Baird, H. C. Carrington, W. N. Haworth, R. Herbert, E. L. Hirst, E. G. V. Percival, F. Smith, and M. Stacey (J.C.S., 1933, 1419—1423; cf. this vol., 936).—*d*- or *l*-Xylosone (prep. described) with $CaCl_2$ and KCN in H_2O and N_2 adds HCN, the product being simultaneously hydrolysed to the acid, which exists as the lactone, identified as *d*- or *l*-ψ-ascorbic acid [osazone, m.p. 210°, different from the osazone of ascorbic acid (I)], since it has a different absorption spectrum from (I), but is converted into (I) (cf. this vol., 1143) by prolonged action of 8% HCl at 40—50° in CO_2. Similarly, glucosone affords the K and NH_4 salts of the ψ-compound, which when heated with 8% HCl at 50° for 24 hr. affords 3-*keto*-d-*glucoheptonofuranolactone*, m.p. 191°. Reduction of K *d* galacturonate in H_2O with Na–Hg at 15° affords *l*-galactonic acid, which at 70° during 2 hr. gives the lactone, converted at 0° by MeOH–NH_3 into *l*-galactonamide,

which is converted into *l*-xylosephenylosazone, m.p. 158—160°, through *l*-xylose (cf. A., 1928, 740). J. L. D.

Induction period in the formation of glycollic acid by the hydrolysis of halogen-substituted acetates. H. M. Dawson and W. Lowson (Proc. Leeds Phil. Soc., 1933, **2**, 435—439).—In the reaction $CH_2X{\cdot}CO_2' + H_2O \longrightarrow OH{\cdot}CH_2{\cdot}CO_2H$ (I) + X′ an induction period is associated with the formation of (I), whereas the halide ion (X′) is eliminated immediately. Experiments on the rates of formation of Cl′ and (I) in the early stages of the hydrolysis of aq. $CH_2Cl{\cdot}CO_2Na$ are consistent with the view that the reaction takes place in two stages, in the first of which Cl′ is a product, whilst no (I) is produced until the second stage. For solutions containing 1—3 mols. per litre the induction period is approx. 3000 min. at 25°. W. R. A.

Preparation of crystalline lactic acid. H. Borsook, H. M. Huffman, and Y. P. Liu (J. Biol. Chem., 1933, **102**, 449—460).—*l*(+)-Lactic acid, m.p. 52·8°, $[\alpha]_{Hg}^{\frac{1}{4}\cdot 22}$ +2·6° (? in H_2O), is separated from the commercial mixture by fractional distillation (avoiding overheating) and crystallisation of the product from Et_2O–Pr^{β}_2O, or by resolution of the Zn NH_4 salt; both methods give the active acid in excess in the mixture, although a little of its optical antimeride is obtainable by the Zn NH_4 salt method. *d*(−)-Lactic acid has m.p. 52·8°, and *dl*-lactic acid, 16·8°; all have the same dissociation const. H. A. P.

Mol. wt. of linear macro-molecules by ultra-centrifugal analysis. I. Polymeric ι-hydroxydecoic acid. E. O. Kraemer and W. D. Lansing (J. Amer. Chem. Soc., 1933, **55**, 4319—4326).—Solutions of a polymeric ι-hydroxydecoic acid (*M* 25,200, by titration) in *s*-$C_2H_2Br_4$ are subjected to ultra-centrifugal analysis. Calculation of the mol. wt. from the sp. sedimentation velocity gives a val. which is considered to be much too low, whilst that calc. from the diffusion coeff. is much too high. The val. calc. from the sedimentation equilibrium (I) agrees fairly well with the above and is considered to be correct. The relationship between osmotic pressure and concn., as calc. from (I), indicates that van 't Hoff's law does not apply at concns. $> 0{\cdot}00025N$. The results confirm the suggestion of Kraemer and Sears (A., 1930, 692) that ultra-centrifugal analysis should be carried out at concns. which are sufficiently low to give a linear relationship between relative viscosity and concn. (diffusion and sedimentation may then be anomalous if the ratio sp. hydrodynamic vol. to partial sp. vol. is much > 1). H. B.

Oxidation and derivatives of *dl*-α-hydroxystearic acid. P. A. Levene and P. S. Yang (J. Biol. Chem., 1933, **102**, 557—562).—*dl*-α-Hydroxystearic acid [*Me* ester, m.p. 64—66°; *Me ether*, m.p. 75—76°; *hydrazide*, m.p. 136—137°; Me_2 *ether-ester* (Me ester, Ag_2O, and MeI in $COMe_2$), m.p. 39—40°; *Ac* derivative, m.p. 64—65°] is readily purified by repeated esterification and hydrolysis with cold NaOH–EtOH without formation of the lactide. Oxidation with $KMnO_4$ gives margaric acid unaccompanied by lower fatty acids. H. A. P.

Course of addition of enolic sodioalkylmalonic esters to phenylthiocarbimide. J. Ross (J. Amer. Chem. Soc., 1933, **55**, 3672—3677).—PhNCS (I) and $CHNa(CO_2Et)_2$ in dry Et_2O give a quant. yield of the Na enolate of $NHPh{\cdot}CS{\cdot}CH(CO_2Et)_2$ [*S-Me ether*, m.p. 58°, hydrolysed (HCl) to SHMe and NH_2Ph]. (I) and $CMeNa(CO_2Et)_2$ similarly afford only 12—15% of the Na enolate of *Et ethane-αα-dicarboxylate-α-thiocarbanilide*, m.p. 92°, which is hydrolysed (10% KOH and acidification) to *methylmalonthioanilic acid*, m.p. 118° (decomp.) (decarboxylated to $NHPh{\cdot}CS{\cdot}Et$). $CMeNa(CO_2Me)_2$ does not give an additive compound. $CN{\cdot}CHNa{\cdot}CO_2Me$ and (I) in MeOH give a quant. yield of the Na enolate of *Me cyanomalonthioanilate*, m.p. 135° (decomp.) (*S-Me ether*, m.p. 83°), whilst $CN{\cdot}CMeNa{\cdot}CO_2Me$ similarly affords 6—10% (reaction does not occur in Et_2O) of the Na enolate of *α-cyanothiopropionanilide*, $NHPh{\cdot}CS{\cdot}CHMe{\cdot}CN$, m.p. 126°, which is apparently derived from $NHPh{\cdot}CS{\cdot}CMe(CN){\cdot}CO_2Me$ by loss of the $\cdot CO_2Me$ group. The reaction mechanism is discussed. H. B.

Determination of hydroxyl number. W. Normann and E. Schildknecht (Fettchem. Umschau, 1933, **40**, 194—197).—Elsbach's method (A., 1923, ii, 796) is unsatisfactory. For mixtures of fats, fatty acids, and alcohols (including volatile alcohols and esters) which give no H_2O-sol. products on acetylation, the Benedikt–Ulzer method can be satisfactorily applied, provided that the acetylated mixture is hydrolysed by boiling for ½—1 hr. under a reflux in order to decompose fatty acid anhydrides. A method applicable in all cases, including mixtures containing or yielding H_2O-sol. esters, has been worked out, whereby 1—1½ g. of the sample is acetylated with a (weighed) excess of Ac_2O and C_5H_5N (cf. Verley and Bolsing, A., 1902, ii, 54); all anhydrides are immediately and completely hydrolysed on the addition of H_2O, and the mixture is then titrated back with 0·5*N*-KOH–EtOH. The OH no. is given by the difference between the titrations (calc. to mg. KOH per g. sample) of a blank and of the sample, plus the acid val. of the sample. E. L.

Oxidative degradation of biologically important sulphur compounds. A. Schoberl [with M. Wiesner] (Annalen, 1933, **507**, 111—127).—When $SH{\cdot}CH_2{\cdot}CO_2H$ (I) (1 mol.) is oxidised with O_2 in aq. $Ba(OH)_2$ (3 equivs.) at 37°, the Ba salts of $H_2C_2O_4$, $H_2S_2O_3$, and (probably) H_2SO_3 and H_2SO_4 are formed; the amount of O_2 absorbed during 14 hr. is approx. six times that required for the production of $(\cdot S{\cdot}CH_2{\cdot}CO_2H)_2$ (II). Oxidation of (I) in aq. NaOH is catalysed by Cu salts; the amount of O_2 consumed increases with rise in the concn. of NaOH. When an excess of 3 equivs. of NaOH per mol. of (I) is used, 1·86 equivs. (mean val.) are consumed; $Na_2C_2O_4$ (68·5% of theory) and $Na_2S_2O_3$ are produced. (II) behaves similarly and gives 68·1% of $Na_2C_2O_4$. (II) and aq. NaOH (8 mols.) in H_2 afford (I) (59·6% yield); $H_2C_2O_4$ is often produced in about 10% yield. A possible reaction mechanism is discussed. $(\cdot S{\cdot}CHMe{\cdot}CO_2H)_2$ is similarly converted (conversion is, in both cases, independent of the time of reaction) into $SH{\cdot}CHMe{\cdot}CO_2H$ (III); $(\cdot S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H)_2$

(IV) is unaffected. (III) is oxidised in aq. NaOH or $Ba(OH)_2$, whilst (IV) is not. Oxidation (O_2) of Na_2S occurs more rapidly in H_2O than in aq. NaOH; in presence of Cu, reaction is more rapid in presence of alkali; Na_2SO_3 and $Na_2S_2O_3$ (main product) are produced. H. B.

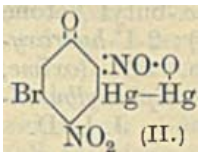
Formation of the hydroxyl radical from the photolysis of water and the generation of formaldehyde.—See this vol., 1255.

Isomerisation of hydroxyaldehydes. V. Oxidation–reduction transformations of α-hydroxy-*iso*butaldehyde. S. Danilov and E. Venus-Danilova (J. Gen. Chem. Russ., 1933, **3**, 559—572).—*iso*Butaldehyde on bromination gives the very stable Br-polymeride (I), m.p. 130°, which when heated at 160° yields the somewhat unstable simple bromoaldehyde, b.p. 113°/750 mm. (I) when heated with freshly pptd. $BaCO_3$ yields α-hydroxybutaldehyde (II), m.p. 74° (semicarbazone, m.p. 164—165°), and when heated for some time in NaOH gives a mixture of hydroxy*iso*butyric acid (III) and *iso*butylene glycol. If, however, hydrated oxides of Pb and Cu are present as catalysts, an internal oxidation–reduction takes place with formation of *iso*butyric acid. Other products [acetylmethylcarbinol (IV), (III), hydroxyketone], in various proportions, are also formed, depending on the conditions. It is considered that an additive compound with the metal hydroxide is first formed, followed by migration of H. If the aldehyde is heated with dil. acid, the OH-ketone rearrangement which occurs to a small extent with alkalis takes place almost quantitatively; (IV), b.p. 104° (semicarbazone, m.p. 185°), is formed. The possible structures and mechanisms of reactions of α-OH-aldehydes are discussed; it is suggested that the liquid (depolymerised) form has the structure $:C<^{CH\cdot OH}_{O}$. M. Z.

Phosphorylated glyceraldehyde. H. K. Barrenscheen and L. Klebermass-Messiner (Biochem. Z., 1933, **265**, 157—158; cf. Fischer and Baer, A., 1932, 834).—From 300 g. of glycerol 2·6 g. of Ca glyceraldehydephosphate are obtained by the methods of Wohl (A., 1898, i, 555) and Sabetay (A., 1926, 1123). The acid is directly fermented by yeast. W. McC.

[Absorption] spectrum of methylglyoxal. L. Marchlewski, J. Pizło, and W. Urbanczyk (Biochem. Z., 1933, **264**, 437—440).—Further work is described aimed at explaining the differences obtained by various authors (Marchlewski *et al.*, A., 1929, 9; Neuberg *et al.*, A., 1927, 203; Fischler *et al.*, A., 1931, 70) in investigations of the change of absorption spectrum during treatment of glucose with OH′. The absorption band previously obtained by the authors at 2682 Å. with alkaline solutions of hexoses, pentoses, and maltose cannot be due to the presence of AcCHO. P. W. C.

Reagent for enols. [Reactions of mercurous nitrate.] A. Dansi and A. Sempronj (Gazzetta, 1933, **63**, 560—565).—$Hg_2(NO_3)_2$ (I) is reduced at once to Hg by COMeEt, $COMe\cdot C_6H_{13}$, $COMe\cdot C_9H_{19}$, and methylheptanone (cf. A., 1932, 362); with COPhEt a yellow intermediate org. *compound* is formed. MeCN from NH_2Ac has no action on (I), but this is reduced by MeCN from Me_2SO_4, owing to presence of MeNC. With (I), p-$NO_2\cdot C_6H_4\cdot ONa$ forms a green *compound*, and with K 5-bromo-2 : 4-dinitrophenoxide a *compound*, $C_6HO\cdot N_2BrHg_2$, for which the structure (II) is proposed. E. W. W.



(II.)

Resinification. II. Transformation of chloro- and bromo-acetone. M. Giua and G. Racciu (Atti R. Accad. Sci. Torino, Cl. Sci. fis. mat. nat., 1932 **67**, 409—412; Chem. Zentr., 1933, i, 3919).—$CH_2Cl\cdot COMe$, when exposed to light for 1 year in a closed vessel, affords a coal-like mass which evolves HCl, and a small quantity of a black liquid. When boiled with H_2O the solid affords a yellow pulverulent substance, decomp. > 350°, which does not react with $NHPh\cdot NH_2$, NH_2OH, or oleum, but with fuming HNO_3 gives a yellow infusible product. The original material is practically insol. in boiling aq. KOH, which becomes coloured yellow. $CH_2Br\cdot COMe$ begins after 2—3 months in light to deposit solid from the brown liquid. A. A. E.

Fluorination of organic compounds. Monofluoroacetone. P. C. Rây, P. B. Sarkar, and A. Rây (Nature, 1933, **132**, 749—750; cf. this vol., 1033).—Refluxing of $CH_2I\cdot COMe$ but not $CH_2Cl\cdot COMe$ with TlF in Et_2O yields *fluoroacetone*, b.p. 72°. L. S. T.

Phosphoric acid in organic reactions. W. M. Dehn and K. E. Jackson (J. Amer. Chem. Soc., 1933, **55**, 4284—4287).—Et *n*-amylacetoacetate is hydrolysed by 85% H_3PO_4 (I) to Me *n*-amyl ketone in 95% yield (H_2SO_4 and alkalis give ≯ 70%). *cyclo*Hexanol is dehydrated by (I) at 160—170° to *cyclo*hexene (96%), whilst menthol gives menthene (96%). Terpin hydrate affords dipentene (II) (65%), terpinene (III) (18%), terpinolene (IV) (2%), and colophene (11%) (V); terpineol and cineole give (II), (III), and (IV), whilst pinene (turpentine) and 98—100% H_3PO_4 at 200° afford (II) (main product), (III), and (V). Pinacol hydrate is dehydrated to βγ-dimethylbutadiene (3·8%), $COMeBu^{\gamma}$ (70%), and dimethyl*iso*propenylcarbinol (10%), whilst $COMe_2$ gives products, b.p. up to 350°. (I) is useful for the hydrolysis of small amounts of substances (*e.g.*, cocaine, alypin, β-eucaine) containing Bz groups (BzOH is readily obtained); o-$OH\cdot C_6H_4\cdot CO_2H$ is similarly obtained from its derivatives (*e.g.*, aspirin, salol). (I) is useful for the identification (cf. A., 1932, 1236) of carbohydrates and glucosides. (I) is recovered from the reaction mixtures and can be used repeatedly. H. B.

Condensation of ketones. V. Grignard and J. Colonge (Bul. Soc. Chim. Romania, 1933, **15**, 5—12).—Interaction of many ketones in C_6H_6 at 20° with $NPhMe\cdot MgBr$ in Et_2O–C_6H_6 affords (cf. this vol., 698) bimol. products in good yield. The following are described: *βγζ-trimethylheptan-γ-ol-ε-one* (77%), b.p. 97°/16 mm. (*semicarbazone*, m.p. 109°) from $COMePr^{\beta}$; *ββγζζ-pentamethylheptan-γ-ol-ε-one* (70%), b.p. 103—105°/15 mm., from pinacolin; *ε-ethyl-δ-propylnonan-δ-ol-ζ-one*, b.p. 104—105°/3 mm.,

from $COPr_2$; *γεη-trimethyl-δ-ethylnonan-δ-ol-ζ-one* (55%), b.p. 104°/3 mm., from Et *sec.*-butyl ketone ($COEtBu^{\gamma}$ and $COPr^{\beta}_2$ do not condense); 2-1′-*hydroxy*-cyclo*hexyl*cyclo*hexanone* (55%), m.p. 56° (*oxime*, m.p. 113°), from *cyclo*hexanone; *βδ-diphenylbutan-β-ol-δ-one*, m.p. 63°, from COPhMe. J. L. D.

Colour and structure of oximes and semicarbazones. (Mme.) Ramart-Lucas and (Mme.) M. Grumez (Bull. Soc. chim., 1933, [iv], **53**, 753—769).—A more detailed account of work previously reviewed (this vol., 159). H. B.

Micro-determination of pentoses, free and combined. I. S. Andrews and J. A. Milroy (Biochem. J., 1933, **27**, 1421—1424).—Pentoses, free and combined, are determined by the colorimetric determination with NH_2Ph,AcOH of furfuraldehyde (I), formed by the action of 50% AcOH on samples capable of producing 0·05 mg. of (I) per c.c. in evacuated glass tubes at 170°. The yields of (I) from the nucleotides (II) of muscle by this method are much > those obtained by other methods (this vol., 612), so that the differences between the (II) from muscle and yeast are < originally believed. H. D.

Analysis of pentosans. B. Peter, H. Thaler, and K. Taufel (Z. Unters. Lebensm., 1933, **66**, 143—158).—The determination of pentosans by conversion into furfuraldehyde (I) and pptn. of (I) with phloroglucinol gives incorrect results owing to the formation of hydroxymethylfurfuraldehyde (II) from hexoses and its inclusion in the ppt. (I) can be determined by pptn. with barbituric acid without interference from (II), which is not pptd. at the concns. met with in practice. In presence of galactose and mannose, either free or in the form of polysaccharides, the yield of (I) is decreased. It is suggested therefore that pentosans should be evaluated by their yield of (I) rather than by a fictitious pentosan content. E. C. S.

Sugar determination. S. Rothenfusser (Z. Unters. Lebensm., 1933, **66**, 182—192).—In pure H_2O, the sugar is pptd. by addition of MeOH (I) and standard $Ba(OH)_2$ in (I). The final concn. of (I) must be ⩽ 90%. The ppt. is filtered off, and an aliquot portion of the filtrate is back-titrated. In physiological fluids and other experimental material, proteins are pptd. with 80% (I), the solution is filtered, and its acid titre determined before the sugar is pptd. E. C. S.

Reducing sugars. IV. W. Gabryelski and L. Marchlewski (Biochem. Z., 1933, **265**, 50—57; cf. this vol., 937).—When glucose is warmed at 40° in a phosphate (I) buffer solution of p_H 7·21 for 192 hr. a band having max. at 3655 Å. appears in its spectrum. Since no such band appears when a buffer containing no (I) is used, a sp. action is attributed to (I). The production of the band at 2670 Å. by OH′ is greatly accelerated by rise (II) of temp. (from room to 40°), but (II) alone has no effect. The spectra of lactose and maltose likewise develop bands (max. at 2635, 3100, 3690 and 2682, 3116, 4025 Å., respectively) by the action of sufficient [OH′] provided that the p_H is ⩽ 10. W. McC.

Hydrolysis of sugars by alkalis. F. Fischler, H. Hauss, and K. Taufel (Biochem. Z., 1933, **265**, 181—190; cf. A., 1931, 70).—Spectroscopic examination and chemical tests (reducing power, CHI_3 test) on alkaline solutions of AcCHO, glucose, galactose, mannose, and xylose confirm the view that alkaline degradation of ketoses leads almost exclusively to production of C_3 compounds, AcCHO being the first substance capable of detection. Some results of Marchlewski *et al.* (this vol., 810) also confirm this view, although certain of their views are open to criticism. W. McC.

Action of pyridine on sugars. P. A. Levene and D. W. Hill (J. Biol. Chem., 1933, **102**, 563—571).—The conversion of aldoses into ketoses by boiling C_5H_5N is reversible, but while the forward action is very rapid, the reverse action is slow, and apparently equilibrium is not reached in experiments starting from the ketose side. The following figures are given for the production of ketose after 4 hr. at the b.p.: *d*-arabinose, 8·0%; *d*-lyxose, 11·1%; *l*-rhamnose, 14·8%; glucose, 11·7% (cf. A., 1930, 1411); and *d*-mannose, 34·6%. *l*-Ribose and *d*-xylose are unaffected. The conversion occurs more readily with the 2 : 3-*cis*- than the 2 : 3-*trans*-sugars, and an explanation based on the formation of a 1 : 2-oxide ring is advanced. H. A. P.

Anhydride formation of 2 : 3 : 6-trimethylglucose. II. K. Hess and O. Littmann (Annalen, 1933, **506**, 298—306).—1-Chloro-2 : 3 : 6-trimethylglucose (I), obtained from fibrous (ramie) trimethylcellulose and Et_2O–HCl, is converted by Na powder (cf. this vol., 596) into (mainly) 3 : 6-dimethylglucal, b.p. 65°/0·04 mm., which is reduced (H_2, Pt-black, EtOH) to 3 : 6-dimethyldihydroglucal, b.p. 66°/0·03 mm., $[\alpha]_D^{\circ}$ +6·26° in H_2O, −16·39° in $CHCl_3$ (4-*p-toluenesulphonate*, m.p. 73—74°; 4-3′ : 5′-*dinitrobenzoate*, m.p. 172—173°). 2 : 3 : 6-Trimethylglucose anhydride (II) is not produced (cf. Freudenberg and Braun, A., 1928, 399; this vol., 596). (I) and active "mol." Ag give (probably) nonamethyltrihexosan (A., 1927, 1058). (II) could not be isolated from the Na-containing by-products formed in the above reaction. H. B.

Syntheses of α- and β-phenyl-*d*-mannoside. B. Helferich and S. Winkler (Ber., 1933, **66**, [*B*], 1556—1558).—β-*d*-Mannose penta-acetate (I) is converted by PhOH and $ZnCl_2$ into *phenyl*-β-d-*mannoside tetra-acetate*, m.p. 169—170°, $[\alpha]_D^{19}$ −62·74° (hydrolysed by NaOMe in MeOH to *phenyl*-β-d-*mannoside*, m.p. 175—176·5°, $[\alpha]_D^{20}$ −71·6° in H_2O), and a little *phenyl*-α-d-*mannoside tetra-acetate*, m.p. 79—80°, $[\alpha]_D^{20}$ +73·9° in $CHCl_3$, better obtained from (I), PhOH, and p-$C_6H_4Me{\cdot}SO_3H$. *Phenyl*-α-d-*mannoside* has m.p. 132—133°, $[\alpha]_D^{23}$ +113·5° in H_2O. H. W.

Galactoseptanoses. II. F. Micheel and F. Suckfull (Annalen, 1933, **507**, 138—143).—α- (I) and β- (II) Galactoseptanose penta-acetates (this vol., 597) are both converted by $TiCl_4$ in $CHCl_3$ into the same β-acetochlorogalactoseptanose, $[\alpha]_D^{19}$ −79·5° in $CHCl_3$, which with Ag_2CO_3 and MeOH gives α-*methylgalactoseptanoside* 2 : 3 : 4 : 5-*tetra-acetate*, m.p. 108°, $[\alpha]_D^{20}$ +17° in $CHCl_3$. This is hydrolysed

(NaOMe in cold MeOH–$CHCl_3$) to *α-methylgalactoseptanoside*, $[\alpha]^{20}$ +26° in H_2O, methylated (Ag_2O, MeOH–MeI) to 2 : 3 : 4 : 5-tetramethylmethylgalactoseptanoside, b.p. 86°/0·005 mm., which is oxidised [HNO_3 (*d* 1·2)] to tetramethylmucic acid (Karrer and Peyer, A., 1922, i, 809), thus proving the presence of the 1 : 6-ring in the above compounds. Hydrolysis of (I) by NaOMe in MeOH–$CHCl_3$ and (II) by 5% H_2SO_4 gives galactopyranose in both cases. H. B.

Solutions of invertase for determination of sucrose. J. Lebouco (J. Pharm. Chim., 1933, [viii], **18**, 292—293).—Using a 1% invertase (I) solution in saturated aq. thymol only 97% of the theoretical sugars was obtained, due to the growth of moulds. With a solution of (I) in 0·1% K 8-hydroxyquinolyl sulphate theoretical yields were obtained. H. D.

Starch. III. Swelling of potato starch in pyridine–water. K. Hess, R. Pfleger, and C. Trogus (Ber., 1933, **66**, [*B*], 1505—1512; cf. A., 1929, 914).—In C_5H_5N–H_2O, air-dried potato starch (16—17% H_2O) exhibits indications of a first swelling max. at 30—40 vol.-% of C_5H_5N and a second marked max. between 80% and 90% C_5H_5N. After desiccation over P_2O_5 at 95—100°/15 mm., starch exhibits a very pronounced first max. and a second less marked max., whilst after re-hydration the first effect is still very pronounced, whereas the second is closely similar to that of the non-dried material. For all concns. of C_5H_5N the volume is const. after about 3 days, but the rate of swelling is very irregular. The experiments are satisfactorily reproducible, but the process is not reversible. The changes produced by swelling in the morphological structure of the starch granules are described. *X*-Ray investigation indicates the probable formation of an additive compound, for which the name "pyridine-starch" (I) is proposed; since it is not produced in 100% C_5H_5N, H_2O is in some manner involved in its formation. The hypothesis that the first swelling max. is due to hydration caused by ion adsorption is in harmony with the behaviour of starch towards NaOH–H_2O; the second max. is attributed to production of (I). Wheat starch swells very little in C_5H_5N–H_2O. H. W.

Starch. IV. Starch tri-*p*-toluenesulphonate, 6-iododi-*p*-toluenesulphonate, and tribenzoate. V. Degradation of starch tri-*p*-toluenesulphonate and 6-iododi-*p*-toluenesulphonate with hydrogen bromide–acetic acid. K. Hess, O. Littmann, and R. Pfleger (Annalen, 1933, **507**, 48—54, 55—61).—IV. Dry potato starch is treated with 90% C_5H_5N at 18—20° until max. swelling occurs, the resultant product washed repeatedly with abs. C_5H_5N, and then treated with *p*-$C_6H_4Me{\cdot}SO_2Cl$ and C_5H_5N at 18—20°; *starch tri-*p*-toluenesulphonate* (I), decomp. about 235—240°, is thus obtained. (I) contains about 1% of Cl, is insol. in all the usual org. solvents, and with anhyd. NaI in $COMe_2$ at 100° (sealed tube) gives *6-iodostarch di-*p*-toluenesulphonate* (II), which contains varying amounts (according to prep.) of $COMe_2$-sol. and -insol. material. *Starch tribenzoate*, also insol. in the usual org. solvents, is prepared [as (I)] using BzCl. *p*-Toluenesulphonylation at higher temp. gives products containing two *p*-$C_6H_4Me{\cdot}SO_2{\cdot}$ groups and one Cl per C_6.

V. (I) (above) and HBr–AcOH at room temp. for 15 days give *1-α-bromo-*d*-glucose* 2 : 3 : 6-*tri*-p-*toluenesulphonate* 4-*acetate* (?), m.p. 162°, $[\alpha]_D^{20}$ +113·1° (all rotations are in $CHCl_3$), converted by Ag_2CO_3 in MeOH into *β-methyl-*d*-glucoside* 2 : 3 : 6-*tri*-p-*toluenesulphonate* 4-*acetate*, m.p. 131—132°, $[\alpha]_D^{20}$ −12·85°, which with excess of NaI in $COMe_2$ at 130° affords a *di-iodomethylhexoside* p-*toluenesulphonate acetate*, m.p. 228°. (II) (above) and HBr–AcOH similarly give *1-α-bromo-6-iodo-*d*-glucose* 2 : 3-*di*-p-*toluenesulphonate* 4-*acetate* (?), amorphous, $[\alpha]_D^{20}$ +114·7°, converted by Ag_2CO_3 in MeOH into *6-iodo-β-methyl-*d*-glucoside* 2 : 3-*di*-p-*toluenesulphonate* 4-*acetate*, m.p. 162—163°, $[\alpha]_D^{20}$ +10·62°, which with AgF in C_5H_5N affords *β-methyl-*d*-glucose-enide* 2 : 3-*di*-p-*toluenesulphonate* 4-*acetate* (?), m.p. 79—80° (decomp.), $[\alpha]_D^0$ −24·18°. This is unsaturated (Br; $KMnO_4$) and is reduced (H_2, Pt-black, EtOH) to *β-methyl-*d*-epirhamnoside* 2 : 3-*di*-p-*toluenesulphonate* 4-*acetate* (?), m.p. 133—134°, $[\alpha]_D^{20}$ −9·35°. H. B.

Potato starch. T. C. Taylor and T. J. Schoch (J. Amer. Chem. Soc., 1933, **55**, 4248—4255).—Gelatinisation (NH_4CNS) and electrophoretic separation (B., 1926, 717) of potato starch (I) (P content 0·069%) give an insol. migratable residue of approx. 3·5% of (I) containing 0·036% P and a sol. fraction containing 0·06% P. Contrary to Samec (cf. A., 1913, i, 17, 1155; 1916, i, 308) and Baldwin (A., 1930, 1167), the main part of the total P is the sol. material (cf. below). (I) (ground for long periods) gives clear dispersions in boiling H_2O; these often deposit insol. material (retrogradation) which cannot be redispersed, especially when the grinding period is relatively short. Sol. or insol. material (containing all the original P) can thus be obtained. Mechanical disintegration of the swollen granules in H_2O and separation of insol. material in an electrophoretic cell give a clear liquid containing about 20% of the original material; pptn. of this with EtOH affords a product (0·003% P) which is stable to alkali (this vol., 261) to the extent of 93%. Disintegration in 85% glycerol and pptn. of solid with EtOH give a product which redisperses completely, but undergoes ready retrogradation; forced dialysis of a solution against H_2O and pptn. of solid from the filtrate with EtOH give a product (containing 0·065% P), 93% of which is stable to alkali. Baldwin's method (*loc. cit.*) of separation affords 17% of sol. material (0·019% P). All the above evidence indicates the presence in (I) of a sol. phase only (provided incomplete disruption of the granule and retrogradation are avoided). The amounts of P in various fractions vary over wide limits, irrespective of solubility and how obtained (cf. Karrer and von Kraus, A., 1930, 72). It is shown (by a method similar to that used for determination of transport nos.) that migration of the high P-containing amylose to the anode and a compensating flow of material with a low P content occur. H. B.

Structure of cellulose. A. Gero (Naturwiss., 1933, **21**, 693—694).—The formation of $C_6(CO_2H)_6$

by oxidation of charcoal is explained by the glucosidic linking of the terminal CH_2·OH and CHO groups of glucose (chain formula) into a six-membered ring in cellulose. Hydrolysis to glucose occurs normally by reversal of the process of formation, but the formation of cellobiose must be regarded as a secondary reaction. H. A. P.

Cellulose. XLIX. Mode of reaction of cellulose. II. Mechanism of methylation of cellulose fibres; formation of a hemimethylcellulose. K. Hess, C. Trogus, W. Eveking, and E. Garthe **L. Formation of a homogeneous [bromodiacetyl]diethylglucose from partly ethylated cellulose.** K. Hess. **LI. Esterification of cellulose with *p*-toluenesulphonyl chloride in presence of pyridine.** K. Hess and N. Ljubitsch (Annalen, 1933, **506**, 260—295, 295—298; **507**, 62—69).—XLIX. The course of methylation of Na cellulose II by 5—70% Et_2O–Me_2SO_4 at 18·5° and by Me_2SO_4 alone at 18°, 38°, and 49° is studied kinetically and by *X*-ray examination of the solid phase. The *X*-ray diagrams of partly methylated celluloses (3—22·43% OMe) show the interferences of hydro- (I) and trimethyl- (II) -celluloses; that due to (I) disappears when the OMe content is 27—31%. The early interference of (II) indicates that reaction starts on the surface of the fibre. Hydrolysis (75% H_2SO_4 or fuming HCl) of methylcelluloses (III) does not give glucose in amounts corresponding with the unattacked cellulose, assuming that all the OMe is present as (II). Extraction of (III) (OMe 6·8—17%) with $CHCl_3$ removes some (II); the residues still contain OMe and their *X*-ray diagrams show only the interference of (I). The residue from (III) (OMe 28·7%) contains 18·7% OMe; the *X*-ray diagram shows the interference of hemimethylcellulose. Dehydration of Na cellulose II with 18% MeOH–NaOH and removal of the surplus MeOH by pressing between filter-paper gives a product (IV), which reacts rapidly with Me_2SO_4 at −5° forming a fibrous hemimethylcellulose (V) (9—11% OMe). When (IV) contains too much MeOH, products with < 9% OMe are obtained; MeOH-free (IV) gives products containing up to 28% OMe. The *X*-ray diagram of (V) is given; it shows no interferences of (I) or (II), and differs from that of (V) in contact with H_2O and MeOH. (V) is hydrolysed to glucose (about 50%) and methylglucoses (about 50%) (probably the 2- and at least one other derivative); the fibre swells considerably in H_2O. (V) is produced during the methylation of Na cellulose [prepared using 30—45% (wt.) aq. NaOH] with Me_2SO_4 or by methylation (Me_2SO_4, 45% aq. NaOH) of cellulose; the *X*-ray diagram of the resultant product (OMe 21·4%) shows interference of (II), but after extraction ($CHCl_3$) interference of (V). All the above results show that methylation of cellulose [to (II)] involves at least two reactions, viz., the formation of (V) and its further methylation.

L. Ethylcellulose (2·5 OEt per C_6) and AcBr–HBr at 0° in absence of moisture give a *bromodiacetyldiethylglucose*, m.p. 126·5°, $[\alpha]_D^{17}$ +257° in $CHCl_3$, in a yield of 20 mols. per 100 mols. of C_6.

LI. Products containing S, Cl, and N are obtained from cellulose (I) (cotton-wool; ramie; Cu silk) and *p*-C_6H_4Me·SO_2Cl (II) in C_5H_5N; the S content decreases, and the N (particularly at > 70°) and Cl contents increase with rise in temp. Treatment of (I) with C_5H_5N at 70° and then with (II) at 15—20° gives products containing two *p*-C_6H_4Me·SO_2· groups per C_6 and small amounts of N and Cl; these swell (and subsequently dissolve) in C_5H_5N, are sol. in $PhNO_2$ and *cyclo*hexanone, and swell in $CHCl_3$, $C_2H_2Cl_4$, dioxan, $CPhCl_3$, and C_6H_6–EtOH (1 : 1). Mercerised natural fibres undergo progressive swelling during *p*-toluenesulphonylation. Treatment of the products (from which the *p*-C_6H_4Me·SO_2 groups are removed only with difficulty; S-free products have not been obtained) with 50% $NHEt_2$ at 90° gives substances containing 1·41—1·7% N (original content, 0·16—0·55%) (cf. Karrer and Wehrli, B., 1926, 659). H. B.

Fractionation of ethylcellulose. I. Okamura (Cellulosechem., 1933, **14**, 135—138).—Ethylcellulose was separated into fractions by pptn. with H_2O from AcOH, and considerable concordance was obtained between determinations of their mol. wts. by measurements of I vals., osmotic pressure in C_6H_6, and viscosity in C_6H_6 at 20° and 50°. A. G.

So-called colloidal coal from carbohydrates. II. B. L. Vanzetti (Rend. Sem. Fac. Sci. Cagliari, 1932, **2**, 41—46; Chem. Zentr., 1933, i, 3902).—The gel obtained by the action of H_2SO_4 on carbohydrates affords when dried a hard, brittle substance containing C 60·93, H 2·94, O 35·88%. Similar products were not obtained from mannitol or glycerol. A. A. E.

Preparation of triethanolamine (ββ′β″-trihydroxytriethylamine). F. E. E. Germann and O. S. Knight (J. Amer. Chem. Soc., 1933, **55**, 4150).—Technical $N(CH_2·CH_2·OH)_3$ is acidified with a slight excess of conc. HCl at 10—15°, the resulting hydrochloride, m.p. 177—178°, washed with EtOH, and then decomposed with NaOH in $Pr^{\beta}OH$. H. B.

Compounds of trihydroxytriethylamine with metallic salts. A. Tettamanzi and B. Carli (Gazzetta, 1933, **63**, 566—570; cf. this vol., 246).—With aq. metallic salts, $N(CH_2·CH_2·OH)_3$ is not hydrolysed, but forms compounds co-ordinated through O or N. Ni, Cd, Ca, Sr, and Mg *compounds* of the type $MCl_2,2N(C_2H_4·OH)_3$ are described; a Ba compound is not obtained. E. W. W.

Alcoholysis of metallic salts by trihydroxytriethylamine. F. Garelli and A. Tettamanzi (Gazzetta, 1933, **63**, 570—575).—$N(CH_2·CH_2·OH)_3$ forms with $CoCl_2$, $CoBr_2$, $Co(CNS)_2$, $Cu(CNS)_2$, and $CdCl_2$, *compounds* of type $N(C_2H_4·OH)_2·C_2H_4·OMX$, with $N(C_2H_4·OH)_3,HX$. With $ZnSO_4$ the *product* is $N(C_2H_4·O·ZnOH)(C_2H_4·O·Zn·)_2SO_4$ (?). E. W. W.

Oxidation of thiol compounds by hydrogen peroxide. II. Catalysis of oxidation of cysteine by thiocarbamides and thioglyoxalines.—See this vol., 1018.

[Preparation of] acetamide and benzamide. F. Govaert (Natuurwetensch. Tijds., 1933, **15**, 149—153).—AcCl or BzCl in Et_2O is added gradually

to Et_2O through which NH_3 is passed fairly rapidly at −20°. The amide is pptd. in 85—90% yield. H. F. G.

***iso*Glutamine.** M. Bergmann and L. Zervas (Z. physiol. Chem., 1933, **221**, 51—54).—*l*(+)-*iso*Glutamine, $[\alpha]_D$ +21°, prepared by the carbobenzyloxy-method (A., 1932, 935) is correctly named. The product, $[\alpha]_D$ −25·5°, of Abderhalden and Nienburg (this vol., 1039) is *l*(−)-pyrrolidonecarboxylic acid. Their starting material, the half-ester of glutamic acid, was the γ- and not the α-ester. J. H. B.

Diketopiperazines. XIV. J. V. Dubsky [with J. Trtilek] (Ber., 1933, **66**, [*B*], 1497—1498; cf. A., 1922, i, 57).—Insolation of a mixture of aldehyde-ammonia and 3% HCN, evaporation of the solution, and extraction of the residue with EtOH yields iminodipropionamide (I) mixed with the diamide and alanine. Sublimation of the mixture at 240—250°/13—15 mm. leads to (I), m.p. 188° (*Ag* salt, decomp. 173—175° after darkening at 150°; *compound* $C_6H_9O_2N_2Ag,HNO_3$, decomp. 192—196° after blackening at 150°). H. W.

ψ-Halogens. XXIII. Reactions and tautomerism of cyanates. L. Birckenbach and H. Kolb (Ber., 1933, **66**, [*B*], 1571—1577).—Electrolysis of KCNO in MeOH with I and *cyclo*hexene (I) in the anode compartment leads to *Me* 2-*iodocyclohexylallophanate* (II), $C_6H_{10}I{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO_2Me$, m.p. 160·5°, which could not be obtained from AgCNO, I, and (I) in MeOH, so that the intermediate production of iodo-oxycyanogen during electrolysis is improbable. (II) is obtained in small yield when AgCNO is replaced by KCNO. Use of $Pb(CNO)_2$ leads smoothly to Me 2-iodo*cyclo*hexylcarbamate (III). Treatment of conc. solutions of Hg^{II} salts with KCNO gives double *salts* (IV) of $Hg(CNO)_2$ with KCl, KNO_3, and KOAc. *Hg^{II} cyanate* (V) is obtained from AgCNO and $HgCl_2$ in MeOH and also yields an additive *compound* with KOAc. (IV) and (V) react with (I) and I in MeOH with production of HCNO and 2-iodo-1-methoxy*cyclo*hexane, but whereas (V) yields (III) in small amount, (IV) gives (II) with a small amount of (III) (20 : 1). Two stable, isomeric Hg^{II} cyanates therefore exist, (IV) having the form $(N{:}C{\cdot}O)_2Hg$ (*O*-cyanates) and (V) the structure $Hg(N{:}C{:}O)_2$ (*N*-cyanates). These observations are confirmed by the Raman spectra. The constitution of (II) is confirmed by synthesis from $ClCO_2Me$ and 2-iodo*cyclo*hexylcarbamide and by its decomp. with boiling conc. HCl to 2-*amino*cyclo*hexano*-4 : 5-*oxazoline* (*picrate*, m.p. 202·5°; *hydrochloride*, m.p. 138°) and 2-hydroxy*cyclo*hexylamine, m.p. 62—66°. (II) is transformed by boiling H_2O into *Me* 2-*hydroxy*cyclo*hexylallophanate*, m.p. 173·5° [*hydriodide*, m.p. 183·5° (decomp.)]. *Et* 2-*iodo*cyclo*hexylallophanate* has m.p. 171°. H. W.

Constitution of the cyanogen halides. IV. Action of silver oxide on cyanogen chloride and iodide. E. V. Zappi (Anal. Asoc. Quím. Argentina, 1933, **21**, 37—46).—CNI and Ag_2O give a mixture of AgCNO, $AgIO_3$, and AgI, formed as a consequence of the initial hydrolysis: $ICN \rightarrow HOI + HCN$. CNCl and Ag_2O yield AgCl and AgOCN. CNCl or CNI yield no explosive products with HgO, Hg_2O, or $Pb(OH)_2$. R. K. C.

α-Bromo-nitriles. R. Merckx and P. Bruylants (Bull. Acad. roy. Belg., 1933, [v], **19**, 681—688).—Interaction of the nitriles of *n*-saturated acids from C_4 to C_{13} at 100° with Br in presence of S affords the corresponding α-bromonitriles, which decompose in air and give additive products with C_5H_5N or quinoline. The following are described: *α-bromobutyro-*, b.p. 65—65·2°/20 mm.; *-valero-*, b.p 67·1—67·3°/10 mm.; *-hexo-*, b.p. 82·3—82·5°/10 mm.; *-hepto-*, b.p. 96·4—96·6°/10 mm.; *-octo-*, b.p. 112·1—112·3°/10 mm.; *-nono-*, b.p. 125·4—125·6°/10 mm.; *deco-*, b.p. 138·9—139·1°/10 mm.; *-undeco-*, b.p. 152·5—152·7°/10 mm.; *-lauro-*, b.p. 164·9—165·1°/10 mm.; *-trideco-nitrile*, b.p. 177·5—178·5°/10 mm. J. L. D.

Unsaturated nitriles. Δ^{α}-Octenonitrile and Δ^{α}-nonenonitrile. P. Bruylants and M. Fonteyn (Bull. Acad. roy. Belg., 1933, [v], **19**, 689—701).—Interaction of heptaldehyde cyanohydrin (cf. A., 1909, i, 293) with P_2O_5 affords cis- (I), b.p. 74—75°/11 mm., and trans-Δ^{α}-*octenonitrile* (II), b.p. 85—86°/11 mm., converted by H_2SO_4 into the *amides*, m.p. 66—66·4°, and 134·7—135·1°, respectively, which with P_2O_5 give the original nitriles. (I) and (II) with dry HCl yield β-*chloro-octonitrile*, b.p. 115—116°/11 mm. Interaction of $CN{\cdot}CH_2{\cdot}CO_2H$ and heptaldehyde in C_5H_5N at 100° during 20 hr. affords cis-, b.p. 88·8—89°/10 mm. (*amide*, m.p. 62·4°), and trans-Δ^{α}-*nonenonitrile*, b.p. 99·8—100°/10 mm. (obtained pure from the trans-*amide*, m.p. 131·1—131·4°, and P_2O_5). J. L. D.

Unsaturated nitriles. Δ^{α}-Dodecenonitrile. A. Gavrilov (Bull. Acad. roy. Belg., 1933, [v], **19**, 815—820).—Bromination of lauronitrile in presence of S affords *α-bromolauronitrile*, b.p. 164·9—165·9°/10 mm., which, on prolonged treatment with hot C_5H_5N, gives an additive product, converted by dry distillation into cis-, b.p. 132·2—132·4°/10 mm., and trans-Δ^{α}-*dodecenonitrile*, b.p. 142·4—142·8°/10 mm. (which are obtained pure only from the corresponding *amides*, m.p. 79·8—80·4° and 115·8—116·7°, and P_2O_5). J. L. D.

Action of phosphorus tribromide on ethylenic α-hydroxynitriles. R. Rambaud (Compt. rend., 1933, **197**, 689—691).—α-Hydroxy-Δ^{β}-butenonitrile isomerises to α-ketobutyronitrile (I) (p-*nitrophenylhydrazone*, m.p. 205—206°) when treated, in CCl_4 or anhyd. Et_2O, with PBr_3, most of which is recovered. (I) is readily hydrolysed by H_2O to $EtCO_2H$ and HCN. Isomerisation is probably due to an initial prototropic change, resulting in the enol form of (I). Similarly, $Pr^{\alpha}CO_2H$ is obtained when α-hydroxy-$\Delta^{\beta\gamma}$-pentenonitrile, b.p. 108—109°/17 mm. (lit. 132—134°/15 mm.), is treated with PBr_3, followed by H_2O. α-Hydroxy-Δ^{β}-butenoic acid and its esters are similarly isomerised by HCl or KOH. A. C.

Negatively substituted alkylarsinic acids. I. Attempted preparation of dichloronitromethylarsinic acids. A. J. Jakubovitsch (J. pr. Chem., 1933, [ii], **138**, 159—166).—Action of $CCl_3{\cdot}NO_2$ on Na salts of alkyl- (or aryl-)arsenious acids gives the corresponding -arsinic acid in good yield. $PhAsO_3H_2$

(82%), (?) $C_6H_4Ph{\cdot}AsO_3H_2$ (80%), $EtAsO_3H_2$ (78%), and $MeAsO_3H_2$ (36%) are thus obtained. With $PhAsO_2Na_2$ there is evidence of formation of an unstable intermediate compound. $COPh{\cdot}CH_2Br$ and $PhAsO_2Na_2$, similarly, give $PhAsO_3H_2$ and some PhAsO. H. A. P.

Effect of traces of carbon disulphide on the yields of Grignard reagents. F. C. WHITMORE and D. E. BADERTSCHER (J. Amer. Chem. Soc., 1933, **55**, 4158—4160).—The yields of $MgPr^{\beta}Br$ (I), $MgBu^{\beta}Br$, and Mg *sec.*-Bu and octyl bromides are increased by addition of a little CS_2 (1 in 1000—4000) to the Et_2O (it is advisable to start the reaction in absence of CS_2, which has a definite retarding action), and the vol. of gas evolved during the prep. of the Grignard reagent is diminished. $Bu^{\gamma}Br$ gives erratic results. Higher yields of $CHMePr^{\beta}{\cdot}OH$ [using (I)] and $CMeEtPr{\cdot}OH$ (from MgPrBr and COMeEt) are obtained when the MgRBr used is prepared in presence of CS_2. The yields of Mg Bu^{γ} and *tert.*-amyl chlorides are not raised appreciably by traces of C_5H_5N, 2-methylpyridine, or acridine. H. B.

Behaviour of metals, particularly lead and bismuth, in atomic hydrogen. [Decomposition of lead tetraethyl.]—See this vol., 1257.

M.-p. curves of alkyl and acetylenic mercury derivatives. T. H. VAUGHN [with R. J. SPAHR and J. A. NIEUWLAND] (J. Amer. Chem. Soc., 1933, **55**, 4206—4209).—*Di(heptylmercuri)-*, m.p. 95·8—96°, *di(octylmercuri)-*, m.p. 108°, *di(nonylmercuri)-*, m.p. 98—98·8°, and *di(decylmercuri)-*, m.p. 110·4—111°, *-acetylenes* are prepared by a slight modification of the method previously described (this vol., 815, 1177). *Hg decyl bromide*, m.p. 111—111·4°, is obtained from Mg decyl bromide and $HgBr_2$. Hexyl, heptyl, octyl, nonyl, and decyl alcohols are prepared in 52—71% yield from $(CH_2)_2O$ and the appropriate MgRBr. The m.-p. curve for HgRBr (R=Me to decyl) shows a small regular alternation. The m.-p. curves for $(R{\cdot}Hg{\cdot}C{:})_2$ and $Hg(C{:}CR)_2$ (this vol., 1033) (in both cases R—Me to decyl) are very similar and lie approx. 29° apart; the former are less fusible. H. B.

Chelated platinammines. H. D. K. DREW and H. J. TRESS (J.C.S., 1933, 1335—1341).—Interaction of $CH_2(CH_2{\cdot}NH_2)_2$ (=tr) with K_2PtCl_4 in H_2O at room temp. affords β-*trimethylenediaminoplatinous chloride* (I), converted by excess of tr in H_2O into β-*bistrimethylenediaminoplatinous chloride* (II) [*plato*-salt (III)], decomposed by 6*N*-HCl at 100° during 7 hr. to an α-*dihydrochloride* [also some (I)], which when treated with conc. aq. K_2PtCl_4 at 80° affords (III). Interaction of (I) and H_2O-en [en=$(\cdot CH_2{\cdot}NH_2)_2$], or Pt enCl$_2$ and H_2O-tr at room temp. and at 100° affords β-*ethylenediaminotrimethylenediaminoplatinous chloride* (IV) [*plato*-salt (V)], indicating that the equivalence of the two pairs of β-positions holds for chelate groups. (IV) is converted as above into an α-*dihydrochloride* (VI) (also some Pt enCl$_2$ and Pt trCl$_2$), showing that again both chelate rings have been opened, which gives, when evaporated with H_2O–K_2PtCl_4, the *chloroplatinite*, $[PtCl(enH)(tr)]PtCl_4$, and subsequently (V). Interaction of (I) with H_2O–NH_3 at room temp. or 100° affords β-*diamminotrimethylenediaminoplatinous chloride* (VII) [*plato*-salt (VIII)], also formed from β-$Pt(NH_3)_2Cl_2$ (1 mol.) and H_2O–tr (2 mols.). α-$Pt(NH_3)_2Cl_2$ and H_2O–tr afford (II), thereby establishing a β-structure for (VII). (VII) with 6*N*-HCl affords β-*amminotrimethylenediaminoplatinous chloride* (IX) [*plato*-salt (X)] (also some Pt trCl$_2$), converted by further treatment with HCl into the α-*monohydrochloride* (XI) of (IX) (and some Pt trCl$_2$), converted by K_2PtCl_4 into (VIII). Evaporation of a solution of the plato-salt of (XI) affords (X), thereby confirming the structure of (XI). (XI) is stable to HCl so that it cannot be a stage in the production of Pt trCl$_2$ from (IX) (cf. A., 1932, 1101); some β-elimination must occur in the reaction. Interaction of the plato-di- and -tetr-ammines in boiling HCl containing H_2O_2 affords the plati-di- and -tetr-ammines, respectively. The following are described: *trimethylenediamino-*; *bistrimethylenediamino-* [*plato*-salt, also obtained from (III) in conc. HCl in air]; *ethylenediaminotrimethylenediamino-* (*plato*-salt); *diamminotrimethylenediamino-platinic chloride* [*plato*-salt, also obtained from (VIII) as above]. Pt enCl$_4$ and $[Pt(NH_3)_4]Cl_2$ in boiling H_2O afford Pt enCl$_3$ (XII) previously obtained by Tschugaev and Tscherniaev (A., 1929, 1157). (XII) with H_2O_2 in HCl affords Pt enCl$_4$ and with $K_2C_2O_4$ in H_2O gives Pt enCl$_2$ (cf. A., 1932, 824). (XII) is different from *bisethylenediaminoplatinous chloroplatinate* and *dichlorobisethylenediaminoplatinic chloroplatinite*, prepared for comparison. β-Pt enCl$_2$ or β-Pt trCl$_2$ with boiling *N*-HCl suffers only oxidation, but with boiling 6*N*-HCl some $[enH_2]PtCl_4$ and $[trH_2]PtCl_4$ is also formed, which indicates that chelated β-plato-diammines may be structurally different from β-$Pt(NH_3)_2Cl_2$. Interaction of tetra- and penta-methylenediamines with K_2PtCl_4–H_2O affords unidentified *substances* which may contain chains of Pt atoms. J. L. D.

Plato- and pallado-sulphines. H. D. K. DREW, G. H. PRESTON, W. WARDLAW, and G. H. WYATT (J.C.S., 1933, 1294—1296; cf. A., 1932, 824).—$(SEt{\cdot}CH_2{\cdot})_2$ (I)(=es) and K_2PtCl_4 at low temp. afford $[Pt\,es_2]PtCl_4$ (II), m.p. about 180° (pink), but at 100°, Pt esCl$_2$ (III), yellow, m.p. 185° [also obtained from (II) with boiling H_2O], is the main product. (III) with Ag_2O affords a base, reconverted into (III) with HCl. Excess of (I) with (II) or (III) affords solutions containing $[Pt\,es_2]Cl_2$ (cf. A., 1910, i, 354). (I) with K_2PdCl_4 at room temp. affords Pd esCl$_2$ (cf. A., 1924, i, 704), which crystallises from H_2O in two forms each of m.p. 182°. $Pd(SEt_2)_2Cl_2$ (IV), m.p. 83° (lit. 78°), with H_2O–$(EtS{\cdot})_2$ affords a solution of $[Pd(SEt_2)_4]Cl_2$ which regenerates (IV) in air. (IV) with Ag_2O affords a base, reconverted by HCl into (IV). $Pd(SMe_2)_2Cl_2$ (V), m.p. 128°, is prepared similarly to (IV). (IV) and (V) are stereochemically and structurally similar to β-$Pt(SEt_2)_2Cl_2$. $(EtS{\cdot})_2$ and acetone-bisethylthioacetal afford no definite products with K_2PtCl_4 or K_2PdCl_4, which indicates that chelate plato- and pallado-disulphines are not formed if the establishment of three- or four-membered rings is involved. J. L. D.

Stereoisomeric 1 : 2-diethyl*cyclo*pentanes. G. CHIURDOGLU (Bull. Soc. chim. Belg., 1933, **42**, 347—

358; cf. A., 1929, 67).—The prep. of 1 : 2-diethyl-*cyclo*pentanol (I), b.p. 82·0—82·6°/8·1 mm., m.p. about —23°, in 54% yield from MgEtBr and 2-ethyl-*cyclo*pentanone is described. Dehydration of (I) with 90% HCO_2H gives 1 : 2-diethyl-Δ^1-*cyclo*pentene, b.p. 149·2—149·3°/760 mm., reduced by Pt-black in AcOH at room temp. to trans-, b.p. 147·53—147·55°/760 mm., m.p. —95·6°, and cis-, b.p. 153·55—153·58°/760 mm., m.p. —118·7°, -1 : 2-*diethyl*cyclo*pentane*, separated by repeated fractionation. Physical consts. are recorded. J. W. B.

Hydrolytic decomposition of *o*-xylenesulphonic acid. N. KISHNER (J. Gen. Chem. Russ., 1933, **3**, 578—580).—Hydrolysis of xylenesulphonic acids (heating with conc. H_2SO_4, diluting with H_2O, and distilling) has shown that the *o*-acid, b.p. 142·5—142·7°/742 mm., is much more stable than the *p*-acid. It is concluded that the stability of the *o*-acid is due to SO_3H being *para* to one of the Me groups. M. Z.

Nitrogenous free radicals. Structure of diarylnitric oxides. L. CAMBI (Gazzetta, 1933, **63**, 579—584).—The magnetic susceptibility of di-*p*-nitrophenyl- and di-*p*-anisyl-nitric oxides (A., 1920, i, 38, 306) has been measured at temp. from 84° to 350° abs., and of Ph_2NO (A., 1914, i, 955) at 291° abs.; it corresponds with 1 Bohr magneton, and with the semipolar double linking structure $R_2N{-}O$. E. W. W.

Syntheses in the di- and tri-phenyl series. II. J. VON BRAUN, G. IRMISCH, and J. NELLES (Ber., 1933, **66**, [*B*], 1471—1483; cf. A., 1927, 655).—The action of CO and HCl on *cyclo*hexylbenzene (I), C_6H_6, $AlCl_3$, and CuCl leads to *cyclo*hexylbenzaldehyde (II), b.p. 160°/12 mm. (*semicarbazone*, m.p. 220°; *oxime*, m.p. 88°; cyclo*hexylbenzylideneaniline* (III), m.p. 77°). (II) and KOH yield p-cyclo*hexylbenzoic acid*, m.p. 198°, and p-cyclo*hexylbenzyl alcohol*, b.p. 162°/12 mm., m.p. 41°. p-cyclo*Hexylbenzyl acetate* has b.p. 184°/12 mm., m.p. 47°. (I), and $CO_2Et{\cdot}COCl$ afford *Et* p-cyclo*hexylbenzoylformate*, b.p. 215—225°/12 mm., hydrolysed to p-cyclo*hexylbenzoylformic acid*, m.p. 111°, converted by protracted heating with NH_2Ph into (III), whence (II) in about 6% yield. (I), $CCl_3{\cdot}CHO$, and $AlCl_3$ give *ααα-trichloro*-β-p-cyclo*hexylphenylethan*-β-*ol*, b.p. 215°/16 mm., smoothly converted by boiling saturated K_2CO_3 into (II). p-cyclo*Hexylbenzaldehyde diethylacetal*, from (II), $CH(OEt)_2$, and NH_4Cl, has m.p. 181°/13 mm. Ph_2 is converted by $(CH_2O)_3$, $ZnCl_2$, and HCl in light petroleum into di-*p*-chloromethyldiphenyl (IV), m.p. 68°, and p-*chloromethyldiphenyl*, b.p. 235°/12 mm., m.p. 136°. (IV) and KCN yield *di*-p-*cyanomethyldiphenyl*, m.p. 184° (*dibenzylidene* derivative, decomp. 256°), hydrolysed to *diphenyl*-4 : 4′-*diacetic acid*, m.p. 270—273° (*Et*$_2$ ester, b.p. 204—206°/0·5 mm., m.p. 55°). Similarly, (I), (CH_2O_3), and HCl afford *chloromethylhexahydrodiphenyl*, b.p. about 120°/0·3 mm., oxidised by 30% HNO_3 to *p*-$C_6H_4(CO_2H)_2$ (Me ester, m.p. 140°) and transformed by $NHEt_2$ into *diethyl*-p-cyclo*hexylbenzylamine*, b.p. 125°/0·1 mm. (*methiodide*, m.p. 186°). A mixture of *cis*- and *trans-cyclo*hexyl-*cyclo*hexanol is converted by 66% HBr at 120° into an inseparable mixture of cis- and trans-p-cyclo*hexyl*-cyclo*hexyl bromide*, b.p. 150—155°/14 mm., transformed by $AlCl_3$ and C_6H_6 into *cyclo*hexyl*cyclo*hexene, b.p. 104—106°/13 mm., a mixture of much m-cyclo*hexyldiphenyl* (dehydrogenated by Se to *m*-$C_6H_4Ph_2$, m.p. 89°), and little p-cyclo*hexyldiphenyl* (dehydrogenated to $C_6H_4Ph_2$, m.p. 209°), and a *hydrocarbon*, $C_{30}H_{46}$, m.p. 145°, oxidised by HNO_3 to *p*-$C_6H_4(CO_2H)$ and dehydrogenated by Se to the *substance* $C_{30}H_{22}$, m.p. 232°, isomeric with quinquephenyl. Treatment of *p-cyclo*hexyl*cyclo*hexanone with MgPhBr and subsequently with boiling 20% H_2SO_4 leads to *tetrahydrodiphenyl*cyclo*hexane* (V),



, b.p. 225—230°/18 mm., m.p. 97—98° directly dehydrogenated to $C_6H_4Ph_2$ by Se at 300–320°, but transformed by Br and subsequent heating at 180°/0·6 mm. into the *hydrocarbon* $C_{18}H_{20}$, b.p. 180—185°/0·6 mm., m.p. 85°. *p*-$C_6H_4Br_2$, Mg, and *cyclo*hexanone (VI) yield p-*dicyclohexenylbenzene*,



, m.p. 110° (whence p-dicyclo-hexadienylbenzene, m.p. 101°), and p-*bromotetrahydrodiphenyl*, m.p. 73°, converted by Br and subsequent distillation at 135°/0·6 mm. into *p*-bromodiphenyl (VII), m.p. 89°. Mg, (VI), and (VII) yield the impure carbinol, transformed by successive treatment with HCl in Et_2O and warm C_5H_5N into a hydrocarbon, m.p. 146—148°, hydrogenated (Pd) to hexahydroterphenyl in very poor yield. Hydrogenation of (V) (Pd–H_2) yields a mixture of *hydrocarbons* $C_{18}H_{26}$, m.p. 86° and b.p. 144°/0·2 mm., respectively, the latter being isomerised to the former by $AlCl_3$ in CS_2. Under more drastic conditions (Ni and H_2 at about 200°) (V) and its less hydrogenated analogues are smoothly transformed into *perhydrophenyldiphenyls* (VIII), $C_{18}H_{32}$, m.p. 162° and 55—57°, respectively, which are not interconverted by $AlCl_3$. Treatment of *p-cyclo*hexyl*cyclo*hexanone with Mg and bromo-*cyclo*hexane affords p-*dicyclohexyl*cyclo*hexene*,



, m.p. 111—113°, hydrogenated (Pd and H_2) to (VIII). Attempts to prepare diphenylylbenzyl chloride were unsuccessful. The liquid dodecahydrophenyldiphenyl is transformed by HCl, $(CH_2O)_3$, and $ZnCl_2$ and subsequent treatment with $NHEt_2$ into small amounts of a *base*, $C_{23}H_{37}N$, b.p. 185—190°/0·4 mm. Treatment of *p*-$C_6H_4Ph_2$ in $C_6H_3Cl_3$ at 100° with Br (4 atoms) and a little I gives the 4 : 4″-Br_2-compound, m.p. 312—313°, in 85% yield. Use of Br (2 atoms) does not lead satisfactorily to the Br_1-derivative. Mg, *p*-$C_6H_4Br_2$, and *p-cyclo*hexyl*cyclo*hexanone give the crude carbinol, transformed by boiling 20% H_2SO_4 into 4-*bromodecahydrophenyldiphenyl*, m.p. 97—98°, transformed by Br at 160° and subsequent distillation into *p*-bromophenyldiphenyl, m.p. 230—232°, and *bromohexahydrophenyldiphenyl*, m.p. 148°; *eicosahydrodidiphenylylbenzene*, b.p. about 250°/0·7 mm., m.p. 240—245°, is obtained as by-product of the Grignard reaction. *p*-$C_6H_4Me{\cdot}MgBr$ and *p-cyclo*hexylhexanone yield *methyldecahydrophenyldiphenyl*, b.p. 165°/0·7 mm., m.p. 108—110°, hydrogenated to *methyldodecahydrophenyldiphenyl*, m.p. 82° and 36—38°, respectively, and dehydrogenated to p-*tolyldiphenyl* (VIII), m.p. 206—208°. (VIII) is oxidised by CrO_3 in AcOH to *diphenyl*-4-*carboxylic acid*, m.p. 305°, and brominated in $C_6H_3Cl_3$ at 140° to

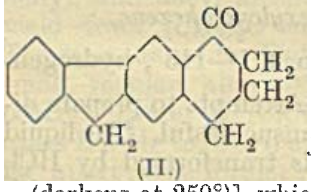
4-p-*diphenylylbenzyl bromide*, m.p. 210°, whence 4-p-*diphenylylbenzyldiethylamine*, m.p. 133° after softening. H. W.

Preparation of 1 : 5- and 1 : 8-dinitronaphthalene and 5-nitro-α-naphthylamine. H. H. Hodgson and J. Walker (J.C.S., 1933, 1346—1348).—Nitration of 1-$C_{10}H_7\cdot NO_2$ (improved method) affords a mixture (I) of 1 : 5- (II) and 1 : 8-$C_{10}H_6(NO_2)_2$ (III), which when reduced in H_2O by Na_2S and Na trisulphide at 65° affords 5-nitro-α-naphthylamine; (III) is relatively unattacked. Reduction of pure (II) occurs better at 90°. (I) when boiled during 1 hr. with Na_2SO_3–H_2O affords (II), (III) dissolving. J. L. D.

Induced oxidation of anthracene in the autoxidation of benzaldehyde.—See this vol., 1252.

Selenium dehydrogenation of sitosterol. L. Ruzicka, M. W. Goldberg, G. Thomann, and E. Brandenberger (Nature, 1933, **132**, 643).—Contrary to Diels (this vol., 1047) the *X*-ray spectra of the hydrocarbons $C_{25}H_{24}$ (I) and $C_{26}H_{26}$ (II) obtained from cholesterol and ergosterol, respectively (*ibid.*, 820), are different. Se dehydrogenation of sitosterol gives a new *hydrocarbon*, $C_{27}H_{28}$, m.p. 202—203° (m.p. of *compound* with dinitroanthraquinone 246—247°), which would not be the case if (I) and (II) were identical. L. S. T.

Synthesis of 2 : 3-benzfluorene. C. F. Koelsch (J. Amer. Chem. Soc., 1933, **55**, 3885—3887).—Fluorene, succinic anhydride, and $AlCl_3$ in C_6H_6 give β-2-*fluoroylpropionic acid* (*γ-keto-γ-2-fluorenylbutyric acid*) (I), m.p. 210—212° [*Me* ester, m.p. 111—112° (*oxime*, m.p. 129—130°)], oxidised by $Na_2Cr_2O_7$–AcOH to *uorenonoylpropionic acid*, m.p. 230—234° (previous darkening), and by alkaline $KMnO_4$ to fluorenone-2-carboxylic acid, m.p. > 295°. Reduction

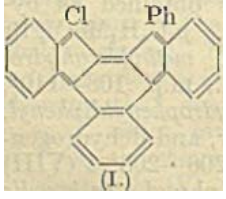


(II.)

(Zn–Hg, conc. HCl, EtOH) of (I) affords *γ-2-fluorenylbutyric acid*, m.p. 151—151·5°, which with PCl_5 in C_6H_6 followed by $AlCl_3$ gives *ketotetrahydrobenzfluorene* (II), m.p. 148—149° [*semicarbazone*, m.p. > 290° (darkens at 250°)], which is reduced (Clemmensen) to the *tetrahydrobenzfluorene*, m.p. 129° (*picrate*, m.p. 123—124°). This is dehydrogenated (S at 250—275°) to 2 : 3-benzfluorene, m.p. 204—206° (lit. 208°). H. B.

Rubenes, organic compounds able to absorb free oxygen and then liberate it. C. Dufraisse (Bull. Soc. chim., 1933, [iv], **53**, 789—849).—A lecture.

Dissociable organic oxides. XIV. Violet chloro-compound of the 1 : 1′-*o*-phenylenerubene series. C. Dufraisse, R. Buret, and R. Girard (Bull. Soc. chim., 1933, [iv], **53**, 782—788).—Dichlorodiphenylrubene (this vol., 57) when heated at 200°/vac. gives HCl and 3-*chloro*-3′-*phenyl*-1 : 1′-*o*-*phenylenerubene* (I), m.p. 274° (Maquenne block), also formed from the compound $C_{30}H_{20}Cl_4$ (*loc. cit.*), at 280°/vac., which affords violet solutions (decolorised rapidly by light in presence of air). The absorption spectrum of (I) is very similar to that of diphenylphenylenerubene (A., 1931, 1407). H. B.



(I.)

[Thermal decomposition of] 3-phenylhydroxylamine. E. Muller and E. Lindemann (Angew. Chem., 1933, **46**, 681—685).—Decomp. of NHPh·OH (I) in boiling xylene (10 hr.) in N_2 is greatly influenced by the nature and cleanliness of the vessel. In SiO_2 9·1% of NH_2Ph (II) and a mixture of NPh:NPhO (III) and N_2Ph_2 (IV) [59—68% of (IV)] are formed. Addition of (III) (5 mols.) decreases the yield of (II) to 0·2% and gives 95% of (IV). Pd-black similarly gives a nearly quant. yield of (IV). Decomp. of (I) is thus primarily a dehydrogenation to PhNO+2H, and (III) sets up the reaction chain: NHPh·OH+NPh:NPhO ⟶ PhNO+NPh:NPh H_2O; NPh:NPh+NHPh·OH ⟶ NPh:NPhO+H_2O. Attempts to isolate PhNO from the decomp. of (I) or its derivatives failed. (I) with CPh_3Na gives the unstable O-*Na* derivative, with the Na_2 derivative of COPh·C_6H_4Ph the *Na_2* derivative of (I); neither compound reacts with alkyl halides. (I), EtCl, and $AlCl_3$ in Et_2O give (IV) (35%) and phenetidine (10%), the latter probably by secondary change of the Me ether of (I). The Bz and Ac derivative (modified prep.) of (I) in boiling xylene give oils, and NBzPh·OMe in boiling cumene gives CH_2O (57%). R. S. C.

Nitro-derivatives of methylaniline. M. M. de Monchy (Rec. trav. chim., 1933, **52**, 833—838).—NAcPhMe and cold abs. HNO_3 give *p*-$NO_2\cdot C_6H_4\cdot$NAcMe; with warm abs. HNO_3+conc. H_2SO_4, *s*-$(NO_2)_3C_6H_2\cdot$NMe·NO_2 results. 2 : 4-*Dinitro*-N-*methylacetanilide*, m.p. 78°, is prepared from 2 : 4-$(NO_2)_2C_6H_3\cdot$NHMe (I), Ac_2O, and a little H_2SO_4. NPhMe·CO·NHEt and abs. HNO_3 afford N′-*nitro*-N-2 : 4-*dinitrophenyl*-N-*methyl*-N′-*ethylcarbamide*, m.p. 96°, which is unaffected by boiling H_2O, MeOH, or EtOH, and is converted by EtOH at 130° (sealed tube) or conc. H_2SO_4 into (I). H. B.

Conjugated systems. XIV. Preparation and properties of δ-amino- and δ-anilino-α-phenylbutadiene. I. E. Muskat and L. B. Grimsley (J. Amer. Chem. Soc., 1933, **55**, 3762—3769).—δ-Bromo-α-phenylbutadiene (I) and a large excess of NH_2Ph at room temp. give *δ-anilino-α-phenylbutadiene* (II) (*hydrochloride*, m.p. 104—106°), which on attempted distillation passes into a resin-like *dimeride*, m.p. 105°. (II) and HCl in C_6H_6 give *γ-chloro-δ-anilino-α-phenyl-Δ^a-butene hydrochloride*, m.p. 124° (ozonolysis product, BzOH), which with excess of Cl_2 in $CHCl_3$ affords *αβγ-trichloro-δ-trichloroanilino-α-phenylbutane hydrochloride*, m.p. 218°. (II) and Br (1 mol.) in $CHCl_3$ give *γδ-dibromo-δ-anilino-α-phenyl-Δ^a-butene*, m.p. 103° (ozonolysis product, BzOH), converted by Br (1 mol.) into *αβγδ-tetrabromo-δ-anilino-α-phenylbutane*, m.p. 88—91°, and by excess of Br into *αβγδ-tetrabromo-δ-tribromoanilino-α-phenylbutane hydrobromide*, m.p. 182°. *γδ-Dichloro-δ-anilino-α-phenyl-Δ^a-butene* (*hydrochloride*, m.p. 135°) is prepared from (II) and Cl_2 (1 mol.) in $CHCl_3$. (I) and EtOH–NH_3 afford *δ-amino-α-phenylbutadiene* (III) (*hydrochloride*, m.p. 111°), which with HCl in C_6H_6 gives (probably) *γ-chloro-δ-amino-α-phenyl-Δ^a-butene hydrochloride*, m.p. 138°. (III) is also prepared (*a*) from (I) and $NaNH_2$ or KNH_2 in liquid NH_3, (*b*) from (I) and *o*-$C_6H_4(CO)_2NK$ followed by

hydrolysis (aq. HCl), and (*c*) by the action of NaOCl on cinnamylideneacetamide. H. B.

Derivatives of 1-phenylnaphthalene. V. Vesely and F. Šturša (Coll. Czech. Chem. Comm., 1933, **5**, 343—347).—Contrary to the orientation assigned by Weiss and Woidich (A., 1926, 509) 1-$C_{10}H_7Ph$ with Ac_2O–HNO_3 (*d* 1·51) gives its 4-NO_2-derivative, m.p. 132°, reduced by Fe–AcOH to the 4-NH_2-compound (I), m.p. 73—74° (*Ac* derivative, m.p. 167—168°), which with Ac_2O–HNO_3 < 30° affords the *Ac* derivative, m.p. 207—208°, of 3-*nitro*-4-*amino*-1-*phenylnaphthalene* (II), m.p. 151—152°, obtained by hydrolysis with conc. HCl. Reduction of (II) with $SnCl_2$–HCl gives the 3 : 4-*diamine*, m.p. 100—101°, the orientation of which is proved by the formation of the 3 : 4-*phenanthrazine*, m.p. 277—228°(?), by condensation with phenanthraquinone in AcOH. By the Sandmeyer reaction (I) gives 4-*bromo*-1-*phenylnaphthalene*, m.p. 76—77°. J. W. B.

Tenacity of organic residues. IX. J. von Braun and R. Michaelis (Annalen, 1933, **507**, 1—14).—The relative tenacities of various substituted benzyl groups in substituted dibenzylmethylamines are determined by investigation of the fission products with CNBr. From these and previous results (A., 1926, 1231; 1931, 1408), the order of tenacity for ·CH_2·C_6H_4R is (R=) : *p*-OMe<*p*-Ph, *p*-*cyclo*hexyl, 4-*p*-diphenylyl<*p*-Et<*p*-Me<*m*-Me<H, F, *o*-Et, *o*-vinyl, *o*-Ph<*o*-Me<*p*-Cl<*p*-Br<*p*-I<*m*-Cl<*m*-Br<*m*-I<*o*-Cl<*o*-Br<*o*-I.

[With (in part) F. Fischer and R. Murjahn.] *p*-OEt·C_6H_4·CHO and conc. aq. NaOH give p-*ethoxybenzyl alcohol*, b.p. 134—135°/12 mm.; the *chloride*, b.p. 95—100°/0·8 mm., and *p*-OMe·C_6H_4·CH_2·NHMe (2 mols.) at 100° afford 4-*methoxy*-4′-*ethoxydibenzylmethylamine*, b.p. 220—225°/14 mm. *p*-*cyclo*Hexylbenzyl chloride and NH_2Me in C_6H_6 at 100° give p-cyclo*hexylbenzylmethylamine* (I), b.p. 165°/11 mm. (*hydrochloride*, m.p. 186°; *chloroplatinate*, decomp. 215°), and some *di*-(p-cyclo*hexylbenzyl*)*methylamine*, b.p. 240°/0·4 mm., m.p. 52° (*methiodide*, m.p. 196°). *p*-C_6H_4Ph·CH_2Cl and (I) afford 4-*phenyl*-4′-cyclo*hexyldibenzylmethylamine*, m.p. 52—53° (*methiodide*, m.p. 200°), which with CNBr yields impure p-*phenyl*- (I), m.p. 67—70°, and p-cyclo*hexyl*-*benzylmethylcyanamides* and the -benzyl bromides. *p*-C_6H_4Ph·CH_2·NHMe, best prepared [together with some di-(*p*-phenylbenzyl)-methylamine, b.p. 255°/0·8 mm. (methiodide, m.p. 205°)] from *p*-C_6H_4Ph·CH_2Cl and NH_2Me in C_6H_6, with 4-*p*-diphenylylbenzyl bromide (II) in $C_6H_3Cl_3$ at 100—130° give 4-*phenyl*-4′-p-*diphenylyldibenzylmethylamine*, m.p. 186° (*hydrochloride*, m.p. 245°), which with CNBr affords (mainly) (I) and (II) with a little 4-p-*diphenylylbenzylmethylcyanamide*, b.p. 160—175°/0·7 mm.; impure 4-p-*diphenylylbenzyltrimethylammonium bromide* has m.p. 225—245°. The following are also described and appear to be new : o-*phenyl*-, b.p. 223°/12 mm. (*methiodide*, m.p. 163°), o-*ethyl*-, b.p. 173°/13 mm. (*hydrochloride*, m.p. 174°; *methiodide*, m.p. 154°), 2-*ethyl*-2′-*vinyl*-, b.p. 195—196°/13 mm. (*hydrochloride*, m.p. 138°; *methiodide*, m.p. 164°), 2 : 2′-*dimethyl*-, b.p. 182°/11 mm., 2 : 2′-*dichloro*-, b.p. 200°/10 mm., 3 : 3′-*dichloro*-, b.p. 198°/11 mm., 4-*chloro*-2′-*methyl*-, b.p. 180—184° (*hydrochloride*, m.p. 170°; *methiodide*, m.p. 215°), 2-*chloro*-2′-*bromo*-, b.p. 150°/0·5 mm. (*hydrochloride*, m.p. 160°; *picrate*, m.p. 129°), 2-*chloro*-3′-*iodo*-, b.p. 200°/0·5 mm., m.p. 55—56° (*hydrochloride*, m.p. 195°; *picrate*, m.p. 123°), 2-*bromo*-2′-*iodo*-, b.p. 200—203°/0·5 mm. (*hydrochloride*, m.p. 200°), 3-*chloro*-4′-*bromo*-, b.p. 186—190°/0·5 mm. (*hydrochloride*, m.p. 187°), 3-*chloro*-4′-*iodo*-, b.p. 210°/0·5 mm. (*hydrochloride*, m.p. 202°; *picrate*, m.p. 110°), 3-*chloro*-3′-*bromo*-, b.p. 180°/0·4 mm. (*hydrochloride*, m.p. 210°; *picrate*, m.p. 147°), 3-*bromo*-3′-*iodo*-, b.p. 200°/0·5 mm. (*hydrochloride*, m.p. 194°; *picrate*, m.p. 140°), 2-*chloro*-3′-*bromo*-, b.p. 185°/0·5 mm. (*hydrochloride*, m.p. 198°; *picrate*, m.p. 133°), and 2 : 3′-*dibromo*-, b.p. 198—200°/0·5 mm. (*hydrochloride*, m.p. 183°), *-dibenzylmethylamines*; *o*-ethyl-, b.p. 92°/12 mm. (*hydrochloride*, m.p. 108°; *picrate*, m.p. 139°), o-*methyl*-, b.p. 100—102°/11 mm. (*hydrochloride*, m.p. 150°; *picrate*, m.p. 129°), o-*chloro*-, b.p. 98—100°/10 mm. (*hydrochloride*, m.p. 135°; *picrate*, m.p. 120°), o-*iodo*-, b.p. 130—132°/10 mm. (*hydrochloride*, m.p. 180°; *picrate*, m.p. 150°), m-*chloro*-, b.p. 122—124°/11 mm. (*hydrochloride* m.p. 170°; *picrate*, m.p. 128°), and m-*bromo*-, b.p. 122°/14 mm. (*hydrochloride*, m.p. 147°; *picrate*, m.p. 135°), *-benzylmethylamines*; o-*phenyl*-, m.p. 205°, o-*ethyl*-, m.p. 220°, and o-*vinyl*-, m.p. 217°(?), *-benzyltrimethylammonium bromides*; o-, b.p. 160—166°/12 mm., m-, b.p. 180°/14 mm., and p-, b.p. 165—167°/10 mm., *-chloro*-, o-, b.p. 180—185°/11 mm., and m-, b.p. 180—184°/14 mm., *-bromo*-, and o-, b.p. 205—210°/11 mm., and m-, b.p. about 160°/0·5 mm., *-iodo-benzylmethylcyanamides*. H. B.

***m*-Phenylenediamine sulphate.** M. S. Roshdestvenski and T. N. Karskaja (J. Gen. Chem. Russ., 1933, **3**, 558).—*m*-$C_6H_4(NH_2)_2$,H_2SO_4 when crystallised from aq. solution is not anhyd. (as has been supposed) but contains $4H_2O$, which can be removed by slow dehydration in a desiccator. M. Z.

Analysis of hair dyes. I. Mol. compounds of polyhydric phenols with aromatic diamines used as hair dyes. C. Naegeli and H. Kaltman (Helv. Chim. Acta, 1933, **16**, 980—988).—The following mol. *compounds* are obtained by melting the components together or mixing them in H_2O, C_6H_6, Et_2O, or $CHCl_3$ or by subliming the mixture in a vac. Usually only one compound can be isolated even when the m.-p. diagram indicates the existence of several. The mol. ratio is stated in parentheses. *m*-$C_6H_4(NH_2)_2$ with pyrocatechol (I) (1 : 1), m.p. 70°, resorcinol (II) (1 : 1), m.p. 84°, quinol (III), (1 : 1), m.p. 135°, pyrogallol (IV), (1 : 1), m.p. 88·5°, and phloroglucinol (2 : 1), m.p. 105°; *p*-$C_6H_4(NH_2)_2$ with (I) (1 : 1 and 1 : 2), m.p. 110·5° and 111°, respectively, (II) (1 : 1), m.p. 118°, (III) (1 : 1), m.p. 194°, and (IV) (1 : 1), m.p. 120°; *p*-tolylenediamine with (I) (1 : 1), m.p. 92·5°, (II) (1 : 1), m.p. 125°, (III) (1 : 1), m.p. 145°, and (IV), (2 : 1), m.p. 104°; 1 : 2-$C_{10}H_6(NH_2)_2$ with (I) (1 : 1), m.p. 104·5°. H. W.

Preparation of derivatives of *m*-phenylenedihydrazine using the tetrazonium salt of *m*-phenylenediamine. H. A. J. Schoutissen (Rec. trav. chim., 1933, **52**, 869—873).—Addition of nitrosylsulphuric acid to *m*-$C_6H_4(NH_2)_2$ hydrochloride in 89% H_3PO_4 at < 0°, subsequent treatment with

$SnCl_2$ and conc. HCl at −5°, and decomp. of the resultant additive compound with aq. NaOAc, give a solution of *m*-phenylenedihydrazine, which when treated with HNO_2 in strongly acid (HCl) solution gives *m*-bistriazobenzene (J.C.S., 1907, **91**, 1953). The m-*phenylenedihydrazones* of *o*-OH·C_6H_4·CHO (m.p. 234°), COPhMe (m.p. 159—160°), $AcCO_2H$ (m.p. 192·5°), $CH_2Ac·CO_2Et$ (m.p. 112—113°), and isatin [m.p. 225° (decomp.)] are described. H. B.

Triarylaminoethylenes. III. Interaction of sulphur and trianilinoethylene. IV. Interaction of sulphur and tri-*o*-toluidinoethylene. R. Shibata, M. Okuyama, N. Kojima, and T. Nishi. **V. Action of sulphur on tri-*p*-tolylaminoethylene.** R. Shibata and T. Nishi (J. Soc. Chem. Ind. Japan, 1933, **36**, 511—514B, 514—517B, 538—540B).—III. Interaction of S and trianilinoethylene at 150° affords dianilinoethylene (I), trianilinothiolethylene, and dithio-oxanilide (cf. A., 1930, 465), also thio-oxanilide and oxanilide as products of oxidation. Interaction of NH_2Ph, CHCl:CHCl, and K_2CO_3 with a catalyst under pressure during 24 hr. at 100—120° affords some (I).

IV. Interaction of *o*-$C_6H_4Me·NH_2$ and $CHCl:CCl_2$ in presence of $Ca(OH)_2$ affords mainly *tri*-o-*toluidinoethylene* (I), m.p. 141° [*hydrochloride*, m.p. 203° (decomp.)], together with a *substance*, $C_{23}H_{23}N_3$, m.p. 115—116°. (I) with S at 130—135° during 1 hr. affords *dithio-ox*-o-*toluidide*, m.p. 118°, which is not oxidised at a higher temp., *tri*-o-*toluidinothiolethylene*, m.p. 88° (*hydrochloride*, m.p. 165—166°), and *di*-o-*toluidinoethylene*, m.p. 69°.

V. (Cf. A., 1930, 465).—Interaction of *p*-$C_6H_4Me·NH_2$ and C_2HCl_3 in boiling 20% NaOH during 40 hr. affords *tri*-p-*tolylaminoethylene* (I), m.p. 161—163° (decomp.), and two *substances*, $C_{23}H_{23}N_3$ (II), m.p. 141°, and $C_{15}H_{13}N_2$ (III), m.p. 207°. (I) is converted by heat into (II) and (III). (I) (5 parts) with S (1 part) at 140° during 1 hr. affords *di*-p-*tolylaminoethylene*, m.p. 121°, *tri*-p-*tolylaminothiolethylene* (?), m.p. 137°, and dithio-ox-*p*-toluidide, $C_{16}H_{16}N_2S_2$. J. L. D.

Glucosidic azo-dyes. B. Helferich, O. Lang, and E. Schmitz-Hillebrecht (J. pr. Chem., 1933, [ii], 275—280).—Condensation of pyrocatechol with β-*d*-glucose penta-acetate at 125° in presence of a little *p*-$C_6H_4Me·SO_3H$ gives *pyrocatechol*-β-d-*glucoside tetra-acetate*, m.p. 114—116·5°, hydrolysed by *N*-NaOH at room temp. to *pyrocatechol*-β-d-*glucoside*, m.p. 129—133°, $[\alpha]_D^{20}$ −71° in H_2O. From this the following azo-dyes are prepared: 3 : 5-*bisbenzeneazo*-, m.p. 244—251° (decomp.); 5-p-*methoxybenzeneazo*-, m.p. 220—222° (decomp.); and 5-p-*sulphobenzeneazo-pyrocatechol*-1-β-d-*glucoside* (as *Na* salt, $[\alpha]_D^{20}$ −41° in H_2O). The last-named is split, but not readily, by emulsin (I). It dyes wool reddish-yellow at 100°, and the dyed fabric on treatment with (I) loses its sugar without changing shade. Wool is also dyed slowly at 37° in presence of (I). All m.p. are corr. H. A. P.

Azo dyes. A. Mironescu and I. V. Nicolescu (Bul. Soc. Chim. Romania, 1933, **15**, 53—57).—Diazonium compounds from *p*-$NH_2·C_6H_4·SO_3H$ (I), *p*-$NO_2·C_6H_4·NH_2$, *o*-$NH_2·C_6H_4·OH$, and (*p*-$NH_2·C_6H_4·)_2$ (II) couple with CHPh:NPh in an alkaline medium in the cold to give benzylideneaminoazobenzene-*p*-sulphonic acid (*Na* salt, m.p. 56°), p-*nitro*-, m.p. 107°, and p-*hydroxy*-p′-*benzylideneaminoazobenzene*, m.p. 158°, and *bisbenzylideneaminobenzeneazodiphenyl*, m.p. 195°, respectively. Similarly, the diazonium compound of (I) with furfurylidene- and anisylidene-aniline (III) affords *Na furfurylidene*-, m.p. 187°, and *Na anisylidene-aminoazobenzene*-p-*sulphonate*, m.p. 170°, whilst (II) (diazonium compound) with (III) affords *bisanisylideneaminobenzeneazodiphenyl*, m.p. 166°. These products dye unmordanted cotton, wool, and silk in shades fast to light and boiling H_2O. The OMe has no influence on the shade. J. L. D.

Atoms and isosteric compounds. II. Comparison of the groups ·N_2· and ·CO·. H. Erlenmeyer and M. Leo (Helv. Chim. Acta, 1933, **16**, 897—904).—Azo- (I) and *p*-aminoazo-benzene (II) do not form mixed crystals with $COPh_2$ and *p*-$C_6H_4Bz·NH_2$, respectively, whereas such crystals are formed with $CO(O·CH_2Ph)_2$ and $N_2(O·CH_2Ph)_2$, whilst benzyl β-phenylpropionate is non-cryst. Since (I) yields mixed crystals with stilbene and CHPh:NPh, it follows that ·N_2· in (I) and (II) is more closely similar to ·CH:CH·, whilst in derivatives of OH·N_2·OH a likeness to ·CO· is manifest. Chemical relations are pointed out in the behaviour of N_2:NH, N_2:CH_2, and CO:CH_2 isosteric with the N_2O and CO_2 groups. Thermal decomp. shows the compounds MgPhCl, PhN_2Cl, BzCl to fall into one group, whereas the polarising action of Hal. in CHPh:CH·Hal. causes a different type of reaction. The behaviour of CO and N_2 towards metals shows marked differences, although contact catalysts for the NH_3 synthesis are metals which readily give carbonyls. H. W.

Determination of the constitution of azo-dyes. V. Křepelka (Chim. et Ind., 1933, **29**, Spec. no., 902—905).—A lecture. A. A. L.

Addition of phenols to the ethylenic linking. Action of phenols on alkylene halides. R. A. Smith and J. B. Niederl (J. Amer. Chem. Soc., 1933, **55**, 4151—4153).—PhOH (1 mol.), allyl chloride (I) (1 mol.), and conc. H_2SO_4 (1 mol.) at room temp. for 6 months give *o*-*iso*propenylphenol; *o*- and *p*-cresols similarly afford 5-*iso*propenyl-*o*- and 3-*iso*propenyl-*p*-cresol, respectively, whilst *m*-cresol (II) yields 4-*iso*propenyl-*m*-cresol (III) (as its dimeride, m.p. 74°). Equimol. amounts of (I), (II), and conc. H_2SO_4 in boiling AcOH for 8 hr. give approx. equal amounts of (III) and (?) impure β-m-*tolyloxypropyl alcohol*, b.p. 218—220° [(?) which when distilled passes into impure β-m-*tolyloxy*-Δ^{α}-*propene*, b.p. about 200°]. The above *iso*propenylphenols are also prepared as previously described (this vol., 270). H. B.

Glucosides of *p*-nitro- and *p*-amino-phenol and their fermentative fission. B. Helferich and O. Peters (J. pr. Chem., 1933, [ii], **138**, 281—283).—*p*-Nitrophenyl-β-*d*-glucoside tetra-acetate is most conveniently prepared from *p*-$NO_2·C_6H_4·OH$, *d*-glucose β-penta-acetate, and $ZnCl_2$ (0·2 mol.) at 115—120°. It is reduced by H_2 (Pd–$BaSO_4$) to p-*aminophenyl*-β-d-*glucoside tetra-acetate*, m.p. 127—130°, $[\alpha]_D^{20}$ −15·5° in $CHCl_3$, which on hydrolysis with

NaOMe in MeOH gives p-*aminophenyl*-β-d-*glucoside*, m.p. 157—160°, $[\alpha]_D^{19}$ −65°; this is hydrolysed by emulsin at 0·1 the rate of the *p*-NO_2-glucoside. H. A. P.

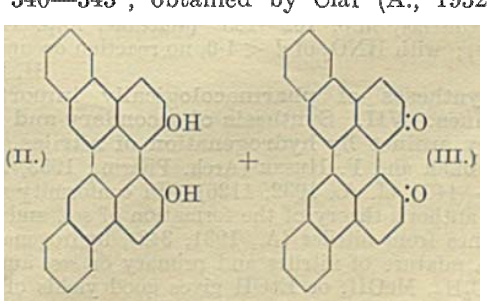
Chloro-derivatives of *m*-cresol. R. C. Huston and P. S. Chen (J. Amer. Chem. Soc., 1933, **55**, 4214—4218).—*m*-Cresol (I) (1 mol.) and Cl_2 (1 mol) in $CHCl_3$ at 0° give 2-chloro- (II), b.p. 198—199°, m.p. 49—50° (lit. 55—56°) (*benzoate*, m.p. 55—56°; *benzenesulphonate*, m.p. 58—58·5°; p-*toluenesulphonate*, m.p. 96°), 6-chloro- (III), b.p. 231—233°, m.p. 55·5° (lit. 52—66°) (benzoate, m.p. 86°; *benzenesulphonate*, m.p. 66°; p-*toluenesulphonate*, m.p. 98°), and 4-chloro-*m*-cresol (IV), b.p. 197—198°, m.p. 46° (benzoate, m.p. 38°; *benzenesulphonate*, m.p. 99°; *p*-toluenesulphonate, m.p. 93—94°); with Cl_2 (2 mols.), 2 : 6-dichloro- (V), b.p. 234°, m.p. 58° (lit. 44—46°) (*benzoate*, m.p. 78—78·5°; *benzenesulphonate*, m.p. 69·5°; p-*toluenesulphonate*, m.p. 100—101°), 2 : 4-*dichloro*- (VI) b.p. 240·5—242·5°, m.p. 27° (*benzoate*, m.p. 90·5°; *benzenesulphonate*, m.p. 70°; p-*toluenesulphonate*, m.p. 92—92·5°), and 4 : 6-dichloro-*m*-cresol (VII), b.p. 235—236°, m.p. 71·5—72·5° (lit. 45—46° and 58°) (*benzoate*, m.p. 57·5°; *benzenesulphonate*, m.p. 86°; p-*toluenesulphonate*, m.p. 104—105°), result. 2 : 4 : 6-Trichloro-*m*-cresol, m.p. 46° (*benzoate*, m.p. 53°; *benzenesulphonate*, 121°; p-*toluenesulphonate*, m.p. 92—93°), is prepared by chlorination of (V)—(VII). (II) and Cl_2 (1 mol.) in cold $CHCl_3$ give (V) and (VI); (III) similarly affords (V) and (VII), whilst (IV) yields (VII) and (VI) (?). (II) is also prepared from 2-amino-*m*-cresol and by chlorination of (I) in oleum (followed by hydrolysis at 200°). Chlorination of *m*-cresoldisulphonic acid in aq. NaOH (5 mols.) and subsequent hydrolysis (acid at 200°) gives (II) and (VI). (III) and (IV) are prepared by the usual methods from 6-chloro-*m*-toluidine and 4-amino-*m*-cresol, respectively. 6-Chloro-4-nitro-*m*-cresol (from 4-nitro-*m*-cresol and Cl_2 in $CHCl_3$ or AcOH) is reduced ($SnCl_2$, conc. HCl) to the amine, which is then converted into (VII) [also prepared (Sandmeyer) from 4 : 6-diamino-*m*-cresol]. 2 : 4-Dichloro-6-nitro-*m*-cresol (from 6-nitro-*m*-cresol and Cl_2 in AcOH) is reduced to the amine which is deaminated to (VI). H. B.

Influence of the migrating group in the Fries isomerisation. R. Baltzly and A. Bass (J. Amer. Chem. Soc., 1933, **55**, 4292—4294).—*m*-Tolyl acylates are isomerised by $AlCl_3$ in $PhNO_2$ at room temp. to (mainly) 4-acyl-*m*-cresols; at 2°, the propionate and butyrate give only 10 and 3%, respectively, of the 6-derivative (cf. Rosenmund and Schnurr, A., 1928, 1010; the results of these authors could only be reproduced with the acetate). The higher esters are isomerised by $AlCl_3$ at 120—140° or as above to the 4-derivative. The following are described (cf. Coulthard *et al.*, A., 1930, 468): 4-propionyl-, m.p. 43—44°; 6-propionyl-, m.p. 117—118°; 4-butyryl-, b.p. 112—115°/4 mm. (phenylhydrazone, m.p. 97—98°); 6-butyryl-, m.p. 98—99°; 4-valeryl-, b.p. 121—125°/3 mm. (phenylhydrazone, m.p. 138—139°); 4-hexoyl- (I), b.p. 134—135°/3 mm. (phenylhydrazone, m.p. 97—97·5°); 4-heptoyl-, b.p. 148°/4 mm. (phenylhydrazone, m.p. 82—83°), and 4-nonoyl-*m*-cresol, b.p. 175—177°/4 mm. Methylation (Me_2SO_4–NaOMe) of (I) and subsequent oxidation (aq. $KMnO_4$) gives methoxyterephthalic acid, also obtained similarly from 4-acetyl-*m*-cresol. H. B.

Action of aromatic alcohols on aromatic compounds in presence of aluminium chloride. VI. Condensation of phenylpropylcarbinol and α-chlorobutylbenzene with phenol. R. C. Huston and H. W. Strickler (J. Amer. Chem. Soc., 1933, **55**, 4317—4318; cf. A., 1927, 659).—CHPhPr·OH (I), b.p. 94—96°/6 mm., or CHPhPrCl (II), b.p. 73—75°/6 mm. (1 mol.), PhOH (1 mol.), and $AlCl_3$ (0·5 mol.) in light petroleum at 25° give 20% of p-, b.p. 154—155°/6 mm., m.p. 49—50° [2 : 6-Br_2-derivative, b.p. 188—189°/6 mm., also prepared from (I), 2 : 6-$C_6H_3Br_2$·OH, and $AlCl_3$; *benzoate*, m.p. 70—71°], and 6% of o-α-*phenylbutylphenol* (III), b.p. 144—146°/6 mm. [4 : 6-Br_2-derivative, b.p. 184—185°/6 mm., also prepared from (I) and 2 : 4-$C_6H_3Br_2$·OH]. Condensation of (II) and PhOH by Claisen's method (A., 1925, i, 656) gives (III) (13%), phenylbutene (12%), and *Ph* α-*phenylbutyl ether*, b.p. 123—125°/6 mm. (10%). H. B.

[4-]Ethyl[-α-]naphthol. G. Levy (Compt. rend., 1933, **197**, 772—774).—Condensed with $CH_2(CO_2Et)_2$, CHPhEtBr affords the *Et* ester, b.p. 154—156°/2 mm., of α-*phenyl*-n-*propylmalonic acid*, m.p. 70—70·5°, decarboxylated at 120° to β-*phenyl*-n-*valeric acid*, b.p. 167—168°/18 mm., the *amyl* ester, b.p. 155—157°/20 mm., of which is reduced (Na–C_5H_{11}·OH) to γ-*phenyl*-n-*amyl alcohol*, b.p. 135—138°/20 mm., converted through the *bromide*, b.p. 130—131°/19 mm., and *nitrile*, b.p. 148—150°/19 mm., into γ-*phenylhexoic acid*, b.p. 185°/22 mm. (*amide*, m.p. 104·5—105·5°), the *chloride*, b.p. 138°/18 mm., of which is cyclised to 1-*keto*-4-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 148—150°/18 mm. [*semicarbazone*, m.p. 183° (corr.)], dehydrogenated by Se at 320° to 4-*ethyl*-α-*naphthol*, m.p. 42° [*picrate*, m.p. 152·5° (corr.)]. No analytical data are given. J. W. B.

Diaryl compounds and their derivatives. III. Oxidation of 2-hydroxyphenanthrene. J. S. Joffe (J. Gen. Chem. Russ., 1933, **3**, 524—527).—By the action of anhyd. $FeCl_3$ in acid solution, 2-hydroxyphenanthrene gives 2 : 2′-*dihydroxy*-1 : 1′-*diphenanthryl* (I), m.p. 283—285°, which, on reduction with Zn dust, yields 1 : 1′-*diphenanthryl*, m.p. 224—226°, together with 2 : 3-10 : 11-*dibenzoperylene*, m.p. 315—318°, not identical with the dibenzoperylene, m.p. 340—343°, obtained by Clar (A., 1932, 731),



which can be prepared by the action of $AlCl_3$ on phenanthrene and is the 2 : 3-8 : 9-isomeride.

Attempts to prepare the $(OH)_2$-derivative of the perylene by the action of $AlCl_3$ on (I) gave apparently only a mixture of the dihydroxydibenzoperylene (II) and its quinone (III). M. Z.

Optically active aryl-sulphoxyaliphatic acids. W. Piechulek and J. Suszko (Rocz. Chem., 1933, **13**, 520—529).—$CMe_2Br{\cdot}CO_2Na$ and NaSPh in aq. EtOH yield *SPh·CMe₂·CO₂H*, m.p. 64—65° [*chloride* (I), b.p. 108—110°/3 mm.; *amide*, m.p. 69—70°], which is oxidised by H_2O_2 to the corresponding dl-*sulphoxide* (II), m.p. 121—122°, which reacts anomalously with $SOCl_2$ to yield (I). l-*PhSO·CMe₂·CO₂H*, m.p. 122—123°, $[\alpha]_D$ −93·8°, is obtained from the racemate by crystallisation of its sparingly sol. *cinchonidine* salt, m.p. 162—163°, $[\alpha]_D$ −136·2°, and the d-*isomeride*, m.p. 122—123°, $[\alpha]_D$ +92·3°, from the *quinine* salt, m.p. 167—169°, $[\alpha]_D$ −40·7°. Pummerer's $PhSO{\cdot}CH_2{\cdot}CO_2H$ (III) (A., 1909, i, 580) is separated into the l-*isomeride*, m.p. 119—120°, $[\alpha]_D$ −179·5° [*cinchonidine* salt, m.p. 174—176° (decomp.), $[\alpha]_D$ −179·1°], and the d-*isomeride*, m.p. 119—120°, $[\alpha]_D$ +180·6° [*cinchonidine* salt, m.p. 117—118°, $[\alpha]_D$ +172°; *cinchonine* salt, m.p. 138—140° (decomp.), $[\alpha]_D$ +220·5°]. (II) and (III) on further oxidation with H_2O_2 yield the corresponding sulphonic acids. The above described optically active acids do not undergo racemisation in solution. R. T.

Behaviour of piperonal derivatives towards bromination and nitration. L. C. Raiford and F. W. Oberst (J. Amer. Chem. Soc., 1933, **55**, 4288—4292).—6-Bromopiperonal (I) and an excess of Br (containing about 1% of $AlBr_3$) at about 100° give (mainly) tetrabromopyrocatechol, m.p. 191° (lit. 187°), (*dibenzoate*, m.p. 197—198°), and its *CH_2 ether* (II), m.p. 208—209°; (II) is the main product when reaction takes place in presence of NaOAc. (II) is also formed by bromination (as above) of the $NaHSO_3$ compounds of (I) and piperonal and the diacetate [of (I) (?)]. 5-Bromo-3 : 4-dinitromethylenedioxybenzene (III) is reduced (NH_4HS) to the 3-*NH_2*-derivative, m.p. 109—110° (*Ac*, m.p. 192—193°, and *Ac_2*, m.p. 146—147°, derivatives), which is reduced [$FeSO_4$, aq. NH_3] to *o-bromo*-3 : 4-*diaminomethylenedioxybenzene*, m.p. 89—90° (decomp.) (*Bz_2*, m.p. 255—256°, and *Ac_4*, m.p. 133—134°, derivatives). (III) is reduced by Sn and EtOH–conc. HCl to 3 : 4-*diaminomethylenedioxybenzene*, m.p. 100—101°. (I) and HNO_3 (*d* 1·6) in Ac_2O at 0° give (cf. Parijs, A., 1930, 343) 5-*bromo*-4-*nitropyrocatechol*, m.p. 162—163° (*diacetate*, m.p. 117—118°); with HNO_3 of $d < 1{\cdot}6$, no reaction occurs. H. B.

Syntheses of pharmacologically important amines. VII. Synthesis of secondary and tertiary amines by hydrogenation of nitriles. K. Kindler and F. Hesse (Arch. Pharm., 1933, **271**, 439—445; cf. A., 1932, 1126).—In conformity with the author's theory of the formation of *sec.* and *tert.* amines from nitriles (A., 1931, 342), hydrogenation of a mixture of nitriles and primary or *sec.* amines in C_6H_6, MeOH, or EtOH gives good yields of *sec.* and *tert.* amines, respectively. Thus were prepared *N* - methyl - β - 3 : 4 - dimethoxyphenylethylamine (epinine Me_2 ether) (78% yield from 3 : 4-dimethoxyphenylacetonitrile and NH_2Me), hordenine Me ether (73% yield) [hydrolysed by HCl at 150—160° to hordenine (90% yield)], *NN*-dimethyl-β-3 : 4-dimethoxyphenylethylamine, b.p. 155—156°/12 mm. (77% yield) (similarly hydrolysed in 64% yield), *NN*-dimethyl- and -diethyl-β-phenylethylamine. R. S. C.

Decomposition of basic and phenolic diphenylmethane derivatives and synthesis of optically active aromatic compounds. II. J. von Braun [with E. Anton, W. Haensel, G. Irmisch, R. Michaelis, and W. Teuffert] (Annalen, 1933, **507**, 14—36; cf. A., 1929, 1058).—Prolonged interaction of COPhMe (1 mol.), PhOH (I) (2 mols.), and conc. HCl gives about 10% of αα*α*-4 : 4′-*dihydroxytriphenylethane*, m.p. 168°, b.p. 235—240°/0·3 mm. (in small amount only), which decomposes at 340° to (I), αα-p-*hydroxydiphenylethane*, m.p. 185—190°/10 mm. (*acetate*, b.p. 180—182°/0·3 mm.; p-*nitrobenzoate*, m.p. 70°), and resinous material. 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene and (I) similarly afford an oil which when distilled gives 1-p-*hydroxyphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 235—240°/10 mm. (*acetate*, b.p. 240°/10 mm.), and resinous material. α-Hydrindone similarly undergoes self-condensation to truxene; definite products were not isolated using CH_2AcCl, CH_2BzCl, or CH_2BzBr. ββ-4 : 4′-*Diacetamidodiphenylpropane*, m.p. 252°, and HNO_3–conc. H_2SO_4 give the 3 : 3′-*$(NO_2)_2$*-derivative, m.p. 190° (the 3-*NO_2*-derivative has m.p. 165°), hydrolysed (EtOH–KOH) to ββ-3 : 3′-*dinitro*-4 : 4′-*diaminodiphenylpropane* (II), m.p. 214°. This is reduced ($SnCl_2$) to the *$(NH_2)_4$*-derivative, m.p. 148° (*phenanthrazine*, m.p. 217°), converted by long heating with AcOH into the corresponding *bis*(*methylbenziminazole*), m.p. 225°. (II) is deaminated to ββ-*di*-m-*nitrophenylpropane*, m.p. 101°, reduced ($SnCl_2$, conc. HCl) to the *$(NH_2)_2$*-derivative (III), m.p. 123° (*hydrochloride*, m.p. 150—155°; *Ac_2* derivative, m.p. 213°), which is then converted into ββ-*di*-m-*hydroxyphenylpropane*, b.p. 190—195°/0·6 mm., m.p. 114° (*dibenzoate*, m.p. 121°); this does not decompose at 350°. 1 : 1-3′ : 3″-*Dinitro*-4′ : 4″-*diacetamido*-, m.p. 157°, 1 : 1-3′ : 3″-*dinitro*-4′ : 4″-*diamino*-, m.p. 245°, 1 : 1-3′ : 4′ : 3″ : 4″-*tetra-amino*-, m.p. 132° (*phenanthrazine*, m.p. 317°), 1 : 1-3′ : 3″-*dinitro*-, m.p. 143°, and 1 : 1-3′ : 3″-*diamino*- (IV), m.p. 147° (*hydrochloride*, m.p. 300°; *Ac_2* derivative, m.p. 226°), -*diphenylcyclohexanes* are similarly prepared from 1 : 1-di-*p*-acetamidophenyl*cyclo*hexane (*loc. cit.*). (III) and (IV) can be distilled unchanged in presence of a little mineral acid (cf. *loc. cit.*).

$COMe_2$ (1 mol.), *o*-toluidine (2 mols.), and 20% HCl (2 mols.) at 150° give 40% of ββ-4 : 4′-*diamino*-3 : 3′-*dimethyldiphenylpropane*, b.p. 216°/1 mm. (*monohydrate*, m.p. 70—72°; *picrate*, m.p. 129°; *Ac_2* derivative, m.p. 205°), which when distilled at about 1 mm. in presence of a little H_2SO_4 affords 5-*iso*propenyl-*o*-toluidine (*Ac* derivative, m.p. 132°) and its *dimeride*, b.p. 233—235°/0·3 mm. (*Ac_2*, m.p. 145°, and *dihydro*-, b.p. 215°/0·1 mm., -derivatives). ββ-3 : 3′-*Dichloro*-4 : 4′-*diaminodiphenylpropane*, b.p. 215°/0·3 mm. (*Ac* derivative, m.p. 189°), from $COMe_2$ and *o*-$C_6H_4Cl{\cdot}NH_2$, similarly gives the *dimeride*, b.p.

250—255°/0·4 mm. (*Ac* derivative, m.p. 84°), of 2-chloro-4-*iso*propenylaniline. ββ-4 : 4′-*Diamino*-3 : 3′-*dimethoxydiphenylpropane*, b.p. 230—232°/0·8 mm. (*hydrochloride*, m.p. 183°), affords 2-*methoxy*-4-*isopropenylaniline*, b.p. 150—155°/13 mm., which polymerises more slowly. 2-Aminodiphenyl, $COMe_2$, and HCl at 150° give a small amount of the *dimeride*, b.p. 250°/0·7 mm. (*Ac*$_2$ derivative, b.p. 260°/0·5 mm.), of 2-amino-5-*iso*propenyldiphenyl. Dimeric *p-iso*propenylaniline is now considered (cf. *loc. cit.*) to be $NH_2{\cdot}C_6H_4{\cdot}CMe{:}CH{\cdot}CMe_2{\cdot}C_6H_4{\cdot}NH_2$.

d-3-Methyl*cyclo*hexanone, *o*-anisidine, and 20% HCl in EtOH at 100° for 200 hr. (at 120° for 8 hr., some racemisation occurs) give 1 : 1-4′ : 4″-*diamino*-3′ : 3″-*dimethoxydiphenyl*-3-*methyl*cyclo*hexane* (V), b.p. 250°/0·3 mm., $[\alpha]_D^{20}$ −14·47° in EtOH (*hydrochloride*, m.p. 215—217°), and 2-*methoxy*-4-3′-*methyl*-Δ^1-cyclo*hexenylaniline* (VI), b.p. 148—150°/0·3 mm., m.p. 34—36°, $[\alpha]_D^{20}$ +42·01° in EtOH [*dihydro*-derivative, b.p. 145—150°/0·7 mm., m.p. 45—47° (*hydrochloride*, m.p. 239°); *hydrochloride*, m.p. 226°; *picrate*, m.p. 162°; *Ac* derivative, m.p. 80° (*dihydro*-derivative, m.p. 82—83°)]. (VI) is also obtained by distillation of (V) with a little acid. 1 : 1-3′ : 3″-*Dichloro*-4′ : 4″-*diaminodiphenyl*-3-*methyl*cyclo*hexane*, b.p. 255—260°/0·3 mm., $[\alpha]_D^{20}$ −11·08° in EtOH, and 2-*chloro*-4-3′-*methyl*-Δ^1-cyclo*hexenylaniline*, b.p. 158—160°/0·3 mm., m.p. 54—57°, $[\alpha]_D^{20}$ +56·64° in EtOH [*dihydro*-derivative, m.p. 17—20° (*Ac* derivative, m.p. 97°); *Ac* derivative, m.p. 127°; *hydrochloride*, m.p. 183°], are similarly prepared from *o*-$C_6H_4Cl{\cdot}NH_2$. *o*-Toluidine affords 1 : 1-4′ : 4″-*diamino*-3′ : 3″-*dimethyldiphenyl*-3-*methyl*cyclo*hexane*, m.p. 169°, $[\alpha]_D^{20}$ −15·73° (*hydrochloride*, m.p. 226°; *picrate*, m.p. 175°; *Ac* derivative, m.p. 176°), and 5-3′-*methyl*-Δ^1-cyclo*hexenyl*-*o*-*toluidine*, b.p. 160°/0·5 mm. The position of the double linking in these and related *cyclo*hexenylanilines is proved by the following oxidations. *p*-3-Methyl*cyclo*hexenylacetanilide (*loc. cit.*) is oxidised (CrO_3–AcOH) to the N-*Ac* derivative, m.p. 110°, of δ-p-*aminobenzoyl*-α-*methylvaleric acid*, m.p. 111°, converted by NaOH at > 220° into α-methyladipic acid (*anilide*, m.p. 170°). p-*cyclo*-Hexenylacetanilide (VII) is oxidised (O_3 followed by alkaline H_2O_2; $KMnO_4$–$COMe_2$) to the N-*Ac* derivative, m.p. 192°, of δ-p-*aminobenzoylvaleric acid*, m.p. 167°; the latter is converted by NaOH at 260° into adipic acid, reacts with isatin to give 2-p-*aminophenyl*-3-γ-*carboxypropylquinoline*-4-*carboxylic acid*, m.p. 303° (decomp.), and is convertible into δ-p-*hydrazinobenzoylvaleric acid*, decomp. 190—192°. 2-*Chloro*-4-cyclo*hexenylacetanilide*, m.p. 143°, is similarly oxidised to δ-3-*chloro*-4-*acetamidobenzoylvaleric acid*, m.p. 154°. (VII) and BzO_2H in cold $CHCl_3$ give (probably) 2-*benzoyloxy*-1-p-*acetamidophenyl*cyclo*hexanol*, m.p. 204° (highest val.) (mixtures, m.p. 142—168°, of isomerides are obtained initially), hydrolysed (conc. HCl) to 1 : 2-*oxido*-1-p-*aminophenyl*cyclo*hexane* (VIII), m.p. 109° (slight previous sintering) (*Ac* derivative, m.p. 142°). Exhaustive methylation of (VIII) gives a quaternary *iodide*, $C_{15}H_{22}ONI$, m.p. 181°, which when heated in a vac. affords 1 : 2-*oxido*-1-p-*dimethylaminophenyl*cyclo*hexane*, m.p. 105° (*picrate*, m.p. 167°), also prepared in poor yield from *p-cyclo*hexenyldimethylaniline and BzO_2H (as above).

[With O. ENGEL.] *dl-p*-3-Methyl*cyclo*hexyl-aniline (IX) (*Ac*, m.p. 126°, and *Bz*, m.p. 155°, derivatives) is converted into the -phenylhydrazine, m.p. 82°, which with $CH_2Ac{\cdot}CO_2Et$ affords 1-p-3-*methyl*cyclo*hexylphenyl*-3-*methyl*-5-*pyrazolone*, m.p. 147—148° [an *isomeride*, m.p. 150°, $[\alpha]_D^{19}$ −2·07° in $CHCl_3$, is similarly obtained from optically active *p*-3-methyl*cyclo*hexylphenylhydrazine (X) (*loc. cit.*)], methylated to the 2 : 3-Me_2 derivative, m.p. 87—88° (*isomeride*, m.p. 90°, $[\alpha]_D^{22}$ −2·64° in EtOH). (IX), $CCl_3{\cdot}CH(OH)_2$, and $NH_2{\cdot}OH,H_2SO_4$ in aq. EtOH give ω-*oximino*-p-3-*methyl*cyclo*hexylacetanilide*, m.p. 116° [*isomeride* (XI), m.p. 121°, $[\alpha]_D^{20}$ −3·5° in EtOH, similarly prepared], converted [as is (XI)] by 90% H_2SO_4 at 70° into 4-3′-*methyl*cyclo*hexylisatin*, m.p. 116°. (XI), COPhMe, and alkali give an inactive 2-*phenyl*-5-3′-*methyl*cyclo*hexylquinoline*-4-*carboxylic acid*, m.p. 216°. dl-p-3-*Methyl*cyclo*hexylacetophenone*, b.p. 179—181°/12 mm. (*semicarbazone*, m.p. 185°), isatin, and aq. EtOH-alkali afford 2-p-3′-*methyl*cyclo*hexylphenylquinoline*-4-*carboxylic acid*, m.p. 234° [*isomeride*, m.p. 254°, $[\alpha]_D^{22}$ −6·13° in C_5H_5N, prepared from the optically active -acetophenone (*loc. cit.*)]. H. B.

ψ-Nitrosite of asarone [**2 : 4 : 5-trimethoxypropenylbenzene**]. V. BRUCKNER (J. pr. Chem., 1933, [ii], **136**, 268—274).—*Asarone*-ψ-*nitrosite* (I), m.p. 130° (decomp.) (dimeric, partly dissociated in warm $CHCl_3$), is formed by regulated action of aq. HNO_2 on asarone (II) in Et_2O; some 5-nitro-1 : 2 : 4-trimethoxybenzene is simultaneously formed. With HNO_2 in aq. AcOH (II) gives 2 : 4 : 5-*trimethoxyphenylmethylglyoxime peroxide*, m.p. 149°. In 8% KOH–EtOH at 30° (I) is converted into β-*nitroasarone* (III), m.p. 101°, dimorphic, red⟶yellow at 90° (and some asaraldehyde), reduced electrolytically (Pb electrodes) to β-*aminodihydroasarone* (β-*amino*-2 : 4 : 5-*trimethoxy*-n-*propylbenzene*) (*hydrochloride*, m.p. 187°). With warm Ac_2O and a little conc. H_2SO_4 (I) gives, among other unidentified compounds, some β-*nitro*-α-*acetoxy*-2 : 4 : 5-*trimethoxy*-n-*propylbenzene*, m.p. 141°, which when dissolved in KOH–EtOH deposits (III). H. A. P.

Structure of dimeric modifications of propenylphenol ethers. II. Synthesis of diasarone. J. HARASZTI and T. SZEKI (Annalen, 1933, **507**, 197—202).—The compound $C_{22}H_{27}O_4Br$ (this vol., 818), formulated as 3-bromo-1 : 2-di-(3 : 4-dimethoxyphenyl)-3 : 4-dimethyl*cyclo*butane, is converted by AgOAc–AcOH and subsequent hydrolysis (2% MeOH–HCl) into the corresponding *alcohol*, m.p. 133°, and by $AgNO_2$ in EtOH into the NO_2-derivative, m.p. 128°. The dibromide, m.p. 86° (improved prep. given), of asarone (2 : 4 : 5-trimethoxypropenylbenzene) (I) is transformed by Cu-bronze in C_6H_6 into a saturated *compound* (II), $C_{24}H_{31}O_6Br$, m.p. 123°, which with MeOH–KOH gives an unsaturated *substance*, $C_{24}H_{30}O_6$, m.p. 101°. (II) is reduced (Zn dust, 90% EtOH) to diasarone (III) [1 : 2-di-(2 : 4 : 5-trimethoxyphenyl)-3 : 4-dimethyl*cyclo*butane], m.p. 101·5°, also formed from (I) and MeOH–HCl. The diasarone, m.p. 98°, previously described (A., 1906, i, 660) is not identical with (III). H. B.

[Halogeno-]derivatives of 2-hydroxydiphenyl.—See B., 1933, 907.

2-Halogeno-4-aminodiphenyl ethers.—See B., 1933, 907.

***C*-Dialkylresorcinols.**—See B., 1933, 956.

Derivatives of 3 : 5-dibromo-2-hydroxybenzyl bromide. W. C. HARDEN (J. Amer. Chem. Soc., 1933, **55**, 4260—4262).—3 : 5-*Dibromo-2-hydroxybenzyl benzoate*, m.p. 154°, *cinnamate*, m.p. 127°, *mandelate*, m.p. 108°, *succinate*, m.p. 161°, *H phthalate*, m.p. 174°, p-*nitrobenzoate*, m.p. 153°, *salicylate*, m.p. 156°, and p-*hydroxybenzoate*, m.p. 148°, are prepared from the bromide (I) (Auwers and Buttner, A., 1899, i, 36) and the requisite Na salt in C_6H_6. (I) and CHNaAc·CO_2Et in PhMe give [after hydrolysis (EtOH–KOH)] β-3 : 5-*dibromo-2-hydroxyphenylpropionic acid*, m.p. 117°. 3 : 5-*Dibromo-2-hydroxybenzylcarbamide* has m.p. 207°. (I), PhOH, and a little mossy Zn in PhMe afford a (3 : 5-*dibromo-2-hydroxybenzyl*)*phenol* (II), m.p. 174° (*Br*$_2$-derivative, m.p. 198°; *diacetate*, m.p. 81°), and *Ph* 3 : 5-*dibromo-2-hydroxybenzyl ether*, m.p. 119° (*Br*$_2$-derivative, m.p. 105°; *acetate*, m.p. 73°). A 0·1% solution of the Na salt of (II) kills *S. aureus*.

H. B.

Production of nuclear-substituted phenylaminoalkylcarbinols [β-amino-α-phenylpropanols].—See B., 1933, 956.

Structure of the second ring of cholesterol. S. MINOVICI and M. VANGHELOVICI (Bul. Soc. Chim., Romania, 1933, **15**, 39—44).—Interaction of the dibasic acid (I), $C_{27}H_{45}O_4Cl$ (cf. A., 1930, 598) with hot Ac_2O affords an *anhydride*, m.p. 106°. This observation confirms the Wieland–Rosenheim formula for cholesterol in which ring II is six-membered.

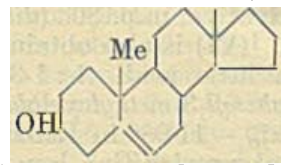
J. L. D.

Sterol group. XVIII. Attempt to define the position of the hydroxyl group in ergosterol. I. M. HEILBRON, K. M. SAMANT, and J. C. E. SIMPSON (J.C.S., 1933, 1410—1413; cf. this vol., 500).—Chloroergostane (modified prep.), m.p. 117—119°, and CrO_3–AcOH give ?-*chloro*allo*norcholanic acid* (I), m.p. 213—214° (*Me* ester, m.p. 158—159°), and an acid, $C_{28}H_{50}(CO_2H)_2$, m.p. 219—221° (Me ester, m.p. 81°) (cf. A., 1929, 61). The prep. of cholesteryl chloride and 3-chloro*allo*cholanic acid (II) is modified. The Me ester, new m.p. 133—134°, of (II) with MgPhBr gives a gummy carbinol, which with CrO_3 gives 3-*chloro*allo*norcholanic acid* (III), m.p. 238° (*Me* ester, m.p. 176°). (I) and (III) are both reduced by Na and Pr$^\beta$OH to *allo*norcholanic acid, m.p. 170—170·5°. The non-identity of (I) and (II) shows that, excluding the improbable occurrence of *cis–trans* isomerism during chlorination of one or other of the sterols, the OH in ergosterol is not in position 3; other reactions, including the formation of ketones by vac. distillation of ergosterol, α- and β-dihydroergosterol, and α- and β-ergostenol (but not of ergostanol), indicate that the OH group is probably near the ethylenic linkings. Oxidation of the acid, $C_{26}H_{46}(CO_2H)_2$, gives inseparable mixtures.

R. S. C.

Constitution of stigmasterol. E. FERNHOLZ (Annalen, 1933, **507**, 128—138).—Oxidation (O_3) of *stigmasteryl acetate dibromide*, m.p. 132—135°, gives α-ethyl*iso*valeraldehyde (showing that the double linking is in the side-chain); treatment of the ozonide with Zn dust and AcOH affords 3-*acetoxybisnorcholenic acid*, m.p. 235° (decomp.) (not perfectly sharp) [*Me* ester (I), m.p. 138—139°]. This is hydrolysed (EtOH–KOH) to 3-*hydroxybisnorcholenic acid*, m.p. 295° (decomp.) (*Me* ester, m.p. 140°), and is reduced (H_2, Pt-black, AcOH) to 3-*acetoxybisnor*allo*cholanic acid*, m.p. 194° [*Me* ester, m.p. 132—133°, prepared by similar reduction of (I)]. 3-*Hydroxybisnor*allo*cholanic acid*, m.p. 270°, is oxidised (CrO_3, AcOH) to 3-*ketobisnor*allo*cholanic acid*, m.p. 244—246° (slight previous sintering), which is reduced (Clemmensen) to *bisnor*allo*cholanic acid* (II), m.p. 213—214°, $[\alpha]_D^{15}$ ±0° in $CHCl_3$ (*Me* ester, m.p. 93—94°, re-solidifying with m.p. 100°, $[\alpha]_D^{16}$ +8° in $CHCl_3$). (II) is also obtained by oxidation (CrO_3, AcOH) of the carbinol from Me nor*allo*cholanate and MgPhBr (cf. Chuang, this vol., 391). The above results show that stigmasterol (III) contains the same ring system as cholesterol and ergosterol; the following constitution is assigned to (III).

Me CHMe·CH:CH·CHEtPr$^\beta$



H. B.

Components of petroleum. II. Preparation of the first homogeneous naphthenic acids. J. VON BRAUN, L. MANNES, and M. REUTER (Ber., 1933, **66**, [*B*], 1499—1505; cf. B., 1931, 957, 1396).—*p*-C_6H_4Et·OH is readily hydrogenated (Ni) to p-*ethyl*cyclo*hexanol*, b.p. 194—196° (*phenylurethanes*, b.p. 165°/0·6 mm., m.p. 116°, and m.p. 57—59°, respectively), oxidised by Beckmann's mixture to p-*ethyl*cyclo*hexanone*, b.p. 192—194° (non-cryst. *oxime*, b.p. 120—124°/10 mm.; *semicarbazone*, m.p. 174°; *di*-p-*nitrobenzylidene* derivative, m.p. 156°; p-*nitrophenylhydrazone*, m.p. 101°). CHEt$(CO_2Et)_2$, $CH_2Cl·CH_2·CO_2Et$, and NaOEt afford *Et*, *ethyl*-β-*carbethoxyethylmalonate*, b.p. 169—172°/11 mm., converted by hydrolysis and decarboxylation into *pentane-αγ-dicarboxylic acid*, b.p. 175°/11 mm. [*Et* ester (I), b.p. 120—123°/11 mm.]. (I) is reduced by Na and EtOH to δ-*hydroxymethyl*-n-*hexanol*, b.p. 140—142°/11 mm., transformed by fuming HBr at 120—130° into δ-*bromomethyl*-n-*hexyl bromide*, b.p. 120°/11 mm., whence β-*ethylpimelonitrile*, b.p. 175—180°/11 mm., and β-*ethylpimelic acid* (II), b.p. 205°/0·4 mm. The *Ca* salt of (II) is transformed by dry distillation into 3-*ethyl*cyclo*hexanone*, b.p. 192—194° (non-cryst. *oxime*, b.p. 116—118°/10 mm.; *semicarbazone*, m.p. 184°; p-*nitrophenylhydrazone*, m.p. 130°; *di*-p-*nitrobenzylidene* derivative, m.p. 176°).

The following experiments were performed with the monocyclic ketone, C_7H_{11}·>CO, derived from the naphthenic acids $C_9H_{17}·CO_2H$ of various origin and yielding a semicarbazone, m.p. 162°, and di-*p*-nitrobenzylidene compound, m.p. 190° (cf. *loc. cit.*). (Neither of the above ethyl*cyclo*hexanones is identical with this ketone.) The *ketoxime*, b.p. 116—120°/14 mm., is reduced (Na–EtOH) to 3 : 3 : 4-*trimethyl*cyclo*pentylamine* (III), b.p. 164—168° (hygroscopic *hydrochloride*; *picrate*, m.p. 174—176°; *chloroplatinate*, decomp. 255° after becoming discoloured at 250°).

Exhaustive methylation of (III) with NaOH and Me_2SO_4 and subsequent distillation of the quaternary base with alkali yields 30% of 3 : 3 : 4-*trimethyl*cyclo*pentyldimethylamine*, b.p. 183—186° (hygroscopic *hydrochloride*; *picrate*, m.p. 153—155°; *chloroplatinate*, m.p. 160—161°; *chloroaurate*, m.p. 60—62°; *methiodide*, m.p. 242—243°), and 53% of a mixture of hydrocarbons, b.p. 117—123°, oxidised by $KMnO_4$ to an apparent mixture of trimethylglutaric acids. The results exclude the possibility of a 3- or 4-membered ring in C_7H_{14}>CO and render very improbable that it is a δ- and γ-methylsuberone.

3 : 3 : 4-Trimethyl*cyclo*pentanone, $CH_2Br{\cdot}CO_2Et$, and Zn yield 1-*hydroxy*-3 : 3 : 4-*trimethyl*cyclo*pentylacetic acid*, b.p. about 140°/15 mm., transformed by $KHSO_4$ at 150° into a mixture of esters $C_{12}H_{20}O_2$, b.p. 112—120°/12 mm., reduced (Pd+H_2) to *Et* 3 : 3 : 4-*trimethyl*cyclo*pentylacetate*, b.p. 113—115°/14 mm. The *acid* (IV), b.p. 144—145°/14 mm., is converted by $SOCl_2$ into the corresponding *chloride*, b.p. 105—108°/16 mm., whence the *amide*, m.p. 122—123°, *anilide*, m.p. 55—58°, and *ureide*, m.p. 197—198°. (IV) is claimed as the first homogeneous naphthenic acid. H. W.

Amino-sulphonic acids. I. Benzoylation of amino-sulphonic acids. B. JOSEPHSON (Biochem. Z., 1933, **264**, 441—451).—Benzoylation of aliphatic amino-sulphonic acids is best effected in saturated $Ba(OH)_2$ and of aromatic acids in C_5H_5N solution by BzCl, good yields of pure products being thus obtained. The benzoylation of $NH_2{\cdot}SO_3H$, taurine, β-aminopropanesulphonic acid, sulphanilic acid, *o*-toluidine-5-sulphonic acid, and naphthionic acid is described. P. W. C.

Preparation of benzoyl hydrogen peroxide. B. T. BROOKS and W. B. BROOKS (J. Amer. Chem. Soc., 1933, **55**, 4309—4311).—BzO_2H (I) is obtained in good yield when BzCl is treated with aq. Na_2O_2 (excess) at 0—5°, the resulting solution of BzO_2Na (freed from Bz_2O_2 which is a by-product) acidified with a slight excess of cold 10% H_2SO_4, and the (I) extracted with $CHCl_3$. Bz_2O_2 and excess of Na_2O_2 similarly give (I). Contrary to Hibbert and Burt (A., 1925, i, 1147), (I) is not decomposed readily by cold aq. NaOH. H. B.

Anhydrides of *N*-arylanthranilic acids. M. GOODMAN, N. ARBITER, and G. POWELL (J. Amer. Chem. Soc., 1933, **55**, 4294—4299).—
o-NHPh·C_6H_4·CO_2H (I) is dehydrated by $PhSO_2Cl$, *p*-$C_6H_4Me{\cdot}SO_2Cl$, or $POCl_3$ in C_5H_5N or C_6H_6–K_2CO_3 to a yellow *anhydride* (II), probably (*o*-NHPh·C_6H_4·$CO)_2O$, m.p. 152—153° (reddens at 149°), which is insol. in HCl or aq. alkali, and is converted by boiling with AcOH or mild treatment with EtOH–KOH into N-*o*-*anilinobenzoyldiphenylamine*-2-*carboxylic acid* (III), m.p. 200—201° (reddens at 198°). (III) is slowly hydrolysed (EtOH–KOH; AcOH–conc. HCl) to (I). (II) and aq. EtOH–NH_3 give (I), (III)(?), and a compound of high N content; with abs. EtOH–NH_3 at 80—90°, (I) and *diphenylamine*-*o*-*carboxylamide*, m.p. 127·5—128·5° [also prepared from *Me diphenylamine*-*o*-*carboxylate*, m.p. 57—58°, from (I) and MeOH–HCl, and EtOH–NH_3 at 120°], result. (II) and (III) heated at 200° and 220°, respectively, give (I) and acridone. *o*-$NPh_2{\cdot}C_6H_4{\cdot}CO_2H$ (IV) and $PhSO_2Cl$ in C_5H_5N at 50° afford the *anhydride*, (*o*-$NPh_2{\cdot}C_6H_4{\cdot}CO)_2O$, m.p. 144·5—146° [which is readily hydrolysed (EtOH–KOH; 80% AcOH) to (IV)], and (probably) a trace of *N*-phenylacridone. H. B.

Syntheses of cinnamic acids. J. VON BRAUN and J. NELLES (Ber., 1933, **66**, [*B*], 1464—1470).—*iso*Amylmalonic acid is immediately converted by Br in Et_2O into *bromoisoamylmalonic acid*, decomp. 132°, transformed by conc. KOH into iso*amyltartronic acid*, m.p. 134—136° (decomp.), which is decarboxylated to α-hydroxy-δ-methylhexoic acid, m.p. 60°. Similarly, hexahydrobenzylmalonic acid affords *bromohexahydrobenzylmalonic acid*, m.p. 146° (decomp.), and *hexahydrobenzyltartronic acid* (I), decomp. 138—140°; decarboxylation of (I) affords α-*hydroxy*-β-cyclo*hexylpropionic acid*, b.p. 170°/0·8 mm., which passes at 120—170° into *cyclo*hexylacetaldehyde (semicarbazone, m.p. 165°) in poor yield. $CH_2(CO_2Et)_2$ and *p*-$C_6H_4Cl{\cdot}CH_2Cl$ yield *Et di*-p-*chlorobenzylmalonate*, b.p. 220—230°/0·8 mm., m.p. 99°, and *Et* p-*chlorobenzylmalonate*, b.p. 190—192°/14 mm., readily hydrolysed by alkali to p-*chlorobenzylmalonic acid* (II), m.p. 149—151° (decomp.). Bromination and subsequent decarboxylation of (II) gives α-*bromo*-β-p-*chlorophenylpropionic acid*, b.p. 190°/0·5 mm., m.p. 99°, smoothly transformed by 30% NaOH into *p*-chlorocinnamic acid (III), m.p. 241°. (III) is converted by the successive action of AcOH–HBr at 100° and Na_2CO_3 into p-*chlorostyrene*, b.p. 33—35°/0·4 mm., which rapidly polymerises. The following compounds are obtained similarly: *Et di*-p-*bromobenzylmalonate*, b.p. 250—260°/0·6 mm., m.p. 104°; *Et* p-*bromobenzylmalonate*, b.p. 193—198°/14 mm.; p-*bromobenzylmalonic acid*, m.p. 151—153° (decomp.), its α-*Br*-derivative, m.p. (indef.) 88—105°, and *p*-bromocinnamic acid, m.p. 250° (corresponding *chloride*, b.p. 175—180°/12 mm., and *anilide*, m.p. 183°); p-*bromocinnamaldehyde*, m.p. 81° (*semicarbazone*, m.p. 240°; *phenylhydrazone*, m. p.145°); α-*bromo*-β-p-*bromophenylpropionic acid*, m.p. 182°, and p-*bromostyrene*, b.p. 88°/13 mm. (*dibromide*, m.p. 64°), which readily polymerises: *Et di*-p-*phenylbenzylmalonate*; *Et* p-*phenylbenzylmalonate*, b.p. about 215°/0·7 mm.; p-*phenylbenzylmalonic acid*, m.p. 185°, and its Br_1-derivative, m.p. 153—155°; α-*bromo*-β-*diphenylylpropionic acid*, m.p. 170°; p-*phenylcinnamic acid*, m.p. 225° (*Na* salt, *Et* ester, m.p. 86°, and its *dibromide*, m.p. 128°, transformed by KOH–EtOH into *diphenylpropiolic acid*, m.p. 168°); α-*amino*-β-*diphenylylpropionic acid*, m.p. 250°; *Et* 3 : 5-*dimethylbenzylmalonate*, b.p. 175—180°/14 mm.; 3 : 5-*dimethylbenzylmalonic acid*, m.p. 145°, and its non-cryst. Br_1-derivative; α-*bromo*-β-m-*o*-*xylylpropionic acid*; 3 : 5-*dimethylcinnamic acid*, m.p. 125°; 1-$C_{10}H_7{\cdot}CH_2Cl$, from $C_{10}H_8$, HCl, and CH_2O, m.p. 30°; Et α-naphthylmethylmalonate; α-naphthylmethylmalonic acid, m.p. 166°, and its Br_1-derivative, m.p. 155°; non-homogeneous α-bromo-β-1-naphthylpropionic acid, m.p. 98—110°; δ-1-naphthylacrylic acid, m.p. 206°, its *chloride*, b.p. 180°/0·4 mm., and *anilide*, m.p. 212°; 1-*naphthylacraldehyde*, m.p. 48° (*oxime*, m.p. 152°; *semicarbazone*, m.p. 228°; δ-*benzoyl*-α-1-*naphthyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 117°). H. W.

General method for preparing di- and tri-arylacetonitriles. J. Hoch (Compt. rend., 1933, **197**, 770—772).—By condensing CHArBr·CN and the appropriate hydrocarbon with $AlCl_3$ in CS_2 good yields (% given in parentheses) of $CHPh_2$·CN (75), *phenyl*-p-*tolyl*-, m.p. 62° (59), -p-*xylyl*, m.p. 52° (55—60), -p-*anisyl*-, m.p. 127° (35), -1-*naphthyl*-, m.p. 98° (67); di-p-*tolyl*-, b.p. 212°/18 mm. (62); p-*tolyl*-p-*xylyl*-, b.p. 212°/18 mm. (62); p-*xylyl*-2-*naphthyl*-, m.p. 106° (40); *phenyl*-1- (? -2-, cf. above) -*naphthyl*-, m.p. 90° (35), -o-*anisyl*-, m.p. 77°, and -o-*tolyl*-, b.p. 200—201°/22 mm., -*acetonitrile* are obtained. Bromination of these and further condensation with the hydrocarbon affords CPh_3·CN, *diphenyl*-p-*tolyl*-, m.p. 111° (62), *phenyl*-p-*tolyl*-p-*xylyl*-, m.p. 148° (45), *phenyl*-p-*xylyl*-p-*anisyl*-, m.p. 164° (45), *phenyl*-*di*-p-*tolyl*-, m.p. 134° (33), and *tri*-p-*tolyl*-, m.p. 191°, -*acetonitrile*. Hydrolysis with KOH–EtOH affords $CHPh_2$·CO_2H, *phenyl*-p-*tolyl*-, m.p. 118°, -p-*anisyl*-, m.p. 103°, -p-*xylyl*-, m.p. 125°, and -1-*naphthyl*-, m.p. 144°, *di*-p-*tolyl*-, m.p. 142°, p-*tolyl*-p-*xylyl*-, m.p. 132°, and p-*xylyl*-1-*naphthyl*-, m.p. 167°, -*acetic acid*. No analytical data are given. J. W. B.

Action of *cyclo*pentanol-2-carboxylic acids on the electrical conductivity of boric acid. Mobility of the *cyclo*pentane ring. J. Boeseken, G. Slooff, J. M. Hoeffelman, and H. E. Hirsch (Rec. trav. chim., 1933, **52**, 881—894).—Reduction (H_2, Ni) of Et *cyclo*pentanone-2-carboxylate to the OH-ester and successive treatment of the OH-acid with $COMe_2$ and P_2O_5 (cf. Smith and Lindberg, A., 1931, 599) gives the *compound*, $C_5H_8<\begin{matrix}O—CMe_2\\CO·O\end{matrix}$, b.p. ±60°/ cathode vac., which is hydrolysed (H_2O) to *cis-cyclo*pentanol-2-carboxylic acid (I). The unchanged acid is probably the slightly impure trans-cyclo*pentanol*-2-*carboxylic acid* (II); during the treatment with $COMe_2$, (II) is converted into (I). The Et methyl-*cyclo*pentanone-2-carboxylate obtained by Dieckmann condensation of Et β-methyladipate is similarly reduced to the OH-ester; the OH-acid with $COMe_2$ and P_2O_5 at −10° gives a *compound*, b.p. 115—117°/2 mm., which is hydrolysed to (probably) *cis*-3-methyl*cyclo*pentanol-2-carboxylic acid (III). The *trans*-acid does not react with $COMe_2$. The conductivity of H_3BO_3 is increased by (I), (III), and *cis*-borneolcarboxylic acid (IV), m.p. 102° (Bredt, A., 1909, i, 498) (*compounds*, m.p. 124° and 191°, with $COMe_2$ and CCl_3·CHO, respectively), but not by the corresponding *trans*-acids. The increase is most marked with (IV) and this is attributed to the greater rigidity of the ring system. The *cyclo*pentane ring may possess some flexibility.

trans-Borneolcarboxylic acid, m.p. 175° (lit. 170°), does not react with $COMe_2$ or CCl_3·CHO. *cyclo*-Hexanol-2-carboxylic acid (V), m.p. 111°, decreases the conductivity of H_3BO_3 but forms a *compound*, m.p. 142°, with CCl_3·CHO; the mother-liquors from several preps. of (V) contain a small amount of an acid, m.p. 57—63°, which enhances the conductivity of H_3BO_3 and may be the impure *cis*-form of (V). H. B.

Salicylberyllates and beryllium salicylate. R. W. Asmussen and E. R. Madsen (Z. anorg. Chem., 1933, **212**, 321—325).—When aq. $BeSO_4$ and Na salicylate are mixed, a complex Be-containing acid is produced, which could not be isolated. It is decomposed by boiling H_2O into Be salicylate and *o*-OH·C_6H_4·CO_2H. Its chemical behaviour is discussed. F. L. U.

Thiols derived from *o*-, *m*-, and *p*-methoxytoluenes and -benzoic acids. M. S. Shah, C. T. Bhatt, and D. D. Kanga (J.C.S., 1933, 1375—1381).—In the following preps., the nitrocresols are methylated by Me_2SO_4 and K_2CO_3 in boiling xylene, and the cresolsulphonic acids, thiolmethoxy-toluenes and -benzoic acids by Me_2SO_4 and 25% aq. NaOH; the thiols were prepared by reduction of the methoxysulphinic acids or chlorosulphonyl compounds by Sn–HCl; the SO_2Me-compounds were obtained from the SMe-compounds by alkaline $KMnO_4$. The following are described: 3-nitro-*o*-tolyl Me ether, m.p. 24°, b.p. 225° (oxidised to 3-nitro-2-methoxybenzoic acid); 3-amino-2-methoxytoluene, b.p. 253° (Bz derivative, m.p. 120°); 3-*methoxytoluene*-3-*sulphinic acid*, an oil, -*sulphonyl chloride*, an oil, and -*sulphonamide*, m.p. 143—144°; 3-*thiol*-2-*methoxytoluene*, b.p. 235—236° (*Hg* and *Pb* salts; *Bz* derivative, m.p. 47°; *disulphide*, an oil; S-*Me ether*, b.p. 254°, oxidised to 3-*methylsulphonyl*-2-*methoxybenzoic acid*, m.p. 166°); *o*-toluidine-4-sulphonic acid [from the NO_2-acid (*Ba*, +H_2O, and *K* salts)] and its *diazo*-compound, decomp. 104° (by nitrous fumes); *o*-cresol-4-sulphonic acid (*Ba* salt, +$2H_2O$); 2-*methoxytoluene*-4-*sulphonic acid*, an oil (*Na*, +H_2O, and *Ba*, +$1·5H_2O$, salts; *chloride*, an oil; *amide*, m.p. 123°); 4-*thiol*-2-*methoxytoluene*, b.p. 238—239° (*Hg* and *Pb* salts; S-*Me ether*, b.p. 255—256°); 4-*methylsulphonyl*-2-*methoxybenzoic acid*, m.p. 151°; 4-*sulpho*-, deliquescent, m.p. 152° (*Ba* salt), 4-*chlorosulphonyl*-, m.p. 149·5°, 4-*amidosulphonyl*-, m.p. 201°, and 4-*methylthiol*-2-*methoxybenzoic acid*, m.p. 112°; 2-methoxytoluene-5-sulphonic acid; 5-amidosulphonyl-, m.p. 137°, and 5-thiol-2-methoxytoluene, m.p. 40° (lit. 38°) (*Bz* derivative, m.p. 80°; S-*Me ether*, b.p. 259°); 5-*methylsulphonyl*-2-*methoxybenzoic acid*, m.p. 190°; 5-*thiol*-2-*methoxybenzoic acid*, m.p. 205° (S-*Me ether*, m.p. 75°) (from the 5-SO_2Cl-acid, m.p. 148·5°); 6-nitro-2-methoxytoluene, m.p. 52° (from 6-nitro-3-amino-2-methoxytoluene, m.p. 103°), the 6-NH_2-compound, 6-sulphinic and 6-sulphonic acid (*K* salt, +H_2O; *chloride*, an oil; *amide*, m.p. 164°), and the 6-*SH*-compound, b.p. 238° (*Bz* derivative, m.p. 62°; *disulphide*, m.p. 80°: *Hg* and *Pb* salts; S-*Me ether*, b.p. 256°, could not be oxidised); 2-nitro-*m*-tolyl Me ether, m.p. 49°; 2-amino-*m*-tolyl Me ether, m.p. 32°: 3-methoxytoluene-2-sulphinic acid, m.p. 94·5°; 2-*thiol*-3-*methoxytoluene*, b.p. 256—257° (*disulphide*, m.p. 148°; S-*Me ether*, b.p. 269—270°); 2-*methylsulphonyl*-3-*methoxybenzoic acid*, m.p. 212°; 3 : 5-dinitrotoluene (modified prep.); 3-methoxytoluene-5-sulphonic acid; 5-*thiol*-3-*methoxytoluene*, b.p. 251—252° (*Hg* and *Pb* salts; *Bz* derivative and *disulphide*, oils; S-*Me ether*, m.p. 155°); 5-methoxytoluene-2-sulphonyl chloride; 2-*thiol*-5-*methoxy*-, b.p. 253—254° (*Hg* and *Pb* salts; *disulphide*, an oil; *Bz* derivative, m.p. 84°), and 6-*methylthiol*-3-*methoxytoluene*, b.p. 272°; 6-*methylsulphonyl*-3-*methoxy*-

benzoic acid, m.p. 180°; 4-*methoxytoluene*-2-*sulphonyl chloride*, an oil, and -*sulphonamide*, m.p. 151°; 2-*thiol*-4-*methoxytoluene*, b.p. 260—261° (*Hg* and *Pb* salts; *Bz* derivative and *disulphide*, oils; S-*Me ether*, b.p. 260—261°); 2-*methylsulphonyl*-4-*methoxybenzoic acid*, m.p. 180°; 3-thiol-2-methoxytoluene, b.p. 252—253°, m.p. 36—37° (*Bz* derivative, m.p. 75°; *disulphide*, m.p. 74°; S-Me ether, b.p. 262°); 3-*methylsulphonyl*-, m.p. 215°, 3-*sulpho*-, m.p. 250—251° (*K* and *Ba* salts, $+2H_2O$; KOH fusion gives protocatechuic acid) (from anisic or 4-methoxytoluene-3-sulphonic acid), and 3-*chlorosulphonyl*-4-*methoxy-benzoic acid*, m.p. 178°, -*benzoyl chloride*, m.p. 70°, and -*benzamide*, m.p. 262°; and 3-*thiol*-4-*methoxybenzoic acid*, amorphous, m.p. 317° (decomp.) (S-*Me ether*, m.p. 205°). R. S. C.

Arylamino-1-hydroxy-2-naphthoic acids. See B., 1933, 908.

Occurrence of isomerism in the fluorenonecarboxylic acid series. Isomeric products from the action of sulphuric acid on 3 : 3′-dichlorodiphenic acid. E. H. Huntress, I. S. Cliff, and E. R. Atkinson (J. Amer. Chem. Soc., 1933, **55**, 4262—4271).—3 : 3′-Dichlorodiphenic acid and conc. H_2SO_4 at 170° (bath) give a *keto-acid* (I), $C_{14}H_6O_3Cl_2$, m.p. 242·5° [*oxime*, m.p. 286° (decomp.); *chloride*, m.p. 183—184°; *amide*, (II) m.p. 296°], which is isomeric but not identical with 1 : 6-dichlorofluorenone-5-carboxylic acid (III), m.p. 242·5° (this vol., 826). (I) sublimes above its m.p., does not titrate consistently, and is formed from (III) and conc. H_2SO_4 at 170°. (II) and aq. NaOBr give an *amine*, $C_{13}H_7ONCl_2$, m.p. 229—230° [1 : 6-*dichloro*-5-*amino-fluorenone*, from the amide of (III) and NaOBr, has m.p. 257°], which is deaminated to 1 : 6-dichlorofluorenone. The formation of isomeric products from other dichlorodiphenic acids is not observed. 5 : 5′-Dichlorodiphenic acid (IV), m.p. 291° (lit. 297°), and conc. H_2SO_4 at 125° give 1 : 6-*dichlorofluorenone*-4-*carboxylic acid*, m.p. 235—236° (*chloride*, m.p. 185°; *amide*, m.p. 301°), which is not decarboxylated at 350° (at 400°, much charring occurs). 4 : 4′-*Dichlorodiphenic acid* (V), m.p. 264—265° (*anhydride*, m.p. 308—310°), and conc. H_2SO_4 at 125° or 175° afford 2 : 7-*dichlorofluorenone*-4-*carboxylic acid*, m.p. 248—249°; at 225°, some 2 : 7-dichlorofluorenone (the sole product at 265—270°) is also formed. 6 : 6′-Dichlorodiphenic acid is unaffected by conc. H_2SO_4 at 175°. (IV) and (V) are prepared from 4- and 5-chloroanthranilic acid, respectively, by the method previously used (*loc. cit.*) for the 3 : 3′-isomeride. All m.p. are uncorr. H. B.

Synthesis of pharmacologically important carboxylic acids. I. Synthesis of arylacetic acids from aromatic aldehydes and of arylpropionic acids from aromatic carboxylic acids. K. Kindler and W. Peschke (Arch. Pharm., 1933, **271**, 431—439).—Methylvanillin and BzCl in Et_2O with aq. KCN at 20° give 3 : 4-dimethoxymandelonitrile benzoate, m.p. 61° (86% yield), reduced by Pd-black and boiling tetrahydronaphthalene to 3 : 4-dimethoxyphenylacetonitrile (70% yield), hydrolysed to a quant. yield of homoveratric acid, m.p. 99—100° (Me ester, b.p. 166°/13 mm.; amide, m.p. 145°). Similarly were obtained good yields of *p*-methoxy- and 3 : 4-dimethoxy-mandelonitrile benzoate and -phenylacetonitriles, and *p*-anisylacetic, homopiperonylic, and phenylacetic acids. Hydrogenation (3 atm.; Pd-black) of $CH_2Bz{\cdot}CO_2Et$ in AcOH in presence of a little conc. H_2SO_4 at 20° gives a 70% yield of Et β-phenylpropionate, probably by way of the β-OH-acid and acrylic acid. Similarly were obtained β-*m*- and -*o*-anisylpropionic acid (Et esters, b.p. 154°/5 mm. and 150—151°/13 mm., respectively). Et *m*-anisoylacetate has b.p. 181°/10 mm. R. S. C.

Tautomerism of phthalyl bromide. W. Davies, A. N. Hambly, and G. S. C. Semmens (J.C.S., 1933, 1309—1315).—*o*-$C_6H_4(CO)_2O$ (I) and PBr_5 or $POBr_3$–PBr_3 first at 100° and then at 160—165°, or ordinary phthalyl chloride and dry HBr at 150—160°, give cyclic *phthalyl bromide*, $C_6H_4<\begin{matrix}CBr_2\\CO\end{matrix}>O$ (II), b.p. 191° (corr.)/24 mm., m.p. about 78—81° (lower if slowly heated), which with NH_3 and NH_2Ph in C_6H_6 gives *o*-$CN{\cdot}C_6H_4{\cdot}CO_2H$ and $C_6H_4(CO{\cdot}NHPh)_2$, respectively. When melted, (I) gives the acyclic *form*, $C_6H_4(COBr)_2$ (III), which, when cooled, slowly reverts to (II). (II) in cold PhMe reacts only slowly at first with NH_2Ph, later more rapidly; if previously heated, it reacts rapidly at once, owing to formation of (III). Pfeiffer's and von Braun's methods for differentiating (II) and (III) fail. (II) forms a double compound with $AlCl_3$, but only unchanged (II) and (I) are isolated by decomp. thereof. The reaction velocities of $Pr^{\beta}OH$ with BzCl, BzF, acyclic phthalyl chloride, (II), and *terephthalyl bromide*, m.p. 84—85°, at 30° are $2{\cdot}64\times10^{-3}$, $5{\cdot}1\times10^{-6}$, $0{\cdot}93\times10^{-2}$, $1{\cdot}6\times10^{-3}$, and very rapid, respectively, thus confirming the structure assigned to (II). Previous heating of (II) greatly increases its rate of reaction with $Pr^{\beta}OH$. The parachor of (III) at 90° is 405·2 [theory for (II) and (III), 390·2 and 404·9, respectively]. (II) and (III) are truly tautomeric. The ease of tautomerisation of phthalyl halides is connected with their reactivity and not with the size of the halogen atom. An attempt to prepare phthalyl iodide failed. R. S. C.

5-Sulpho-3-nitro- and 5-sulpho-3-hydroxybenzoic acid. M. S. Shah and C. T. Bhatt (J.C.S., 1933, 1373—1375).—The structure of 3-sulpho-5-nitrobenzoic acid (I) is confirmed. (I) (modified prep.), $+H_2O$, m.p. 70°, and anhyd. 152° (*Na H*, $+0{\cdot}5H_2O$, and *H* salts), affords 5-*chlorosulphonyl*-3-*nitrobenzoic acid* (II), m.p. 170°, by way of the *chloride*, m.p. 64°, which with NH_3 gives 5-*amidosulphonyl*-3-*nitrobenzamide* (III), m.p. 226° after sintering at 213°. (II) with aq. NH_3 or (III) with hot conc. HCl gives 5-*amidosulphonyl*-3-*nitrobenzoic acid*, m.p. 230°, reduced by $(NH_4)_2S$ to 5-*amidosulphonyl*-3-*aminobenzoic acid*, m.p. 242° (decomp.). Similar reduction of (I) gives the 3-NH_2-acid, which with nitrous fumes gives the *diazo*-compound, decomp. 137°, whence was obtained 5-sulpho-3-hydroxybenzoic acid (IV), $+2H_2O$, softens from 70°, and $+H_2O$, m.p. 142° (softens at 135°) [K_2, $+3H_2O$, *Na H*, *K H*, $+1{\cdot}5H_2O$, and NH_4 *H* salts: 3-*Me ether* (V), $+2H_2O$,

m.p. 125° (*K H*, $+H_2O$, *Na H*, and *Ba* salts)]. This yields *5-chlorosulphonyl-3-methoxybenzoic acid*, m.p. 160° (*chloride*, m.p. 51·5°), *5-amidosulphonyl-3-methoxybenzoic acid*, m.p. 214° (also obtained from 3-methoxytoluene-5-sulphinic acid), and *-benzamide*, m.p. 184°. (IV) or (V) with KOH at 220—290° gives α-resorcylic acid. R. S. C.

Hydrogenation of derivatives of diphenyl. C. R. Waldeland, W. Zartman, and H. Adkins (J. Amer. Chem. Soc., 1933, **55**, 4234—4237).—Di-*m*- and -*p*-tolyls are reduced [H_2, Ni catalyst (NH_4HCO_3 type), methyl*cyclo*hexane (I) at 200° and 100 atm.] to 3 : 3′, b.p. 254—256°/740 mm., and 4 : 4′-, b.p. 119—121°/10 mm., -dimethyldi*cyclo*hexyl, respectively. (p-OH·C_6H_4·)$_2$ is similarly reduced (in EtOH) to 78% of 4 : 4′-*dihydroxy*-, m.p. 204—207°, and 22% of 4-*hydroxy*-, m.p. 94—98°, -di*cyclohexyl*, whilst (p-OMe·C_6H_4·)$_2$ affords 50% of 4-*methoxydicyclohexyl*, b.p. 120—121°/7 mm. Et diphenate [in (I)] yields *Et* cis (?)-, b.p. 155—158°/1—2 mm., and trans (?)-, m.p. 84—85°, -*dicyclohexyl*-2 : 2′-*dicarboxylates*. (p-NH_2·C_6H_4·)$_2$ could not be reduced successfully owing to the formation of NH_3 and compounds of high mol. wt.; in EtOH, 26% of (p-NEt_2·C_6H_4·)$_2$ is produced, whilst in (I) a little 4-aminodi*cyclo*hexyl is formed. *dl*-6 : 6′-Dimethoxydiphenic acid and *d*-3 : 3′-diamino-2 : 4 : 6 : 2′ : 4′ : 6′-hexamethyldiphenyl could not be reduced. It is possible that the same factors which prevent rotation of the rings in resolvable derivatives of Ph_2, also prevent reaction between the C_6H_6 ring and the catalyst and thus inhibit the first stage in the reduction. H. B.

Stereochemistry of diphenyls. XXXI. Preparation and properties of 5 : 5′-dichloro-2 : 6 : 2′ : 6′-tetrafluorodiphenyl-3 : 3′-dicarboxylic acid. E. C. Kleiderer and R. Adams. **XXXII. Preparation and properties of 2 : 6 : 2′ : 6′-tetramethoxydiphenyls.** A. M. VanArendonk, M. E. Cupery, and R. Adams. **XXXIII. Preparation and properties of 2 : 3′-dinitro-2′ : 6′-dimethoxydiphenyl-6-carboxylic acid and 2′-fluoro-2-nitro-6′-methoxydiphenyl-6-carboxylic acid.** A. M. VanArendonk, B. C. Becker, and R. Adams (J. Amer. Chem. Soc., 1933, **55**, 4219—4225, 4225—4230, 4230—4234).—XXXI. 5-Chloro-4-nitro-*o*-toluidine, m.p. 123—124° (all m.p. are corr. unless stated otherwise) [Ac derivative, m.p. 140—141° (lit. 262°)], prepared from 5-chloro-*o*-toluidine and HNO_3–H_2SO_4 at 0—5°, is deaminated to 3-chloro-4-nitrotoluene; the *diazonium borofluoride*, decomp. 153°, at 170°/vac. gives *5-chloro-2-fluoro-4-nitrotoluene*, b.p. 247°/750 mm., reduced ($SnCl_2$, conc. HCl, AcOH) to *5-chloro-2-fluoro-p-toluidine* (I), m.p. 55—56° (*Ac* derivative, m.p. 138—139°). The 3-*acetoxymercuri*-derivative (II), m.p. 216—218° (decomp.), of (I) [from (I) and MeOH–$Hg(OAc)_2$] and aq. KI give the 3-*iodomercuri*-derivative, m.p. 275—279° (decomp.), converted by MeOH–I into *5-chloro-3-iodo-2-fluoro-p-toluidine*, m.p. 67—68° (*Ac* derivative, m.p. 203—204°); the *diazonium borofluoride*, decomp. 218°, affords *5-chloro-3-iodo-2 : 4-difluorotoluene* (III), b.p. 244—246° (corr.). Successive treatment of (II) with aq. NaBr and Br–$CHCl_3$ gives 5-chloro-3-bromo-2-fluoro-*p*-toluidine, m.p. 61—62°, also prepared from (I) and Br in AcOH. (III) and activated Cu (Cu-bronze treated with 2% I in $COMe_2$ and then with dil. HCl in $COMe_2$) give (at 200°) 5 : 5′-*dichloro*-2 : 6 : 2′ : 6′-*tetrafluoro*-3 : 3′-*dimethyldiphenyl*, m.p. 137—138°, oxidised (dil. HNO_3) to 5 : 5′-*dichloro*-2 : 6 : 2′ : 6′-*tetrafluorodiphenyl*-3 : 3′-*dicarboxylic acid*, m.p. 295—298° (shrinks at 285°) (the *cinchonidine*, *strychnine*, and *morphine* salts do not exhibit mutarotation), which, in accordance with theory (A., 1930, 762), could not be resolved. Sidgwick's discussion (Ann. Repts., 1932, **29**, 69) of the structure of 2 : 2′-difluoro-6 : 6′-diamino-3 : 5 : 3′ : 5′-tetramethyldiphenyl (A., 1931, 720) is criticised.

6-Fluoro-*m*-4-xylidine (IV) and MeOH–$Hg(OAc)_2$ afford the 5-*acetoxymercuri*-derivative (V), m.p. 207—208° (decomp.); the 5-*iodomercuri*-derivative and MeOH–I give *5-iodo-6-fluoro*-m-4-*xylidine*, m.p. 53—54° (uncorr.). The corresponding diazonium borofluoride, decomp. 235°, yields *5-iodo-4 : 6-difluoro*-m-*xylene*, m.p. 42—43°, oxidised (dil. HNO_3) to *5-iodo-4 : 6-difluoroisophthalic acid*, m.p. 223—226° (uncorr.), and converted by active Cu at 200° into 2 : 6 : 2′ : 6′-*tetrafluoro*-3 : 5 : 3′ : 5′-*tetramethyldiphenyl*, m.p. 149—150°. Successive treatment of (V) with aq. NaBr and Br–$CHCl_3$ gives 5-bromo-6-fluoro-*m*-4-xylidine, m.p. 56°, also obtained from (IV) and Br in AcOH.

XXXII. 2-Iodoresorcinol Me_2 ether (VI) (modified preps. of this and intermediates described) and Cu-bronze at 170—210° give 2 : 6 : 2′ : 6′-*tetramethoxydiphenyl* (VII), m.p. 175—176°; the 3 : 3′-*Ac*$_2$ derivative (VIII), m.p. 113—115° [from (VII), AcCl, and $FeCl_3$ in CS_2], is oxidised (method; A., 1931, 1156) to 2 : 6 : 2′ : 6′-*tetramethoxydiphenyl*-3 : 3′-*dicarboxylic acid* ($+H_2O$)($+$EtOAc), m.p. 231—232° [5 : 5′-*Cl*$_2$-derivative, m.p. 202—203°, prepared from (VIII) and Cl_2 in AcOH containing a little I and subsequent oxidation (*loc. cit.*); the *brucine*, *strychnine*, and *cinchonine* salts do not exhibit mutarotation], which could not be resolved. (VII) and "conc." HNO_3 (fuming HNO_3 heated until colourless) in warm Ac_2O afford the 3 : 3′-(*NO*$_2$)$_2$-derivative, m.p. 174° [the 3 : 5 : 3′ : 5′-(*NO*$_2$)$_4$-derivative, m.p. 194—195°, is obtained with fuming HNO_3 at 0°], reduced (H_2, PtO_2, EtOH) to 3 : 3′-*diamino*-2 : 6 : 2′ : 6′-*tetramethoxydiphenyl*, m.p. 159—160° [*di*-d-*camphorsulphonate*, m.p. 229—232° (softens at 220°), $[\alpha]_D^{-17}$ (in MeOH) +85° (< 2 min.)—→ +32·5° (const.); mutarotation is rapid at 0°]. Four OMe groups represent about the lower limit for the production of restricted rotation at > −17°. Successive treatment of (VII) with 40% HBr and Ac_2O gives 2 : 6 : 2′ : 6′-*tetra-acetoxydiphenyl*, m.p. 190°. 2 : 6 : 2′ : 6′-*Tetramethoxy*-3 : 5 : 3′ : 5′-*tetra-acetyldiphenyl*, m.p. 340—350° (decomp.), is prepared from (VII), Ac_2O, and $AlBr_3$.

XXXIII. Me 2-iodo-3-nitrobenzoate, (VI) (above), and Cu at 240—300° give (after hydrolysis) (VII) and 2-*nitro*-2′ : 6′-*dimethoxydiphenyl*-6-*carboxylic acid* (IX), m.p. 248—249° (the *brucine*, *cinchonine*, *strychnine*, and *cinchonidine* salts do not exhibit mutarotation), which could not be resolved. 2 : 3′-*Dinitro*-2′ : 6′-*dimethoxydiphenyl*-6-*carboxylic acid* (X), m.p. 192—193° [from (IX) and "conc." HNO_3 in warm Ac_2O], is resolved by brucine into d-, m.p. 174—175°, $[\alpha]_D$ +123·9° in EtOH, and l-*acids*, m.p. 175—176°,

$[\alpha]^{25}$ −109·2° in EtOH (hydrated *brucine* salts, m.p. 146—152° and 142—148°, $[\alpha]^{25}$ +225° and −226·8° in $CHCl_3$, respectively). *2′-Fluoro-2-nitro-6′-methoxydiphenyl-6-carboxylic acid* (XI), m.p. 173—174° (from 2-iodo-3-fluoroanisole, Me 2-bromo-3-nitrobenzoate, and Cu-bronze at 210—240° with subsequent hydrolysis), is similarly resolved into d-, m.p. 157°, $[\alpha]_D^{25}$ +61·6° in EtOH, and l-*acids*, m.p. 157°, $[\alpha]_D^{25}$ −65·6° in EtOH (*brucine* salts, m.p. 215° and 207°, $[\alpha]_D^{25}$ +103·9° and −104·8° in $CHCl_3$, respectively). The active forms of (X) racemise less readily than those of (XI), showing that F has less effect than OMe in restricting rotation. H. B.

Constitution of pyromellitic, mellophanic, and prehnitic acids. L. I. Smith and G. D. Byrkit (J. Amer. Chem. Soc., 1933, **55**, 4305—4308; cf. Baeyer, A., 1871, 372; 1873, 755; Jacobsen, A., 1885, 166; Tohl, A., 1888, 584; Carre, A., 1910, i, 620; Bamford and Simonsen, J.C.S., 1910, **97**, 1904).—Durylic acid (from acetyl-ψ-cumene and NaOBr) is oxidised by Mills' method (J.C.S., 1912, **101**, 2191) to pyromellitic acid [1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$]. Dinitrodurylic acid, m.p. 212·5—214·5° (corr.), is oxidised by Nef's method (A., 1887, 255) to dinitropyromellitic acid; the Et ester is reduced (cf. Nef, *loc. cit.*), subsequently hydrolysed (EtOH–KOH), and the resultant product heated with soda-lime [thus giving *p*-$C_6H_4(NH_2)_2$]. 2 : 4 : 6-$C_6H_2Me_3{\cdot}CO_2H$ (from Mg mesityl bromide and CO_2 or, in poor yield, from ωωω-tribromo-2 : 4 : 6-trimethylacetophenone and 40% alkali), is oxidised (as above) to 1 : 2 : 3 : 5-$C_6H_2(CO_2H)_4$, m.p. 238—253° (Me ester, m.p. 107—109°), which should be designated mellophanic acid. 3 : 5-Dinitro-2 : 4 : 6-trimethylbenzoic acid is oxidised ($KMnO_4$, aq. K_2CO_3) to 4 : 6-*dinitrobenzene*-1 : 2 : 3 : 5-*tetracarboxylic acid* (+3H_2O), m.p. 216—218°, which is decarboxylated (quinoline, Cu chromite) to *m*-$C_6H_4(NO_2)_2$. The $C_6H_2(CO_2H)_4$, m.p. 238—240°, is (by exclusion) the 1 : 2 : 3 : 4-derivative, and should be termed prehnitic acid. H. B.

Attempted synthesis of "diamantoid" substances. H. Kleinfeller and W. Frercks (J. pr. Chem., 1933, [ii], **138**, 184—206).—Attempts to bring about cyclisations leading to substances having an arrangement of C atoms similar to the diamond space lattice were unsuccessful. Interaction of $NO_2{\cdot}C(CH_2Cl)_3$ (I) with *s*-$C_6H_3(OH)_3$ in MeOH in presence of excess of NaOMe gives $CHCl{:}C(CH_2{\cdot}OEt)_2$ and a reddish-brown resin. With $CHNa(CO_2Et)_2$ (II) (3 equiv.) (I) gives *Et*$_4$ *γ-chloromethylenepentane-αααε-tetracarboxylate* (III), b.p. 165—171°/0·3 mm. [*tetrahydrazide*, m.p. 190° (+1H_2O, lost at 135°)], also obtained from $CHCl{:}C(CH_2Cl)_2$ and (II); the corresponding *tetracarboxylic acid*, m.p. 100° (alkaline hydrolysis), is decarboxylated by heat to *γ-chloromethylenepimelic acid*, m.p. 92°, which with O_3 gives $CO(CH_2{\cdot}CO_2H)_2$. Attempts at cyclisation of (III) by heating with dry NaOEt or Na gave a *compound*, $C_{25}H_{32}O_7Cl_2$, b.p. 151—161°/0·8 mm. [*dihydrazide*, m.p. 230° (decomp.); free acid not obtained cryst.], formed from 2 mols. of (III) by elimination of 2 H_2O and 3 CO_2Et. With 4 equivs., of (II) (I) gives the *Et*$_6$ ester, $CH(CO_2Et)_2{\cdot}CH{:}C[CH_2{\cdot}CH(CO_2Et)_2]_2$, which is decomposed by distillation/high vac. into the corresponding tricarboxylic acid. Et hexahydrobenzylmalonate is not appreciably altered by dry NaOEt at 180° or conc. H_2SO_4 at 100°. Condensation of 3 : 5-dibromo-4-acetoxybenzyl bromide in C_6H_6 with (II), even in excess, gives mainly *Et*$_2$ *bis-(3 : 5-dibromo-4-acetoxybenzyl)malonate*, m.p. 117°, hydrolysed by KOH–EtOH to *Et*$_2$ *bis-(3 : 5-dibromo-4-hydroxybenzyl)malonate*, m.p. 142°, but with 3 equivs. of (II) some *Et*$_2$ *3 : 5-dibromo-4-acetoxybenzylmalonate* is formed. Both of these products on catalytic dehalogenation (Pd–$CaCO_3$+KOH) give resins, probably on account of the alkali necessary. Et_2 *p*-nitro-benzyl- (HNO_3, *d* 1·49 at <−10°) and -benzylidene-malonates are reduced by H_2 and Pd–$CaCO_3$ to *Et*$_2$ p-*aminobenzylmalonate*, m.p. 64° (*hydrochloride*, m.p. 120°; p-*aminobenzylmalonic acid hydrochloride*, m.p. 178°), but this could not be converted into the phenol by the diazo-reaction. Its H_6-derivative, m.p. 94° (H_2–PtO_2) (*PhNCO* derivative, m.p. 206—209°), at 200°/vac. loses EtOH with formation of the complex *amide* $NH_2{\cdot}C_6H_{10}{\cdot}CH_2{\cdot}CH[CO{\cdot}NH{\cdot}C_6H_{10}{\cdot}CH_2{\cdot}CH(CO_2Et)_2]_2$, and on diazotisation in 5*N*-HCl and heating gives *Et*$_2$ p-*hydroxyhexahydrobenzylmalonate*. This is oxidised (H_2SO_4–$Na_2Cr_2O_7$) to *Et*$_2$ p-*ketohexahydrobenzylmalonate*, b.p. 150—167°/0·3 mm., which with dry NaOEt at 200°/high vac. loses 2 EtOH, but the only isolable product is the *semicarbazone*, decomp. about 80°, of a ketone $C_{24}H_{12}O_9$. H. A. P.

Tetracarboxylic acid, $C_{27}H_{44}O_8$, from cholesterol. A. Windaus and M. Deppe (Ber., 1933, **66**, [*B*], 1563—1565).—Repetition of the work of Windaus *et al.* (A., 1904, i, 1010) confirms the production of the tetracarboxylic acid $C_{27}H_{44}O_8$ (I) (cf. Minovici *et al.*, A., 1930, 598); the fourth CO_2H cannot be titrated with KOH–EtOH in presence of phenolphthalein, but the acid is characterised by its *Me*$_5$, m.p. 165—166°, and *Me*$_4$ esters. (I) loses H_2O at 175° and CO_2+2H_2O at 230°, thereby giving a *ketodicarboxylic anhydride*, $C_{26}H_{40}O_4$, m.p. 232°, hydrolysed by alkali to the *ketodicarboxylic acid*, $C_{26}H_{42}O_5$, m.p. 167—168° and m.p. 232° after resolidification. The conclusions of Minovici *et al.* (A., 1929, 440) are adversely criticised. H. W.

Enzymes of lichens and constitution of umbilicaric acid.—See this vol., 1216.

Inhibitor actions. K. Bodendorf (Ber., 1933, **66**, [*B*], 1608—1611).—The autoxidation of PhCHO is restricted by *m*- and *p*-$C_6H_4(OH)_2$, *m*- (I), and *p*-$C_6H_4(OMe)_2$ (II), but not by *m*- (III) or *p*-$C_6H_4(OAc)_2$ (IV). (I), (II), (III), and (IV) do not inhibit the autoxidation of α-terpinene. Photochemical decomp. of Eder's solution is restricted by (III). The results support the conclusions of Eisenbrand (this vol., 886). H. W.

Elimination of the aldehydic group as formic acid from aromatic aldehydes. I. Polychlorobenzaldehydes. S. Lock (Ber., 1933, **66**, [*B*], 1527—1533).—Aromatic aldehydes containing Cl in positions 2 and 6 lose ·CHO as HCO_2H quantitatively under the influence of hot 50% KOH or NaOH, but not of Na_2CO_3, NH_3, or NH_2Ph. The following

examples are cited : 2 : 6-$C_6H_3Cl_2$·CHO to *m*-$C_6H_4Cl_2$ and HCO_2K; 2 : 3 : 6-$C_6H_2Cl_3$·CHO to 1 : 2 : 4-$C_6H_3Cl_3$, b.p. 211°(corr.)/742 mm., and HCO_2K; 2 : 4 : 6-$C_6H_2Cl_3$·CHO, m.p. 58—59° (prep. by hydrolysis of 2 : 4 : 6-*trichlorobenzylidene chloride*, b.p. 158°/15 mm., m.p. 27°, obtained from Cl_2 and 2 : 4 : 6-$C_6H_2MeCl_3$ at 200°), to 2 : 4 : 6-$C_6H_3Cl_3$, m.p. 63·5°, and HCO_2K; C_6Cl_5·CHO, m.p. 202·5° [from *pentachlorobenzylidene chloride*, b.p. 199° (corr.)/13 mm.], to C_6HCl_5, m.p. 87°, and HCO_2K. Benzaldehydes containing *m*-OH or *m*-OMe behave similarly provided that the 2 and 6 positions are occupied by Cl or Br. 2 : 5-$C_6H_3Cl_2$·CHO under similar conditions affords 2 : 5-dichloro-benzyl alcohol and -benzoic acid. H. W.

Lignin. VI. A. Hillmer (Ber., 1933, **66**, [*B*], 1600—1607; cf. A., 1932, 558).—Comparison of ultraviolet absorption spectra of aromatic compounds shows that many "U.V. colour families" may be derived, of which the following are the respective initial members : C_6H_6, PhOH, *o*-$C_6H_4(OH)_2$, 1 : 3 : 5-$C_6H_3(OH)_3$, PhCHO, *p*-OH·C_6H_4·CHO, protocatechu-, gall-, cinnam-, and ferul-aldehyde. Examination of the optical and chemical behaviour of lignin shows it to have an aromatic structure of such a type that C_6H_6 nuclei are united according to a simple plan with two or three partly or completely etherified OH groups and a side-chain with about 3 C which does not contain a double linking or CO in conjugation with the C_6H_6 ring. The principle of spectral additivity of polymeric homologues (*loc. cit.*) is confirmed by observations on Me gallate, ethylene glycol digallate, glyceryl trigallate, erythrityl tetragallate, and mannityl hexagallate. Application of this principle to lignin shows that a uniform plan of structure must maintain in the mol. and that it is almost entirely constructed from aromatic units. H. W.

Constitution of jasmone. W. Treff and H. Werner (Ber., 1933, **66**, [*B*], 1521—1527).—Jasmone (I), obtained by distillation with steam of the extract of jasmine flowers and purified by fractional distillation and through the semicarbazone, m.p. 204—266°, has b.p. 108—110°/5—6 mm. It is hydrogenated (Skita) to *tetrahydrojasmone* (II), b.p. 91°/7 mm. (semicarbazones, m.p. 165—166°, and 191—192°, respectively), identical with the tetrahydropyrethrone of Staudinger *et al.* (A., 1924, i, 522). (II) is oxidised by $KMnO_4$ to hexoic (III), lævulic (IV), and δ-keto-γ-methyl-*n*-decoic acid [*semicarbazone*, m.p. 111—112°, further oxidised to (III) and (IV)]. The identity of (II) with 3-*methyl*-2-n-*amyl*cyclo*pentanone* is established synthetically. Et *n*-amylsodiomalonate and Et γ-bromovalerate under defined conditions afford *Et*$_3$ *γ-methylnonane-ααδ-tricarboxylate*, b.p. 180—184°/5—6 mm., hydrolysed and decarboxylated to the dicarboxylic acid, the Ba salt of which is converted by dry distillation into (II), b.p. 91°/7 mm. (semicarbazone, m.p. 165—166°). Hydrogenation of (I) (Paal) leads to *dihydrojasmone*, b.p. 101—102°/5 mm., identified as 3-methyl-2-*n*-amyl-Δ^2-*cyclo*pentenone by comparison of the *semicarbazone*, m.p. 175—176°. (I) is oxidised by 1% $KMnO_4$ to lævulic acid, $EtCO_2H$, and probably AcOH; $PrCO_2H$, $(\cdot CH_2\cdot CO_2H)_2$, or glutaric acid could not be detected. (I) is therefore 3-methyl-2-Δ^β-pentenyl-Δ^2-*cyclo*pentenone. H. W.

Skita's *trans*-2 : 6-dimethyl*cyclo*hexanone is the *cis*-isomeride. R. Cornubert and M. de Demo (Compt. rend., 1933, **197**, 843—845).—2 : 6-Dimethyl*cyclo*hexanol, m.p. 40·5°, prepared by hydrogenation (Pt-black) of *vic.-m*-xylenol in acid solution (cf. Skita, A., 1924, i, 25) (phenylurethane, m.p. 158°), gives with CrO_3 2 : 6-dimethyl*cyclo*hexanone (*A*) [oximes, (I), m.p. 79°, and (II), 119°; semicarbazones, m.p. 183° and 197°; diphenyltetrahydropyrone derivatives, m.p. 175° and 216°; does not give a $NaHSO_3$ compound]. (I) gives the amine obtained by Skita and is identical with the oxime (III), previously given m.p. 65°, now obtained with m.p. 79°, of the ketone obtained by methylation of 2-methyl*cyclo*hexanone (A., 1928, 416).

[With P. Lobinet.] The ketone, regenerated from (III), gives a semicarbazone, m.p. 180°, that from (II) a semicarbazone, m.p. 197° (lit. 193° and 180°, respectively). Only one form of (*A*) is thus known, and this is the *cis*-isomeride. R. S. C.

Production of methylated *cyclo*heptanones and *cyclo*octanones.—See B., 1933, 906.

Action of bromine on acetomesitylene. Polyhalogeno-derivatives of 3 : 5-dibromoacetomesitylene. C. H. Fisher (J. Amer. Chem. Soc., 1933, **55**, 4241—4245).—Acetomesitylene or ωωω-tribromo-2 : 4 : 6-trimethylacetophenone and excess of Br (no solvent) at 0° to room temp. give ωωω : 3 : 5-*pentabromo*-2 : 4 : 6-*trimethylacetophenone* (I), m.p. 113—114°, and a 1 : 1-*mixture* (II), m.p. 108—109°, of (I) and (IV) (below). 3 : 5-*Dibromoacetomesitylene* (III), m.p. 147·5—148·5°, and Br (2 mols.) in AcOH afford ωω : 3 : 5-*tetrabromo*-2 : 4 : 6-*trimethylacetophenone* (IV), m.p. 143—144°. (III) is prepared by reduction (Zn dust, AcOH) of (I), (II), and (IV). (III) and aq. NaOCl in C_5H_5N give ωωω-*trichloro*-3 : 5-*dibromo*-2 : 4 : 6-*trimethylacetophenone*, m.p. 102—103°, converted by conc. aq. NaOH in dioxan into a little 3 : 5-dibromo-2 : 4 : 6-trimethylbenzoic acid. (II), (III), and (IV) are all converted by NaOBr into (I), which with Br and 48% HBr in AcOH affords (II). (III) and Br (excess) in AcOH give (mainly) (II) [treatment of this with 10% aq. KOH gives alkali-sol. material (from IV) and (I)]. H. B.

Substances with the odour of violets. III. Empirical formula and reactions of irone. L. Ruzicka, C. F. Seidel, and H. Schinz (Helv. Chim. Acta, 1933, **16**, 1143—1154).—Analyses of irone (I) separated from its compound with *p*-NH_2·NH·C_6H_4·SO_3H, of its *p*-bromophenylhydrazone, m.p. 175° when rapidly heated, thiosemicarbazone, m.p. 120—122° becoming transparent at 127°, and *phenylsemicarbazone* (II), m.p. 178—179°, establish the composition $C_{14}H_{22}O$ (instead of $C_{13}H_{20}O$). The homogeneity of derivatives obtained from oil of iris is examined in detail and the possibility is indicated that the present differs from the former technical product. (I) can be regenerated from its derivatives by phthalic anhydride in H_2O, whereas $H_2C_2O_4$ induces further change; the only suitable derivative is (II). Dehydrogenation of irene (III) with Se leads

to 1 : 2 : 6-$C_{10}H_5Me_3$. Since ozonisation of (I) affords trimethylpimelic acid, it appears that it contains a 7-membered ring from which (III) results by a pinacolin transformation. To irene is ascribed the constitution 1 : 1′ : 2 : 6-tetramethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. H. W.

Product of oxidation of styryl methyl ketone by peracetic acid. J. Boeseken and A. L. Soesman (Rec. trav. chim., 1933, **52**, 874—880) CHPh:CHAc (1 mol.) and AcO_2H (1 mol.) in AcOH at < 40° give (cf. A., 1931, 1050) β-phenylvinyl acetate (I), m.p. 32—33° [identical with that prepared by Semmler (A., 1909, i, 239)], and a liquid isomeride (II) (*dibromide*, m.p. 115°). Acetylation (Ac_2O–C_5H_5N) of $CH_2Ph{\cdot}CHO$ also affords (I) and a liquid isomeride (III) (*dibromide*, m.p. 90°). (II) and (III) give approx. the same amount of MeOAc when treated with MeOH–HCl, and they are oxidised by an excess of AcO_2H to HCO_2H and BzOH. (I) rearranges slowly when kept in a desiccator or in a vac. into a liquid isomeride. β-Acetyl-α-phenylethylene oxide is unaffected by Br or AcOH; it is not an intermediate in the above oxidation. H. B.

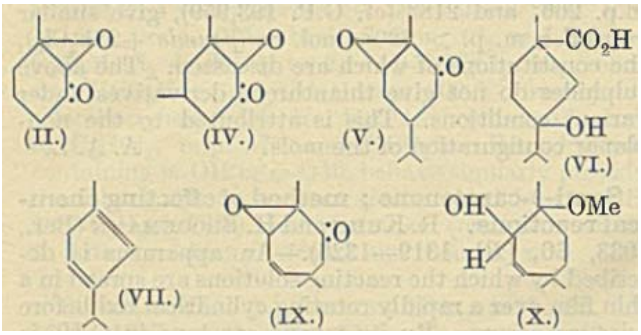
Vat dyes of the benzanthrone series. V. Preparation of *Bz*-1-chlorobenzanthrone. II. T. Maki and T. Nagai (J. Soc. Chem. Ind. Japan, 1933, **36**, 529—531B; cf. B., 1933, 741).—The best conditions for the prep. of *Bz*-1-chlorobenzanthrone consist in passing a current of Cl_2, 0·3 g. per mm., into a solution of 12·5 g. of benzanthrone in 150 c.c. of glacial AcOH at 100° for 17 min. The yield is 69·4% of theory. J. L. D.

***o*-Dihalogenobenzanthrones and their reactions with sodium sulphide.** K. Brass and C. Lauer (Chim. et Ind., 1933, Spec. no., 876—882).—In the following reactions % yields are given in parentheses. 6 : 7-Dibromo-1 : 9-benzanthrone (I) (from 2 : 3-dibromoanthraquinone) with CrO_3 in AcOH gives 6 : 7-*dibromoanthraquinone*-1-*carboxylic acid*, m.p. 298—299° (47·2) [*Bu*$^{\alpha}$ ester, m.p. 148—149° (90·2); *amide* (II), m.p. 292—293°], which is converted by alkaline fusion into 6 : 7-*dihydroxyanthraquinone*-1-*carboxylic acid*, m.p. > 320° (43·1). (II) with NaOBr gives 6 : 7-*dibromo*-1-*aminoanthraquinone*, m.p. 292—293° (87·8) [*Ac* derivative, m.p. 240° (decomp.)], converted by diazotisation into 6 : 7-*dibromo*-1-*hydroxyanthraquinone*, m.p. 320° (63·8), which with H_2O, $Ca(OH)_2$, and a little Cu at 200° gives 1 : 6 : 7-*trihydroxyanthraquinone* (80·1). The constitutions of the above substances follow from that of the last-named compound. The following are similarly obtained from 1 : 2 - dibromoanthraquinone : 7 : 8 - dibromo - 1 : 9-benzanthrone (III), 7 : 8-*dibromoanthraquinone*-1-*carboxylic acid*, m.p. 320° (47·3) (*Bu*$^{\alpha}$ ester, m.p. 310°; *amide*, m.p. 300°), 7 : 8-dibromo-1-amino-, m.p. 229—230° (77·3) (*Ac* derivative, m.p. 219—220°), 7 : 8-*dibromo*-1-*hydroxy*-, and 1 : 7 : 8-trihydroxy-anthraquinone (44·0). (I) with Na_2S at 250—255° yields a *di*(*bromobenzanthronyl*) *sulphide*, m.p. 320° (96·0). Similar treatment of (III) gives 8 : 8′-*dibromo*-7 : 7′-*dibenzanthronyl sulphide*, m.p. > 320° (95·0) (mol. *compound* +2Sb_2Cl_6), oxidised by HNO_3 to the *sulphoxide*, m.p. > 320° (99·3), which may be reduced to the sulphide. This oxidation supports the 7 : 7′-position of the sulphide linking deduced from the greater reactivity of the α-Br atoms. A *Bz*-dibromo-, m.p. 254—255°, and two *Bz*-dichloro-benzanthrones, m.p. 266° and 218° (cf. G.P. 193,959), give similar *sulphides*, m. p. > 320° (mol. *compounds* +2Sb_2Cl_6), the constitutions of which are discussed. The above sulphides do not give thianthrene derivatives under various conditions. This is attributed to the non-planar configuration of the mols. A. A. L.

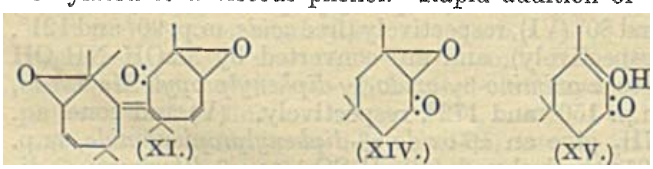
Semi-β-carotenone; method of effecting chemical reactions. R. Kuhn and H. Brockmann (Ber., 1933, **66**, [*B*], 1319—1326).—An apparatus is described by which the reacting solutions are spread in a thin film over a rapidly rotating cylindrical rod before mixture occurs. By its means carotene in C_6H_6 is oxidised by CrO_3 in AcOH–H_2O in such a manner that only one ring system is ruptured, thus leading to *semi*-β-*carotenone* (I), $CH_2<\begin{matrix}CH_2{\cdot}CMe_2\\CH{\cdot}CM\end{matrix}>C{\cdot}[CH{:}CH{\cdot}CMe{:}CH]_2{\cdot}[CH{:}CH{\cdot}CH{:}CMe]_2{\cdot}CH{:}CH{\cdot}CO{\cdot}CMe_2{\cdot}[CH_2]_3{\cdot}COMe$, m.p. 118—119° (corr.; Berl.; vac.) (adsorption, distribution, reduction, and colour reactions described). (I) yields an *oxime*, m.p. 134—135° (corr.; Berl; vac.), and is oxidised to β-carotenone (II) (A., 1932, 749). Reduction of (II) (Zn and AcOH in C_5H_5N) affords *dihydro*-β-*carotenone*, m.p. 130° (corr.; Berl: vac.) [*oxime*, m.p. 151° (corr.; Berl; vac.)]. H. W.

Reactions of halogenated ketones. II. Action of potassium cyanide on desyl chloride. E. P. Kohler and F. W. Brown (J. Amer. Chem. Soc., 1933, **55**, 4299—4304).—Desyl chloride (1 mol.) and KCN (1·5 mols.) in aq. MeOH at room temp. for 4 days give two stereoisomeric α-*cyano*-αβ-*diphenylethylene oxides*, m.p. 52° (I) and 74° (II), and two α-*imino*-βγ-*oxido*-βγ-*diphenylpropyl Me ethers*, m.p. 85° (III) and 110° (IV); MeOBz, NH_2Bz, deoxybenzoin, and other products (cf. Madelung and Oberwegner, A., 1932, 62) are also formed. (I) and (II) are converted by MeOH–KCN into (III) and (IV), respectively. (III) and (IV) are hydrolysed (MeOH–H_2SO_4) to *Me* αβ-*oxido*-αβ-*diphenylpropionates*, m.p. 35° (V) and 80° (VI), respectively (free *acids*, m.p. 90° and 121°, respectively), and are converted by MeOH–NH_2OH into α-*oximino*-βγ-*oxido*-βγ-*diphenylpropyl Me ethers*, m.p. 150° and 172°, respectively. (V) and conc. aq. NH_3 give an αβ-*oxido*-αβ-*diphenylpropionamide*, m.p. 205°, hydrolysed (dil. H_2SO_4) to αβ-*dihydroxy*-αβ-*diphenylpropionamide* (VII), m.p. 135°; (VI) and conc. aq. NH_3 afford an isomeric αβ-*dihydroxy*-αβ-*diphenylpropionamide* (VIII), m.p. 235°. Passage of HCl into solutions of (III) and (IV) in C_6H_6 or Et_2O until the pptd. hydrochlorides redissolve gives α-*chloro*-β-*hydroxy*-αβ-*diphenylpropionamides*, m.p. 180° and 210°, respectively, converted by dil. Na_2CO_3 into (VII) and an αβ-*oxido*-αβ-*diphenylpropionamide*, m.p. 124°, respectively. (VII) and (VIII) with MeOH–acid afford the same mixture of α(or β)-*hydroxy*-β(or α)-*methoxy*-αβ-*diphenylpropionamides*, m.p. 178° and 250°. (V) and (VI) are hydrolysed (acid) to *Me* αβ-*dihydroxy*-αβ-*diphenylpropionates*, m.p. 144° and 153°, respectively (free *acids*, m.p. 184° and 204°, respectively). H. B.

Autoxidation of αβ-unsaturated ketones. VII. W. TREIBS (Ber., 1933, **66**, [*B*], 1483—1492; cf. this vol., 509).—Treatment of 3-methyl*cyclo*hexenone (I) with H_2O_2 yields the *oxide* (II), b.p. 201—202°, trans-



formed by boiling 10% MeOH–KOH into 2-*methoxy*-3-*methyl*cyclo*hexenone*, b.p. 220°, also obtained from the autoxidation product of (I). 3 : 5-Dimethylcyclohexenone (III) similarly yields the *oxide* (IV), b.p. 212—215°, and 2-*methoxy*-3 : 5-*dimethyl*-Δ$^{\alpha}$-cyclo*hexenone*, b.p. 228—230°, also obtained by autoxidation of (III). *Carvotanacetone oxide* (V), b.p. 118—120°/20 mm., is converted by KOH–MeOH partly into hydroxycarvotanacetone, m.p. 181°, unstable to air, and partly into the Me ether of the ketoglycol, b.p. 145—150°/15 mm. (cf. *loc. cit.*); these products are obtained also from the autoxidation of carvotanacetone. *Carvenone oxide*, b.p. 118—122°/18 mm., is isomerised by alkali to the OH-acid (VI), m.p. 78° [obtained previously by autoxidation (*loc. cit.*)], and an isomeric *OH-acid*, m.p. 114—115°, converted by 20% H_2SO_4 into the unsaturated acid, $C_{10}H_{16}O_2$, b.p. 246—248°. Treatment of carvenone with an excess of H_2O_2 or incidence of autoxidation at raised temp. leads to a *tert.* alcohol which readily loses H_2O with formation of the *hydrocarbon* (VII), b.p. 152—158°/1 atm., 50—55°/20 mm. Eucarvone (VIII) readily absorbs 1 O_2 in KOH–EtOH, but is transformed with difficulty by H_2O_2 into the *oxide* (IX), b.p. 105—110°/20 mm., which in boiling alkaline solution slowly adds MeOH, yielding the *ether* (X), b.p. 135—137°/20 mm., demethylated to a viscous phenol. Rapid addition of



H_2O_2 without cooling to an alkaline alcoholic solution of (VIII) yields a small proportion of the *substances* $C_{20}H_{36}O_3$ (XI), m.p. 215° and 217°, respectively (*monosemicarbazones*, decomp. 266° and 254°, respectively), which are stable towards $KMnO_4$, Br, and H_2 and are obtained in better yield (15%) with (X) by autoxidation of (VIII). The main product of the autoxidation of (VIII) is a *resin*, $C_{20}H_{28}O_6$, sol. in alkali. l-*Verbenone oxide* (XII), b.p. 118—120°/20 mm., α_D −105·6° (*semicarbazone*, decomp. 216°), is slowly converted by boiling MeOH–KOH into *hydroxyverbenone* (XIII), m.p. 119—121° [*semicarbazone*, m.p. 191°; *monoacetate*, b.p. 158—160°/20 mm.], which is very stable in alkaline solution but readily affected by O_2 when solid or in acid solution. Addition of alcohol to (XII) is not caused by alkali. Verbenone readily absorbs 1 O_2 in alkaline solution with production of small amounts of (XII), identified by conversion into (XIII). *iso*Phorone is autoxidised with difficulty although readily transformed into the *oxide* (XIV), b.p. 208—211° (*semicarbazone*, decomp. 216°). Under the influence of alkali it is partly converted into *hydroxyisophorone* (XV), m.p. 92—93°, mainly into the *Me ether*, b.p. 221—223°, demethylated to (XV). Pulegone is readily converted by H_2O into the *oxide*, b.p. 125—127°/25 mm., m.p. 40°, but its autoxidation is slow and incomplete. H. W.

Mixed benzoins. X. Conversion of benzanisoin into anisbenzoin. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1933, **55**, 4312—4317).—α-Benzoinoxime (I) is reduced (H_2, PtO_2, EtOH at 70—75°) to β-amino-αβ-diphenylethyl alcohol (II), the N-*Ac* derivative (III), m.p. 197°, of which is oxidised (CrO_3, aq. AcOH) to *Ph* α-*acetamidobenzyl ketone*, m.p. 132°. Hydrolysis (conc. HCl) of this gives Ph α-aminobenzyl ketone (desylamine) [*hydrochloride*, m.p. 245° (decomp.)], also formed by oxidation (CrO_3, dil. H_2SO_4) of (II), which with HNO_2 affords benzoin. (III) is also obtained by reduction (as above) of the Ac derivative of (I) [OH·CHPh·CPh.N·OAc] and acetyl-α-benzilmonoxime. Benzanisoinoxime is similarly reduced to β-*amino*-α-*phenyl*-β-*anisylethyl alcohol*, m.p. 123° (N-*Ac* derivative, m.p. 183°). *Ph* α-*amino*-p-*methoxybenzyl ketone*, decomp. 94° (softens at 88°) [N-*Ac* derivative, m.p. 112°; *hydrochloride*, m.p. 236° (decomp.)], and HNO_2 give anisbenzoin (benzoylanisylcarbinol). *o*-Chlorobenzanisoinoxime (anisyl 2-chloro-α-hydroxybenzyl ketoxime) is reduced to a mixture of β-amino-α-phenyl- [*hydrochloride*, m.p. 233° (decomp.)] and β-*amino*-α-p-*chlorophenyl*-, m.p. 115° [N-*Ac* derivative, m.p. 122°; *hydrochloride*, m.p. 252° (decomp.)], -β-*anisylethyl alcohol*. *p*-Dimethylaminophenyl α-hydroxybenzyl ketoxime is reduced to β-*amino*-α-*phenyl*-β-p-*dimethylaminophenylethyl alcohol*, m.p. 151° (N-*Ac* derivative, m.p. 187°). H. B.

Phenolic ketones derived from diphenylmethane, -ethane, and -propane, and their reduction products. H. WOJAHN (Arch. Pharm., 1933, **271**, 417—431).—The following are prepared from the acid chloride or acid and $POCl_3$: o-*acet*-, b.p. 195°/25 mm., -*propion*-, b.p. 203°/25 mm., -*butyr*-, b.p. 213°/24 mm., and -iso*valer-oxydiphenylmethane*, b.p. 217°/25 mm.; p-*acet*-, b.p. 195°/19 mm., -*propion*-, b.p. 205°/20 mm., -*butyr*-, b.p. 220°/23 mm., and -iso*valer-oxydiphenylmethane*, b.p. 222°/20 mm.; p-*acet*-, b.p. 215°/18 mm., m.p. 38—40°, -*propion*-, b.p. 220°/18 mm., m.p. 38—39°, -*butyr*-, b.p. 227°/18 mm., m.p. 45°, and -iso*valer-oxydiphenylethane*, b.p. 233°/19 mm., m.p. 36°; *Ph* β-*phenylpropionate*, b.p. 195°/27 mm.; p-*acetoxydiphenylpropane*, b.p. 217°/19 mm.; 2 : 4-*di-acet*-, b.p. 248°/16 mm., m.p. 48°, -*propion*-, b.p. 240°/16 mm., -*butyr*-, b.p. 245°/19 mm., and -iso*valer-oxydiphenylmethane*, b.p. 250°/20 mm.; 2 : 4-*di-acet*-, b.p. 258°/17 mm., m.p. 82°, -*butyr*-, b.p. 255°/21 mm., and -iso*valer-oxydiphenylethane*, b.p. 257°/20 mm.; 2 : 4-*di-acet*-, b.p. 2oo°/20 mm., -*butyr*-, b.p. 258°/19 mm., and -iso*valer-oxydiphenylpropane*, b.p. 260°/20 mm. By $AlCl_3$ in

$PhNO_2$, first at room temp. and then at 50—60°, are obtained *p*-hydroxyphenyl β-phenylethyl ketone, m.p. 65° (from Ph β-phenylpropionate), and the following 5-acyl derivatives of *o-hydroxydiphenylmethane* (I) (numbering of these and other substances as in the annexed formula): *Ac*, m.p. 137—138° (*phenylhydrazone*, m.p. about 122—124°; *Me ether*, m.p. 101—102°), *propionyl*, m.p. 153° (*Me ether*, m.p. 119°), *butyryl*, m.p. 142° (*Me ether*, m.p. 106°), and iso*valeryl*, m.p. 121° (*Me ether*, m.p. 66°). The esters of (I) with $AlCl_3$ at 110—170° give only *p*-derivatives. By $AlCl_3$ in boiling PhCl are obtained 4-*hydroxy*-5-*acetyl*-, m.p. 56° (*Me ether*, b.p. 223°/23 mm.), -*propionyl*-, m.p. 75—76°, -*butyryl*-, m.p. 52°, and -iso*valeryl-diphenylmethane*, b.p. 223°/22 mm.; 4-*hydroxy*-5-*acetyl*-, m.p. 52°, -*propionyl*-, m.p. 47—48°, b.p. 220°/18 mm., -*butyryl*-, b.p. 240—242°/18 mm., and -iso*valeryl*-αβ-*diphenylethane*, b.p. 247°/19 mm.; and 4-*hydroxy*-5-*acetyldiphenylpropane*, b.p. 232°/18·5 mm. 2 : 4-Dihydroxydiphenylmethane (1 mol.), its diacyl derivative (1 mol.), and $AlCl_3$ (2·4 mol.) in $PhNO_2$ at 50° give 2 : 4-*dihydroxy*-5-*acetyl*-, m.p. 149° (*phenylhydrazone*, m.p. 146°; *Me*$_2$ *ether*, m.p. 110°), -*propionyl*-, m.p. 92°, -*butyryl*-, m.p. 72°, and -iso*valeryl-diphenylmethane*, m.p. 115°; similarly were prepared 2 : 4-*dihydroxy*-5-*acetyl*-, m.p. 136°, -*butyryl*-, m.p. 85—86°, and -iso*valeryl-diphenylethane*, m.p. 102°, and 2 : 4-*dihydroxy*-5-*acetyl*-, m.p. 106°, -*butyryl*-, m.p. 78°, and -iso*valeryl-diphenylpropane*, m.p. 105°. Clemmensen reduction of the appropriate ketones affords 2-*hydroxy*-5-*ethyl*-, b.p. 197°/17 mm., -*propyl*-, b.p. 205°/17 mm., -*butyl*-, b.p. 211°/18 mm., and -iso*amyl-diphenylmethane*, b.p. 222°/18 mm.; 4-*hydroxy*-5-*ethyldiphenylmethane*, b.p. 212—215°/23 mm.; *p*-hydroxy-αβ-diphenylethane, m.p. 100—101° (from *p*-phenylacetylphenol); -hydroxy-αγ-diphenylpropane, b.p. 215°/19 mm. (from *p*-β-phenylpropionylphenol); 2 : 4-*dihydroxy*-5-*ethyl*-, b.p. 237—240°/11 mm., -propyl-, b.p. 225°/12 mm., -*butyl*-, b.p. 238—240°/15 mm., and -iso*amyl-diphenylmethane*, b.p. 241°/16 mm. R. S. C.

Reductic acid, a strongly reducing product of the degradation of carbohydrates. T. Reichstein and R. Oppenauer (Helv. Chim. Acta, 1933, **16**, 988—998).—Treatment of tetragalacturonic acid *a* with 5% H_2SO_4 at 150—155° leads to reductic acid, m.p. 213—213·5° (corr., decomp.) (*Na* salt), which is identified as 3-*keto*-Δ^1-cyclo*pentene*-1 : 2-*diol*, and is apparently identical with the product obtained by Thierfelder from glycuronic acid; its formation from pectin, *d*-xylose, and 1% H_2SO_4 at 150° and from *d*-galacturonic acid and 1% H_2SO_4 at 155—160° is described. (I) reduces cold Fehling's solution, $AgNO_3$, and dichlorophenol-indophenol. In H_2O it neutralises 1 NaOH and reacts with 2 I, giving probably 1 : 2 : 3-triketo*cyclo*pentane, reconverted into (I) by H_2S. (I) has no antiscorbutic action. Distillation of (I) with 12% HCl yields furfuraldehyde. It is oxidised by $KMnO_4$ in alkaline solution to $(\cdot CH_2 \cdot CO_2H)_2$ in good yield. With CH_2N_2 (I) affords a *Me*$_1$, m.p. 138° (corr.), and *Me*$_2$, b.p. 120°/12 mm., *ether*. With excess of $NHPh \cdot NH_2$ (I) affords the *substance* $C_{17}H_{16}ON_4$ or $C_{17}H_{18}ON_4$, m.p. 247·5—248·5° (corr., decomp.). H. W.

Cymorcinol [2 : 6-dihydroxy-*p*-cymene]. W. Treibs (J. pr. Chem., 1933, [ii], **138**, 284—288).—Hydroxycarvone is converted by a little I at its m.p. into cymorcinol (I) [3 : 5-*Br*$_2$-, m.p. 65°, and 3-*NO*-derivative (II), m.p. 142°]; its acetate similarly gives the *Ac* derivative of (I), b.p. 270°. Reduction of (II) with $SnCl_2$ and treatment of the amine produced with HNO_2 gives hydroxythymoquinone, also obtained by direct oxidation of (I) with aq. HNO_3, H_2O_2 in aq. AcOH, or air in KOH–MeOH; further air-oxidation gives *dihydroxythymoquinone*, m.p. 220°, which with Zn dust and alkali or H_2 (Skita) gives readily oxidisable (?) leuco-compounds. Oxidation of (I) in presence of NH_3 does not give compounds containing N. Attempts at prep. of the derived aldehyde and carboxylic acid failed. H. A. P.

Constitution of reaction products of benzo- and naphtho-quinones with compounds containing a methylene group and two adjacent negative groups. W. Kesting (J. pr. Chem., 1933, [ii], **138**, 215—220).—Interaction of $CH_2(CN)_2$, benzoquinone, and NH_3 in dry Et_2O gives the deeply coloured unstable *compounds*, $CH_2(CN)_2,C_6H_4O_2,NH_3$, and $CH_2(CN)_2,2C_6H_4O_2,2NH_3$, to which the formulæ $NH_4[CH(CN)_2,C_6H_4O_2]$ and $[NH_4]_2[C(CN)_2\cdot(C_6H_4O_2)_2]$ are assigned. With acids these form H_2O- and Et_2O-insol. compounds of unknown structure. H. A. P.

Manufacture of aminoanthraquinonesulphonyl chlorides.—See B., 1933, 908.

Preparation of 1 : 2- and 2 : 3-diaminoanthraquinones. P. H. Groggins and H. P. Newton (Ind. Eng. Chem., 1933, **25**, 1030—1033).—*o*-3 : 4-Dichlorobenzoylbenzoic acid [improved prep. from *o*-$C_6H_4Cl_2$, *o*-$C_6H_4(CO)_2O$, and $AlCl_3$] is cyclised by H_2SO_4 (7·5 hr. at 135°) to 13% of 1 : 2- and 87% of 2 : 3-dichloroanthraquinone, separated by crystallisation from H_2SO_4 followed by EtOH, and converted into the corresponding NH_2-derivatives by a mixture of aq. NH_3, $KClO_3$, NH_4NO_3, and Cu_2O or CuO. F. R. S.

Polycyclic aromatic hydrocarbons. XI. Acetylation of 1 : 2-benzanthracene. J. W. Cook and C. L. Hewett (J.C.S., 1933, 1408—1410; cf. A., 1932, 74).—1 : 2-Benzanthracene gives mixtures by the Friedel–Crafts reaction; under various conditions are obtained poor yields of the ?-*Ac*, m.p. 147° (*picrate*, m.p. 192°; *quinone*, m.p. 196—197°), 7-*Ac* (I), m.p. 151—152° (*picrate*, m.p. 147—148°; *quinone*, m.p. 219°), 9- or 10-*Ac* (II), m.p. 104—105° (*picrate*, m.p. 153·5—154·5°; gives 1 : 2-benzanthraquinone when oxidised), and 6-*Ac* (III), m.p. 192·5—193·5° (*quinone*, m.p. 197—199°), derivatives. (II) gives (I) with $AlCl_3$ in $PhNO_2$ at 40°. Oxidation of (I) and (III) gives anthraquinone-1 : 2 : 7- (*Et*$_3$ ester, m.p. 204—204·5°) and -1 : 2 : 6-tricarboxylic acid (*Et*$_3$ ester, m.p. 233·5—234·5°), respectively. (I) and MgMeI in Et_2O give 7-(1 : 2-*benz*)*anthranyldimethylcarbinol*, m.p. 135°, which with hot HCl–AcOH gives a *dimeride*, m.p. 248—251°, of 7-iso*propenyl*-1 : 2-*benzanthracene*. R. S. C.

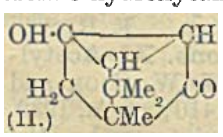
Resinols. I. β-Amyrin of *Manila elemi*. F. S. Spring (J.C.S., 1933, 1345—1346).—α- and β-Amyrin

(I) may be separated by fractional dissolution of the anisates in $CHCl_3$. β-Amyrin acetate is oxidised (H_2O_2–AcOH) to the oxy-compound, m.p. 291—292°, hydrolysed to *oxy-β-amyrin*, m.p. 201—202°. β-*Amyrin formate*, m.p. 238°, is hydrolysed to (I), whilst (I) and AcOH–HCl give β-amyrin acetate and iso-*acetate*, m.p. 246°. Reduction of β-amyrilene with amyl alcohol and Na gives β-amyrene and with Pd–H_2 yields iso-β-*amyrene*, m.p. 82—83°. F. R. S.

Nitrosopinene. G. VITTE (Bull. Inst. Pin, 1933, 216).—An improved prep. is described (yield 50%). A. A. L.

Camphor and terpenes. X. Cause, source, and elimination of partial racemisation in the conversion of *D*- into *L*-camphor. J. HOUBEN and E. PFANKUCH (Annalen, 1933, **507**, 37—47).—Optically pure 4-chloro*iso*bornyl trichloroacetate (I) could not be obtained from α- or 4-chlorocamphene (II) and $CCl_3{\cdot}CO_2H$ under various conditions. The partial racemisation occurs in the 4-chloro*iso*bornyl ion (which arises from the intermediate 4-chlorocamphene hydrate trichloroacetate); (I) is not racemised by $CCl_3{\cdot}CO_2H$ under the conditions used in its prep. Optically pure (II), $[\alpha]_D$ −107·6°, is converted by HBr–AcOH into 4-chloro*iso*bornyl bromide, $[\alpha]_D^{18}$ +50·5° in EtOH, which with C_5H_5N and *m*-cresol (cf. this vol., 613) affords (II), $[\alpha]_D^{18}$ −108° in EtOH. Hydrolysis of (I), $[\alpha]_D$ +42°, gives 4-chloro*iso*borneol, $[\alpha]_D$ +22·6°; the bromide, $[\alpha]_D$ +35°, from this is converted (as above) into (II), $[\alpha]_D^{20}$ −75·5° in EtOH (*i.e.*, optical purity is 70%). Mg *L-d*-4-chloro*iso*bornyl bromide and CO_2 give L-d-4-*chlorocamphane*-2-*carboxylic acid*, m.p. 159—160°, $[\alpha]_D^{21}$ +9·5° in EtOH; with O_2, optically pure *L-d*-4-chloro*iso*borneol, m.p. 235°, $[\alpha]_D^{18}$ +32·5° in EtOH (small amount), 4 : 4′-*dichlorodiisobornyl*, m.p. 187—189°, $[\alpha]^{18}$ +45·05° in $CHCl_3$, 4-chlorocamphane, and (II) result. H. B.

Physiologically active isomeride of Bredt's 5-ketocamphor. K. TAKEUCHI and Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **22**, 59—68).—5-Ketocamphor, or the mixture obtained from 5-hydroxycamphor (I) with H_2SO_4 and $K_2Cr_2O_7$ (cf. A., 1928, 524), when boiled with C_6H_{14} or ligroin, or at 200° in vac., is converted into the enolic *isomeride* regarded as (II), m.p. 209—210°, $[\alpha]_D^1$ +147·3° in ligroin (*semicarbazone*, m.p. 230—231°), which is reduced (H_2–Pt, AcOH) to (I). The physiological action of (II) is described. A. A. L.



(II.)

Camphenilone and some derivatives. I, II. P. SNITTER (Bull. Inst. Pin, 1933, 178—180, 200—211).—I. A review of sources of camphene.

II. Camphenilone (I), m.p. 37° (semicarbazone, m.p. 224°), is obtained from camphene (improved prep.) by an improved process with N_2O_5, and is stable to SeO_2, and to H_2 and Pt. The Raman spectrum of (I) is described. (I) dissolves cellulose nitrate, and is recommended as a cryoscopic solvent (const., 605). The chloride (improved prep.) from camphenylol with NaOEt gives camphenylene (II), m.p. 26·5° (yield 38%), containing a little *apo*bornylene (III), but no santene (Raman spectrum). (III) is similarly found to contain a little (II). A. A. L.

Optical isomerism and diminution of blood pressure. J. VON BRAUN and A. JACOB (Ber., 1933, **66**, [*B*], 1461—1464).—*d*-Fenchone is converted by $NaNH_2$ into *d*-fencholamide and thence by Br–KOH into the carbimide $CH_2{<}\begin{matrix}CH_2\\CHPr^{\beta}{\cdot}CH_2\end{matrix}{>}CMe{\cdot}N{:}C{:}O$, which with $NMe_2{\cdot}[CH_2]_2{\cdot}OH$ affords the carbamic ester $C_9H_{17}{\cdot}NH{\cdot}CO_2{\cdot}[CH_2]_2{\cdot}NMe_2$ [*methiodide* (I), m.p. 74°, $[\alpha]_D$ +5·18° in EtOH]. *l*-Fenchone, m.p. +5·2°, $[\alpha]_D^{20}$ −66·8°, is obtained from thuja oil by distillation, treatment with HNO_3 and then with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, and finally with $NaNH_2$ in C_6H_6, which removes a previously undetected impurity. *l*-Fencholamide (II), m.p. 94°, $[\alpha]_D^{20}$ −5·85° in MeOH, is converted by alkali or by HCl at 120° into l-*fencholic acid*, b.p. 144—145°/13 mm., f.p. 16—18°, $[\alpha]_D^{20}$ −3·66° (corresponding *chloride*, b.p. 118—119°/24 mm., *Et* ester, b.p. 115—117°/25 mm., $[\alpha]_D^{20}$ −3·753°). (II) is converted into the l-*carbimide*, b.p. 82—83°/13 mm., $[\alpha]_D^{18\cdot5}$ −2·96° and thence into the *carbamic* ester [*methiodide* (III), m.p. 75°, $[\alpha]^{24}$ −6·39° in EtOH]. The diminution of blood pressure caused by (I) is at least 50 times that effected by (III). H. W.

Antioxidants of rubber latex. I. H. F. BONDY [with G. G. LAUER](Ber., 1933, **66**, [*B*], 1611—1621).—Rubber latex contains a material which restricts the autoxidation of rubber (I) and balata (II). By means of viscosity measurements, the degree of autoxidation of (I) and (II) can be determined and the presence of the antioxidant established. In the dark, solutions do not become autoxidised, and in light and in solution the antioxidant is inoperative. It is active only in the solid condition. Results are much more rapidly obtained in ultra-violet than in daylight and are much more readily reproduced. Examination of various fractions of (I)–$COMe_2$ extracts shows that the basic components are particularly active. Possibly the restrictive action is caused by the dark brown colour of the basic material as well as by their chemical nature, since the colour prevents the penetration of the rays which cause autoxidation. Azo-dyes and azobenzene are strongly restrictive, whereas alizarin and carotene have little action. The action of the dye appears sp.; it cannot be chemical and only the colour appears important. H. W.

Mol. wt. and chain-length of natural and synthetic rubber. A. J. WILDSCHUT (Rec. trav. chim., 1933, **52**, 935—940).—The mol. wts. of natural rubber (I) and synthetic Me-rubber (II) (from βγ-dimethylbutadiene) are determined by Staudinger's viscosimetric method using dil. solutions in C_6H_6. Staudinger's formula is not valid for (I), but gives good results for (II) and plasticised (I), which possess approx. the same chain-length. The mol. wt. of (I) from different sources varies appreciably; the differences in behaviour during plasticisation are thus explicable. Kraemer and van Natta's conclusions (this vol., 218) are criticised. H. B.

Super-aromatic properties of furan. II. Friedel-Crafts reaction. H. GILMAN and N. O. CALLOWAY (J. Amer. Chem. Soc., 1933, **55**, 4197—4205).—Ph 2-furyl ketone (I), $Bu^{\gamma}Cl$, and $AlCl_3$ in

CS_2 give *Ph* 5-tert.-*butyl*-2-*furyl ketone* (30%), b.p. 180—182°/20 mm., 187—189°/22 mm., also obtained from 5-tert.-*butyl*-2-*furoyl chloride*, b.p. 220°, C_6H_6, and $AlCl_3$. 2-*Propionyl*- (II), b.p. 78—80°/17 mm., m.p. 27—28°, 2-n-*butyryl*-, b.p. 95—97°/19 mm., 2-iso-*butyryl*-, b.p. 86—87°/18 mm., 2-n-*valeryl*-, b.p. 108—109°/18 mm. (*semicarbazone*, m.p. 158—159°), and 2-n-*hexoyl*-*furan*, b.p. 116—119°/16 mm. (*semicarbazone*, m.p. 110—112°), are prepared in 23—52% yield from furan, the appropriate acyl chloride, and $AlCl_3$ in CS_2. Me 2-furoate (III), Pr$^{\alpha}$Cl or Pr$^{\beta}$Cl, and $AlCl_3$ in CS_2 give *Me* 5-iso*propyl*-2-*furoate*, b.p. 110—112°/20 mm. (free *acid*, m.p. 65—66°); *Me* 5-tert.-*butyl*-2-*furoate*, b.p. 110—114°/15 mm. (free *acid*, m.p. 104—105°), is obtained in 45, 66, 1·6, and 46% yield from Bu$^{\alpha}$Cl, Bu$^{\beta}$Br, *sec.*-BuBr, and Bu$^{\gamma}$Br, respectively, and in 41·3% yield from (III), Bu$^{\gamma}$Cl, and $FeCl_3$ in CS_2, whilst *Me* 5-*amyl*-, b.p. 112—116°/13 mm. (free *acid*, m.p. 69—70°), and 5-*hexyl*-2-*furoates*, b.p. 132—136°/19 mm. (free *acid*, m.p. 36—37°), are prepared using *n*-amyl chloride and *n*-hexyl bromide, respectively. (III), MeCl, and $AlCl_3$ in CS_2 give *Me* 5-*carbomethoxyfuran*-2-*dithiocarboxylate* (?), m.p. 102—103°. Furfuraldehyde and Pr$^{\beta}$Cl similarly give an *aldehyde*, $C_8H_{12}O_2$, b.p. 101—103°/21 mm. (*semicarbazone*, m.p. 174—176°), which may be a dihydrofuran derivative; it is oxidised (alkali–Ag_2O) to an *acid*, $C_8H_{12}O_3$, m.p. 76—77°, and with Ac_2O and NaOAc affords an *acid*, $C_{10}H_{14}O_3$, m.p. 102—103°. (II) and MgMeI give 2-*furylmethylethylcarbinol*, b.p. 77—78°/19 mm., which when dehydrated (Ac_2O) and then reduced (Adams) affords 2-sec.-*butylfuran*, b.p. 132—135° (5-*chloromercuri*-derivative, m.p. 88°). 2-n-*Propyl*-, b.p. 114—116° (5-*chloromercuri*-derivative, m.p. 99°), 2-n-*butyl*-, b.p. 137—138° (5-*chloromercuri*-derivative, m.p. 79—80°), and 2-iso*butyl*-*furan*, b.p. 123—127° (5-*chloromercuri*-derivative, m.p. 95—96°), are prepared by reduction (Wolff–Kishner) of the appropriate 2-acylfurans, whilst 2-iso*propyl*-, b.p. 106—109° (5-*chloromercuri*-derivative, m.p. 117—118°), and 2-tert.-*butyl*-*furan*, b.p. 119—120° (5-*chloromercuri*-derivative, m.p. 136—137°), are obtained by decarboxylation (quinoline and Cu-bronze) of the 5-alkyl-2-furoic acids. Acylation of (III) or Et 2-furoate (IV) could not be effected using $AlCl_3$; (IV), Ac_2O, and $SnCl_4$ in C_6H_6 give *Et* 5-*acetyl*-2-*furoate*, m.p. 85—86° (the free *acid* blackens and decomposes gradually when heated), whilst (III) and $(PrCO)_2O$ similarly afford *Me* 5-n-*butyryl*-2-*furoate*, m.p. 67—68° (free *acid*, m.p. 172°). 2 : 5-Dimethylfuran, Ac_2O, and FeCl, give the 3-Ac derivative (42%); *Ph* 2 : 5-*dimethyl*-3-*furyl ketone*, b.p. 140°/15 mm., 152°/17 mm., is obtained in 7% yield using BzCl and $AlCl_3$ in CS_2 and in 29% yield using Bz_2O and $FeCl_3$ in CS_2. The exclusive substitution in the furan residue of (I), the alkylation and acylation of (III) and (IV) (not of EtOBz), and the use of C_6H_6 as a medium for some of the above reactions, indicate that furan is more aromatic than C_6H_6 (cf. this vol., 71).

Me anisate, Pr$^{\beta}$Cl, and $AlCl_3$ in CS_2 give 33·6% of *Me* 4-*methoxy*-3-iso*propylbenzoate*, b.p. 162—165°/25 mm. [free *acid*, m.p. 162—163° (softens at 158°)]; α-$C_{10}H_7$·CO_2Et similarly affords 33% of *Et* iso*propyl*-α-*naphthoate*, b.p. 198—203°/20 mm. [hydrolysis (EtOH–KOH) gives a mixture of acids, m.p. 68—72°]. An *Et butyl*-α-*naphthoate*, b.p. 230—235°/18 mm., is obtained using Bu$^{\alpha}$Cl. H. B.

Molecular rearrangement of some *o*-acyloxyacetophenones. Mechanism of the production of 3-acylchromones. W. Baker (J.C.S., 1933, 1381—1389).—*o*-Aroyloxyacetophenones (*A*) rearrange in presence of K_2CO_3 in C_6H_6 at $> 35°$ to the (enolic) K salts of *o*-hydroxydibenzoylmethanes (*B*), which by ring-closure afford hydroxy- or acyloxyflavones. When (*A*) are produced by acylation of substances containing other acyloxy substituents, the yields of (*B*) are reduced by hydrolysis by the H_2O liberated; under some conditions exchange of acyl groups may occur. The formation of 3-acylchromones from *o*-hydroxyacetophenones, acid anhydrides, and their Na salts is a general reaction, and the reputed nature of many substances formed by this method is suspect. The reaction proceeds by way of a 2-hydroxyflavone, di- and tri-acylmethane, other interpretations being now untenable. Resacetophenone (I) gives (Schotten–Baumann) the 4-O-*Bz* (II), m.p. 106—107° [*Ac* derivative (by boiling Ac_2O), m.p. 82—83°], (by BzCl and C_5H_5N at 100°) Bz_2 (III), m.p. 80—81°, (by Ac_2O and NaOAc at 50°) 4-O-*Ac* (IV), m.p. 75—76°, and [from (IV), BzCl, and C_5H_5N] 2-O-*Bz*-4-O-*Ac* (V), m.p. 67°, derivatives. ω : 4-*Dibenzoylresacetophenone* (VI), m.p. 167° (sol. in warm NaOH), is obtained (*a*) from (II), K_2CO_3, and BzCl (1 mol.) in hot PhMe (20% yield), (*b*) similarly (20%) from (I) and BzCl (2 mols.), (*c*) from K_2CO_3 and (III) (40%) or (V) (1%) in hot PhMe, and (*d*) from (II), K_2CO_3, and CH_2PhCl in hot PhMe (20%). (VI) with cold H_2SO_4 gives 7-hydroxyflavone (76% yield), with hot AcOH and NaOAc a 90% yield and some 7-Ac derivative, and with hot AcOH and a little conc. HCl rapidly 7-*benzoyloxyflavone*, m.p. 157—158°. ω : 4-*Dianisoylresacetophenone* (VII), m.p. 170—171°, is similarly obtained from *resacetophenone dianisate* (prepared in C_5H_5N), m.p. 118°, from 4-O-*benzoyl*-2-*anisoylresacetophenone* [prepared from (II) in C_5H_5N], m.p. 109°, and as in (*b*) above using *p*-OMe·C_6H_4·COCl, which gives also much 3-*anisoylresacetophenone*, m.p. 151° (best obtained by the Schotten–Baumann method). (VII) with hot AcOH–NaOAc, followed by dil. KOH–MeOH, gives 7-hydroxy-4′-methoxyflavone, m.p. (rapid heating) 263—264° (Ac derivative, dimorphic, m.p. of both forms 176—177° owing to change of the less stable into the more stable form), but with conc. H_2SO_4 a non-cryst. product is formed. *o*-Benzoyloxyacetophenone (prepared in C_5H_5N), m.p. 87—88°, with hot K_2CO_3–PhMe gives *o*-hydroxydibenzoylmethane, m.p. 121° (lit. 120°), whence flavone was prepared by both methods. *p*-Hydroxyacetophenone (Bz derivative, prepared in C_5H_5N, m.p. 134—135°) was prepared from PhOAc. *Resacetophenone diveratrate*, m.p. 151—152°, with K_2CO_3–PhMe gives the ω : 4-*diveratroyl* derivative, m.p. 159—160°, and thence (AcOH–NaOAc) 7-*hydroxy*-3′ : 4′-*dimethoxyflavone*, m.p. 255°. *Gallacetophenone tribenzoate* (prepared in dry C_5H_5N at $< 50°$), m.p. 118—119°, gives similarly ω : 3 : 4-*tribenzoylgallacetophenone*, m.p. 193—194°, and 7 : 8-dihydroxyflavone, m.p. 243° (varies with rate of heating) (Ac derivative, m.p. 198°). (I), K_2CO_3, and

cinnamoyl chloride (2 mols.) in hot PhMe give 4-O-*cinnamoylresacetophenone*, m.p. 131°, and 7-*cinnamoyloxy*-2-*styrylchromone*, m.p. 216—217°. 2 : 4-Dihydroxyphenyl benzyl ketone (prepared from resorcinol and $CH_2Ph{\cdot}CN$) (4-O-*Bz* derivative, m.p. 121—122°), BzCl, and K_2CO_3 in PhMe give 7-hydroxy-2 : 3-diphenylchromone and 2 : 4-dihydroxybenzoic acid. (I), Bz_2O, and NaOBz at 200° give 7-benzoyloxy- and 7-*benzoyloxy*-3-*benzoyl-flavone*, m.p. 167°, the latter product being also obtained similarly from (III) and giving 7-hydroxyflavone with hot KOH–aq. EtOH. 3-Acetyl-*p*-cresol [obtained from *p*-tolyl acetate (modified prep.), m.p. 214°], Na, and $EtCO_2Et$ at 100° give 3-*propionoacetyl*-p-*cresol* (VIII), m.p. 75—76°, which with hot AcOH–HCl rapidly gives 6-*methyl*-2-*ethylchromone*, m.p. 51°. 3-Acetoacetyl-*p*-cresol (IX) and 2 : 6-dimethylchromone (X), new m.p. 99° and 103°, respectively, are similarly obtained. (VIII), Ac_2O, and NaOAc give 3-propionyl-2 : 6-dimethylchromone (XI), m.p. 82°, also obtained with (X) from (IX), $(EtCO)_2O$, and $EtCO_2Na$. (XI) with Na_2CO_3–aq. EtOH gives (X), but with aq. Na_2CO_3 mostly *p*-cresotinic acid, m.p. 152°, which is the sole product from (XI) or (X) and hot 2*N*-NaOH.

R. S. C.

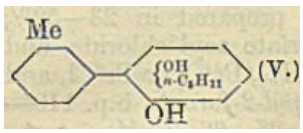
Synthesis of dihydro*iso*osthol. Constitution of osthol. M. YAMASHITA (Bull. Chem. Soc. Japan, 1933, **8**, 276—280).—*iso*Valeronitrile and resorcinol in Et_2O with $ZnCl_2$ and HCl gives 2 : 4-dihydroxyphenyl Bu^{β} ketone (oxime, m.p. 203—205°), reduced (Zn–Hg, HCl) to 2 : 4-dihydroxy*iso*amylbenzene (cf. A., 1926, 838). This with malic acid and H_2SO_4 gives 7-*hydroxy*-6-iso*amylcoumarin*, m.p. 108—110°, the *Me ether* ("dihydro*iso*osthol"), m.p. 61—62°, of which is not identical with dihydro-osthol. The constitution for osthol suggested by Spath (this vol., 614) is preferred. A. A. L.

Cichoriin and the constitution of æsculin and scopolin. K. W. MERZ (Arch. Pharm., 1933, **271**, 449).—Concerning priority (cf. this vol., 72).

R. S. C.

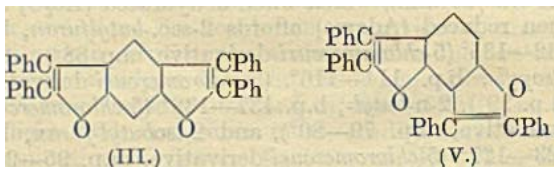
Natural colouring matters and their analogues. R. ROBINSON (Nature, 1933, **132**, 625—628).—From the presidential address to section B (Chemistry) of the British Association, 1933. L. S. T.

***Cannabis Indica* resin. IV. Synthesis of some 2 : 2-dimethyldibenzopyrans, and confirmation of the structure of cannabinol.** R. S. CAHN (J.C.S., 1933, 1400—1405).—o-*Bromophenyl* o-*bromobenzoate*, b.p. 247°/26 mm., m.p. 39°, does not react with Mg, nor does diazotised Ph anthranilate on elimination of N give the lactone of 2-hydroxydiphenyl-2′-carboxylic acid (I), which has been prepared from anthranilic acid diazonium sulphate (II) and PhOH. (I) and MgMeI yield 2-*hydroxy*-2′-α-*hydroxy*iso*propyldiphenyl*, m.p. 147—150°, dehydrated (P_2O_5) to 2 : 2-*dimethyldibenzopyran*, b.p. 186—187°/27 mm. (II) and *p*-cresol form the *lactone* of 2-*hydroxy*-5-*methyldiphenyl*-2′-*carboxylic acid*, m.p. 134—135°, which with MgMeI gives 2-*hydroxy*-5-*methyl*-2′-α-*hydroxy*iso*propyldiphenyl*, m.p. 112° (2-*acetoxy*-, m.p. 78—79°, and -*methoxy*-derivatives, m.p. 122°), dehydrated (P_2O_5) to 2 : 2 : 5′-*trimethyldibenzopyran* (III), b.p. 201°/30 mm., m.p. 58°. The lactone of 2-*hydroxy*-3-*methoxydiphenyl*-2′-*carboxylic acid*, m.p. 167°, from guaiacol, gives impure 3″-methoxy-2 : 2-dimethyldibenzopyran. (III) and HCl–AcOH afford 2-*hydroxy*-5-*methyldiphenyl* (IV), m.p. 110—111° (*Me ether*, m.p. 90°; *Bz* derivative, m.p. 109—110°), which with HNO_3–AcOH is nitrated and oxidised to a *substance*, m.p. 199—200°. Acetylcannabinol and HCl–AcOH yield a *phenol*, (V), b.p.



about 255°/27 mm., m.p. 61—62°, similar to (IV) in properties, which forms a NO_2-derivative, oxidised (HNO_3) to 6-nitro-*m*-toluic acid. This confirms the structure assigned to cannabinol (cf. A., 1932, 747), and the possible constituents of crude *Cannabis* resin are discussed in view of the results obtained. F. R. S.

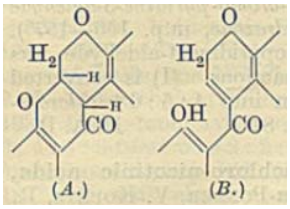
Condensation of benzoin with resorcinol. O. DISCHENDORFER (Monatsh., 1933, **62**, 263—283).—The initial product obtained by Japp and Meldrum (J.C.S., 1899, **75**, 1035) by condensation of benzoin (I) with resorcinol (II) is 6-hydroxy-2 : 3-diphenylcoumarone, m.p. 118—120° (*Ac* derivative, m.p. 112°), since oxidation of its *Bz* derivative, m.p. 160—162°, with CrO_3–AcOH affords 2 : 4-*dibenzoyloxybenzophenone* [synthesised from (II), BzCl, and $AlCl_3$ in CS_2], hydrolysed by 10% NaOH in EtOH to the 2 : 4-(*OH*)$_2$-compound, m.p. 146°. The ultimate product from (I) and (II) (*loc. cit.*) is s-*tetraphenyl*-1 : 2 : 4 : 5-*difuranobenzene* (III), since similar oxidation gives



4 : 6-dibenzoylresorcinol (IV) as its Bz_2 derivative (Doebner, A., 1879, 319). With Br in $CHCl_3$ (III) affords the *meso*-Br_2-derivative, m.p. 291—292°, similarly oxidised to the Bz_2 derivative, m.p. 246—247°, of 2 : 5-*dibromo*-4 : 6-*dibenzoylresorcinol*, m.p. 256°, which is obtained on hydrolysis, and is oxidised by alkaline $KMnO_4$ to BzOH free from Br. With Br in $CHCl_3$ at 0° (IV) gives only the 2-(or 5-)Br_1-derivative, m.p. 212°. With HNO_3 (*d* 1·4) in hot AcOH (III) affords a 4-(or 8-)NO_2-derivative, m.p. 281°, reduced by $NHPh{\cdot}NH_2$ to the corresponding NH_2-compound, m.p. 260° (sinters at 250°), and oxidised to the Bz_2 derivative, m.p. 255°, of the 2-(or 5-)NO_2-derivative of (IV) (BzOH on oxidation). With excess of HNO_3 in boiling AcOH (III) gives a $(NO_2)_4$-derivative, sinters 239°, m.p. 242—243°; as-*tetraphenyl*-1 : 2 : 3 : 4-*difuranobenzene* (V), m.p. 203—204°, is also isolated in small yield in the condensation of 2 mols. of (I) with 1 mol. of (II), and is oxidised to the Bz_2 derivative (resin) of 2 : 4-*dibenzoylresorcinol*+AcOH, m.p. 103—104°. A mixed m.-p. curve of (I) and (II) gives a eutectic but no indication of a mol. compound. J. W. B.

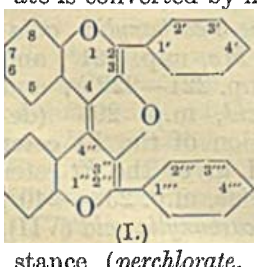
Vegetable, fish, and insect poisons. VI. Relation of toxicarol to rotenone. A. BUTENANDT and G. HILGETAG (Annalen, 1933, **506**, 158—171; cf. A., 1932, 751).—Rotenone (I) (as *A*) probably

reacts in alkaline solution as *B*; the formation of toxicaric (=dehydronetoric) acid (*loc. cit.*) [isolated in about 1% yield from the mixture of acids obtained by oxidation (H_2O_2, EtOH–KOH) of (I)], and the optical inactivity of *iso*rotenol and *isorotenone*isoxime, m.p. 194° (prepared by oxidation of *iso*rotenone in alkaline solution) are thus readily explained.



β-Dihydrorotenone is reduced (Zn dust, EtOH–KOH) to β-*dihydrorotenol*, m.p. 110°. (I) can also react in its enolic form. The reactions (lit.) of toxicarol (II) are discussed from a similar viewpoint (cf. *loc. cit.*; Clark, A., 1932, 855). The *monoacetate*, m.p. 182·5°, of (II) is oxidised (EtOH–I) to acetyldehydrotoxicarol, m.p. 235—236°. Similar oxidation of dihydrotoxicarol gives iododihydrodehydrotoxicarol, which is reduced (Zn, AcOH) to *dihydrodehydrotoxicarol* (III), m.p. 260° [*acetate*, m.p. 108—110° (to a turbid melt), decomp. 230°]; oxidation with H_2O_2 and EtOH–KOH affords a little toxicaric acid. The diacetates of (I) and dihydrotoxicarol are not oxidised (EtOH–I) to any appreciable extent. Dihydrotoxicarol hydrate, $C_{23}H_{24(26)}O_8$ (cf. *loc. cit.*) (*acetate*, m.p. 192°; *benzoate*, m.p. 174°), is prepared by reduction of toxicarol hydrate (*loc. cit.*) or from dihydrotoxicarol and cold alkali; it is converted by EtOH–conc. HCl into (III). H. B.

Pyrylium salts. XXI. Diflavylene oxides. W. Dilthey and W. Höschen (J. pr. Chem., 1933, [ii], **138**, 145—158).—3-Hydroxyflavylium perchlorate is converted by hot Ac_2O and NaOAc or HCO_2Na and HCO_2H into 4 : 4″-*diflavylene* 3 : 3″-*oxide* (I), m.p. 252—260° (decomp.). With NaOAc in EtOH the intermediate 3 : 3″-*dihydroxy*-4 : 4″-*diflavylene*, m.p. 192—193° (+0·5C_6H_6, lost at 100°/vac.) [converted into (I) by hot AcOH, but not by H_2SO_4 or $HClO_4$], and an unidentified substance (*perchlorate*, m.p. 236·5—237·5°; red halochromism in conc. H_2SO_4) are isolated in addition to (I). With I in PhCl (I) gives a *di-iodide*, and with Br an unstable bromide; (I) is readily oxidised (*e.g.*, in Ac_2O) by air to its 4 : 4″-*glycol*, m.p. 201—202° (decomp.). The following derivatives are similarly prepared: 4′ : 4‴-*di*-, m.p. 278—283°; 7 : 7″ : 4′ : 4‴-*tetra*-, m.p. 226—254°; 3′ : 4′ : 3‴ : 4‴-*tetra*-, m.p. 235—240°, and 7 : 7″ : 3′ : 4′ : 3‴ : 4‴-*hexa-acetoxy*-4 : 4″-*diflavylene* 3 : 3″-*oxide*, m.p. 260° (sinters 200°). The deep red colour of (I) is ascribed to partial dissociation at the 4 : 4″-linking into a bivalent radical.



H. A. P.

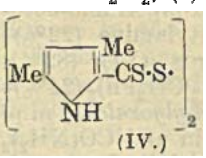
Spirans. J. Böeseken (Inst. int. Chim. Solvay, Conseil Chim., 1931, **4**, 61—100; Chem. Zentr., 1933, i, 227—229).

1 : 3 : 5-Trithian perchlorate. O. Hinsberg (J. pr. Chem., 1933, [ii], **138**, 207—213).—1 : 3 : 5-Trithian, m.p. 216°, is converted by 70% aq. $HClO_4$ at 100° into a basic *perchlorate*, $3C_3H_6S_3,2HClO_4$ (I), m.p. 138° (decomp.), converted by Na picrate into the *picrate*, $C_3H_6S_3,C_6H_3O_7N_3,H_2O$, decomp. 134°. Oxidation of (I) with H_2O_2 in AcOH–Ac_2O gives the normal sulphone, $C_3H_6O_6S_3$, and Ac_2O and NaOAc at the b.p. give s-*diacetylthioldimethyl sulphide*, m.p. 37°. (I) is completely decomposed by boiling H_2O with formation of MeSH etc.; with bases it gives amorphous products and with KOH–EtOH a *substance*, m.p. 93°.

H. A. P.

Trimethylene trisulphide of m.p. 247°. O. Hinsberg (J. pr. Chem., 1933, [ii], **138**, 214).—1 : 3 : 5-Trithian, m.p. 247°, has the formula $C_3H_6S_3$ and is not formed from the isomeride, m.p. 216°, with all reducing agents; therefore it cannot be a hydroderivative as suggested by Chattaway and Kellett (A., 1931, 1071). H. A. P.

Reactions of magnesyl-2 : 4-dimethylpyrrole. F. Ingraffia (Gazzetta, 1933, **63**, 584—591).—The Mg derivative (I) of 2 : 4-dimethylpyrrole treated with $ClCO_2Et$ gives *Et* 2 : 4-*dimethylpyrrole*-5-*carboxylate* (II), m.p. 124° (the 3-carboxylate has m.p. 75—76°). With SO_2Cl_2, (I) forms 3 : 5 : 3′ : 5′-*tetramethyldipyrryl*-(2 : 2′)-*sulphone*, decomp. 95°; with CS_2 the products are 2 : 4-*dimethylpyrrole* - 5 - *dithiocarboxylic acid* (III) (*Pb* and *Ag* salts), and the *disulphide* (IV), m.p. 156°, into which (III) is at once converted when isolated. The Mg derivative of (II) does not react with CS_2 or AcCl; the Mg may be attached through the enolic form of the ester.



E. W. W.

Synthesis and reactions of nitrogen ring-compounds over nickel. C. F. Winans and H. Adkins (J. Amer. Chem. Soc., 1933, **55**, 4167—4176).—Pyrroles are obtained by reduction (H_2 at 100—200 atm., Raney Ni catalyst) of equimol. mixtures of α-oximinoketones (I) and ketones containing a reactive CH_2 group in EtOH at 50—90°; (I) similarly give pyrazines. γ-Cyanopropionic esters are similarly reduced in Et_2O to 2-pyrrolidones. Thus,
CN·CHPh·CO·CO_2Et gives 26% of 2 : 3-*diketo*-4-*phenylpyrrolidine*, m.p. 288—289°;
CN·CHPh·CH_2·CO_2Et affords 89% of 4-phenyl-2-pyrrolidone; CN·CH_2·CH_2·CO_2Et yields 38% of 2-pyrrolidone; Et γ-oximinovalerate furnishes 63% of 5-methyl-2-pyrrolidone; (·CMe:N·OH)$_2$ gives (·CHMe·NH_2)$_2$ (18%) and 2 : 3 : 5 : 6-tetramethylpyrazine (76%); benzilmonoxime affords
NH_2·CHPh·CHPh·OH (36%) and 2 : 3 : 5 : 6-tetraphenylpyrazine (42%); Et oximinoacetoacetate (II) yields 43% of Et 2 : 5-dimethylpyrazine-3 : 6-dicarboxylate; OH·N:CH·COPh (III) furnishes 54% of 2 : 5-diphenylpyrazine; 2-oximino-α-hydrindone (IV) gives 78% of 2 : 3 : 5 : 6-*di-indenopyrazine*, m.p. 270—271°; (II) + CH_2Ac_2 afford 63% of Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate; (II) + CH_2Ac·CO_2Et (V) yield 67% of Et 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate; (III) + (V) furnish 35% of Et 4-phenyl-2-methylpyrrole-3-carboxylate; CAc_2:N·OH+(V) give 74% of Et 5-acetyl-2 : 4-dimethylpyrrole-3-carboxylate; CBz_2:N·OH+(V) afford *Et* 2-*benzoyl*-3-*phenyl*-5-*methylpyrrole*-4-*carboxylate* (51%), m.p. 156—157°; (IV)+(V) yield *Et* 4 : 5-*indeno*-2-*methylpyrrole*-3-*carboxylate* (44%), m.p. 199—200°, and *Et* β-(1-*hydroxy*-2-*hydrindenylamino*)*butyrate* (39%), m.p. 95—96°;

CBzAc:N·OH+(V) furnish 56% of Et 5-benzoyl-2 : 4-dimethylpyrrole-3-carboxylate; (II) + $CH_2Bz·CN$ give 23% of *Et* 3-*cyano*-2-*phenyl*-4-*methylpyrrole*-5-*carboxylate*, m.p. 85—86°.

Hydrogenation of glyoxalones at 200° using a Ni-kieselguhr catalyst gives saturated derivatives. Pyrazolones undergo hydrogenolysis (usually with loss of NH_3) at 120—150° in EtOH. α-Aminonitriles give some αβ-diamines (a satisfactory general method has not been developed) at 80—100° in EtOH, whilst α-piperidinonitriles generally undergo hydrogenolysis ($C_5H_{10}N·CHR·CN \longrightarrow C_5H_{10}NH + CH_2R·CH_2·NH_2$). Thus, CH_2:N·CH_2·CN gives $NHMe·CH_2·CH_2·NH_2$ (66%) and di-(β-methylaminoethyl)amine (18%), b.p. 95—100°/25 mm. (*tripicrate*, m.p. 172—173°); $NEt_2·CH_2·CN$ affords $NEt_2·CH_2·CH_2·NH_2$ (37%) and di-(β-diethylaminoethyl)amine (23%), b.p. 130—135°/26 mm. (*tripicrate*, m.p. 165—166°); piperidinoacetonitrile yields β-piperidinoethylamine (50%) and di-(β-piperidinoethyl)amine, b.p. 160—170°/22 mm. (*tripicrate*, m.p. 210—211°); α-piperidinoisobutyronitrile furnishes 78% of piperidine (VI); α-piperidino-octonitrile gives (VI) (79%) and *n*-octylamine (22%); α-piperidinophenylacetonitrile affords (VI) (82%), $CH_2Ph·CH_2·NH_2$ (50%), and $NH(CH_2·CH_2Ph)_2$ (24%); 4 : 5-diphenyl- and 4 : 5-*dicyclohexyl*-*glyoxalone*, m.p. 287—289° [from dodecahydrobenzoin and $CO(NH_2)_2$ in AcOH], both yield 4 : 5-*dicyclohexyldihydroglyoxalone*, m.p. 237—239°; 4 : 5-*diethylglyoxalone*, m.p. 293—294° [from propionylethylcarbinol and $CO(NH_2)_2$ in AcOH], furnishes 4 : 5-*diethyldihydroglyoxalone*, m.p. 192—193°; 1-phenyl-3-methyl-5-pyrazolone gives 68% of butyranilide; 1 : 3-diphenyl-5-pyrazolone affords 95% of β-phenylpropionanilide; 1-phenyl-4-benzylidene-3-methyl-5-pyrazolone yields 80% of β-amino-α-benzylbutyranilide (*hydrochloride*, m.p. 155—156°) (NH_3 is not formed in this case). H. B.

Electrochemical reduction of pyridine.—See this vol., 1254.

Action of ultra-violet light on pyridine. IV. Formation of photo-products from pyridine derivatives in spectrally resolved ultra-violet light. H. Freytag (J. pr. Chem., 1933, [ii], **138**, 264—267; cf. this vol., 513).—Formation of photopyridine derivatives by irradiation with individual lines of the ultra-violet spectrum is determined for C_5H_5N and its 2-, 3-, and 4-Me, 2 : 4- and 2 : 6-Me_2, 2 : 4 : 6-Me_3 (I), 2 : 3 : 4 : 5-$(CO_2H)_4$, 2-NH_2- (II), and 3-NH_2- (III) derivatives. With the exception of (III), which is most affected at λ 365, 313, and 302 mμ, the active lines have λ 265, 254, and to a smaller extent 248 and 240 mμ. (I) is almost and (II) quite unaffected after 2 hr. H. A. P.

Rosenmund aldehyde synthesis in pyridine series. R. Graf [with P. László] (J. pr. Chem., 1933, [ii], **138**, 231—238; cf. A., 1932, 1039).—The Rosenmund reaction proceeds the more rapidly the more Cl groups are present in the nucleus. Replacement of Cl by the less negative Br results in very low conversion into aldehyde. The following are described: 4 : 5 : 6-*trichloropyridine*-2-*aldehyde* (I), m.p. 94—95° [(+$2H_2O$), m.p. 65—67° (sealed tube); *phenylhydrazone*, m.p. 216—217° (rapid heating)] (accompanied by 2 : 3 : 4-*trichloropyridine*, m.p. 45—47°); 5-*chloro*-, m.p. 69—70° [*phenylhydrazone*, m.p. 159—161° (rapid heating)], and 5-*bromo*-*pyridine*-3-*aldehyde* (only isolated as *phenylhydrazone*, m.p. 156—157°). Formation of 2 : 6-dibromopyridine-4-aldehyde was detected only by colour reactions. (I) is converted by the Cannizzaro reaction into 4 : 5 : 6-*trichloro*-2-*hydroxymethylpyridine*, m.p. 84°. H. A. P.

5-Chloro- and 5 : 6-dichloro-nicotinic acids. R. Graf [with E. Lederer-Ponzer, V. Kopetz, R. Purkert, and P. László] (J. pr. Chem., 1933, [ii], **138**, 244—258).—Interaction of nicotinic acid hydrochloride with a large excess of $SOCl_2$ at the b.p. for 5 days and then at 180° for 12 hr. gives 5-chloro- (I) and 5 : 6-dichloro-nicotinic acid (II), separated by the insolubility of the hydrochloride of (I) in $SOCl_2$. 5-*Aminopyridine*-3-*carboxylic acid*, m.p. 288—290° (decomp.) (from the Me ester, cf. A., 1928, 1379), is converted by standard methods into the following: 5-bromopyridine-3-carboxylic acid, m.p. 182—183° (identical with Claus' acid, A., 1887, 158) [*chloride*, m.p. 74—75°, b.p. 112°/12 mm.; *Me*, m.p. 98—99°, and *Ph*, m.p. 86—87°, esters; s-*di*-(5-*bromo*-3-*pyridoyl*)*hydrazine*, m.p. 308° (decomp.); 5-*bromo*-3-*pyridoyl*-*hydrazide*, m.p. 193—194° (*CHPh*: derivative, m.p. 191—193°), and -*azide* (III), m.p. 88—89° (decomp.)], *Et*, m.p. 150—151° (IV), and *Me* 5-*bromo*-3-*pyridylcarbamate*, m.p. 169—170° (decomp.) [from (III) and EtOH or MeOH]; *Na* 5-*bromo*-3-*pyridylcarbamate* (V) [from (IV) and 30% aq. NaOH]; 5-bromo-3-aminopyridine, m.p. 66—67°, b.p. 149—150°/12 mm. [from (V) and dil. HCl] {*Ac* derivative, m.p. 127—128° [(+$2H_2O$), m.p. 76—78° (sealed tube, rapid heating)]; *picrate*, m.p. 212—213°; *chloroaurate*, m.p. 185—187°}; ɔ-*iodopyridine*-3-*carboxylic acid*, m.p. 220° (*Ph*, m.p. 100—101°, *Me*, m.p. 121°, and *Et* ester, m.p. 86—87°; *amide*, m.p. 221—222°); and 5-*hydroxypyridine*-3-*carboxylic acid*, m.p. 299° (decomp., rapid heating). Interaction of the Et ester of (II) with N_2H_4,H_2O in EtOH gives the *Et* ester (VI), m.p. 137—138°, and *hydrazide*, m.p. 238—240°, of ɔ-*chloro*-6-*hydrazinopyridine*-3-*carboxylic acid* (VII), m.p. 248—249° [alkaline hydrolysis of (VI)]. HNO_2 converts (VI) into *Et* 5-*chlorobenztetrazole*-3-*carboxylate*, m.p. 95—96° (free *acid*, m.p. 195—196°), oxidised by alkaline $KMnO_4$ to tetrazole. With hot HCO_2H (VII) gives 5-*chlorobenztriazole*-3-*carboxylic acid*, m.p. > 300°. Excess of aq. NH_3 at 180—190° converts (II) into 5-*chloro*-6-*amino*-, m.p. 323° (decomp.) (*Me* ester, m.p. 163—165°), which with HNO_2 gives 5-*chloro*-6-*hydroxy*-*pyridine*-3-*carboxylic acid*, m.p. 218°. H. A. P.

Nuclear-substituted pyridine-β-carboxydiethylamides. R. Graf [with A. Theyerl and R. Purkert] (J. pr. Chem., 1933, [ii], **138**, 259—263).—The *diethylamides* of *pyridine*-3 : 5-*dicarboxylic acid*, m.p. 73—75°, ɔ-*bromo*-, b.p. 189°/12 mm., and 5 : 6-*dichloro*-*pyridine*-3-*carboxylic acid* (I), b.p. 191—192°/12 mm., are prepared from the acid chloride and $NHEt_2$ in $CHCl_3$; those of 2-*methylpyridine*-5-*carboxylic acid*, b.p. 160—164°/12 mm., and 2 : 6-*dimethylpyridine*-3 : ɔ-*dicarboxylic acid*, m.p. 82—83°, b.p. 236°/12 mm., from the azide and $NHEt_2$ in Et_2O. Interaction of (I) with N_2H_4,H_2O in EtOH gives the 6-hydr-

azino-derivative, converted by HNO_2 into 5-*chlorobenztetrazole*-3-*carboxydiethylamide*, m.p. 113—115°. H. A. P.

Aliphatic keto-anils. W. H. Cliffe (J.C.S., 1933, 1327—1331).—Interaction of equimol. quantities of $COMe_2$ and NH_2Ph (containing 1% I) affords 2 : 2 : 4-trimethyl-1 : 2-dihydroquinoline (I) (cf. A., 1932, 1142), bromination of which in MeOH affords 3 : 4 : 6 : 8-*tetrabromo*-2 : 2 : 4-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 160°, with a *substance*, m.p. 181—182°. (I) with oleum at room temp. during 16 hr. affords 2 : 2 : 4-*trimethyl*-, decomp. above 360°, and 1 : 2 : 2 : 4-tetramethyl-1 : 2-dihydroquinoline (II) (cf. A., 1924, i, 205) similarly gives 1 : 2 : 2 : 4-*tetramethyl*-1 : 2-*dihydroquinoline*-7-*sulphonic acid*, decomp. 323°. (I) and (II) with CH_2O, dil. H_2SO_4, and a trace of *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ afford respectively 6 : 6′-*bis*-(2 : 2 : 4-*trimethyl*-, and -(1 : 2 : 2 : 4-*tetramethyl*-1 : 2-*dihydroquinolino*)*methane*, oxidised to hydrols by PbO_2 in AcOH. (I) with PhCHO and $ZnCl_2$ at 100° in 2 hr. affords 6 : 6′-*bis*-(2 : 2 : 4-*trimethyl*-1 : 2-*dihydroquinolino*)*phenylmethane*, m.p. 158°, oxidised (PbO_2) to a dye. Similar dyes are obtained from (I) with *o*-$OMe{\cdot}C_6H_4{\cdot}CHO$ or *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$, and from (II) with PhCHO. These substances dye tannin-mordanted cotton. 2 : 2 : 4 : 7-Tetramethyl-1 : 2-dihydroquinoline (III) (cf. A., 1921, i, 785) (*hydrochloride*, m.p. 224°; *nitrate*, m.p. 149—151°; *Ac* derivative, m.p. 85°; *Bz* derivative, m.p. 108·5°) affords with Me_2SO_4 in EtOH, followed by NaOH, 1 : 2 : 2 : 4 : 7-*pentamethyl*-1 : 2-*dihydroquinoline*, b.p. 162—163°/18 mm. (*picrate*, m.p. 171°; *hydriodide*, m.p. 242·5°), whereas with PhNCO, (III) affords 1-*phenylcarbamyl*-2 : 2 : 4 : 7-*tetramethyl*-1 : 2-*dihydroquinoline*, m.p. 149°. Interaction of *m*-$C_6H_4Cl{\cdot}NH_2$, boiling $COMe_2$, and I in 30 hr. affords 7-*chloro*-2 : 2 : 4-*trimethyl*-1 : 2-*dihydroquinoline*, m.p. 38·5° [*hydrochloride*, m.p. 202° (decomp.); *nitrate*, m.p. 131—132° (decomp.); *methosulphate*, m.p. 140°; *Ac* derivative, m.p. 76—77°; N-*methylhydriodide*, m.p. 142—144°; *PhNCO* derivative, m.p. 160°]. Similarly, *p*-$C_6H_4Cl{\cdot}NH_2$ affords 6-*chloro*-2 : 2 : 4-*trimethyl*-1 : 2-*dihydroquinoline*, m.p. 61·5° [*hydrochloride*, m.p. 196° (decomp.)]. The analogous 8-Cl-compound is formed only in poor yield. COMeEt affords 2-methyl-2 : 4-diethyl-1 : 2-dihydroquinoline (IV) (*Ac* derivative, b.p. 173—179°/12·5 mm.; *nitrosoamine*) together with some 2-methyl-4-ethylquinoline (V) (cf. A., 1921, i, 785), into which it is easily converted. Similarly, *o*- and *p*-$C_6H_4Me{\cdot}NH_2$, and *m*-xylidine with COMeEt afford compounds analogous to (IV) and (V). J. L. D.

Synthesis of quinoline derivatives. IV. K. Dziewoński, J. Moszew, T. Chechliński, and I. Pietrzykowska (Rocz. Chem., 1933, **13**, 530—539).—*p*-Tolyl Me ketone (I) when heated at 180—260° during 6 hr. with $CS(NHPh)_2$ yields 4-*anilino*-2-*p*-*tolylquinoline* (II), m.p. 139—140° [*picrate*, m.p. 246°; *hydrochloride*, m.p. 175—176°; 4-N-*NO*-, m.p. 185—186° (decomp.), and 4-N-*Ac* derivative, m.p. 154—155°]. (II) when fused with KOH yields 4-*hydroxy*-*p*-*tolylquinoline*, m.p. 277—278°. 4-*p*-*Tolylamino*-2-*p*-*tolylquinoline*, m.p. 171—172° (*picrate*, m.p. 267—268°; *hydrochloride*, m.p. 302—303°; 4-N-*NO*-, m.p. 202°, and 4-N-*Ac* derivative, m.p. 164—165°), is prepared from (I) and di-*p*-tolylthiocarbamide, and 4-*anilino*-2-*p*-*anisylquinoline*, m.p. 190° [*picrate*, m.p. 257°; *nitrate*, m.p. 205° (decomp.); 4-N-*NO*-, m.p. 212° (decomp.), and 4-N-*Ac* derivative, m.p. 132°], is obtained from *p*-anisyl Me ketone (III) and $CS(NHPh)_2$, or from the anil of (III) and PhNCS. 4-Hydroxy-2-phenylquinoline when heated at 220—240° with $(NH_4)_2SO_3$ and aq. NH_3 yields the corresponding 4-NH_2-derivative; on coupling with the appropriate diazonium salts it gives the corresponding 3-*p*-*nitrobenzeneazo*-, m.p. 235—236°, 3-α-, m.p. 243—244°, and 3-β-*naphthaleneazo*-, m.p. 145—146°, -derivatives. 4-Amino-2-phenyl-6-methylquinoline (*picrate*, m.p. 210°; 4-N-*Ac* derivative, m.p. 164—165°) and 4-*hydroxy*-3-*p*-*nitrobenzeneazo*-2-*phenyl*-6-*methylquinoline*, m.p. 252° (decomp.), are prepared analogously from 4-hydroxy-2-phenyl-6-methylquinoline. R. T.

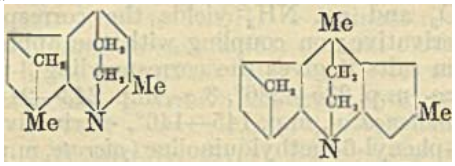
Nitrogen compounds in petroleum distillates. IV. Cumulative extraction of kerosene bases. Isolation of 2 : 4 : 8-trimethylquinoline. T. S. Perrin and J. R. Bailey. **V. Use of sulphur dioxide in the separation of petroleum bases.** B. S. Biggs and J. R. Bailey. **VI. Occurrence of 2 : 8-dimethylquinoline in the crude kerosene distillate of California petroleum.** G. R. Lake and J. R. Bailey. **VII. Reactions of the naphthenic base, $C_{16}H_{25}N$. New naphthenic base, $C_{13}H_{21}N$.** B. F. Armendt and J. R. Bailey (J. Amer. Chem. Soc., 1933, **55**, 4136—4140, 4141—4142, 4143—4145, 4145—4149).—IV. A "cumulative extraction" method of separation of the aromatic (I) and non-aromatic (II) kerosene bases, involving the wide difference in the distribution ratio of their hydrochlorides between H_2O and $CHCl_3$, is described in detail. The hydrochlorides of (II) are readily sol. in $CHCl_3$ [whilst those of (I) are less sol.] and in H_2O (whereas the hydrochlorides of some of the methylquinolines crystallise readily from H_2O). The base $C_{16}H_{25}N$ (A., 1930, 788), and 2 : 3 : 8- (*loc. cit.*) and 2 : 4 : 8-trimethylquinoline, b.p. 280°(corr.)/746 mm. (lit. 269—270°) [which with *o*-$C_6H_4(CO)_2O$ at 200° gives a *phthalone*, m.p. 282°], are now extracted from a base fraction, b.p. 273°. A small amount of a new base, $C_{12}H_{13}N$, and 2 : 3-dimethylquinoline are also separated from the residual bases from the fraction, b.p. 263—267°, after separation of 2 : 3- and 2 : 4-dimethylquinoline with SO_2 (see below). The results of the cumulative extraction of kerosene bases, b.p. 182—350°, are given; quinoline, *iso*quinoline, and 2- and 4-methylquinolines could not be detected.

V. Treatment of a base fraction, b.p. 263—267°, with SO_2 in Et_2O gives a viscous product, which when treated with *s*-$(NO_2)_3C_6H_2{\cdot}OH$ in EtOH affords a mixture of the picrates of 2 : 3-, b.p. 273°/750 mm., m.p. 67° (*H sulphate*; *picrate*, m.p. 231°), and 2 : 4-, b.p. 274°/756 mm. (lit. 264—265°) (*chloroplatinate*; *picrate*, m.p. 194°), -dimethylquinolines.

VI. 2 : 8-Dimethylquinoline, b.p. 252·4°/754 mm., m.p. 24° (lit. 27°) [*H sulphate*, m.p. 187°; *perchlorate*, m.p. 189°; *hydrochloride mercurichloride*, m.p. 211°; *phthalone*, m.p. 283° (decomp.)], is isolated by the cumulative extraction process from the base fraction, b.p. 253—256°.

VII. A *base*, $C_{13}H_{21}N$, b.p. 225·6°/750 mm., m.p.

24·5° [*picrate*, m.p. 158·7°; *hydrochloride mercurichloride*, m.p. 131·6°; *chloroplatinate*, m.p. 205° (decomp.); *H sulphate*, m.p. 155°], has been isolated in 0·004% yield from the base fraction, b.p. 215—216°; structure (I) is assigned provisionally. The base $C_{16}H_{25}N$ (*loc. cit.*) reacts unexpectedly with *o*-$C_6H_4(CO)_2O$ at 200° to give a *phthalone*, m.p. 208°,

(I.)  (II.)

and forms a *dibenzylidene* derivative, m.p. 120—121° [*picrate*, m.p. 249—250° (decomp.); *hydrochloride*, m.p. 241—242°]; structure (II) is now assigned (cf. A., 1931, 631). Neither of the above bases could be oxidised (alkaline $KMnO_4$), reduced (Adams), or dehydrogenated; a methiodide and phthalone could not be obtained from the former. Methyl*cyclo*pentane does not condense with *o*-$C_6H_4(CO)_2O$ in absence or presence of $ZnCl_2$. H. B.

***iso*Quinoline derivatives. II. Synthesis of 6 : 7-dimethoxy-1-aminomethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline.** H. J. Harwood and T. B. Johnson (J. Amer. Chem. Soc., 1933, **55**, 4178—4180).—Homoveratrylamine (I), phthalimidoacetyl chloride, and 6% aq. Na_2CO_3 give *phthalimidoacethomoveratrylamide*, converted by $POCl_3$ in PhMe into 6 : 7-*dimethoxy*-1-*phthalimidomethyl*-3 : 4-*dihydroiso*-*quinoline* [*sulphate* (+H_2O), m.p. 229—231°; "phosphate" (II), obtained by crystallisation of the reaction product from H_2O]. This is reduced (H_2, PtO_2, dil. HCl) to 6 : 7-dimethoxy-1-phthalimidomethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline [*hydrochloride*; "phosphate" (III), m.p. 244—245° (decomp.), prepared by reduction (H_2, PtO_2, H_2O) of (II)]. (III) is hydrolysed (N_2H_4,H_2O method) to 6 : 7-dimethoxy-1-aminomethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline [sulphate, m.p. about 274—275° (decomp.)]. Ring closure of *triazoacethomoveratrylamide* [from (I), triazoacetyl chloride, and aq. NaOH] or *aminoacethomoveratrylamide* could not be accomplished; *phthalimidoacet*-β-*phenylethylamide* gives a trace of product. H. B.

Reactivity of groups in substituted acridones. II. Cationoid activity at position 4 in acridones. H. B. Nisbet (J.C.S., 1933, 1372—1373).—The following have been prepared (cf. this vol., 74): 2 : 5-*dichloro*-, m.p. 232°, 2 : ɔ-*dibromo*-, m.p. 229—230°, 5-*chloro*-2-*methyl*-, m.p. 180—181°, and ɔ-*chloro*-2-*nitrodiphenylamine*-6′-*carboxylic acid*, m.p. 228°; 1 : 4-*dichloro*-, m.p. 268°, 1 : 4-*dibromo*-, m.p. 232—233°, 4-*chloro*-1-*methyl*-, m.p. 298°, and 4-*chloro*-1-*nitroacridone*, m.p. 240°. The last-named and $C_5H_{11}N$ give 1-*nitro*-4-*piperidinoacridone*, m.p. 192°. F. R. S.

Ethyl γ-phenylacetoacetate. A. Sonn and W. Litten (Ber., 1933, **66**, [*B*], 1512—1520).—Agitation of Et α-phenylacetylacetoacetate with 0·5% NH_3 affords Et γ-phenylacetoacetate (I), b.p. 153—155°/9 mm., in 40% yield; the *Cu* salt, m.p. 176—178°, *semicarbazone*, m.p. 113—116°, non-cryst. *oxime*, and *anil*, m.p. 96—98·5°, are described. (I) and N_2H_4,H_2O in Et_2O yield 3-*benzylpyrazol*-ɔ-*one*, m.p. 197—198°. (I) and $NHPh{\cdot}NH_2$ at 140° give 3-benzyl-1-phenylpyrazol-5-one, more readily obtained from $CH_2Ph{\cdot}CO{\cdot}CH(CO_2Et)_2$ and $NHPh{\cdot}NH_2$ in AcOH, converted by MeI in MeOH at 100—110° or by Me_2SO_4 and NaOMe at 60—70° into 1-*phenyl*-3-*benzyl*-2-*methylpyrazol*-ɔ-*one* (II), m.p. 105—106° [*hydrochloride*, m.p. 175—181° (decomp.) after softening at 165°; *NO*-derivative; 4-NO_2-compound, m.p. 193—195°]. (II) and Br in $CHCl_3$ yield 3 : 4-*dibromo*-1-*phenyl*-3-*benzyl*-2-*methylpyrazol*-ɔ-*one*, m.p. 204—206°, transformed by recrystallising from H_2O into 4-*bromo*-1-*phenyl*-3-*benzyl*-2-*methylpyrazol*-ɔ-*one*, m.p. 116—117°, whence 4-*dimethylamino*-1-*phenyl*-3-*benzyl*-2-*methylpyrazol*-5-*one*, m.p. 111—113° (*hydrochloride*, m.p. 168—171° after softening at 150°). Condensation of Et α-formyl-β-phenylpropionate with $NHPh{\cdot}NH_2$ leads to 1-*phenyl*-4-*benzylpyrazol*-5-*one*, m.p. 146—147°, whence 1-*phenyl*-4-*benzyl*-2-*methylpyrazol*-5-*one*, m.p. 77·5—79°. 1-*Phenyl*-3 : 4-*dibenzylpyrazol*-5-*one* has m.p. 139—141° after softening at 138°. (I) is converted by Na and subsequently by I in Et_2O into *Et*$_2$ *di*-αβ-*phenylacetylsuccinate*, m.p. 119—120°. (I), conc. H_2SO_4, and phloroglucinol or *m*-$C_6H_4(OH)_2$ give respectively 5 : 7-*dihydroxy*-, decomp. 260°, and 7-*hydroxy*-4-*benzylcoumarin*, m.p. 214—215°. 4-*Hydroxy*-2-*thiol*-6-*benzylpyrimidine*, m.p. 216—219° (gradual decomp.), is derived from (I), $CS(NH_2)_2$, and NH_4CNS in presence of a little conc. HCl. ω-Aminoacetophenone hydrochloride and (I) in boiling 90% EtOH yield *Et* 4-*phenyl*-2-*benzylpyrrole*-3-*carboxylate*, m.p. 94—95°; the corresponding *acid*, m.p. 203—205° (decomp.) after darkening at 193° and softening at 195—196°, is decarboxylated by Cu powder at about 200° to 4-phenyl-2-benzylpyrrole, m.p. 91—93°. 2 : 4-*Diketo*-3-*phenylacetyl*-6-*benzyl*-3 : 4-*dihydropyran*, m.p. 127—128°, is obtained as by-product in the prep. of (I). 1-Phenyl-2 : 4-dimethyl-3-bromomethylpyrazol-5-one is transformed by $CNaEt(CO_2Et)_2$ into *Et*$_2$ 4-*methyl*-3-*antipyrylethylmalonate*, m.p. 115—117°, which condenses with NaOEt and $CO(NH_2)_2$ to 4-*methyl*-3-*antipyryl*-C-*ethylbarbituric acid*, m.p. > 250° (*Na* salt. Antipyrine and Br in $CHCl_3$ yield *antipyrine perbromide*, m.p. 159—161° after softening at 156°, transformed by hot H_2O into 4-bromoantipyrine, m.p. 117°. H. W.

Alkylation of pyrazolones. A. Sonn and W. Litten (Ber., 1933, **66**, [*B*], 1582—1588).—"Technical pyrazolone" (I) is unaffected by boiling Pr$^\alpha$Br, whereas at 130—135° much decomp. occurs with production of small amounts of the *compound* $C_{13}H_{16}ON_2$, m.p. 90—91° (*picrate*, m.p. 155—158°). Antipyrine (II) and Pr$^\alpha$Br reacted at 190°, yielding unchanged material and (I). (II) and boiling CH_2PhCl yield dibenzylpyrazolone (III), m.p. 140°, whereas at 180° unchanged (II), (I), (III), and 1-phenyl-4-benzyl-3-methylpyrazolone result. 1-Phenyl-2-benzyl-3-methyl- and the corresponding 4-benzylpyrazolones and CH_2PhCl afford only (III). The behaviour of (I) and CH_2PhCl under widely varied conditions is described. 1-*Phenyl*-2-*benzyl*-3 : 4-*dimethylpyrazol*-ɔ-*one*, m.p. 128·5—130°, is formed from the 1-phenyl-3 : 4-dimethyl compound and 1-

phenyl-2-benzyl-5-methylpyrazol-3-one, m.p. 103—104° (*picrate*, m.p. 106—109°; *hydrochloride*, m.p. 155—158°), from the 1-phenyl-5-methyl derivative. 1-*Phenyl-2-benzylpyrazol-5-one*, m.p. 125—126°, results from 1-phenylpyrazol-5-one. Pyrazolone and MeCl at 150° give unchanged material, (I), and (II), whereas at 180° small amounts of 1-phenyl-4-benzyl-3-methylpyrazolone, m.p. 146°, result. The dibenzylpyrazolone, m.p. 91°, is regarded as 4 : 4-dibenzylpyrazolone, since it is reduced by Na and amyl alcohol to 4-benzylpyrazolone and small amounts of a compound with the colour reactions characteristic of hydroxypyrazolines. (II) is regarded as 5-benzyloxy-4-benzylpyrazole on account of its colour reactions with $FeCl_3$ and $C(NO_2)_4$ and its behaviour towards Br. H. W.

Action of chlorine on the 3-carbethoxy-4-hydroxy-1-nitrophenylpyrazoles. F. D. Chattaway and D. R. Ashworth (J.C.S., 1933, 1389—1393).—Cl_2 with 3-carbethoxy-4-hydroxy-1-nitrophenylpyrazoles in $CHCl_3$ or AcOH gives 5 : 5-*dichloro-3-carbethoxy*-1-p- (I), m.p. 131°, -o-, m.p. 98°, and -m-*nitrophenyl*-, m.p. 135°, and -1-(2′-*chloro*-4′-*nitrophenyl*)-4-*pyrazolone*, m.p. 87°, which with KI–AcOH form, respectively, I and 5-*chloro*-3-*carbethoxy*-4-*hydroxy*-1-p-, m.p. 146° (*Ac* derivative, m.p. 121·5°), -o-, m.p. 142°, and -m-*nitrophenyl*-, m.p. 109°, and -1-(2′-*chloro*-4′-*nitrophenyl*)-*pyrazole*, m.p. 191°. (I) and EtOH yield *Et diketosuccinate*-p-*nitrophenylhydrazone* (II), m.p. 125°, identical with that from diazotised p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and Et oxalacetate. Similarly, (I) and the appropriate alcohol give 2-*Me* 1-*Et*, m.p. 138°, 1-*Et* 2-*Pr*$^{\alpha}$, m.p. 92°, and 1-*Et* 2-CH_2Ph *diketosuccinate*-1-p-*nitrophenylhydrazone*, m.p. 147°; 2-*Me* 1-*Et diketosuccinate*-1-(2′-*chloro*-4′-*nitrophenylhydrazone*), m.p. 115°, and 2′-*Br*-compound, m.p. 126°; 2-*Me* 1-*Et diketosuccinate*-1-o-, m.p. 116°, and -m-*nitrophenylhydrazone*, m.p. 105°; and *Et diketosuccinate*-m-*nitrophenylhydrazone*, m.p. 84°. 3-Carbethoxy-4-hydroxy-1-(2′ : 6′-dichloro-4′-nitrophenyl)pyrazole and Cl_2 yield the 5-*Cl*-derivative, m.p. 200°. (II) and p-nitrophenylhydrazine form *Et diketosuccinate*-p-*nitrophenylosazone*, m.p. 190°, which with C_5H_5N gives *Et* 4 : 5-*diketo*-1-(4′-*nitrophenyl*)*pyrazolone*-3-*carboxylate*-4-(4″-*nitrophenyl*-*hydrazone*), m.p. 257° (decomp.), and (II) with NH_2OH,HCl affords *Et diketosuccinateoximino*-p-*nitrophenylhydrazone*, m.p. 163° (decomp.), which with NaOAc–AcOH gives 3-*carbethoxy*-4-*keto*isooxazolone-4-p-*nitrophenylhydrazone*, m.p. 186° (decomp.). (II) and Br form Et α-bromoglyoxylate-p-nitrophenylhydrazone and with Cl_2 the Cl-compound is obtained. (I) and NaOH yield 1-*Et* 2-*H diketosuccinate*-p-*nitrophenylhydrazone*, m.p. 141°, which with EtOH–HCl gives *diketosuccinic anhydride* p-*nitrophenylhydrazone*, m.p. 243° (decomp.), and with Ac_2O forms 3-*carbethoxy*-4 : o-*diketo*-1-p-*nitrophenylpyrazolone hydrate*, m.p. 95—105°, converted by NH_2OH,HCl into 4-*oximino*-3-*carbethoxy*-1-p-*nitrophenyl*-5-*pyrazolone*, decomp. > 222°. F. R. S.

Extractives of muscle. XXXV. Biological transformation of carnosine. A. Parschin (Z. physiol. Chem., 1933, **219**, 245—248).—Carnosine is degraded by yeast and *Oidium lactis* probably to NH_3 and CO_2, since intermediate products could not be isolated. J. H. B.

Pyrimidines. CXXXVII. Synthesis of 5-acetyluracil. W. Bergmann and T. B. Johnson (Ber., 1933, **66**, [*B*], 1492—1496).—Et ureidomethyleneacetoacetate (I) is rapidly converted by NaOEt in hot EtOH into *Et* 2-*keto*-6-*methyl*-1 : 2-*dihydropyrimidine*-5-*carboxylate* (II), m.p. 248—250° (decomp.) (*benzylidene* derivative, m.p. 194°), reduced (Pt-black–H_2) to Et 2-keto-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate, m.p. 161—162°, also obtained by hydrogenation of (I) with subsequent ring closure (cf. Folkers *et al.*, A., 1932, 1144). Dissolution of (I) in hot 7·5% KOH followed rapidly by acidification of the solution leads to 5-*acetyluracil* (III), m.p. 294° (decomp.), also obtained from (II). (III) gives an *oxime*, m.p. 254° (decomp.), and *phenylhydrazone*, m.p. 238°, and is reduced (Pt–H_2, H_2O at 60°) to 5-*acetyldihydrouracil*, m.p. 204°. H. W.

Pyrimidines. Molecular rearrangement of 6-thiocyano-2-ethylthiol-5-phenylpyrimidine. Y. F. Chi and Y. L. Tien (J. Amer. Chem. Soc., 1933, **55**, 4181—4184).—2-*Ethylthiol*-5-*phenyluracil*, m.p. 153—154° [from SEt·C(:NH)·NH_2,HBr and the Na salt of CHO·CHPh·CO_2Et in aq. NaOH], and $POCl_3$ at 130—140° give 6-*chloro*-2-*ethylthiol*-5-*phenylpyrimidine* (I), b.p. 218°/10 mm., 231—232°/20 mm., m.p. 38—39°, which with KCNS in EtOH or C_6H_6 affords 6-*thiocyano*-2-*ethylthiol*-5-*phenylpyrimidine* (II), b.p. 215°/2 mm., m.p. 90°. (II) and SH·CH_2·CO_2H at 100° give 2-*ethylthiol*-5-*phenyl*-6-*thiopyrimidine*, m.p. 171°, also prepared from (I) and EtOH–NaHS. When (II) is heated in xylene for 30 hr. it rearranges to 2-*ethylthiol*-6-*thiocarbimido*-5-*phenylpyrimidine* (III), m.p. 84—85°, which with conc. aq. NH_3 in light petroleum gives the 6-*thiocarbamido*-derivative, m.p. 204°; with NH_2Ph, the 6-*phenylthiocarbamido*-derivative, m.p. 149°, results. (III) and MeOH and EtOH give the corresponding *thiourethanes*, m.p. 79—80° and 85—85·5° (IV), respectively. (II) also rearranges when heated with EtOH at 140°; the (III) formed then reacts to give (IV). (II) does not react with NH_3, NH_2Ph, or alcohols. H. B.

Pyrimidines. Synthesis of 5-phenylcytosine. Y. F. Chi and Y. L. Tien (J. Amer. Chem. Soc., 1933, **55**, 4185—4186).—6-*Amino*-2-*ethylthiol*-5-*phenylpyrimidine*, m.p. 87—88° (from the 6-Cl-derivative and conc. EtOH–NH_3 at 150°), and 48% HBr give EtSH and the *hydrobromide*, m.p. 280—281° (decomp.), of 5-*phenylcytosine*, $NH\langle \overset{CO\text{—}N}{CH{\cdot}CPh} \rangle C{\cdot}NH_2$, m.p. > 310° [*hydrochloride*, m.p. 277—278° (sinters at 270°)]. H. B.

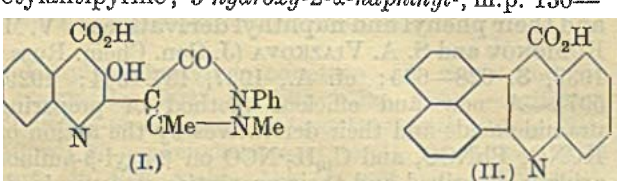
Synthesis of α-aryl-β-uramidopropionic acids and their phenyl and naphthyl derivatives. V. M. Rodionov and S. A. Viazkova (J. Gen. Chem. Russ., 1933, **3**, 628—635; cf. A., 1927, 137, 804; 1929, 557).—A new and efficient method of preparing uramido-acids and their derivatives by the action of KCNO, PhNCO, and $C_{10}H_7{\cdot}NCO$ on β-aryl-β-amino-acids is described and their properties are examined. With KCNO β-phenylalanine gives α-uramido-β-phenylpropionic acid, m.p. 190°, which, when heated

with HCl, gives 4-phenyl-4 : 5-dihydropyrimidine, m.p. 218°. β-Piperonylalanine gives β-uramido-β-piperonylpropionic acid, m.p. 176°, but ring closure to form 4-piperonyl-4 : 5-dihydropyrimidine, m.p. 255°, could be effected only through the Et ester of the acid, m.p. 65°. The Ph and $C_{10}H_7$ derivatives of the above β-NH_2-acids are obtained by using PhNCO and $C_{10}H_7$·NCO instead of KNCO. The $C_{10}H_7$ derivatives do not cyclise. M. Z.

4-*N*-Piperidylpyridine [4-piperidinopyridine]. R. Graf [with R. Lehmann] (J. pr. Chem., 1933, [ii], **138**, 239—243).—Interaction of $C_5H_{11}N$ with 4-chloro-α-picolinic acid gives *4-piperidinopyridine-2-carboxylic acid* (+$4H_2O$), m.p. 58—77° [*Cu* salt, purple; *hydrochloride*, m.p. 225° (sinters 210°); *hydriodide*, m.p. 200—210° (decomp.); *Me* ester, m.p. 52—53°], decarboxylated by heat to *4-piperidinopyridine*, m.p. 80°, b.p. 164°/13 mm. (*chloroaurate*, m.p. 161—163°; *picrate*, m.p. 142°; *methiodide*, m.p. 159°; *methochloride*). H. A. P.

Tautomerism in the phthalazine series. *N*- and *O*-Derivatives of 1-methylphthalaz-4-one and phthalaz-1 : 4-dione. F. M. Rowe and A. T. Peters (J.C.S., 1933, 1331—1335).—1-Methylphthalaz-4-one exists in alkali hydroxide solution and forms the 1 : 3-Me_2 derivative, which cannot be demethylated. In neutral or acid solution, the tautomeric form, 1-hydroxy-4-methylphthalazine, is stable and forms the 1-*OMe*-derivative, m.p. 53—54° (*picrate*, m.p. 198°; also obtained from 1-chloro-4-methylphthalazine), and 1-*OAc*-derivative, m.p. 130—132°. "Phthalylhydrazide" (I) exists in alkali hydroxide solution as 1-hydroxyphthalaz-4-one, which with Me_2SO_4–KOH gives the 3-*Me* derivative (II), m.p. 238° (1-*OAc*-compound, m.p. 142°), regarded by Radulescu and Georgescu (A., 1925, i, 1185) as the *O*-ether, and 1-*methoxy*-3-*methylphthalaz*-4-*one*, m.p. 93°, demethylated to (II). (I) exists in neutral and acid solution as 1 : 4-dihydroxyphthalazine. 4-Hydroxy-1-methoxyphthalazine is obtained from the Ag salt and MeI–MeOH and gives the 4-*OAc*-derivative, m.p. 137°, easily hydrolysed by EtOH. Acetylation (Ac_2O–AcOH) of (I) yields 1 : 4-*diacetoxyphthalazine*, m.p. 134°. F. R. S.

Substituted quinoline-4-carboxylic acids. E. Benary (Ber., 1933, **66**, [*B*], 1569—1571).—The following *-quinoline-4-carboxylic acids* have been prepared: 2-2′-*methyl*-5′-*pyridyl*-, m.p. 262—264°, from 5-acetyl-2-methylpyridine, isatin, and 33% KOH in boiling EtOH: 2-6′-*methoxy*-4′-*quinolyl*-, decomp. about 230°, analogously from 6-methoxy-4-acetylquinoline; 2-2′-*phenyl*-4′-*quinolyl*- (I), m.p. 260—263°, from 4-acetyl-2-phenylquinoline; 3-*hydroxy*-2-*antipyryl*- (I), m.p. 160—162° (decomp.), from chloroacetylantipyrine; 3-*hydroxy*-2-α-*naphthyl*-, m.p. 130—145°, from ω-bromoacetonaphthone; 2 : 3-peri-*naphthylene*- (II), decomp. about 320°, from acenaphthenone: 3-benzyl-2-phenyl-, from benzylacetophenone. H. W.



Sandmeyer indigo synthesis. R. Shibata, M. Okuyama, and K. Okamura (J. Soc. Chem. Ind. Japan, 1933, **36**, 569—571B).—Interaction of diphenylamidino-oxalthioamide with conc. H_2SO_4 at 105—110° during 3 hr. affords β-isatinanil (cf. A., 1914, i, 519) (also α-isatinanil at 50°) and isatin. J. L. D.

Glycosine, $C_6H_6N_4$, of Debus. II. Carbon salts of tetranitrodiglyoxalinyl and methylation of nitroglyoxaline. K. Lehmstedt and (in part) O. Zumstein (Annalen, 1933, **507**, 213—225).—The hydrated (univalent) dimetallic salts of 1 : 5 : 1′ : 5′-tetranitro-2 : 2′-diglyoxalinyl (I) (A., 1927, 979) [*di-pyridine*, decomp. 233°, and *di*(*glyoxaline*), decomp. 325°, salts] are formulated as $\left[-C\langle^{N(NO_2)\cdot C:NO_2M}_{N\quad\quad CH\cdot OH}\right]_2$; these are dehydrated readily to $\left[-C\langle^{N(NO_2)\cdot C\cdot NO_2}_{N\quad\quad CM}\right]_2$ (*A*; M=metal). (I) is a "true" acid (see Hantzsch, this vol., 142); it reacts instantaneously with CH_2N_2 (2 mols.) in Et_2O at −5° to give 1 : 5 : 1′ : 5′-*tetranitro*-4 : 4′-*dimethyl*-2 : 2′-*diglyoxalinyl* (II), decomp. 239—240°, also formed from the anhyd. Na_2 salt (III) (*A*, M=Na) of (I) and Me_2SO_4 at 100° (bath). (I) and Me_2SO_4 in aq. NaOH give 1 : 5 : 1′ : 5′-*tetranitro*-4-*methyl*-2 : 2′-*diglyoxalinyl* (+$2H_2O$) (IV), decomp. 273—274°, indicating the existence of both of the above salts in solution; in one case, a small amount of the *compound* $NO_2\cdot C\cdot N(NO_2)\rangle C\cdot C\langle N(NO_2)\cdot C:NO_2Me$ / $MeC\quad\quad N\quad\quad C:CH_2$ +H_2O, decomp. 127°, was also formed. The *Na*$_2$ salt (+$4H_2O$) of (IV) is reduced ($Na_2S_2O_4$) to the *Na*$_2$ salt (+$4H_2O$) of 5 : 5′-dinitro-1 : 1′-diamino-4-methyl-2 : 2′-diglyoxalinyl. (III) and Et_2SO_4 at 100° (bath) give 1 : 5 : 1′ : 5′-*tetranitro*-4-*ethyl*- (+$2H_2O$), m.p. 259° (decomp.) [*Na*$_2$ salt (+$2H_2O$)], and -4 : 4′-*diethyl*-, decomp. 203 -2 : 2′-*diglyoxalinyl*; (I) does not react with Et_2SO_4 in aq. NaOH. (II) and 5*N*-NaOH in $COMe_2$ give the *salt* (V), $\left[-C\langle^{N(ONa)\cdot C\cdot NO_2}_{N\quad\quad CMe}\right]$,$H_2O$, which when acidified (cold dil. HCl) affords a blue *dye*, $C_8H_{10}O_4N_4$. (II) and MeOH–NaOMe give 5 : 5′-*dinitro*-1 : 1′-*dimethoxy*-4 : 4′-*dimethyl*-2 : 2′-*diglyoxalinyl*, decomp. 242° (previous darkening), which is hydrolysed (aq. NaOH) to (V).

The production of 4-nitro-1-methylglyoxaline (VI) by methylation of 4(5)-nitroglyoxaline (*Na* salt) in alkaline solution (cf. Pyman *et al.*, A., 1925, i, 699, and preceding abstracts) involves the intermediate formation of the nitronic ester $CH\langle^{N:CH}_{N\cdot C:NO_2Me}$; this then rearranges to (VI). The yield of (VI) is increased when methylation (Me_2SO_4, KOH) is carried out in EtOH, owing to the hydrolysis of the above ester being suppressed. H. B.

Chlorophyll. XXXVIII. Fission of chlorophyll *a* and its derivatives by diazomethane. Crystalline allomerised ethylphæophorbide *a*. XXXIX. Catalytic hydrogenation in the chlorophyll series. H. Fischer and J. Riedmair. H. Fischer and E. Lakatos (Annalen, 1933, **506**, 107—

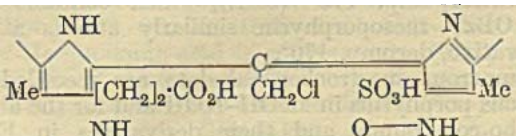
123, 123—157).—XXXVIII. The yield of chlorin *e* Me_3 ester (I) from phæophorbide *a* (II) and Et_2O–CH_2N_2 in MeOH–C_5H_5N (cf. A., 1932, 1263) decreases when the amount of MeOH is diminished, but is independent of the concn. of CH_2N_2. (I) is also produced when the reaction is carried out in N_2, showing that oxidation is not a part of the process (cf. Stoll and Wiedemann, this vol., 838). (II) which has been kept in contact with acid for a long time gives only about 30% of (I); about 30% of a substance (pyrophæophorbide) (III), dimethylphæopurpurin 7 (IV), and a chlorin-like (spectrum) substance [which slowly changes to (IV)] are also formed. (III) has the same spectrum as (II), and is degraded (HI) to phylloerythrin; the phase test is negative. Pure methylphæophorbide *a* (V) and Et_2O–CH_2N_2 in MeOH–C_5H_5N and N_2 give about 80% of (I) and small amounts of purpurin (VI), methylpyrophæophorbide [degraded (HI) to phylloerythrin ester], and residual chlorins [these are not formed in presence of O_2, but the amount of (VI) is increased]. Pure (II) and native (V) afford almost quant. yields of (I), native methylchlorophyllide *a* gives (after removal of Mg) mainly (I), whilst methylphæophorbide *a*+*b* yields (I) and rhodin *g* Me ester. Allomerised ethylchlorophyllide *a*+*b* (VII) [using benzoquinone (VIII) in EtOH and N_2] and allomerised (II) (using I) do not give (I). Native (II) and the product from MgMeI and PrOH in N_2 afford (after decomp. with NaH_2PO_4) a bluish-green cryst. compound, which is degraded (HI) to phæoporphyrin a_5. (V) (from chlorophyllide) similarly affords an amorphous chlorophyllide *a*; allomerisation [(VIII)] of this and subsequent degradation (HI) gives phæoporphyrin a_6. 10-*Ethoxyethylphæophorbide* a (allomerised ethylphæophorbide *a*), $C_{39}H_{44}O_6N_4$, m.p. > 280°, is separable from (VII) by fractionation of the Et_2O solution with 18% HCl; it probably arises by addition of EtOH to dehydroethylphæophorbide *a*. The O_2 absorption of chlorophyll and its derivatives in various solvents at 21·5° is measured. Compounds containing Mg show max. absorption (up to 1·1 mols.); C_5H_5N and phæophorbide (which does not absorb O_2) have a retarding influence.

XXXIX (cf. A., 1930, 932). Reduction [H_2, PtO_2 (simplified prep. given), AcOH (unless stated otherwise)] of the following results in the absorption of approx. 3 mols. of H_2; oxidation (atm. O_2) of the resulting leuco-compounds regenerates (mainly) the original substance: pyrroporphyrin; phylloporphyrin (I) (also in $CHCl_3$); deoxophylloerythrin (II); phylloerythrin (III); phæoporphyrin a_5 (IV). In the following cases, the nos. quoted after the compounds are the approx. nos. of mols. of H_2 absorbed, and the substances enclosed in brackets are the oxidation products of the leuco-compounds: chlorin *e*, 3 [chloroporphyrin e_5 and a little (I)]; chlorin *e* Me_3 ester (in AcOH–HI), 3 [chloroporphyrin e_6 (V)]; phæophorbide *a* (Sandoz and native), 4 [(III), (IV), (V), and phæoporphyrin a_7 (VI)]; ψ-verdoporphyrin Me_2 ester, 4 [rhodoporphyrin Me_2 ester]; (I) (in $CHCl_3$–light petroleum), 2 [(I) and a little phyllochlorin]; synthetic deoxophylloerythrin, 6, and its Me ester, 5 [blue basic dye] [in one case (II) absorbed 5 mols. and oxidation gave little of the original product]; native phæophorbide *a* (using Pd-black), 3 [(III), (IV), and (VI)]; native methylphæophorbide *a* (using Pd-black), 3 [phæoporphyrin a_5 Me_2 ester].

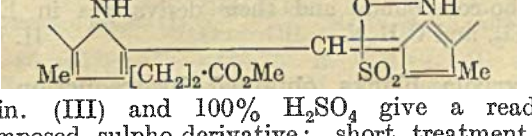
Reduction [H_2 (1 mol.), PtO_2, HCO_2H] of phæophorbide *a* gives *dihydrophæophorbide* a (VII), $C_{35}H_{38}O_5N_4,H_2O$ [*Me* ester (=*dihydromethylphæophorbide* a), m.p. 218° (corr.); *oxime*, decomp. 236°, degraded by HI–AcOH to (after esterification) *phæoporphyrin oxime Me* ester, m.p. 280° (darkens at 260°), which is hydrolysed (Et_2O–conc. HCl) to phylloerythrin Me ester (VIII)], and traces of (IV) and (V). Prolonged treatment of (VII) with HCO_2H gives (III) (62%) and (IX) (below). (VII) is degraded by HBr–AcOH at 100° to (II) and (III), and by HI–AcOH at 60° to (IV); it absorbs 4 H (Pd-black) and oxidation of the leuco-compound gives (IV). (VII) heated with C_5H_5N gives *pyrodihydrophæophorbide* a (IX), $C_{33}H_{36}O_3N_4$ [*Me* ester, m.p. 239°, degraded (HI–AcOH at 55—60°) to (VIII)]. The Me esters of (IX) and pyrophæophorbide *a* absorb 2 and 3 mols. of H_2, respectively, in presence of Pd-black; subsequent oxidation gives (VIII) in both cases. Hydrolysis (MeOH–KOH) of (VII) in C_5H_5N gives *dihydrochlorin* e (X), probably $C_{33}H_{38}O_6N_4$ [Me_3 ester (XI), m.p. 184°, degraded (HI–AcOH) to chloroporphyrin e_6 Me_3 ester, which is also obtained by oxidation of the leuco-compound from (XI) (Pd-black; 4 H absorbed)], and some (IX). (VII) and Et_2O–CH_2N_2 in MeOH–C_5H_5N give (XI) (m.p. 188°); in air, some chlorin is produced also. Ring closure of (XI) [to the Me ester of (IX)] is effected with Na_2CO_3 in C_5H_5N. (X) heated with C_5H_5N gives *pyrodihydrochlorin* e (*dihydrochlorin* e_4), $C_{33}H_{38}O_4N_4$ (Me_2 ester, m.p. 154°). Formulæ are suggested for (VII), (X), and (XI). Phæopurpurin 7 Me_3 ester absorbs 6 H (Pd-black); subsequent oxidation gives *allo*phæoporphyrin a_5. Phæopurpurin 18 Me_2 ester also absorbs 6 H. H. B.

Sulpho-derivatives of chlorophyll porphyrins; structure of porphyrins. A. TREIBS (Annalen, 1933, **506**, 196—259).—Phylloporphyrinsultone (I) (Fischer *et al.*, this vol., 286) [stable 1 : 1-*compound* with C_5H_5N; the Me ester (II) (*Cu*, decomp. 250—280°, *Zn*, and *Fe* complex salts) is obtained with m.p. 294° (corr.) (using MeOH–HCl), 320° (corr) and 335° (block) (CH_2N_2), and 302° (corr.) (when prepared from phylloporphyrin Me ester and oleum)] and warm MeOH–KOH give the K_2 salt (+4H_2O and +2MeOH) of the hydroxyphylloporphyrinsulphonic acid. Contrary to Fischer *et al.* (*loc. cit.*), (I) and conc. HCl give a *chlorophylloporphyrinsulphonic acid* (as *A*), $C_{32}H_{37}O_6N_4ClS$ [Me_2 ester, decomp. 270—290° (to phyllo- and pyrro-porphyrin esters), converted by conc. H_2SO_4 into (II)]. (I) and MeOH–KOH at 150—155° give phyllo- (III) and some pyrro- (IV) -porphyrin. (III) and 100% H_2SO_4 give a readily decomposed sulpho-derivative; short treatment of

(*A.*)

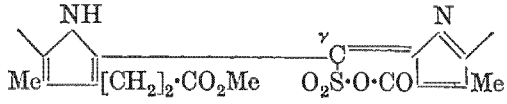


(*B.*)

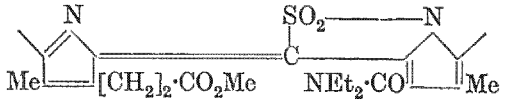


the Me ester with H_2SO_4,H_2O and subsequent esterification (CH_2N_2) affords *Me_2 phylloporphyrinsulphonate* (as *A*, with CH_2Cl=Me), m.p. 224° (corr.) (decomp.) (*Cu* and *Fe* complex salts), which with $Fe(OAc)_2$ and NaCl in hot aq. AcOH affords (by the reduction of ·SO_3Me to ·SOMe and introduction of Cl) a *salt*, $C_{34}H_{37}O_3N_4Cl_2SFe$. Pyrroporphyrin Me ester (V) is converted by cold oleum (20% SO_3) or *N*-pyridiniumsulphonic acid (VI) (Baumgarten, A., 1926, 844) at 185—190° into a *sulpho*-derivative (as *B*), $C_{32}H_{36}O_5N_4S$,H_2O, decomp. 260—290° [largely to (IV) and (V)] (*K* salt; *hydrochloride*; *Cu* and *Fe* complex salts; *compound* with C_5H_5N), which with Et_2O–CH_2N_2 in $CHCl_3$ affords the *Me_2* ester, m.p. 238° (corr.) [*Cu*, m.p. 241° (corr.), and *Fe* complex salts], of (VII) (below). (IV) is rapidly decomposed by oleum, but with 100% H_2SO_4 pyrrorhodin and *pyrroporphyrinsulphonic acid* (VII), $C_{31}H_{34}O_5N_4S$, decomp. 305° [to (IV)], result. Deuteroporphyrin Me_2 ester and (VI) at 165° give a *disulphonic acid*, decomp. about 300° (*K_2* salt; *Cu* and *Fe* complex salts; *compound*, decomp. 300°, with C_5H_5N), esterified (CH_2N_2 in Et_2O–$CHCl_3$) to the *Me_4* ester, m.p. 246° (corr.) (*Cu* and *Fe* complex salts), of deuteroporphyrindisulphonic acid (*K_4* salt). Rhodoporphyrin Me ester and cold oleum (20% SO_3) afford a neutral *compound* (as *C*), $C_{33}H_{34}O_6N_4S$, m.p. 271° (decomp.) [(V) is isolated from the melt] (*Fe*, *Mg*, and *Cu* complex salts, converted by prolonged treatment with very dil. MeOH–KOH into a *K_2* salt,

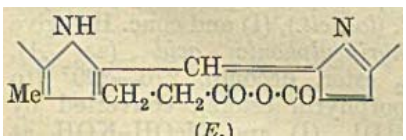
(*C.*)



(*D.*)



$C_{33}H_{34}O_6N_4SK_2$, and by $NHEt_2$ into the *diethylamide* (as *D*) (*Cu* and *Mg* complex salts). Rhodin formation from porphyrins containing the ·CH_2·CH_2·CO_2H grouping (by treatment with H_2SO_4) is considered to involve sulphonation at C*γ*, anhydride formation between the ·CO_2H and ·SO_3H, and subsequent elimination of SO_3 to give a stable six-membered C ring. Rhodoporphyrin (VIII) and BzCl in C_5H_5N afford an impure *compound*, $C_{46}H_{42}O_6N_4$; in one case, *rhodoporphyrin anhydride* (as *E*), $C_{32}H_{32}O_3N_4$, was isolated. (VIII) and Bz_2O at 140—150° give a *Bz_2* derivative, m.p. 170° (corr.), which contains two ·CO·OBz; mesoporphyrin similarly affords a *Bz_2* derivative, decomp. 170°.



(*E.*)

Numerous spectrochemical data are recorded for various porphyrins in MeOH–KOH and for the above sulpho-compounds and their derivatives in Et_2O, $CHCl_3$, and C_5H_5N. H. B.

Pyrrole blacks obtained by reduction. G. Illari (Gazzetta, 1933, **63**, 591—596).—Pyrrole when warmed with aq. HCO_2H and treated with KOH yields a brown condensation *product*, $C_{22}H_{29}O_2N_5$, no m.p. (*picrate*). E. W. W.

Derivatives of furan. A. Mironescu and G. Ioanid (Bul. Soc. Chim., Romania, 1933, **15**, 49—52).—Interaction of furil (I) in boiling EtOH with benz-, anis-, or furfur-aldehyde and NH_3 does not result in further ring closure, but with piperonal, (I) affords an *oxazole* (cf. A., 1882, 1063). J. L. D.

Leucopterin, the wing-pigment of common white butterflies (*Pieridæ*). II. H. Wieland, H. Metzger, C. Schöpf, and M. Bülow (Annalen, 1933, **507**, 226—265; cf. A., 1926, 1168).—Leucopterin (I), probably $C_{19}H_{19}O_{11}N_{15}$ (cf. *loc. cit.*), does not react with CH_2N_2, is unaffected by HI, Na–Hg, or Al–Hg, does not absorb O_2 in alkaline solution, but is oxidised by $K_3Fe(CN)_6$ [7·7—7·8 mols. per mol. of (I)]; (I) gives the murexide reaction, but the colour differs from that obtained with uric acid. (I) and Ac_2O–conc. H_2SO_4 at 100° (bath) give a *Ac_3* derivative, $C_{19}H_{14}O_{10}N_{15}Ac_3$, the formation of which involves loss of 1 mol. of H_2O per mol. of (I). (I) is converted by PCl_5+$POCl_3$ into *leucopteryl chloride*, $C_{19}H_{16}O_8N_{15}Cl_3$, and by HNO_2 into *deiminoleucopterin* (II), $C_{19}H_{14}O_{13}N_{12}$. (I), which titrates (NaOH in EtOH) as a tetrabasic acid, is isomerised by dissolution in cold conc. H_2SO_4 and subsequent pptn. to *isoleucopterin*, which titrates as a hexabasic acid. (I) (1 mol.) is hydrolysed by conc. HCl at 160—170° to NH_2·CH_2·CO_2H (III) (3 mols.), NH_3 (12 mols.), CO_2 (9 mols.), and CO (3 mols.); uric acid similarly affords (III) (1 mol.), NH_3 (3 mols.), and CO_2 (3 mols.), whilst guanine gives NH_3 (4 mols.), CO_2 (2 mols.), and CO (1 mol.). Treatment of (I) with Cl_2 in MeOH and decomp. of the resulting trihydrochloride with C_5H_5N in MeOH give a *triglycol Me_6 ether* (IV), $C_{19}H_{19}O_{11}N_{15}(OMe)_6$, becomes brown at 160° and very dark at 200°, which when crystallised from H_2O passes into a *compound*, $C_{19}H_{17}O_{10}N_{15}(OH)_3(OMe)_3$, darkens at 180°. Decomp. of the trihydrochloride with aq. C_5H_5N affords a *substance*, $C_{19}H_{19}O_{11}N_{15}(OH)_3(OMe)_3$,$4H_2O$,$2C_5H_5N$; the *salt*, $C_{19}H_{19}O_{11}N_{15}(OH)_3(OMe)_3$,3HCl (+1 and $8H_2O$), is obtained from (IV) and dil. HCl. (I) and Cl_2–H_2O give a *triglycol* (V), $C_{19}H_{19}O_{11}N_{15}(OH)_6$ (anhyd. and +$6H_2O$) (*trihydrochloride*), which does not give the murexide reaction and is hydrolysed (0·1*N*-HCl at 140—150°) to CO_2 (4·3—4·9 mols.), $NH_4HC_2O_4$ (3—3·4 mols.), and guanidine (VI) (1·27 mol.) (*chloroaurate*; *acetate*, m.p. 224—226°). (I) and Cl_2 in AcOH–2*N*-HCl afford a *diglycol* (VII), $C_{19}H_{21}O_{12}N_{15}(OH)_4$,$H_2O$ (*trihydrochloride*); (II) similarly gives a *compound*, $C_{16}H_{22}O_{17}N_{12}$,3HCl [hydrolysis (0·1*N*-HCl at 170°) of this does not yield (VI)]. A *substance*, $C_{16}H_{24}O_{17}N_{14}$, is obtained from (I) and Br.

(IV) is hydrolysed by H_2O at 65° to CO, MeOH, (VI), an acid, probably NH_2·CO·CH(OMe)·NH·CO·CO_2H (*Me* ester, hydrolysed by 2*N*-HCl to $H_2C_2O_4$ and by alkali to CHO·CO_2H), and a OMe-free *compound*, $C_{17}H_{29}O_{15}N_{15}$; the last two compounds are isolated by pptn. with $Hg(OAc)_2$ and subsequent decomp. with H_2S. $H_2C_2O_4$ is also formed by hydrolysis (alkali) of (IV), (V), and (VII). (VII) is hydrolysed by aq. $Ba(OH)_2$ to (VI) and by H_2O to a *compound*,

$C_{16}H_{31}O_{16}N_{15}$, darkens at 220°. During the purification of (I) by dissolution in Na_2CO_3 and repptn. with HCl, some *anhydroleucopterin*, $C_{19}H_{13}O_8N_{15}$, is produced.

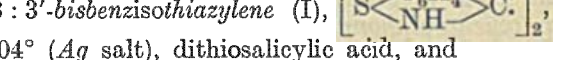
The pigment obtained by extraction of the whole animals with aq. NH_3 differs from (I) and is termed *ψ-leucopterin*. It does not give concordant analyses, it is converted by conc. H_2SO_4 into an *isomeride* of (I), and with HNO_2 affords *deimino-ψ-leucopterin*, $C_{19}H_{16}O_{11}N_{12}$. Xanthine and Cl_2 in MeOH give NH_4Cl and Me 5-methoxyuramil-*N*(5)-carboxylate. Contrary to Wigglesworth (A., 1924, i, 1372), uric acid could not be found in the wings of *Pieridæ*; it is readily isolable from the body and excrement. Alternative structures (all containing guanine residues) are suggested for (I). H. B.

Occurrence of pterins in wasps and butterflies; leucopterin and xanthopterin. C. Schöpf and E. Becker (Annalen, 1933, **507**, 266—296).—Dissolution of xanthopterin (I), probably $C_{19}H_{19}O_7N_{15}$ (cf. A., 1925, i, 1464), in hot half-saturated (at 20°) aq. $Ba(OH)_2$ and subsequent cooling give *Ba β-xanthopterin* (II), $C_{19}H_{15}O_8N_{15}Ba_3$ [the Ba salt previously described (*loc. cit.*) is designated Ba α-xanthopterin], which when crystallised from H_2O is hydrolysed to the *salts*, $(C_{19}H_{16}O_8N_{15})_2Ba_5$ and $(C_{19}H_{18}O_8N_{15})_2Ba_3$. The absorption spectrum of (II) (from various sources) in AcOH is given. Treatment of a relatively conc. solution of (II) in 2*N*-HCl with conc. aq. NaOAc gives amorphous (I); in more dil. solutions products of differing cryst. form are obtained, and these are designated *xanthopterin hydrates* a and b, probably $C_{19}H_{22}O_{10}N_{14}$. These may result by hydrolysis of >C:NH to >CO. (I) does not contain NMe groups; it couples with diazotised 2 : 5-$C_6H_3Cl_2{\cdot}NH_2$ to give a *compound*, $C_{55}H_{31}O_7N_{27}Cl_{12}$ (xanthine similarly affords a *compound*, $C_{11}H_6O_2N_6Cl_2$), and when hydrolysed [aq. $Ba(OH)_2$] gives 1 mol. of

[In part with E. Bumm and H. Stober.] A mixture of leucopterin *a* (III) and leucopterin *b* (IV) is isolated from *Gonepteryx rhamni* (yellow male) in addition to (I); the white female contains (III) but no (I). (III) and (IV) are also isolated from the aurora butterfly (*E. cordamines*). (III) gives a Na_2 salt, whilst (IV) affords a Na_3 salt; (IV) may arise from (III) by the action of the HCl (used in purification) and may be identical with *iso*leucopterin (cf. preceding abstract).

Details are given for the isolation of (I), (III), (IV), and a new *pterin* from *Vespa germanica*, *V. crabro*, and *V. vulgaris*. H. B.

Effect of substituents on the bromination of diaryl-ψ-thiohydantoins. Application of the theory of singlet linkings to the formation of polybromide complexes by heterocyclic compounds. M. R. Chowdhury, R. D. Desai, R. F. Hunter, and F. M. K. Solangi (Rec. trav. chim., 1933, **52**, 853—861; cf. this vol., 284).—2-*p*-Tolylimino-4-keto-3-*p*-tolyltetrahydrothiazole (di-*p*-tolyl-ψ-thiohydantoin), m.p. 128—129° (lit. 127°) [from $(p\text{-}C_6H_4Me{\cdot}NH)_2CS$ and $CH_2Cl{\cdot}CO_2H$ in EtOH–C_5H_5N (method *A*) or $CH_2Cl{\cdot}CO_2Et$ in EtOH–NaOEt], and Br in $CHCl_3$ at 0° give an unstable *hydro-octabromide* (I), m.p. 60° (decomp.) (sinters at 45°) [which when exposed to air affords a more stable *hydrotribromide* (II), m.p. 125—130°], of 2-p-*tolylimino*-4-*keto*-3-o-*bromo*-p-*tolyltetrahydrothiazole* (III), m.p. 183°. (III) is obtained from (I) and (II) by successive treatment with H_2SO_3 and aq. NH_3, and is synthesised from α-p-*tolyl*-γ-o-*bromo*-p-*tolylcarbamide*, m.p. 169—170° (from *o*-bromo-*p*-toluidine and $p\text{-}C_6H_4Me{\cdot}NCS$) by method *A*. 2-p-*Nitroanilo*-4-*keto*-3-p-*nitrophenyltetrahydrothiazole*, m.p. 175—176° [from $(p\text{-}NO_2{\cdot}C_6H_4{\cdot}NH)_2CS$ by method *A*], does not form additive compounds with Br, whilst 2-p-*chloroanilo*-4-*keto*-3-p-*chlorophenyltetrahydrothiazole* (IV), m.p. 166—167° [best prepared from $(p\text{-}C_6H_4Cl{\cdot}NH)_2CS$, $CH_2Br{\cdot}CO_2Et$, and EtOH–NaOEt], furnishes a *pentabromide* (V), m.p. 116—118° (decomp.) (sinters at 101°), which when kept in a vac. over KOH passes into a *tetrabromide*, m.p. 122—125°. When (V) is kept in air or treated with H_2SO_3 or HgO, (IV) is regenerated. 2-p-*Bromoanilo*-4-*keto*-3-p-*bromophenyltetrahydrothiazole* (VI), m.p. 178° (cf. Dains *et al.*, A., 1921, i, 362) [formed together with a substance, m.p. 145—146° (decomp.), from $(p\text{-}C_6H_4Br{\cdot}NH)_2CS$ by method *A*; more conveniently prepared as (IV)], similarly gives a *pentabromide* (VII), m.p. 108—110° (decomp.), which is re-converted [as (V)] into (VI). (V) and (VII) probably contain the :$NBr(Br_4)$ grouping; this formulation necessitates " singlet " linkings. H. B.

2 : 3 : 2′ : 3′-Tetrahydro-3 : 3′-bisbenz*iso*thiazylene. R. Stolle and M. Merkle (J. pr. Chem., 1933, [ii], **138**, 221—224; cf. A., 1925, i, 1466).—3-Amino*iso*benzthiazole is prepared in good yield from the 3-carboxylamide by Hofmann's method. With HNO_2 in 25% H_2SO_4 at 0° it gives 2 : 3 : 2′ : 3′-*tetrahydro*-3 : 3′-*bisbenziso*thiazylene (I),  , m.p. 104° (*Ag* salt), dithiosalicylic acid, and $o\text{-}CO_2H{\cdot}C_6H_4{\cdot}SO_3H$ (II). Oxidation of (I) with HNO_3 gives (II) and (in the cold) ? benzil-2 : 2′-disulphonic acid (NH_4 salt, m.p. 238°). H. A. P.

Formation of heterocyclic iodine, nitrogen, and oxygen rings. L. Mascarelli (Mem. R. Accad. Ital., Sci. fis. mat. nat., 1931, **3**, Chim., No. 2, 5—15; Chem. Zentr., 1933, i, 3194).—A discussion. A. A. E.

Photosynthesis of nitrogenous compounds.—See this vol., 1256.

Alkaloids of *Jaborandi* leaves. III. Synthesis of pilocarpine and pilocarpidine. N. A. Preobrashenski, A. F. Wompe, V. A. Preobrashenski, and M. N. Schtschukina. **IV. Diazomethyl-*r*-*iso*pilopyl ketone and its transformation products.** N. A. Preobrashenski and M. J. Kabatschnik (Ber., 1933, **66**, [*B*], 1536—1541, 1541—1545).—III. *d*-Homopilopic acid is converted by $SOCl_2$ into d-*homopilopyl chloride* and thence by the successive action of CH_2N_2 in Et_2O and HCl into d-*homopilopyl chloromethyl ketone* (I), $\begin{matrix}CO{\cdot}CHEt\\ O\text{——}CH_2\end{matrix}>CH{\cdot}CH_2{\cdot}CO{\cdot}CH_2Cl$, m.p. 86—87°, $[\alpha]_D^{17}$ +115·35° in $C_2H_2Cl_4$. (I) and $o\text{-}C_6H_4(CO)_2NK$ in boiling EtOH afford *phthalimidomethyl* d-*homopilopyl ketone*, m.p. 157—158·5°, $[\alpha]_D^{16}$ +66·77° in $C_2H_2Cl_4$, converted by 20% HCl into

aminomethyl d-*homopilopyl ketone hydrochloride*, m.p. 179—181°, $[\alpha]_D^{17\cdot05}$ +90·0° in H_2O, and thence by KCNS into 2-*thiol*-4(5)-d-*homopilopylaminazole* (2-*thiolpilocarpidine*) (II), m.p. 207—208·5° (decomp.), $[\alpha]_D$ +122·96° in MeOH. Treatment of (II) with $FeCl_3$ leads to pilocarpidine (*nitrate*, m.p. 132·5—133°, $[\alpha]_D^{19}$ +71·78° in H_2O), transformed by MeI and HNO_3 into pilocarpine nitrate, m.p. 175·5—176·5°, $[\alpha]_D^{18}$ +81·09° in H_2O.

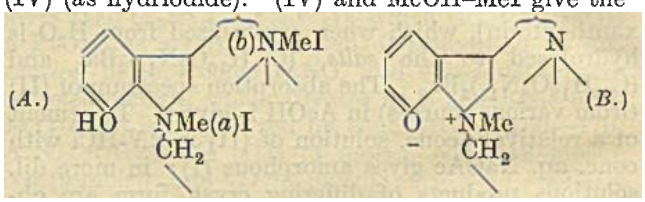
IV. Gradual addition of r-iso*pilopyl chloride*, from the acid and $SOCl_2$, to excess of CH_2N_2 in Et_2O leads to r-iso*pilopyl diazomethyl ketone* (III), converted by I in Et_2O and Br in CCl_4, respectively, into the corresponding *di-iodomethyl*, decomp. 109°, and *dibromomethyl*, m.p. 76·5—77·5°, *ketone*. Treatment of (III) with *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ in xylene at 140° or of the CH_2Cl ketone with *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2Na$ leads to *keto*-r-*homo*iso*pilopyl* p-*nitrobenzoate*, m.p. 129·5—130°; the corresponding *benzoate*, m.p. 70—71°, is prepared analogously. H. W.

Synthesis of α-nicotine, 2-(2′-pyridyl)-1-methylpyrrolidine. J. P. Wibaut and A. G. Oosterhuis (Rec. trav. chim., 1933, **52**, 941—944).—2 : 2′-Nicotyrine [2-(2′-pyridyl)-1-methylpyrrole] is reduced (Zn, conc. HCl, and a little $PtCl_4$] to *α-nicotine*, b.p. about 120°/1 mm. [*dipicrate*, m.p. 179° (decomp.) (sinters at 177—178°); *chloroplatinate*, decomp. about 218—219°], and (probably) a little dihydronicotyrine. 2-(2′-Pyridyl)pyrrole could not be reduced (Zn and HCl under varying conditions). H. B.

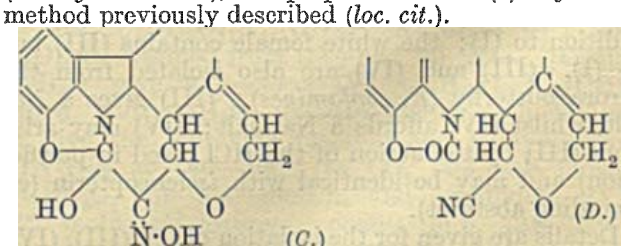
***apo*Quinine.** L. Jarzynski, R. Ludwiczakówna and J. Suszko (Rec. trav. chim., 1933, **52**, 839—846).—*apo*Quinine (β-*iso*cupreine) (I), m.p. 186—195° (decomp.) (according to prep.), $[\alpha]_D^{20}$ −190·5° (mean val.) in H_2O {*hydrochloride*, m.p. 236—237° (decomp.); p-*toluenesulphonyl* derivative, amorphous [*dinitrate* (+1·5H_2O), m.p. 180—182° (decomp.)]; *carbethoxy*-derivative, m.p. 201—202°; *H oxalate* (+2H_2O), m.p. 142—144° (decomp.)}, is obtained (*a*) from quinine sulphate and boiling 60% H_2SO_4, (*b*) from quinine dihydrobromide and 65% HBr (first at room temp. and then up to 100°) and treatment of the resulting *hydrobromo*apo*quinine* (+0·5H_2O), m.p. 179° (decomp.) [*dihydrobromide*, m.p. 209—210° (decomp.)], with 10% EtOH–KOH or, better, $AgNO_3$ in dil. HNO_3, and (*c*) from quinine and $AlCl_3$ in $PhNO_2$ at 130—135°. (I) is methylated (CH_2N_2) to β-*iso*quinine (A., 1925, i, 1448). H. B.

Cupreidine, the phenolic base corresponding with quinidine. R. Ludwiczakówna, J. Suszko, and R. Zwierzchowski (Rec. trav. chim., 1933, **52**, 847—852).—Demethylation (boiling 60% H_2SO_4) of quinidine (I) gives almost entirely *cupreidine* (II), m.p. 186—190°, $[\alpha]_D^{20}$ +219·4° in EtOH [*hydrochloride* (+H_2O), m.p. 215—216° (decomp.); *picrate*, m.p. 208—209°; *methiodide*, m.p. 277° (decomp.); *dimethiodide*, m.p. 248° (decomp.); *dibenzoate*, m.p. 100—105°; *benzeneazo*-, m.p. 145—146°, and p-*sulphobenzeneazo*-derivatives], which is methylated (CH_2N_2) to (I). (II) is also prepared from (I) by the successive action of 65% HBr at 50—80° and EtOH–KOH. The so-called *apo*conquinine of Hesse (A., 1881, 615) contains (II). H. B.

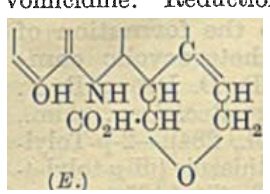
***Strychnos* alkaloids. XIV. Vomicidine.** H. Wieland, F. Holscher, and P. K. Bose. **XV. Deoxyvomicine and oximinovomicine.** H. Wieland and G. Varvoglis (Annalen, 1933, **507**, 69—82, 82—91).—XIV. Vomicidine (I) (improved prep. given; cf. A., 1932, 179) [*Ac* derivative, m.p. 229—230° (decomp.); in one case, acetylation (AcCl–C_5H_5N) gave a *compound*, $C_{24}H_{30}O_6N_2$, m.p. 304—305° (decomp.)], is reduced (H_2, PtO_2, 60% EtOH) to *dihydrovomicidine* (+0·5H_2O) (II), decomp. 296—298° (sinters at 278°) (*H sulphate*), also obtained by electrolytic reduction of dihydrovomicine. (I) is methylated (MeI or Me_2SO_4 and NaOH) to *vomicidine* O-*Me ether* (III), m.p. 295° (decomp.) [b-*methiodide*, m.p. > 300° (sinters and darkens at 280°), also obtained from (I) and MeI in boiling EtOH, which gives the characteristic $FeCl_3$ reaction]. (I) and MeI in EtOH and N_2 at 100° (sealed tube) afford a *dimethiodide* (as *A*), darkens gradually from 250°, which when treated with Et_2O–MeOH–CH_2N_2 loses 2 MeI and passes into the *phenolbetaine*, $C_{23}H_{28}O_3N_2$ (as *B*), m.p. 246° (sinters at 200°). This passes when heated into (III) and is converted by HI into vomicidine *a*-methiodide (IV) (as hydriodide). (IV) and MeOH–MeI give the



a-*methiodide*, m.p. 295° (decomp.) (sinters at 200°), of (III), which does not give a colour with oxidising agents. The *dimethiodide*, m.p. 230° (decomp.), of (II) is converted by CH_2N_2 into a *phenolbetaine*, $C_{23}H_{30}O_3N_2$, m.p. > 300°. Oxidation (CrO_3=15O in cold dil. H_2SO_4) of (I) gives a small amount of an *acid*, $C_{19}H_{24}O_8N_2$, m.p. 242° (decomp.; loss of CO_2), which probably contains a ·$CH(CO_2H)_2$ group; a partial structure is suggested. Divomicidyl, $C_{44}H_{50}O_6N_4$ (*tetrahydrochloride*), is prepared from (I) by the method previously described (*loc. cit.*).



XV. Deoxyvomicine (V) (A., 1929, 708) is reduced electrolytically to a *dihydro*-derivative (VI), $C_{22}H_{26}O_3N_2$, m.p. 161°, and (probably) a little deoxyvomicidine. Reduction (H_2, PtO_2, AcOH) of (V) gives *bases*, $C_{22}H_{28}O_2N_2$, m.p. 185° [also formed by reduction (H_2, PtO_2, EtOH) of (VI)], $C_{22}H_{30}O_2N_2$, m.p. 211°, and $C_{22}H_{28}O_3N_2$, m.p. 220° (cf. *loc. cit.*).



Vomicine, Et nitrite, and EtOH–NaOEt in N_2 at 40—60° give *oximinovomicine* (III) (as *C*) [*hydrochloride*, m.p. > 350° (darkens at 250°)], converted by $SOCl_2$ into the *carbamic acid lact-*

one (as *D*), m.p. 218° (slight darkening), which is hydrolysed (2*N*-NaOH) to *norvomicinic acid* (as *E*), m.p. > 350° (blackens at 320°) (O-*Me ether Me* ester, m.p. 194°), and reduced (H_2, PtO_2, EtOH) to a *dihydro*-derivative, m.p. 208°. (III) is reduced (Zn dust, 2*N*-HCl) to aminovomicine, converted by HNO_2 into *diazovomicine*, darkens at 200°. H. B.

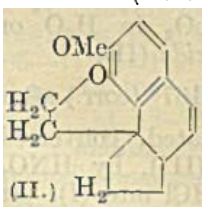
Production of ψ-morphine from morphine. C. C. Fulton (Amer. J. Pharm., 1933, **105**, 503—510).—ψ-Morphine is obtained by oxidising morphine in alkaline solution with the following reagents (yield in parentheses): $K_3Fe(CN)_6$ (90%), Hg salt (90%), $K_2S_2O_8$ in presence of Cu and C_5H_5N (75%). Morphine can be detected at a dilution of 1 : 3000 by oxidising with $K_3Fe(CN)_6$ and treating the solution with conc. H_2SO_4 and CH_2O (green colour). S. C.

Identity of Karrer's corynanthine and Fourneau's amorphous alkaloid from *Pseudocinchona africana*. Raymond-Hamet (Compt. rend., 1933, **197**, 860—862).—Identity is established by means of the hydrochloride, m.p. 185—200° after decomp. from 180° (block, preheated to 170°), $[\alpha]_D^{18}$ +7·20° to 7·60° in MeOH (cf. A., 1927, 64). R. S. C.

Oxyacanthine and berbamine. III. F. von Bruchhausen, H. Oberembt, and A. Feldhaus (Annalen, 1933, **507**, 144—159; cf. A., 1931, 636).—6 : 5′-Dialdehydo-2 : 3 : 2′-trimethoxy-5 : 4′-diethyldiphenyl ether (*loc. cit.*) is reduced (Clemmensen) to 2 : 3 : 2′-*trimethoxy*-6 : 5′-*dimethyl*-5 : 4′-*diethyldiphenyl ether* (I), m.p. 86·5°, the constitution of which is proved by synthesis. 4-Methoxy-*m*-tolyl acetate and $AlCl_3$ in $PhNO_2$ at room temp. give 4-*hydroxy*-5-*methoxy*-2-*methylacetophenone*, m.p. 124° [*semicarbazone*, m.p. 224° (sintering); *oxime*, m.p. 174°; Me ether, m.p. 76° (lit. 68°), prepared by methylation (Me_2SO_4) and from 3 : 4-dimethoxytoluene, AcCl, and $AlCl_3$], reduced (Clemmensen) to 4-*methoxy*-6-*ethyl*-m-*cresol* (II), m.p. 57·5° [*benzoate*, m.p. 71°; 2-*Br*-derivative (III), m.p. 51·5°]. Clemmensen reduction of 2-bromo*iso*vanillin gives 2-*bromo*-4-*methoxy*-m-*cresol*, m.p. 98°, which with AcCl and $AlCl_3$ in CS_2 affords 3-*bromo*-4-*hydroxy*-5-*methoxy*-2-*methylacetophenone*, m.p. 82° [*semicarbazone*, m.p. 214° (darkening and sintering)]. This is reduced (Clemmensen) to (III), which is methylated (CH_2N_2) to 2-*bromo*-3 : 4-*dimethoxy*-6-*ethyltoluene*, b.p. 80°/0·05 mm. Condensation (Ullmann) of this with the K derivative of (II) gives (I).

The dimethiodide of berbamine Me ether (IV), $C_{38}H_{42}O_6N_2$ (cf. Santos, Diss., München, 1929), m.p. 182°, treated successively with TlOH and hot aq. NaOH gives a methine base *A* (V), α 0° (Santos, *loc. cit.*), and a methine *base* B, $C_{40}H_{46}O_6N_2$, m.p. 146—147°, $[\alpha]^{20}$ −162° in $CHCl_3$. (V) and O_3 in 0·1*M*-H_3PO_4 afford 5 : 4′-dialdehydo-2-methoxydiphenyl ether, m.p. 82° (lit. 72°), and 6 : 5′-dialdehydo-2 : 3 : 2′-trimethoxy-5 : 4′-bis-(β-dimethylaminoethyl)-diphenyl ether. (IV) and tetrandine (Kondo *et al.*, A., 1932, 1048) appear to be optical isomerides, whilst oxyacanthine (Me ether) is a structural isomeride. The above results support the structures previously assigned to oxyacanthine and berbamine. H. B.

Sinomenine. XXXVIII. Dihydrosinomenilane and its degradation. K. Goto and H. Shishido (Annalen, 1933, **507**, 296—300).—Reduction (H_2, Pd–$BaSO_4$) of 6 : 6-*dichlorodihydrosinomenilane*, m.p. 110—116° (sinters at 105°) (from dihydrosinomenilone and PCl_5 in $CHCl_3$), gives *dihydrosinomenilane*, m.p. 145—150° (sinters at 140°), $[\alpha]_D^{28}$ +34·15° in EtOH,



the *methiodide*, m.p. 85—87°, decomp. 113—120°, of which with 16·5% KOH affords *de*-N-*methyldihydrosinomenilane* (I), m.p. 183—185°, $[\alpha]_D^{28}$ −98·22° in EtOH. The *methiodide*, m.p. 225—227°, of (I) is similarly converted into *sinomelane* (II), m.p. 85—90°, $[\alpha]_D^{28}$ −178·03° in EtOH. Reduction (H_2, Pd–C, dil. AcOH) of (I) gives *dihydrode*-N-*methyldihydrosinomenilane*, m.p. 143—146°, $[\alpha]_D^{28}$ +45·48° in EtOH, the *methiodide* of which with 16·5% KOH affords *dihydrosinomelane*, m.p. 55°, $[\alpha]_D^{28}$ −104·63° in EtOH, also obtained by reduction (H_2, Pd–C, 70% AcOH) of (II). H. B.

Arsine derivatives of silver salts. G. J. Burrows and R. H. Parker (J. Amer. Chem. Soc., 1933, **55**, 4133—4135).—$AsPh_2Me$ and AgCl in EtOH give the *chloride*, $[Ag(AsPh_2Me)_2]Cl$, m.p. 121°; the *bromide*, m.p. 110°, and *nitrate* (I), m.p. 112°, are similarly prepared, whilst the *iodide*, m.p. 132°, is obtained from (I) and HI in aq. EtOH. $AsPhMe_2$ similarly affords the analogous *chloride*, m.p. 97°, and *bromide*, m.p. 79°. These compounds are decomposed by conc. HNO_3 and hot MeOH or EtOH. Cryst. compounds could not be obtained from $AsPh_2Me$ or AsPhMeEt and Ag *d*-mandelate or *d*-bromocamphorsulphonate. H. B.

Course of oxidation of primary hydrazines. II. Action of oxidising acids on primary aromatic hydrazines. O. A. Seide, S. M. Scherlin, and G. J. Bras (J. pr. Chem., 1933, [ii], **138**, 225—230; cf. this vol., 946).—Oxidation of NHPh·NH_2 (I) (or *p*-C_6H_4Me·NH·NH_2) with aq. H_3AsO_4 in presence of Cu-bronze at about 75° gives mainly Ph_2AsOH (or C_6H_4Me·AsOH, etc.) with some PhAsO and Ph_3As; in strongly acidic solution (HCl), PhAsO (? $PhAsCl_2$) is the main product, and in presence of EtOH (using $CuSO_4$ as catalyst) some COPhMe is formed. The reaction mechanism is regarded as involving intermediate formation of a diazonium salt (? diazoarsenite). Similarly, with $HClO_3$ or HIO_3 and traces of Cu salts PhCl or PhI are formed. 1-Quinolylhydrazine with aq. HIO_3 at 40° gives 1-iodoquinoline (25%) and carbostyril (20%). $PhAsO_3H_2$ and (I) give approx. equal amounts of PhAsO and Ph_2AsOH and some Ph_3As. *Phenylhydrazine arsenate*, *phenylarsinate*, m.p. 84° (decomp.), and *phenylarsenite*, m.p. 100—101° (decomp.), are described. H. A. P.

Hydrates of sodium *p*-aminophenylarsinate. E. Kahane (J. Pharm. Chim., 1933, [viii], **18**, 334—339).—The monohydrate is obtained by air-drying at 42°, the trihydrate at 20°, and the penta- and hexahydrates are stable at 20° in an atm. saturated with H_2O. S. C.

Thermal decomposition of lead tetraphenyl. M. F. Dull and J. H. Simons (J. Amer. Chem. Soc.,

1933, 55, 4328—4329).—$PbPh_4$ decomposes at 252° in sealed Pyrex-glass tubes to Ph_2 (quant. yield). At 345—450°, Ph_2 (22—50%), C_6H_6, and p-$C_6H_4Ph_2$ are formed. H. B.

Action of selenium dioxide and selenium oxychloride on methone. H. Stamm and K. Gossrau (Ber., 1933, 66, [*B*], 1558—1563).—Methone [dimethylhydroresorcinol] (I) with SeO_2 in H_2O or EtOH yields *Se anhydrodimethone oxide* (II), CH_2–CO–C·SeO·C–CO–CH_2 / CMe_2·CH_2·C·O—C·CH_2·CMe_2, m.p. 167° (corr.) after softening at 148° when slowly heated, converted by Br into 4 : 4-dibromomethone (III), by HNO_3 into 4-nitromethone, and by dil. HCl into (I). It does not react with $FeCl_3$ or CH_2O and cannot be acetylated. The action of Na–Hg or Al–Hg gives non-uniform products. H_2S in EtOH is without action, whereas H_2Se immediately causes separation of 1 Se (from the H_2Se) and yields a very unstable (?) selenide. Oxidation of (II) by N_2O_3 in $CHCl_3$ yields the *substance* $C_{16}H_{20}O_5Se$ (? selenone), decomp. about 150°; it is feebly acidic, indifferent to $FeCl_3$ or CH_2O. With Br it affords (III) and with SO_2 in EtOH it gives (II). An analogous reaction does not occur between (I) and SO_2 at 70°. (I) and $SeOCl_2$ in $CHCl_3$ react (*a*) $2C_8H_{10}O_2+SeOCl_2 \longrightarrow H_2O+Se+2C_8H_{11}O_2Cl$ and (*b*) $2C_8H_{12}O_2+SeOCl_2 \longrightarrow H_2O+2HCl+$(II); separation of Se commences immediately the solutions are mixed. Since reaction between (I) and SeO_2 occurs rapidly and fairly completely, it can be used for the detection of H_2SeO_3, particularly in presence of H_2SeO_4. H. W.

Manometric micro-method for determination of carbon in organic compounds. D. D. Van Slyke, I. H. Page, and E. Kirk (J. Biol. Chem., 1933, 102, 635—649).—Backlin's method (A., 1930, 508) has been modified to give an accuracy of 0·2—0·5% using 1—3 mg. of C. H. G. R.

Determination of halogens in organic substances by Gasparini's method. K. Heller and G. Patzelt (Annali Chim. Appl., 1933, 23, 391—396).—This method (A., 1907, ii, 650; B., 1908, 430) is not to be recommended for compounds which sublime readily or are difficult to decompose. The authors' electrolytic method (A., 1929, 528, 1158; 1931, 1257) is simpler than that of Illari (A., 1930, 101; 1932, 955). T. H. P.

Micro-determination of iodine [in organic substances].—See this vol., 1260.

Micro-analytical determination of methoxyl groups in liquid compounds. A. F. Colson (Analyst, 1933, 58, 594—600).—Pregl's apparatus and technique give satisfactory results in most cases, but have been modified for liquids (*e.g.*, anisole) which tend to distil from the reaction vessel. Provision is made to regulate the stream of CO_2, and to avoid the escape of HI into the $AgNO_3$. BzOH, Ac_2O, CCl_4, and o-$C_6H_4(CO)_2O$ are equally efficient as catalysts; warm solutions in the absorption traps may give rise to low results through hydrolysis of MeI. J. G.

Diffusion as an aid in the analysis of gaseous paraffin hydrocarbon mixtures. R. A. Baxter and L. J. Beckham (J. Amer. Chem. Soc., 1933, 55, 3926—3936).—The Maxwell diffusion equation is extended to a mixture of gases diffusing out through an orifice, large compared with the mean free path, against air diffusing in at 1 atm. and const. temp. The calc. changes in composition of known ternary mixtures of hydrocarbons after diffusion accord with experimental vals. obtained with a simple apparatus, and thus, by means of the triangular charts described, a much closer approximation to the actual composition of an unknown hydrocarbon mixture can be obtained by using the diffusion method in conjunction with the usual combustion and absorption data. J. G. A. G.

Iodometric determination of substances forming oxalic acid and of methyl alcohol. K. Szahlender (Magyar gyogysz. Tarsas. Ert., 1933, 9, 125—147; Chem. Zentr., 1933, i, 3223).—$(CH_2·OH)_2$, glycerol, erythritol, adonitol, mannitol, glucose, fructose, sucrose, and lactose are quantitatively oxidised to $H_2C_2O_4$ in alkaline BrO′ solution in the light of the C arc. Mols. with an odd no. of C atoms also afford CO_2. The $H_2C_2O_4$ is determined iodometrically. MeOH is completely oxidised. A. A. E.

Titrimetric determination of carbonyl compounds by means of hydroxylamine hydrochloride. R. E. Meyer (Deut. Parfüm.-Ztg., 1933, 19, 3—5; Chem. Zentr., 1933, i, 2983).—Good results are obtained only when the oxime is easily formed. 0·003—0·004 mol. of the substance is dissolved in 20 c.c. of 5% EtOH–NH_2OH,HCl containing bromophenol-blue, treated with exactly 10 c.c. of 0·5*N*-EtOH–KOH, kept (with shaking) at room temp. for 1 hr., and then titrated back with 0·5*N*-HCl, a control determination being performed. Keeping in contact with a solution containing free NH_2OH is important. A. A. E.

Colour reactions of *m*-dinitrobenzene in alkaline media. M. Peronnet and R. Truhaut (J. Pharm. Chim., 1933, [viii], 18, 339—343).—Aldehydes, which give no colour reaction with a cold alcoholic solution of m-$C_6H_4(NO_2)_2$ and NaOH, do so on warming. Among purine derivatives only uric acid gives a stable violet colour, which may be used for the detection of this compound. Some NH_2-acids, particularly glycine and β-phenylalanine, give similar colorations, but none is obtained with camphor. S. C.

Thermal analysis of picrates.—See this vol. 1257.

Checking various concentrations of solutions of novocaine hydrochloride. F. W. Co Tui and A. Bengalia (J. Lab. Clin. Med., 1933, 18, 636—637).—An indicator method is described. Ch. Abs.

Microchemical contributions. IX. [Detection of alkaloids and alkylamines.]—See this vol., 1262.

Biochemistry.

Photometric determination of carbon monoxide in blood. I. J. K. PARNAS and J. SIENIAWSKI (Biochem. Z., 1933, **266**, 102—106).—The step photometer is used to determine CO-hæmoglobin in presence of hæmoglobin or oxyhæmoglobin. W. McC.

Significance of carbon dioxide in the diffusion of ammonium salts through the blood corpuscle-membrane. S. L. ØRSKOV (Pflüger's Archiv, 1933, **231**, 680—684; Chem. Zentr., 1933, i, 3731).—CO_2 assists hæmolysis by NH_4Cl; the effect is sp. A. A. E.

Action of erythrocytes on acetoacetic acid. P. E. GRÉGOIRE (Bull. Soc. Chim. biol., 1933, **15**, 1094—1106).—Erythrocytes (I) from 25 c.c. of dog's blood decompose 8—9 mg. $CH_2Ac{\cdot}CO_2H$ to $COMe_2$ per hr. in PO_4'''–NaCl media. The action of serum is < that of (I). Methylene-blue and glucose do not influence the reaction. H. D.

Oxidations by erythrocytes and catalytic influence of methylene-blue. I. Oxidation of lactate to pyruvate. II. Methæmoglobin and effect of cyanide. W. B. WENDEL (J. Biol. Chem., 1933, **102**, 373—383, 385—401).—I. Blood or erythrocytes (I) incubated at 37° with methylene-blue (II) show a decreased lactic acid (III) formation with a const. glucose (IV) consumption. Removal of (IV) from the cells and addition of (III) produces a slight decrease in (III) in the presence of (II). In glycolysed or washed (I) free from (IV) but containing (III) there is a moderate agreement between the loss of (III) and the gain of $AcCO_2H$ (V). No MeCHO is found. Added (V) is not oxidised by (I). With unwashed (I) more (IV) disappears than is accounted for by the (III) or (V) formed. A loss of O_2 capacity of (I) accompanies the oxidation of (IV) corresponding with the formation of methæmoglobin (VI).

II. Glycolytically active (I) in buffered NaCl containing (III) and (VI) show a formation of (V). Concns. of HCN up to 0·01*M* slightly inhibit the rate of (III) disappearance. Higher concns. caused an increased rate of (III) loss in the presence of (II). 0·02*M*-HCN completely inhibits the oxidation of (III) by (VI). Addition of (II) overcomes the HCN inhibition. Semicarbazide behaves similarly to HCN, indicating that the accelerating effect of the latter is due to fixation of (V). The presence of additional (V) inhibits (III) oxidation. H. D.

Blood-regenerative action of various chemical substances. H. MATSUO (Fukuoka-Ikwad.-Zasshi, 1932, **25**, 64—119).—Rapid blood regeneration (I) followed administration of a small dose of Cu combined with injections of tryptophan. Na glutamate has no effect on (I). CH. ABS.

Isoelectric point of hæmoglobin at high altitude. M. RUBOWITZ (Biochem. Z., 1933, **266**, 190—196).—Life at high altitude (Davos) or reduction of atm. pressure to 330—400 mm. leads to a shift to the alkaline side in the isoelectric points of hæmoglobin and of reduced and CO-hæmoglobin (man, calf, ox, rabbit, guinea-pig, rat). The alteration is accompanied by a change in colloidal character. W. McC.

Hæmoglobin content of the blood of infants. C. A. ELVEHJEM, W. H. PETERSON, and D. R. MENDENHALL (Amer. J. Dis. Children, 1933, **46**, 105—112).—The blood-hæmoglobin decreases from 22 g. per 100 c.c. at birth to a min. val. at 8—12 weeks; at 12—24 weeks it reaches 11—12 g., the val. remaining const. to 2·5 years and thereafter gradually increasing. CH. ABS.

Crystallisation of a compound of hæmoglobin and carbon dioxide. D. D. VAN SLYKE, R. T. DILLON, and A. HILLER (Proc. Nat. Acad. Sci., 1933, **19**, 828—829).—Crystals of oxyhæmoglobin, containing as much CO_2 as O_2, have been prepared from rat blood. At physiological CO_2 tensions, these contain 1/15—1/20 as much CO_2. H. G. R.

Blood-iron in hæmocyanin animals, and ease of elimination of copper from hæmocyanin. G. BARKAN (Klin. Woch., 1933, **12**, 546—547; Chem. Zentr., 1933, i, 3589).—Blood of *Astacus fluviatilis*, incubated for 24 hr. with 0·4% HCl, afforded only slight traces of Fe, but all the Cu, in the ultra-filtrate. A. A. E.

Crystalline chlorocruorin. H. M. FOX and J. ROCHE (Compt. rend., 1933, **197**, 874—876, and Nature, 1933, **132**, 516).—Addition of H_2O (1 vol.) and then of saturated aq. $(NH_4)_2SO_4$ (1 vol.) to the blood of *Spirographis Spallanzanii* at 0° gives cryst. chlorocruorin (I) (photomicrographs), containing C 47·2, H 7·3, N 15·4, S 2·6, and Fe 1·2%, and having absorption bands at 602·5, 562·5, 515, 445, 360, and 275 mμ. The differences between (I) and hæmoglobin are discussed. R. S. C.

Proteins of ox serum. H. F. HOLDEN and M. FREEMAN (Austral. J. Exp. Biol., 1933, **11**, 185—195).—Variations in [α] of the proteins of ox serum indicate that they are probably not individuals, but variable and unstable mixtures. It is suggested that the production of euglobulin (I) on treatment of pseudoglobulin (II) with dil. acid indicates that (I) may be a mixture of (II) with a metaprotein. A. L.

Tryptophan in the hæmolymph of the silkworm. L. MAMOLI (Giorn. Chim. Ind. Appl., 1933, **15**, 437—438).—Six samples showed 0·15—0·163 (mean 0·152) % of tryptophan, determined by Fürth and Nobel's modification (A., 1921, i, 74) of Voisonet's reaction (A., 1906, ii, 59). It is suggested that in the silkworm, and possibly in other insects, digestion of proteins proceeds as far as the liberation of NH_2-acids. T. H. P.

Free and combined amino-nitrogen in deproteinised blood and tissue under normal and pathological conditions. I, II. E. BECHER and E. HERRMANN (Deut. Arch. klin. Med., 1933, **171**, 529—546, 547—564; Chem. Zentr., 1933, i, 3991—3992).—I. An analytical method based on Folin's procedure gives results to ±0·6 mg. per 100 c.c. The influence of various substances is recorded.

II. Normal human blood contains 5—7 (average 6·6) mg. NH_2-N per 100 c.c. (free) and 1—3 (2·3) (combined). On keeping, deproteinised blood shows a diminution in NH_2-N, whilst non-deproteinised blood shows an increase. Free NH_2-N in total blood is > in serum and plasma and < in erythrocytes. Mammalian blood contains practically the same, blood of animals with nucleated erythrocytes a markedly greater, content of NH_2-N. A. A. E.

Comparison of gasometric, colorimetric, and titrimetric determinations of amino-nitrogen in blood and urine. D. D. Van Slyke and E. Kirk (J. Biol. Chem., 1933, **102**, 651—682).—The gasometric method (I) and the CH_2O titration (II) are satisfactory for blood and urine. The $COMe_2$ titration with blood is invalidated by the presence of large amounts of org. acids. Folin's method gave unsatisfactory results. For blood, (I) is recommended, whilst (II) is advocated for urine. H. G. R.

Micro-determination of residual nitrogen and of urea in blood. F. Rappaport (Mikrochem., 1933, **14**, 49—74).—Satisfactory results can be obtained with 0·2 c.c. of blood. For the determination of residual N the sample, after removal of proteins, is submitted to a micro-Kjeldahl operation, and the NH_3 is distilled into standard NaOBr solution buffered to the degree of alkalinity appropriate to the reaction $2NH_3+3NaOBr \longrightarrow N_2$. Excess of NaOBr is determined iodometrically with 0·01*N*-$Na_2S_2O_3$. Urea is determined by decomp. with urease, followed by removal of proteins. To prevent production of NH_3 from NH_2-acids the NH_3 formed is distilled from a borate buffer. F. L. U.

Micro-determination of indican in blood. F. Rappaport and H. Engelberg (Mikrochem., 1933, **14**, 75—80).—A modification of Jolles' method is described. F. L. U.

Determination of uric acid in blood. Fischer and Huppmann (Süddeut. Apoth.-Ztg., 1932, **72**, 2; Chem. Zentr., 1933, i, 3992).—In Flatow's method deproteinisation with uranyl acetate (I) and C_5H_{11}·OH gives higher results than that with (I) and $COMe_2$. A. A. E.

Histamine-like and "delayed" toxic substances in blood. K. Zipf and P. Hulsmeyer (Arch. exp. Path. Pharm., 1933, **173**, 1—14).—Aq. and aq.-EtOH extracts and the $COMe_2$-pptd. material from aq.-EtOH extracts of fresh and old blood contain a significant amount of an adenosine-like substance (I), but no appreciable amount of histamine. Aq. and aq.-EtOH extracts also contain a substance which, like (I), stimulates the intestine and uterus, but, unlike (I), has no depressor action and is probably identical with the "delayed" toxic substance of Freund (*ibid.*, 1920, **86**, 226). F. O. H.

Phenolic substance in spider's blood. J. Millot and R. Jonnart (Compt. rend., 1933, **197**, 1002—1003).—Coincidental with the approach of moulting, the granular leucocytes and also the plasma of spider's blood give reactions for a free phenolic group. These reactions disappear after each moulting. F. O. H.

Determination of blood-fat. O. Muhlbock and C. Kaufmann (Klin. Woch., 1932, **10**, 1128—1129; Chem. Zentr., 1933, i, 3757).—In Bloor's method cholesterol is pptd. from the extract containing that and fatty acids with 1% EtOH–digitonin, and the fatty acids are then oxidised with $K_2Cr_2O_7$. A. A. E.

Spontaneous variations in blood-sugar. P. Mauriac, P. Broustet, and A. Dupin (Compt. rend. Soc. Biol., 1933, **112**, 587—590).—Determinations of the blood-sugar level of man, fasting and at rest, showed spontaneous variations, at fairly regular intervals (average val. 0·01—0·02 g. per 100 c.c.). With the diabetic subject these variations were also observed, but they were not so marked after feeding combined with insulin administration. Nutr. Abs. (*b*)

Variations in blood-lactic acid. L. Binet and J. Klukowski (J. Physiol. Path. gen., 1933, **31**, 372—379).—Increases were observed in lactic acid (I) content of the blood of dogs due to anæmia produced by repeated bleedings, and after raising the body-temp. by injection of $OH{\cdot}C_6H_3(NO_2)_2$. After pancreatectomy it was lowered, but hypophysectomy caused an increase. Perfusion of the liver and lungs caused considerable increase in (I); the elevation after lung perfusion persisted in depancreatised dogs and was as great as the corresponding fall in blood-glucose. Nutr. Abs. (*b*)

Blood-phosphorus. I. Partition of phosphorus in whole blood and serum; serum-calcium and plasma-phosphatase from birth to maturity. G. Stearns and E. Warweg (J. Biol. Chem., 1933, **102**, 749—765).—Inorg., lipin-, ester-, and total P vary through the period of growth and reach a max. at varying ages. The % of blood-corpuscles is highest at birth, the adult val. being slightly less. Serum-Ca is also highest at birth and remains const. after the third month. Plasma-phosphatase is low at first, rising rapidly to a max. in the first month and remaining high until the second year. H. G. R.

Mineral content of blood of children in the first year of life. J. A. Kotikoff (Jahrb. Kinderheilk., 1933, **138**, 280—318).—During the first 3 months, blood-Ca and -org. P are >, and -inorg. P is somewhat <, later. In the third month the mineral content is very low. Between the fifth and sixth month the mineral content again becomes lower, whilst the ninth month is the time of greatest variability. The composition of the blood is in very close relationship with the feeding in respect of some minerals, particularly Na and to a smaller extent inorg. P. All the minerals except Na increase in spring. Nutr. Abs. (*b*)

Variations in dry matter of blood and their relationship to constitution and production in Hohenfleck cattle. E. Diem (Arch. Tierernahrung, 1933, **9**, 123—155).—The blood of cattle showed individual variations in dry matter (I) up to 25% of the smallest val. An increase in (I) was associated with rising barometer, with excitement of the animals during blood sampling, and with the beginning of pregnancy. Œstrus, age and sex, stage of lactation,

body-wt., and milk yield could not be correlated with (I). NUTR. ABS. (*b*)

Carius digestion for the measurement of chloride in biological material. F. W. SUNDERMAN and P. WILLIAMS (Biochem. J., 1933, **27**, 1578—1580).—In cases where Cl is not completely measured by the Carius method, preliminary digestion with alkali is effective. Failure to measure Cl completely is due to factors other than a loss during the digestion. H. G. R.

Micro-determination of bromine in blood. A. G. FRANCIS and C. O. HARVEY (Biochem. J., 1933, **27**, 1545—1550).—A method whereby Br may be determined in 1—2 c.c. of blood with an accuracy of 10% is described. H. G. R.

Conductivity of normal and pathological serum. F. STEIGERWALDT and B. REISER (Arch. exp. Path. Pharm., 1933, **173**, 15—25).—For normal sera, κ has a const. val. of 0·0146—0·0155. This val., which primarily depends on the NaCl content, is diminished by carcinoma, a change apparently not due to formation of Na lactate. No significant changes occur in many other diseases investigated. F. O. H.

Fibrinogen content of fish plasma. E. ZUNZ (Bull. Acad. roy. Belg., 1933, [v], **19**, 929—937).—9 c.c. of blood are added to 1 c.c. of 7% Na citrate (3·55% for Teleosteans). An equal vol. of 1—2% $CaCl_2$ is added to the plasma, which is then kept at 2—4° for 24—48 hr. The clot of fibrin is freed from serum and dried to const. wt. at 105°. The content varies greatly in different samples from the same species. Many Teleosteans have a fibrin content similar to that of mammals, whilst other fish contain less. P. G. M.

Coagulation of fish blood. E. ZUNZ (Bull. Acad. roy. Belg., 1933, [v], **19**, 938—944).—Muscle extracts of *Scylliorhinus stellaris* (Selachian) and *Conger vulgaris* (Teleostean) contain sp. substances capable of activating serum (deprived of thrombin), so that it coagulates the fibrinogen of the same genus. Rabbit-muscle extract exhibits similar properties. P. G. M.

Influence of cod-liver oil on the hæmolytic complement of human beings. T. W. B. OSBORN (Biochem. J., 1933, **27**, 1425—1429; cf. A., 1932, 184).—Ingestion of a dose of cod-liver oil by 50 humans produced, on the average, a rise in hæmolytic complement > that produced by olive oil. A micro-pipette for the measurement of vols. of the order of 0·005 c.c. is described. H. D.

Individual differences in chicken blood. K. LANDSTEINER and P. LEVINE (Proc. Soc. Exp. Biol. Med., 1932, **30**, 209—212).—Agglutination tests are described; two general types were differentiated. CH. ABS.

Precipitin reaction. Antibody production in rabbits injected with an azo-protein. M. HEIDELBERGER, F. E. KENDALL, and C. M. S. HOO (J. Exp. Med., 1933, **58**, 137—152). CH. ABS.

Phenylcarbimide-protein compounds and their immunological properties. II. Gelatin compounds. S. J. HOPKINS and A. WORMALL (Biochem. J., 1933, **27**, 1706—1715).—*Phenyl-* (I) and *p-bromophenyl-ureidogelatin* (II) have been prepared by the action of phenyl- and *p*-bromophenyl-carbimide on gelatin at p_H 8. (I) and (II) give positive precipitin (III) and complement-fixation (IV) reactions with anti-sera to phenylureido-horse-serum-globulin, the best reactions being obtained at room temp. and with higher dilutions of the antigen. (I) and (II), on injection into rabbits, give no antibodies detectable by (III) or (IV) tests. The non-antigenicity of gelatin is not due solely to a deficiency in aromatic groupings. A. W.

Chemical nature of lipin antigens, particularly of cerebral antigen. H. RUDY (Klin. Woch., 1933, **12**, 433; Chem. Zentr., 1933, i, 3210).—Cerebral antigen contains no P; short treatment with EtOH–alkali hydroxide does not decompose it. It does not dialyse through parchment. A. A. E.

Serological differentiation of steric isomerides. K. LANDSTEINER and J. VAN DER SCHEER (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1261—1263).—Immune sera sp. for *l*- and *d*-tartaric and *l*-malic acid have been obtained. An immune serum for *l*-malanilic acid reacted with the *l*- but not the *d*-tartranilic antigen. CH. ABS.

Carbohydrate antibodies. Gum arabic. P. UHLENHUTH and E. REMY (Klin. Woch., 1933, **12**, 911—912).—When a drop of pharmaceutical olive oil–gum arabic emulsion is added to normal horse serum and the mixture shaken, pptn. occurs. Ass serum also gives the reaction strongly, but the sera of rabbits, guinea-pigs, and man generally do not react. If a rabbit is injected for a long time with the emulsion, antibody formation occurs. Pure arabic acid and its salts suffice to produce the results, but not emulsions of starch, dextrin, tragacanth, cherry gum, etc. NUTR. ABS. (*b*)

Heparin. I. Preparation. II. Heparin in various tissues. III. Purification of heparin. D. A. SCOTT and A. F. CHARLES (J. Biol. Chem., 1933, **102**, 425—429, 431—435, 437—448).—I. Minced ox liver allowed to autolyse for 24 hr. is extracted with 0·5*N*-NaOH and saturated $(NH_4)_2SO_4$; after keeping for 1 hr. at 50° the proteins are coagulated by heating rapidly to 70° and filtered off. Heparin (I) is pptd. with H_2SO_4 at p_H 2—2·5, collected, and washed with hot dil. H_2SO_4. The ppt. is then suspended in 95% EtOH, the EtOH decanted, and the ppt. dissolved in H_2O. Further purification is effected by incubation with trypsin and xylene, pptn. with EtOH, re-dissolution in H_2O, and pptn. with $COMe_2$. The product contains 3·5 units per mg.

II. A purified (I) was obtained by treating the product obtained as above with Lloyd's reagent in 2% AcOH, and addition of 2 vols. of $COMe_2$. The white ppt. was washed with EtOH and dried in vac. (I) occurs in greatest quantities in the muscle, liver, and lung. Dog liver contains twice as much (I) as ox liver.

III. Crude (I) containing 5 units per mg. is purified first by Howell's technique with Lloyd's reagent (A., 1928, 318), giving a powder containing 15 units per mg. It is further purified by dissolution in HCl at p_H

5 and pptn. with $CdCl_2$. The supernatant liquor is treated with $COMe_2$, giving a further ppt., which was repeatedly redissolved in NaCl and pptd. with $COMe_2$, giving a final product containing 421 units per mg. By pptn. as the Na salt from EtOH an activity of 480 units per mg. was attained, whilst the hydrochloride contained 471 units per mg. All the products contained N, their activity being destroyed by treatment with $NaNO_2$. Tests with resorcinol, phloroglucinol, and naphthoresorcinol were negative. H. D.

Astacene from the eggs of the spider-crab (*Maia squinado*). R. KUHN, E. LEDERER, and A. DEUTSCH (Z. physiol. Chem., 1933, 220, 229—234).—Vitellorubin (I), m.p. 242—243° (decomp.), obtained from the eggs of the spider crab is probably identical with the ovo-ester of astacene (II) (cf. this vol., 509). (I) gives (II) on alkaline hydrolysis. (II) [*Ac* derivative, m.p. 235° (decomp.)] is probably a highly unsaturated OH-lactone. It yields 5 AcOH on oxidation with CrO_3. Vitellolutein, from the same source as (I), agrees optically and chromatographically with β-carotene. J. H. B.

Cytoflav. K. LAKI (Biochem. Z., 1933, 266, 202; cf. A., 1932, 537).—The absorption spectrum curve of cytoflav (I) (from heart muscle) exhibits a max. between 450 and 460 mμ, and hence (I) is identical with the coloured component of Warburg's yellow enzyme. W. McC.

Nucleoproteins. IV. Native nucleoproteins. S. J. VON PRZYŁECKI, S. FRAJBERGER, and W. GIEDROYĆ (Biochem. Z., 1933, 266, 107—127).—Mononucleoproteins probably do not occur naturally, being incapable of existence under ordinary biological conditions. Native nucleins (I), which are complex mixtures, exist, *e.g.*, in liver. As regards the linking between the nucleic acid (II) and the protein (III), they are probably intermediate between the hetero- and homo-polar type of compound, being certainly heteropolar below the isoelectric point. In the individual (I) the ratio of (II) to (III) varies greatly. Native polynucleins are found less frequently than is usually supposed. Compounds (*e.g.*, lipins) similar to nucleoproteins but containing additional different org. components also occur in biological material. W. McC.

Colloidal behaviour of muscle-proteins. V. Composition of proteins of rabbit muscle and structure of the muscle. H. H. WEBER and K. MEYER (Biochem. Z., 1933, 266, 137—152; cf. this vol., 624).—Minced rabbit muscle repeatedly extracted with 0·6*N*-KCl first at p_H 8—9 and then at 9·5 yields extracts (I) containing 75 [red muscle (VII)] to 85% [white (VI)] of the total N (V). Myosin (II), myogen (III), and a "globulin *X*" (IV) are obtained from (I) by dialysis and pptn., whilst only (III) and (IV) are obtained if mechanical pressure is substituted for extraction. (II) is pptd. by 0·03—0·04*N*-KCl at p_H about 7, (IV) by 0·016*N*-KCl–KOAc at $p_H < 6$; under these conditions (III) remains in solution. (II), (III), and (IV) are present in living muscle. Residual N is 12—13% of (V). (VI) contains 22% of (III), 22% of (IV), 40% of (II), and 17% of stroma. The corresponding amounts in (VII) are 17, 17, 40, and 27%. (III) and part of (IV) constitute the liquid portion of muscle [concn. of (III) < 7%]. There is no (II), (III), or (IV) in stroma. W. McC.

Determination of the phosphorus fractions in muscle and of phosphagen in the warm-blooded heart. H. MUGGE (Arch. exp. Path. Pharm., 1933, 173, 333—340).—The material is dried in vac. at low temp. and extracted with cold 4% $CCl_3{\cdot}CO_2H$, the extract being subsequently treated by a method based on those of Eggleton and Eggleton (A., 1930, 109) and Fiske and Subbarow (A., 1926, 443). The "phosphagen index" (phosphagen/orthophosphate ratio) of heart-muscle is approx.=that of skeletal muscle (approx. 2·5). The contents of pyrophosphate and other P fractions are given. F. O. H.

Lipins in cell protoplasm. Lipoidal inclusions in cells of mesenchyme origin. J. B. GOLDMAN (Arch. sci. biol., U.S.S.R., 1932, 32, 459—470).—A method of staining is described, and the nature of the lipoidal bodies is discussed. CH. ABS.

Choline. II. Choline in the organism. T. AOKI (Trans. Japan. Path. Soc., 1932, 22, 201—209).—Administration of lecithin into the stomach or duodenum is followed by increase in blood- and lung-choline. CH. ABS.

Choline (acetylcholine?) content of animal tissue. E. STRACK, E. NEUBAUR, and H. GEISSENDORFER (Z. physiol. Chem., 1933, 220, 217—228).—Free choline (I) is practically absent from fresh ox and dog liver. (I) is quickly formed by hydrolysis when blood circulation ceases; the increase is most rapid in the first and fourth hr. A substance present, probably a H_2O-sol. sphingomyelin, readily liberates (I) in presence of too high a concn. of mineral acid, which should therefore be avoided in determination of (I). EtOH is unsuitable as a fixing agent, since it does not immediately inhibit the liberation of (I) from its complexes. J. H. B.

Detection of an acetylcholine-like substance in the skin. K. GOLLWITZER-MEIER and A. BINGEL (Arch. exp. Path. Pharm., 1933, 173, 173—179).—An acetylcholine-like substance (I) occurs in the transudate of blisters induced by injection of 0·9% aq. NaCl (especially when the limb is heated to 45—48°) and in the protein-containing fluid of cantharides blisters; in the latter case, however, the action of (I) is almost completely masked by that of histamine-like substances. F. O. H.

Urea precursor depot in kidney tissue. E. KIRK (J. Biol. Chem., 1933, 102, 683—690).—More NH_3 is formed in a mixture of urease from jack bean (I) and frog kidney (II) than corresponds with the urea in (II). This arises from a substrate in (I) which is decomposed by an arginase-like enzyme in (II), which is not present in dog and rat kidney or in (I). H. G. R.

Effect of lipins of cells on swelling of gelatin. P. BAMBERGER (Biochem. Z., 1933, 266, 175—189).—The state of combination of the H_2O in gelatin gels is independent of the extent of swelling, but is altered by substances (I) of low mol. wt. (II) and by finely dispersed (I) of high (II), the proportion of bound H_2O being increased by K_2SO_4<Na taurocholate<

OH′ and decreased by KI and lecithin. H·, cholesterol, triolein, Na oleate, and glycogen have no effect. Account must be taken of delays in freezing. From about −7° to −35° the ratio between freezable and non-freezable H_2O remains const., probably because H_2O of the "H_2O of crystallisation" type is then no longer present. The biological significance of these results, indicating that H_2O in tissues exists in at least two forms, is discussed. W. McC.

Electrolytes in human tissue. I. Digestion of tissue and determination of various electrolytes. G. E. CULLEN and W. E. WILKINS. **II. Electrolyte content of tissues from cases with various diseases.** G. E. CULLEN, W. E. WILKINS, and T. R. HARRISON (J. Biol. Chem., 1933, **102**, 403—413, 415—423).—I. Tissue is digested with HNO_3, followed by ashing completed with $(NH_4)_2S_2O_8$. Ca is determined by oxalate analysis of the supernatant liquors after pptn. of CaC_2O_4. P is determined in the HNO_3 digest by heating with $Mg(NO_3)_2$ and MgO and determining the P by the Fiske–Subbarow method (A., 1926, 443).

II. The H_2O, Cl′, P, K·, Ca··, and Mg·· contents of various tissues of persons suffering from various diseases are determined. H. D.

Iron in hen's ovary. V. D. MARZA, E. MARZA, and L. CHIOZA (Bull. Histol., 1932, 9, 213—225).—Inorg. Fe is present in the interstitial cells and org. Fe in the yolk of rapidly growing eggs. For determining org. Fe the incineration method is preferred; for inorg. Fe Macallum's method is satisfactory. Staining with hæmatoxylin is unsatisfactory. The nuclei of the ova contain no Fe. CH. ABS.

Clinical determination of the protein content of body-fluids. E. H. FISHBERG (Klin. Woch., 1932, **10**, 988; Chem. Zentr., 1933, i, 3991).—For serum 5 c.c. are diluted with 5 c.c. H_2O and treated with 0·25 c.c. 0·1*N*-HCl and 2 drops of Me-red. The colour indicates the protein content: yellow > 6%, yellowish-orange 5—6%, reddish-orange 4—5%, pink 3—4%, red < 3%. For exudates and transudates 1 c.c. is used undiluted; red < 1%, yellow > 3%. The error is ± 0·5 g. per 100 c.c. A. A. E.

Calcium content of human cerebrospinal fluid and of an ultrafiltrate of serum. O. M. SEARLE and J. J. MICHAELS (Amer. J. Physiol., 1933, **103**, 455—457).—Over the normal range of serum-Ca vals. the cerebrospinal-fluid Ca approximates closely to the diffusible Ca of blood. NUTR. ABS.

Bromide and chloride distribution between serum and cerebrospinal fluid. M. MISHKIS, E. B. RITCHIE, and A. B. HASTINGS (Proc. Soc. Exp. Biol. Med., 1933, **30**, 473—475).—When NaBr was given in doses of 0·01 g. per lb. body-wt. per day for 5 days, serum(I)- : cerebrospinal fluid(II)-Br was > 1; hence bromides are not freely diffusible between (I) and (II). (I)-Br + -Cl : (II)-Br + -Cl was 0·87, in agreement with the reported ratio for Cl alone. CH. ABS.

Osmotic relations between blood and body-fluids. II. Osmotic relation of blood and gastric juice. A. GILMAN and G. R. COWGILL (Amer. J. Physiol., 1933, **103**, 143—152). NUTR. ABS.

Sodium formate as salt substitute. J. FREUND (Klin. Woch., 1933, **12**, 226—227).—4—5 g. of HCO_2Na had no effect on gastric secretion. NUTR. ABS.

Influence of acid secretion of the stomach on variations in blood-sugar level after administration of caseinogen and hydrochloric acid. S. MARINO and F. ROMEO (Arch. Farm. sperim., 1933, **56**, 407—442).—The fasting blood-sugar level is no index of hypo- or hyper-chlorhydria. However, hyperglycæmia (I) follows administration of caseinogen (II) by mouth, whilst when (II)+HCl is given (I) is more marked in hyper- than in hypo-chlorhydrics, and when HCl alone is given hyperchlorhydrics become hyperglycæmic and hypochlorhydrics become hypoglycæmic. The results are discussed in relation to neuro-endocrine regulation. R. K. C.

Acetylcholine and gastric juice. F. GEBHARDT and J. KLEIN (Klin. Woch., 1933, **12**, 535—538; Chem. Zentr., 1933, i, 3590).—For sub- and an-acid vals. of gastric juice, injection of acetylcholine leads in 50% of the cases to an increase in aq. secretion, and in a small no. of cases to a rapidly falling increase in the acid curve. The Cl secretion is in almost all cases increased. A. A. E.

Peculiarities of goat's milk and the composition of goat's blood. F. E. NOTTBOHM and K. PHILIPPI (Z. Unters. Lebensm., 1933, **66**, 289—301).—Goat's milk (I) differs from cow's milk only in the Cl content, which is twice as high in (I). Goat's blood has a higher K content than the blood of other ruminants. The constituents of the ash of the serum are not appreciably different from those of the sheep and ox. E. C. S.

Milk and fat secretion during lactation in women. C. VINCENT and J. VIAL (Compt. rend. Soc. Biol., 1933, **112**, 910—912).—The yield of morning milk was invariably > that at midday or in the evening. NUTR. ABS.

Buffer intensities of milk and milk constituents. II. Buffer action of calcium phosphate. E. O. WHITTIER (J. Biol. Chem., 1933, **102**, 733—747).—Equations for the ionic equilibria of Ca phosphate solutions, with both $CaHPO_4$ and $Ca_3(PO_4)_2$ as the solid phase, are given. Initial concns. of $Ca^{··}$ and $PO_4^{'''}$ have been calc. for acid whey, and the effect of increased ionic strength of these vals. has been used to explain some of the peculiarities of whey. H. G. R.

Effect of ultra-violet irradiation and administration of iodine on biological value of milk. L. ANDRIK and C. KUCERA (Compt. rend. Soc. Biol., 1933, **113**, 622—624).—Addition of dried milk from a thyroidectomised goat to a ration of bread, starch, and dried meat inhibited growth and delayed metamorphosis of tadpoles. Milk from the same goat after irradiation of the udder gave somewhat better results. Subcutaneous injection of I into the goat improved the val. of the milk to that of green food. Thyroids from tadpoles on milk from the untreated goat were under-developed; on milk after irradiation of the udder they contained more colloid, and on milk after I treatment were normal in structure.

Daily injection of 40 mg. of KI caused a marked rise in milk-Ca and a small increase in fat.

NUTR. ABS. (*b*)

Flavins isolated from white of egg and milk. R. KUHN and T. WAGNER-JAUREGG (Ber., 1933, **66**, [*B*], 1577—1582).—Treatment of ovoflavin (I) (this vol., 522) and lactoflavin (II) (*ibid.*, 298) with Ac_2O in C_5H_5N gives cryst. *acetates* (III), m.p. 240° (decomp.) and 242° (decomp.), which do not cause mutual depression of m.p., so that possibly, in spite of certain differences, (I) and (II) are identical. (III) are not removed from $CHCl_3$ by Na_2CO_3, whereas NaOH causes hydrolysis with regeneration of the pigment which retains vitamin-B_2 characteristics. Determination of the mol. wt. of (III) in $CHCl_3$ and $COMe_2$ gives the val. 500±60 and establishes the presence of 4 N. Irradiation of (I) in $CHCl_3$ leads to a pigment $C_{13}H_{12}O_2N_4$±C±H_2, presumably identical with that obtained by Warburg *et al.* (this vol., 313, 533). Reaction consists not in isomerisation but in elimination of a portion, $C_4H_8O_4$, of the mol. which is not a sugar-like residue. (I) and (II) are not affected by HNO_2, showing absence of NH_2. Treatment of (II) with alkali affords urea, indicating the group ·NH·CO·NH·. The flavins therefore contain this grouping, with a second containing OH and yielding lumiflavins when irradiated and a third relatively stable grouping with two feebly basic, probably *tert.* N atoms distributed at the double linkings causative of colour. Alloxazine differs so considerably from the natural flavins that an analogous constitution is excluded. Treatment of lactoflavin *C* (Ellinger *et al.*, this vol., 298, 847) with 2*N*-AcOH and subsequent purification leads to a colourless *material* (32·08% N); it is therefore probably not a homogeneous pigment. H. W.

Composition of sweat collected in Turkish baths. M. CHATRON (Bull. Soc. Chim. biol., 1933, **15**, 1107—1112).—The sweat contains a high % of fixed base; vals. for urea-, NH_2-, and total N, org. acids, Cl′, total base, and total acidity are determined. H. D.

Is glycogen a constituent of urine? P. JUNKERSDORF and M. MISCHNAT (Z. ges. exp. Med., 1932, **83**, 711—717; Chem. Zentr., 1933, i, 3590).—Normal or pathological urine does not contain glycogen. The reducing power of normal urine is due to uric acid, purine substances, creatinine, dyes, and glycuronic acid derivatives; that of pathological urine is due also to sugar, homogentisic acid, quinol, and bile acids etc. A. A. E.

Determination of sugar in urine. L. DINKIN (Med. Klinik, 1932, **27**, 1793—1794; Chem. Zentr., 1933, i, 3993—3994).—5 c.c. of urine, diluted if necessary, are boiled with 1 c.c. of Nylander's reagent until blackening is complete, the time taken being determined and the % of glucose read from a diagram. The accuracy is 0·25—0·5%. A. A. E.

Fermentable sugar in fasting urine. V. J. HARDING and D. L. SELBY (Biochem. J., 1933, **27**, 1598—1608).—Filtrates suitable for "sugar" determinations may be cleared by KH_2PO_4 followed by MgO. The val. for fermentable sugar (I) varies with the dilution previous to the application of H_2SO_4–Lloyd's reagent, the clearing and the Cu reagents. Ingestion of glucose (II) results in slight increase in (I), but when the renal threshold is passed, larger amounts appear. Some substance removable by yeast other than (II) exists in normal urine. H. G. R.

Threshold for the renal excretion of inorganic phosphates in the sheep. R. H. WATSON (Austral. J. Exp. Biol., 1933, **11**, 197—207).—The level of the threshold in the animals examined varied between 2·8 and 6·2 mg. of P per 100 c.c. of blood, the vals. for any animal being variable. A. L.

Colorimetric determination of phosphate in urine. J. FOUCRY (Union pharm., 1933, **72**, 257—258; Chem. Zentr., 1933, i, 3993).—The dark yellow sol. complex afforded by vanadates and NH_4 phosphomolybdate is employed. A. A. E.

Nitrate-nitrogen in the urine of children. E. S. HEWITT and A. S. HURT (Amer. J. Dis. Children, 1933, **46**, 24—29).—For infants aged 2—20 days, fed on milk, urinary NO_3-N is 0—1·31 mg. per 100 c.c.; at 1—5 years (general diet) it is 0—2·31 mg. High vals. are found in disease of the digestive tract. CH. ABS.

Determination of urinary total nitrogen. M. WIRBEL (Union pharm., 1931, **72**, 1; Chem. Zentr., 1933, i, 3752).—Urine (1 c.c.) is heated until colourless with H_2SO_4 (*d* 1·84, 1—2 c.c.), $KHSO_4$, and $HClO_4$ (4—6 drops), diluted, neutralised with NaOH (phenolphthalein), treated with 2 c.c. of neutral 10% aq. CH_2O, and titrated with NaOH. A. A. E.

Casts and protein in urine. L. MEYLER (Ned. Tijdschr. Geneeskunde, 1933, **77**, 759—773; Chem. Zentr., 1933, i, 3211).—The presence of albumin (usually little) and casts (usually many) in urine is always associated with acidosis; it is also found after respiratory disturbance and great bodily exertion. Presumably with strongly acid urine the renal cells become penetrable to protein, the globulin fraction flocculating in the renal canals in cylindrical form. A. A. E.

Solubility of calcium oxalate and uric acid in solutions of urea. G. MEDES (Proc. Soc. Exp. Biol. Med., 1932, **30**, 281—284).—The solubility of CaC_2O_4,H_2O increases with increasing concn. of urea; that of uric acid is max. at 10% urea. The amount of CaC_2O_4 dissolved by 1500 c.c. of 3% urea solution is approx.=, and of uric acid and Na urate is much >, the daily output in urine. CH. ABS.

Excretion of uric acid and urates by the bird. E. G. YOUNG and N. B. DREYER (J. Pharm. Exp. Ther., 1933, **49**, 162—180).—The urine of cockerels contains uric acid (I) in supersaturated solution (0·2—0·7%) and its colloidal nature is demonstrated by ultrafiltration experiments. In the blood, (I) is probably in true solution and even during anuria does not exceed 0·091%. Various (I) solvents [Li salts, piperazine, piperidine, and $(\cdot CH_2\cdot NH_2)_2$] increase the excretion of (I) but to a degree largely determined by their diuretic effect. Other diuretic agents similarly increase excretion of (I). W. O. K.

Kidney secretion in reptiles. E. K. MARSHALL, jun. (Proc. Soc. Exp. Biol. Med., 1932, **29**, 971—

973).—By determination of blood- and urinary glucose and uric acid in the iguana injected with phloridzin followed by urethane, it is calc. that 6% of the uric acid is eliminated by glomerular filtration and 94% presumably by tubular secretion. Experiments with chickens are also described. CH. ABS.

Relation between amyloid degeneration and hydrogen-ion concentration of organs. II. M. MURATA and M. FUJII (Trans. Japan. Path. Soc., 1932, 22, 140—145).—[H^+] of organs in which amyloid degeneration (I) was produced by injection of Na silicate or *Staphylococcus pyogenes aureus* was closely related to (I). CH. ABS.

Silicic acid content of organs involved in amyloid degeneration. II. M. MURATA and K. KAGEYAMA (Trans. Japan. Path. Soc., 1932, 22, 153—156).—The SiO_2 content was generally increased. CH. ABS.

Iron and copper, and reticulocyte response in anæmic rats. M. O. SCHULTZE and C. A. ELVEHJEM (J. Biol. Chem., 1933, **102**, 357—371).—Anæmic rats depleted of their stores of Cu show a typical reticulocyte response (I) only when both Fe and Cu are administered; the min. daily doses for the production of (I) are 0·3 mg. of Fe and 0·005—0·01 mg. of Cu. It is assumed that the (I) produced by Beard (A., 1932, 79) with Fe alone was due to the presence of Cu in the rats. A slight increase in hæmoglobin (II) is observed when a (I) is obtained. Intraperitoneal injection of a (II) prep. produces a (I). Any stimulation of (I) due to feeding liver-extract preps. is due to the presence of Fe and Cu in the preps. H. D.

Iron deposition and anæmia of adult guinea-pigs into which "hæmosol" colloidal iron has been injected subcutaneously and intraperitoneally. K. MORITO (Trans. Japan. Path. Soc., 1932, 22, 137—140).—Anæmia was observed. Fe was deposited in the liver, but not in the kidneys or the mucous membrane of the cæcum. CH. ABS.

Catalase and glutathione content of red blood-corpuscles in experimental anæmia. I. BACH and B. KORPASSY (Magyar Orvosi Arch., 1933, **34**, 44—50; Chem. Zentr., 1933, i, 2968).—In anæmia caused by bleeding or $NHPh{\cdot}NH_2$ there is a relative increase in catalase and glutathione which is independent of megalocytosis. A. A. E.

Prevention of cholesterol atherosclerosis in rabbits. I. Effect of whole thyroid and of potassium iodide. K. B. TURNER. **II. Influence of thyroidectomy on the protective action of potassium iodide.** K. B. TURNER and G. B. KHAYAT (J. Exp. Med., 1933, **58**, 115—125, 127—135).—I. Simultaneous administration of thyroid or KI, but not KBr or KCl, with cholesterol (I) has a protective effect; thyroxine is less effective. Development of atherosclerosis (II) is related to blood-I. Aortic lesions are accompanied by hypercholesterolæmia.

II. Thyroidectomy does not cause a rise in blood-(I) or the development of (II) in young rabbits. Feeding (I) produces hypercholesterolæmia and atherosclerotic lesions. The protective action of KI disappears when the thyroids are removed. CH. ABS.

Cholesterol metabolism and chlorophyll. C. BLUMER, T. GORDONOFF, and L. REZNIKOFF (Arch. exp. Path. Pharm., 1933, **173**, 42—61).—Administration of chlorophyll to rabbits suffering from arteriosclerosis induced by feeding with cholesterol (I) favourably influences the disease, especially if given simultaneously with (I). F. O. H.

Nitrogen and sulphur metabolism in Bright's disease. IV. Retention of urea in the nephrosis syndrome. G. P. GRABFIELD (Arch. Int. Med., 1933, **52**, 632—636).—The addition of urea to the diet of a woman suffering from lipoid nephrosis resulted in a considerable apparent retention of the urea, and in increases of the urinary N/S ratio from 18·3 to 42·5, and in the ratio of N retained to S retained from 10·4 to 44·5. W. O. K.

Stone. XIII. *X*-Ray diffraction of calculi. S. RANGANATHAN (Indian J. Med. Res., 1932, **19**, 1153—1161).—The *X*-ray diffraction patterns of cholesterol (I) stones and vesical calculi suggest cryst. deposition of (I) or uric acid. In non-pigmented (I) stones the presence of larger crystals is suggested. CH. ABS.

Effect of calcium chloride, vigantol, and parathormone on the blood serum-calcium of sarcoma rabbits. S. E. RHEE and C. H. KIM (Trans. Japan. Path. Soc., 1932, 22, 974—984).—Serum-Ca increases more markedly in sarcoma rabbits than in normal rabbits after injection of $CaCl_2$ solution or vigantol, but not after that of parathormone. CH. ABS.

Relation between internal secretions and blood-calcium, especially in tumour animals. Response of serum-calcium to hormones. K. SUZUKI (Trans. Japan. Path. Soc., 1932, 22, 985—988).—Blood-Ca (I) and Ca tolerance of tumour animals are normal, but decrease in (I) caused by injections of thymoglandol, pituglandol, insulin, adrenaline, interenine, gynandol, and epiglandol was greater and recovery was slower. (I) decreased slightly and recovery was more rapid after injection of testiglandol and anteglandol. Thyroxine scarcely increased (I) in sarcoma rabbits. CH. ABS.

Induced oxidation of lactic acid by ascorbic acid and the cancer problem.—See this vol., 1252.

Determination of hydrogen-ion concentration of the blood of sarcoma rabbits. Y. FUJIMAKI, K. ARIMOTO, T. KIMURA, and I. TANI (Trans. Japan. Path. Soc., 1932, 22, 971—974).—The alkalinity of the blood increases parallel with the growth of the inoculated tumours. CH. ABS.

Potassium content of cancerous tumours. A. EPSTEIN (Z. Krebsforsch., 1932, **38**, 63—74, 535—540; Chem. Zentr., 1933, i, 3465).—Malignant tumour-K is > normal tissue-K. A diet rich in K increases the K content of implanted tumours and appears to accelerate their growth. A. A. E.

Influence of magnesium chloride on the urinary C : N ratio of rats with experimental tumours. B. BRAIER (Semana med., 1933, i, 2006—

2010).—Oral or subcutaneous administration of $MgCl_2$ has a favourable effect; increase in the urinary C : N ratio is also prevented. CH. ABS.

Preparation of the carcinogenic substance of fowl sarcoma. A. GOLDFEDER (Z. Krebsforsch., 1933, **38**, 585—586; Chem. Zentr., 1933, i, 2839).—The substance is pptd. at p_H 4. When dissolved in a buffer solution of p_H 8 it always causes tumours when injected. A. A. E.

Iodine content of the thyroid gland. II. K. MITSUI (Trans. Japan. Path. Soc., 1932, **22**, 250—252).—Increased thyroid gland-I was found in struma colloides, carcinoma of digestive organs, and diabetes mellitus; decreased vals. were found in exophthalmic goitre and tuberculosis. CH. ABS.

Respiratory quotient of exercise in pancreatic diabetes. A. CANZANELLI and M. KOZODOY (Amer. J. Physiol., 1933, **103**, 298—302).—In some experiments the R.Q. rose during exercise, but in these a compensatory fall occurred during recovery, and the average exercise and recovery R.Q. was the same as that before exercise. NUTR. ABS.

Effects of adrenal medulla and thyroid on the respiratory metabolism of pancreatic diabetes. G. C. RING and C. W. HAMPEL (Amer. J. Physiol., 1933, **104**, 298—302).—The high basal metabolic rate of depancreatised cats, since it is not lowered by adrenal inactivation or by thyroidectomy, cannot be ascribed to hyperactivity of these glands. NUTR. ABS. (*b*)

Carbohydrate dosage in insulin therapy. F. MEYTHALER (Klin. Woch., 1933, **12**, 533—535; Chem. Zentr., 1933, i, 3588).—By administering carbohydrate in small increasing doses instead of in one dose large variations in blood-sugar can be avoided. A. A. E.

Storage of glycogen and glycogen-storing disease. P. JUNKERSDORF (Klin. Woch., 1933, **12**, 899—900). NUTR. ABS. (*b*)

Relation of diet to goitre. I. Dietary technique for the study of goitre in the rat. II. Iodine requirement of the rat. H. LEVINE, R. E. REMINGTON, and H. VON KOLNITZ (J. Nutrition, 1933, **6**, 325—345, 347—354).—I. Physiological effects and the reduction in the I content of the thyroid following the administration of an I-deficient diet are described. The recovery process caused by re-administration of I is examined.

II. The min. I requirement of rats is $1—2\times10^{-6}$ g. daily. This produces 0·11—0·18% of I (dry wt.) in the thyroid. The min. requirement for man is calc. as $60—120\times10^{-6}$ g. daily. A. G. P.

Determination of urinary amino-acids in exophthalmic goitre. W. KRECH (Klin. Woch., 1933, **12**, 341—344; Chem. Zentr., 1933, i, 2985).—Except in severe cases the NH_2-N in morning urine is 5—7 mg. per 100 c.c. In the course of treatment with I the NH_2-acid excreted falls. In severe cases the NH_2-N is 2 mg. per 100 c.c.; on treatment with I the NH_2-N first rises and then falls. A. A. E.

Effect of irradiating non-goitrogenic cabbage on its goitrogenic activity. J. J. WESTRA and V. HUNTER (Proc. Soc. Exp. Biol. Med., 1933, **30**, 1157—1158).—The feeding to rats of an irradiated non-goitrogenic variety of cabbage did not produce thyroid enlargement. Non-goitrogenic cabbage does not therefore contain the precursors of a goitrogenic substance which can be synthesised by prolonged irradiation. NUTR. ABS. (*b*)

Role of di-iodotyrosine in hyperthyroidism. Comparison of the therapeutic effect of di-iodotyrosine with inorganic iodine. A. B. GUTMAN, L. W. SLOAN, E. B. GUTMAN, and W. W. PALMER (J. Amer. Med. Assoc., 1933, **101**, 256—259).—The therapeutic effect of di-iodotyrosine (I) given to patients with hyperthyroidism is similar to that produced by an equiv. amount of I given as Lugol's solution or as NaI. Conclusive evidence that (I) is specifically antagonistic to the action of thyroxine was not found. NUTR. ABS. (*b*)

Hypoproteinæmia probably due to deficient formation of plasma-proteins. W. K. MYERS and F. H. L. TAYLOR (J. Amer. Med. Assoc., 1933, **101**, 198—200). NUTR. ABS. (*b*)

Avitaminosis and infection. II. Animal experiments with human leprosy. Pathological and histological condition of avitaminous animals inoculated with an emulsion from leprous nodules. III. Relation between vitamins and infection with pus-forming bacteria. S. KOBASHI (J. Chosen Med. Assoc., 1933, **23**, 32—33, 39).—II. Pathological changes were observed in the livers and spleens of mice, rats, and guinea-pigs receiving a vitamin-free diet and inoculated with an emulsion from leprous nodules. Thus the avitaminosis seemed to favour infection.

III. Subcutaneous injection of *Staphylococcus aureus* produced more serious effects in rats deprived of vitamin-*A* and -*D* than in normal animals or in those deprived of vitamin-*B*. Doses of vigantol prevented the appearance of abscesses and other symptoms. NUTR. ABS. (*b*)

Serum-proteins in leprosy; *Hydnocarpus* treatment. G. R. RAO (Indian J. Med. Res., 1932, **19**, 993—1011).—In leprosy the serum-globulin is generally increased and the -albumin decreased. Injection of a *Hydnocarpus* prep. usually causes a further increase in the globulin. The CH_2O-gel test is never positive in uncomplicated cases, and bears no definite relationship to the serum-globulin. CH. ABS.

Lipolytic activity of rat tissues in experimental leprosy. G. EMERSON, H. H. ANDERSON, and C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1932, **30**, 150—152).—The lipolytic activity (I) of leprous rat tissues is < that of other tissues from infected or normal animals. In leprosy (I) of most of the body tissues is lowered. CH. ABS.

Carbohydrate metabolism following extensive experimental liver damage. F. RATHERY and Y. DEBIENNE (Compt. rend. Soc. Biol., 1933, **113**, 30—32).—After injection of dil. H_2SO_4 into the bile ducts of dogs, the liver-glycogen was considerably decreased, but the production of sugar by the liver, as determined by the difference in sugar content of the blood of the portal and hepatic veins, was not seriously affected; the arterial blood-sugar remained

normal. The amount of glycogen in the liver is not directly related to the production of sugar by that organ. NUTR. ABS. (*b*)

Gaseous metabolism during cardiac insufficiency. I. Histamine. A. RUHL (Arch. exp. Path. Pharm., 1933, **172**, 568—585).—With heart–lung preps., the cardiac insufficiency due to histamine is accompanied by a marked diminution of O_2 consumption (due to œdematous changes in the capillaries) despite the increased dilation of the heart, whilst an increase in the R.Q. indicates partial suffocation. The decrease in the rate of work by the heart indicates that the energy is supplied by non-oxidative sources. F. O. H.

Influence of experimental mitral insufficiency on metabolism. D. JAHN (Arch. exp. Path. Pharm., 1933, **173**, 221—241).—Mitral insufficiency in dogs produces an increase in the blood-lactic acid (I) due to the retardation in the peripheral blood supply and the consequent lack of O_2. This acidosis may lead to a prolonged increase in the R.Q. without change in the basal metabolism (II). Muscular work produces dyspnœa, whilst (I) and (II) are increased. Following ingestion of glucose the sp. dynamic action and the resulting hyperglycæmia are increased, whilst (I) exhibits a rise in place of the normal fall. F. O. H.

Influence of mineral metabolism on nephrotic œdema. W. S. HOFFMAN and W. E. POST (J. Clin. Invest., 1933, **12**, 613—638).—Ingestion of H_2O, Na, or Cl causes their transudation across capillary walls, so that the osmotic relations of the plasma and extracellular fluids are kept nearly normal until kidney excretion restores the normal body content. Low serum-protein produces a tendency for accumulation of extracellular fluid, determined partly by the speed of excretion of H_2O, Na, and Cl. Serum-Na and erythrocyte-K appear related. CH. ABS.

Blood-cholesterol in osteomalacia. T. A. HUGHES, D. L. SHRIVASTAVA, and K. S. MALIK (Indian J. Med. Res., 1932, **19**, 1205—1208).—Plasma-cholesterol is sometimes decreased. CH. ABS.

Avian paludism : a quinoline derivative acting on schizonts and gametes. D. BOVET and L. DEMANCHE (Ann. Inst. Pasteur, 1933, **51**, 528—534).—Some products used in the treatment of paludism are lethal to gametes, others only to schizonts; the latter group has no effect on infections of the Java sparrow. 8-Diethylamino-*n*-undecylamino-6-methoxyquinoline (852 F) is lethal to both schizonts and gametes. The chemotherapeutic index is 3, < that of plasmoquin, but > that of quinine. All activity is lost if the MeO is replaced by Me, whilst substitution of Me_2 for Et_2 in the terminal NH_2 of the side-chain lowers the activity. P. G. M.

Urea clearance test in pregnancy. A. CANTAROW and G. RICCHIUTI (Arch. Int. Med., 1933, **52**, 637—646).—In normal pregnancies, the urea clearance test tends progressively to give subnormal vals. towards the end of term, whilst in cases complicated with glomerulonephritis and in one case of myocardial failure abnormally low figures were obtained. W. O. K.

Beri-beri of pregnancy, puerperium, and infancy. I. Vitamin-*B* content of urine and various tissues of normal rabbits fed with complete diet. II. Pregnant rabbit, fœtus, placenta, and show. III. Urine, milk, and tissues of puerperal rabbits. H. SHIN (J. Chosen Med. Assoc., 1932, **22**, 1011—1024, 1143—1155; 1933, **23**, 242—256).—I. The order of vitamin-*B* content of adequately fed rabbits is liver, spleen, kidney, lung and brain, heart, muscle, mammary gland. The amount in blood (dry) is about 50% of that in the liver. 80 c.c. of rabbit's urine contain an appreciable amount; 80 c.c. of human urine do not.

II. Kidney and mammary gland of the pregnant rabbit are high in vitamin-*B*; liver, lung, brain, and blood are low, whilst heart, skeletal muscle, and urine are normal. The fœtus and placenta contain much; 50 c.c. of show contain none.

III. The brain tends to return to normal vitamin content, whilst the mammary gland shows an increase. Lung, heart, muscle, and spleen contain < the tissues of pregnant rabbits. Puerperal urine contains > normal or pregnancy urine. CH. ABS.

Ketones of the blood and urine of the cow and ewe in health and disease. J. SAMPOON, A. C. GONZAGA, and C. E. HAYDEN (Cornell Vet., 1933, **23**, 184—207).—In general there is a slight decrease in the alkali reserve of the cow during pregnancy. The strong similarity that exists in some cases of milk fever and acetonæmia (I) suggests that they are not separate diseases. Analytical data for blood are tabulated.

There is a definite (I) in cases of so-called "pregnancy disease" of ewes, and the blood and urine picture resembles that found in typical cases of "(I) of cows." In addition to ketosis in pregnancy disease of ewes, the terminal stage is characterised by uræmia. The use of daily intravenous injections of glucose (500 c.c. of a 5% solution) is suggested to overcome the ketosis and restore impaired renal function. NUTR. ABS. (*b*)

Beryllium "rickets." B. L. GUYATT, H. D. KAY, and H. D. BRANION (J. Nutrition, 1933, **6**, 313—324).—Replacement of $CaCO_3$ in a rachitogenic diet by basic Be carbonate or the addition of this to a normal diet produced a condition resembling rickets in young rats. The severity of the bone lesions was approx. proportional to the amount of Be ingested. Mineral deposition failed and there was a reduction in the inorg. P of the blood-plasma, in the acid-sol. phosphoric esters of the liver, and in the phosphatase activity of the kidneys. Deposition of Be in bones was insignificant. The condition was not alleviated by the customary antirachitic treatments. A. G. P.

Total calcium content of whole blood and its elimination through the kidneys during chronic and acute scurvy. A. MICHOUX (Compt. rend., 1933, **197**, 865—867).—The Ca content of the whole blood of guinea-pigs during chronic and acute scurvy is 0·095 (mean) and 0·117—0·153 g. per litre, respectively (normal, 0·075). 0·029—0·037 g. of Ca is excreted in the urine during 24 hr. in both cases (normal, 0·139). R. S. C.

Uric acid metabolism in pulmonary tuberculosis. M. PELLEGRINI (Arch. Ist. biochim. Ital., 1933, **5**, 225—270).—Sufferers have low uric acid levels in blood and urine, particularly when in low general condition, and the levels are of prognostic val. When two doses of calf thymus are given on successive days after a period on a diet free from nucleic acid, in contrast to normal subjects, the blood-uric acid rises less, the urinary elimination is lower, and the second dose provokes less reaction. R. K. C.

Changes in gastric acidity in peptic ulcer, cholecystitis, and other diseases. F. R. VANZANT, W. C. ALVAREZ, J. BERKSON, and G. B. EUSTERMAN (Arch. Int. Med., 1933, **52**, 616—631).—Data are presented regarding the vol. and free acidity of the gastric juice and incidence of achlorhydria in various diseases, and compared with normal vals. previously obtained (A., 1932, 534). W. O. K.

The ketogenic diet and its use. C. J. BARBORKA (J. Amer. Diet. Assoc., 1933, **8**, 471—481) NUTR. ABS.

Influence of diet in adsorptive disinfection with Adsorgan and Silargel. H. BECHHOLD and M. SCHLESINGER (Z. ges. exp. Med., 1933, **87**, 58—80; Chem. Zentr., 1933, i, 3097).

Changes in blood-sugar after intravenous administration of sugar in various pathological conditions. T. IRAWASHIRO (Tohoku J. Exp. Med., 1930, **20**, 577—543).—Studies on rabbits are described. CH. ABS.

Hyperglycæmia produced by surgical operations. J. P. LAMARE, M. LARGET, F. DARNIS, and R. LECOQ (Bull. Soc. Chim. biol., 1933, **15**, 1124—1145).—The hyperglycæmia (I) produced by different surgical operations under different anæsthetics (II) are determined. General (II) produce (I) > do local (II); sympathetic stimulation produces (I). In four cases of post-operative (I) subcutaneous injection of insulin reduced the blood-sugar to normal. H. D.

Metabolism of normal and tumour tissue. XI. Measurement of respiratory quotient, respiration, and glycolysis. F. DICKENS and G. D. GREVILLE (Biochem. J., 1933, **27**, 1479—1486).—The const.-vol. manometer (this vol., 481) is applied to the measurement of R.Q., respiration, and glycolysis in HCO_3' media, permitting accurate measurement of the aerobic acid production of highly glycolysing tissue. H. D.

Oxygen consumption without carbon dioxide production in acidified tissues. W. R. AMBERSON, P. B. ARMSTRONG, and W. S. ROOT (Proc. Soc. Exp. Biol. Med., 1931, **29**, 31—32).—Respiration experiments with the egg and embryo tissues of *Fundulus heteroclitus* are described. CH. ABS.

Oxygen consumption by acidified tissues. J. NEEDHAM (Proc. Soc. Exp. Biol. Med., 1932, **30**, 182—184).—O_2 consumption without CO_2 production was observed with hen's and shore crab's eggs after acidification. It may be due to oxidation of org. S to SO_4, conversion of lactic into pyruvic acid and glucose into glycuronic acid, formation of $CH_2Ac{\cdot}CO_2H$ from fat, or oxidation of reduced glutathione and lipins. CH. ABS.

Influence of diet on the course of the combustion processes in the body. A. BICKEL (Z. Volksernahrg., 1933, **8**, 17—19, 34—37, 52—54; Chem. Zentr., 1933, i, 2968).—A discussion of factors and processes concerned in physiological oxidation. A. A. E.

Intracellular oxidation-reduction studies. VI. Effects of penetrating and non-penetrating acids and bases on the oxidation-reduction phenomena in starfish eggs. L. V. BECK (J. Cell. Comp. Physiol., 1933, **3**, 261—276).—The apparent reduction potential of intact, living starfish eggs is rendered more negative by a penetrating base (NH_3), and more positive by a penetrating acid (CO_2). Addition to sea-H_2O of non-penetrating alkali (NaOH) or acid (HCl) to produce p_H 10·0 and 5·0, respectively, did not influence the aerobic or anaerobic potential nor the rate of reduction of indicators. A. G. P.

Urochrome and the part played by lyochromes in cellular respiration. K. G. STERN and G. D. GREVILLE (Naturwiss., 1933, **21**, 720).—The urochrome fraction of urine contains a substance of lyochrome type with general absorption in the shorter visible region, showing fluorescence in ultraviolet rays, and having a mol. wt. of about 2600. It accelerates respiration of erythrocytes of man or rabbit, but not of the rat. Urochrome or liver-lyochrome converts hæmoglobin into methæmoglobin and reduces oxidised cytochrome-*c* and helicorubin. The scheme suggested for cellular respiration is: O_2 ⟶ Warburg's respiratory enzyme ⟶ cytochrome ⟶ lyochrome ⟶ substrate —— dehydrogenase. R. K. C.

Chemistry of muscular contraction. ANON. (Nature, 1933, **132**, 683—684).—A review. L. S. T.

Effect of muscular work on urinary excretion of nitrogen, phosphorus, and creatinine. S. F. LIBIKH and G. A. DMITRIEV (Arch. Sci. biol., U.S.S.R., 1932, **32**, 386—393).—Control of conditions in metabolic studies is discussed. CH. ABS.

Relation between muscle metabolism and formation of ketone substances. C. BRENTANO (Deut. med. Woch., 1933, **59**, 448—451; Chem. Zentr., 1933, i, 2970).—Creatinuria (I), ketonuria, and decomp. of glycogen in muscle are parallel. In (I) there is an increased formation of ketone substances which are excreted after injection of adrenaline. A. A. E.

Essential difference between the protein degradation by depletion of reserves and a temporary degradation through ingestion. I, II. G. SANT (Pharm. Weekblad, 1933, **70**, 1153—1158, 1175—1180).—From measurements of the hydrolysis no. (I) (cf. this vol., 627) and the protein (II) content of blood-serum it follows that (I) is not an abs. measure of (II) content. Max. resorption of (II) takes place —3 hr. after a meal. With an inadequate diet the initial α before hydrolysis gradually increases after a meal, whereas with sufficient (II) it remains const., although in both cases degradation occurs. S. C.

High-protein diets and acid-base mechanism. M. E. Bell (Biochem. J., 1933, 27, 1430—1437).—The retarded growth of rats fed on a diet containing caseinogen 7, yeast 5, and McCollum's salt mixture 5% is restored to normal by increasing the yeast fraction to 15%; Na citrate and K_2CO_3 are without effect. Subnormal growth occurs in rats receiving 20—66% egg-white; in the latter case acute nephritis sometimes occurs, the fæces containing 0·06 g. N per g. and indican occurring in the urine, indicating excessive putrefaction in the intestine. H. D.

Relative values of whole and separated milk fortified with tapioca or with plant oils and cod-liver oil. H. Isaachsen, O. Unvesli, M. Husby, and K. Breirem (37th Rep. Inst. Animal Nutrit., Roy. Agric. Coll. Norway, 1933).—Replacement of the fat of whole milk in the diet by tapioca of equiv. energy val. gave satisfactory results with both pigs and calves. With pigs, replacement by an equiv. amount of a mixture of soya and cod-liver oils gave no better results. There was no indication of deficiency of fat-soluble vitamins on the tapioca ration. Nutr. Abs. (*b*)

Nutritive value of Indian vegetable foodstuffs. IV. *Phaseolus mungo* and *P. radiatus*. S. P. Niyogi, N. Narayana, and B. G. Desai (Indian J. Med. Res., 1932, 19, 1041—1054).—The globulins have been isolated and analysed. At 10% intake level about 50% of the total protein is metabolised. Ch. Abs.

Arginine metabolism. II. Arginine content of diet and creatine-creatinine production during growth. C. E. Meyer and W. C. Rose (J. Biol. Chem., 1933, 102, 461—471; cf. A., 1931, 255).—Rats fed on a low-arginine (I) diet show an excretion and storage of creatine (II) and creatinine (III) far too large to be accounted for by the (I) intake, showing that the production of (II) and (III) is not dependent on the quantity of preformed (I) in the food. H. D.

Sulphur metabolism of the dog. XII. Preparation and metabolism of *d*-acetylcysteine. N. W. Pirie and T. S. Hele (Biochem. J., 1933, 27, 1716—1718).—Since it has been suggested that the acetylcysteine previously used for metabolic work was partly racemic, the *d*-compound, m.p. 111°, $[\alpha]_{546}$ +6·3° in H_2O, has been prepared by the action of keten on an alkaline cystine solution. After oral administration to dogs, 48% of the dose is excreted as sulphate and 32% as neutral S; with subcutaneous injection the figures are 28 and 42%. A. W.

Growth and longevity of the white mouse. II. Influence of vegetable nucleic acid and thyroid on growth and longevity. T. B. Robertson, M. C. Dawbarn, J. W. Walters, and J. D. O. Wilson (Austral. J. Exp. Biol., 1933, 11, 219—235).—The growth of mice receiving daily 25 mg. of nucleic acid throughout life and small amounts of thyroid up to 3·0 mg. daily for one, two, or three 28-day periods was < that of control animals. The administration of thyroid for one period only (6th—10th week) reduced senescent loss of wt. and prolonged the mean life duration. This effect was negatived by a second period of thyroid and reversed by a third. A. L.

Absorption of *n*-hexadecane from the alimentary tract of the rat. M. A. H. E. Mahdi and H. J. Channon (Biochem. J., 1933, 27, 1487—1494; cf. A., 1929, 1194).—Rats given 0·035—0·12 c.c. of *n*-hexadecane (I) daily for 20 days showed no significant change in the liver-unsaponifiable matter (II) or -sterol content, nor in the I vals. of the non-sterol fractions of (II). Analysis of the fæces indicated an absorption of 50 mg. per day. Rats fed on a diet containing 5% of (I) absorb 108 mg. per day, the absorption producing a decrease in the I val. of the non-sterol fraction of (II) from 122 to 66. An average of 0·15 g. of (I) was found in the tissues. H. D.

Fatty acids in nutrition. II. Diets composed of rice, oil, and lipin containing linoleic or linolenic acid. U. Tange (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 1—14; cf. this vol., 183).—Addition of linoleic acid to the diet does not influence the vitamin-B_1 or -B_2 requirements. Good growth occurs in rats receiving 1% of lecithin as the sole source of fatty acid; soya-bean oil and chrysalis oil are equally effective owing to their unsaturated fatty acid content. EtOH yeast extract cannot replace dried yeast as a curative agent for rats fed on a fat-free diet containing 76% of polished rice. The deficiency disease resulting from the use of rice-bran oil as a sole source of fat cannot be cured by administration of linoleic acid. P. G. M.

Spleen and fat metabolism. S. Leites, A. Koslowa, and W. Jussin (Deut. med. Woch., 1933, 59, 214—215).—In normal animals, the fat content of the liver after feeding with hempseed and linseed oils increased by 120% and of the spleen by 307%, and whereas the I val. of liver- and tissue-fat increased somewhat, that of the spleen-fat decreased. In splenectomised animals the liver-fat increased but the I val. was > in normal animals. Nutr. Abs.

Role of phosphatides in fat metabolism. I. Parenteral administration of iodised fats. C. Artom (Arch. int. Physiol., 1933, 36, 101—128; Chem. Zentr., 1933, i, 3464).—A large part of the parenterally injected fat is rapidly deposited in the liver. Part of the fat-I is then decomposed affording I, and part passes into the blood unchanged. Almost all the fat-I in the liver is sol. in $COMe_2$, whilst with blood ≯ 43% of the fat-I is present in the $COMe_2$ ppt. A. A. E.

Influence of side-chains on the oxidation processes in the animal body. II. Model experiments on the biological degradation of the carotenoid pigments. R. Kuhn and K. Livada (Z. physiol. Chem., 1933, 220, 235—246).—Various branched-chain acids are metabolised in the animal body (dog or rabbit) as follows: $CHPh{:}CMe{\cdot}CO_2H \longrightarrow NHBz{\cdot}CH_2{\cdot}CO_2H$, $CHPh{:}CEt{\cdot}CO_2H \longrightarrow$ 30% unchanged, $CH_2Ph{\cdot}C(:CHMe){\cdot}CO_2H \longrightarrow$ 50% unchanged, $CPhMe{:}CH{\cdot}CO_2H \longrightarrow$ the *acylglycine*, m.p. 145°, $CHPhMe{\cdot}CH_2{\cdot}CO_2H$ (*amide*, m.p. 105°) $\longrightarrow$ the acylglycine, $CHPh{:}CH{\cdot}CMe{:}CH{\cdot}CO_2H \longrightarrow$ trace of BzOH, $Ph{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H \longrightarrow$ possible trace of

BzOH, citral—→dibasic acid (cf. Hildebrandt, A., 1901, ii, 669), in which the new CO_2H appears to be terminal (ω-oxidation). Thus dealkylation of fatty acids with branched chain during oxidation in the animal body is by no means general. J. H. B.

Relation of carbohydrates and lipins in the perfused liver. D. E. Gregg (Amer. J. Physiol., 1933, **103**, 79—88).—Perfusion of the liver by Jost's method, using fat-fed cats' and dogs' livers, gave no evidence of the conversion of fatty acids into carbohydrates. Nutr. Abs.

Avian carbohydrate metabolism. IV. Factors influencing the maintenance of respiration in surviving brain tissue of the normal pigeon. R. A. Peters and H. M. Sinclair (Biochem. J., 1933, **27**, 1677—1686).—The fall in respiration rate which takes place in minced pigeon-brain is decreased in the presence of lactate (I) and more markedly by pyrophosphate (II) in presence of (I), although (II) alone has little effect. Na α-glycerophosphate (III) has also a stimulating effect on the respiration, but its action is not dependent on the presence of (I). The effect of (I) and (II) is inhibited by F′ (IV), but that of (III) is insensitive to (IV). The fall in respiration is not decreased by galactose, mannitol, Na β-glycerophosphate, hexose di- (V) and hexose monophosphate (VI), but (V) and (VI) may influence the rate of fall initially. W. O. K.

Salivary glands and carbohydrate metabolism. E. Glaser and I. Bannet (Klin. Woch., 1933, **12**, 345—346; Chem. Zentr., 1933, i, 2832—2833).—Hypoglycæmic substances were not detected in the salivary glands of the ox. Peroxidases, oxidases, ptyalin, and lipase are present. A. A. E.

Mannitol and mannitan in the animal body. C. J. Carr, R. Musser, J. E. Schmidt, and J. C. Krantz (J. Biol. Chem., 1933, **102**, 721—732).—Mannitan (I) cannot be stored as glycogen in the liver and is ineffective in relieving insulin shock. Mannitol (II) does not affect the R.Q., whereas (I) produces a slight rise. There is no difference in the toxicities when administered orally, but (II) produces a slight rise in blood-sugar. H. G. R.

Development of an alkali reserve in *Fundulus* eggs. J. F. Manery, V. Warbritton, and L. Irving (J. Cell. Comp. Physiol., 1933, **3**, 277—290).—Unfertilised eggs of *F. heteroclitus* and those in early cleavage stages contain practically no alkali reserve. A HCO_3' system is established during the first day of development and increases until hatching occurs. A. G. P.

Iodine metabolism. I. T. Yuzuriha (Trans. Japan. Path. Soc., 1932, **22**, 245—250).—The rate of metabolism of exogenous I introduced into the blood is controlled by the activity of the reticulo-endothelial system; the thyroid acts as a brake on this system, but does not directly affect I metabolism. Ch. Abs.

Morphological studies of iron metabolism. II. T. Kosugi, K. Umeda, M. Mikami, and S. Tachibana (Trans. Japan. Path. Soc., 1932, **22**, 129—133). Ch. Abs.

Histology and chemistry of iron metabolism. G. Wallbach (Z. ges. exp. Med., 1932, **83**, 641—656; Chem. Zentr., 1933, i, 3593).—Administration of "nutrose" or dried ovalbumin reduces retention and accumulation of Fe in the liver, spleen, and bone marrow when Ferrum reductum or Ferrum oxydatum saccharatum is given. A. A. E.

Iron resorption. G. Wallbach (Z. ges. exp. Med., 1932, **83**, 657—681; Chem. Zentr., 1933, i, 3593).—Accumulation of Fe after administration of various Fe preps. and the influence thereon of As preps. have been studied. A. A. E.

Liver-glycogenesis without insulin. Theory of carbohydrate substitutes. H. Kosterlitz (Arch. exp. Path. Pharm., 1933, **173**, 159—172).—With depancreatised dogs, ingestion of fructose or *d*-sorbitol produces liver-glycogenesis (I) and, to a smaller extent, muscle-glycogenesis; with glucose (II) neither occurs. The heart maintains a glycogen level of 1·0—1·5% under all conditions. Hence (I) is possible in the absence of insulin, but it is not evident unless the enhanced glycogenolysis is balanced by a high sugar intake. Whilst the normal assimilation of (II) occurs in both the liver and peripheral tissues, that of substitutes is confined to the liver; in the latter case (II) is probably not an intermediary in glycogen formation. F. O. H.

Microscopical examination of calcium and iron deposition in human tissues. T. Tsunoda and S. Shirai (Trans. Japan. Path. Soc., 1932, **22**, 126—129).—Ca and Fe deposition occurs in the interstitium of the anthracotic lung and lymph gland, in the intima and media of arteriosclerotic arteries, and in the ovarian arteries of middle-aged and old women. Ch. Abs.

Mineral metabolism of pullets. R. H. Common (J. Agric. Sci., 1933, **23**, 555—570).—The retention of Ca and P by pullets is related to the NaCl content of the food. Egg laying involves additional excretion of P, but no corresponding change in K elimination. Small increases in Na excreted may occur if the Na and Cl contents of the ration are small. Retention of K is recorded on the following day. The increased P excreted during laying is possibly related to the withdrawal of reserve Ca for shell formation and is in a form other than Ca phosphate. A. G. P.

Effect of calcium-phosphorus relationship of the diet on growth and bone formation in the pig. R. M. Bethke, B. H. Edgington, and C. H. Kick (J. Agric. Res., 1933, **47**, 331—338).—The Ca : P ratio (I) and the [Ca] and [P] of the diet of pigs are factors controlling growth and bone formation, optimal results being obtained with (I)=1·0—2·0 and [P] $\lessdot$ 0·6%. With (I) $>$ 3·0, rickets develops and the requirement of vitamin-*D* is increased. F. O. H.

Metabolism studies on dry and milking animals. B. Singh (Agric. Live Stock India, 1933 **3**, 411—431).—Effects of supplementing various rations with limestone and bone meal are recorded. The balance of Ca and P is mainly controlled by the total intake. Heavily yielding cows showed the greatest assimilation of Ca and P. With a general

maintenance diet there was no relationship between total intake and the digestibility of the different forms of Ca and P. A. G. P.

Soya-bean flour in infant feeding. G. STEARNS (Amer. J. Dis. Children, 1933, **46**, 7—16).—Infants maintained on diets of soya-bean foods containing Ca, P, and N in approx. the same proportions as in cow's milk retain adequate quantities of these elements. Increase in the relative intake of Ca results in insufficient retention of P and Ca and of other fixed bases. CH. ABS.

Temperature and sensitivity to poisons. H. FUHNER and W. BREIPOHL (Arch. exp. Path. Pharm., 1933, **173**, 146—158).—Colchicine has a toxicity to frogs at 30° or to normal mice approx. 400 times that to frogs at 20°, and readily oxidised physostigmine (I) and adrenaline (II) are more toxic to the mouse than to the normal frog, but little difference is shown by (I), (II), sympatol, ephedrine, strophanthin, cymarin, MeOH, and EtOH in their respective toxicities to cold and warm frogs. F. O. H.

Combination of morphine with local anæsthetics and the assay of the analgesic constituent. H. KILLIAN and G. SCHWORER (Arch. exp. Path. Pharm., 1933, **173**, 242—247).—Administration of morphine (I) with cocaine, novocaine, or percaine increases the anæsthetic action on the rabbit's cornea; for one series of experiments the increase averaged 9·2, 24·6, and 5·1%, respectively. The variations in the results indicate, however, that the use of such determinations for the assay of (I) and similar substances is not feasible (cf. A., 1932, 1061). F. O. H.

Intestinal motility. VI. Effect of morphine alkaloids. W. STRAUB and M. OZAKI (Arch. exp. Path. Pharm., 1933, **173**, 374—380).—Of morphine (I), codeine, thebaine, narcotine, and papaverine (II), (I) has the greatest and (II) the least action on the tonus of the isolated small or large intestine (III). No marked distinction exists between alkaloids of the phenanthrene and those of the *iso*quinoline series. The action of opium on (III) is due almost entirely to (I). F. O. H.

Mechanism of phenylcinchoninic intoxication. O. FURTH and R. SCHOLL (J. Lab. Clin. Med., 1933, **18**, 991—1001).—Phenylcinchoninic acid (I) intoxication appears to be associated with changes in the colloidal state of the proteins of the nervous centres; toxicity is increased (rats, rabbits, guinea-pigs) by injection of thyroxine, but not by ingestion (rats) of carbohydrates. (I) increases the rate of swelling of gelatin in 0·9% NaCl, and the rate of diffusion of various dyes through 10% gelatin gel. The spontaneous coagulation of solutions of brain-, liver-, and muscle-protein is accelerated by anions of (I), salicylic acid, quinine, antipyrine, "phenocoll," and "melubrin." CH. ABS.

Colloid changes produced by antipyretics and analgesics and their supposed relation to excitability of nervous centres and to liver injury. O. FURTH and R. SCHOLL (Klin. Woch., 1933, **12**, 511—512; Chem. Zentr., 1933, i, 3214—3215).—Pathological effects of administration to rats of phenylcinchoninic acid are discussed. Experiments using Na phenylcinchoninate and salicylate, quinine, "phenocoll," "melubrin," morphine, novocaine, and cocaine with colloidal systems (brain, gelatin, lecithin, etc.) indicated no parallelism between physiological and physico-chemical synergism and antagonism. A. A. E.

Atropine-like parasympathetic inhibitors. K. FROMHERZ (Arch. exp. Path. Pharm., 1933, **173**, 86—128).—A series of tropic esters of alkylamines and of similarly constituted compounds exhibited no wide differences in toxicity. Curare-like action was shown only by two quaternary derivatives. The parasympathetic inhibition as indicated by the salivary secretion in rabbits etc. was determined for each compound and comparison made with atropine (I). The *l*- were more active than the *d*-isomerides. $NMe_2 \cdot CMe_2 \cdot CH_2$ benzilate is nearly as effective as (I) in its action on the intestine. F. O. H.

Optical isomerism and diminution of blood-pressure.—See this vol., 1300.

Excretion of veronal and "quadronox." H. SCHLOSSMANN (Arch. exp. Path. Pharm., 1933, **173**, 129—132).—With rabbits to which 0·2 g. per kg. body-wt. of veronal (I) or of (I) combined with 20% of antipyretics etc. ("quadronox") is orally administered, the urinary excretion of (I) is 50% and 80% of the total dose within 24 and 72 hr., respectively. Somewhat lower % excretion follows higher dosage. F. O. H.

Assay of *Digitalis* in the cat. H. BAUER and K. FROMHERZ (Arch. exp. Path. Pharm., 1933, **172**, 693—698).—The assay of strophanthin (I) in cats with light Et_2O narcosis gives results 20% > those when numal is used. Digitoxin (II), however, gives results within the limit of experimental error when either narcotic is used. Lower results are given for preps. of (II) with the continuous infusion method than with the method of infusing (II) for 15 min. and, after a 20-min. interval, substituting (I) for (II) in the infusing liquid (cf. B., 1926, 719). The "cat dose" for *Digitalis* preps. is of use only when the method employed for the assay is clearly defined. F. O. H.

Active constituents of *Curcuma* (Temoelavac). E. FRANQUELO (Münch. med. Woch., 1933, **80**, 524—526; Chem. Zentr., 1933, i, 3465).—The cholagogue action of *Curcuma* is due to curcumin. A. A. E.

Effect of benzine on blood-fats and -lipins. M. NIKULIN and Z. HETMANN (Arch. Gewerbepath. Gewerbehyg., 1933, **4**, 653—664).—Prolonged exposure of men to benzine vapour causes an increase in neutral fat, cholesteryl esters, and total cholesterol in the blood, and a decrease in phosphatides and free cholesterol. A. G. P.

Determination of alcohol in blood and brain. H. KLAUER (Deut. Z. ges. gerichtl. Med., 1933, **17**, 89—91; Chem. Zentr., 1933, i, 3992).—Fellenberg's method is modified. A. A. E.

Blood-sugar after administration of alcohol. E. KOLTA (Deut. Arch. klin. Med., 1933, **175**, 376—380).—Simultaneous administration of glucose with

EtOH produced in both normals and diabetics a brief fall of blood-sugar and then a slow rise; the immediate hyperglycæmia noted in diabetics after EtOH alone was abolished. EtOH, as normally dispensed to diabetics, has little influence apart from its caloric and digestive properties. NUTR. ABS. (*b*)

Pharmacology of optically active secondary butyl alcohol. F. VIDITZ (Arch. exp. Path. Pharm., 1933, **172**, 668—680).—No significant differences are shown by *d*- (I), $[\alpha]_D^{20}$ +13·37°, *l*- (II), $[\alpha]_D^{20}$ −12·33°, and *dl-sec.*-BuOH (III) in their narcosis of the central nervous system, stimulation of isolated muscle, or action on the isolated frog's heart. The hydrolysis of BuOAc by liver-esterase is, however, inhibited by (II) to an extent > that by (I), whilst the anaerobic oxidation in presence of yeast occurs more readily with (I) than with (II). F. O. H.

Dependence of the structure of tissue-proteins on the metabolism of the organism. II. Protoplasm damage, hormones, and metabolic products. III. Cystine and tyrosine. IV. Senility and avitaminosis. E. G. SCHENCK and H. WOLLSCHITT (Arch. exp. Path. Pharm., 1933, **173**, 260—268, 269—277, 278—282; cf. this vol., 631).—II. Changes in the % protein, free and bound tryptophan (I), and free NH_2-acids of the tissues of rat's liver, kidney, heart, and muscle after treatment with agents injurious to protoplasm (*X*-rays, pneumococcus infection, poisoning with As, quinine, $CH_2Br{\cdot}CO_2H$, or Witte's peptone), with hormones (adrenaline, insulin, thyroxine), with catabolic products (urea, lactic acid), and with nerve poisons (atropine, choline) indicate in many cases marked changes in the tissue-proteins.

III. The cystine (II) and tyrosine (III) content of the proteins of various organs of rats were determined under the following conditions: (*a*) normal, (*b*) fed on various diets with and without added (I), (II), or (III), and (*c*) under the influence of protoplasmic damage, hormones, etc. (as above). With *b*, administration of an NH_2-acid causes displacement of others from the tissue-protein to an extent dependent on the organ concerned. (I) and (II) mutually oppose each other in this displacement.

IV. Age and avitaminosis in rats produce marked changes in the amount and composition of the tissue-proteins. F. O. H.

Influence of emotional excitement on the composition of the blood. G. D. OBRASTZOV, E. T. MINKER-BOGDANOVA, and M. N. KALINNIKOVA (Arch. Sci. biol., U.S.S.R., 1932, **32**, 502—512).—In emotional states in rabbits there was increased blood-sugar, decreased -fat, and unusually great variations in -amylase. In psychoneurotic children in emotional states the blood-K and -Ca were increased. CH. ABS.

Permeability of living tissue to carbonic acid. J. WEHRLI-HEGNER and O. A. M. WYSS (Biochem. Z., 1933, **266**, 46—67).—The passage (measured potentiometrically) of CO_2 (saturated solution at 4 atm.) through surviving tissue (Vena abdominalis, frog) is rapid, although other acids (0·01*N*-HCl, $-H_2SO_4$, $-H_3PO_4$) in the absence of CO_2 do not pass through. Dead tissue exhibits increased permeability to HCl, but not to CO_2. W. McC.

Behaviour of skin towards solutions of various kinds and various concentrations. II. Swelling of normal human skin; change in weight. III. Is change in weight of normal skin influenced by the temperature of the solutions? IV. Pathological skins. E. NISHIMURA (Japan. J. Dermat. Urol., 1933, **33**, 1—34). CH. ABS.

Exchanges between blood and tissues. VII. Sugar and sodium chloride in capillary and venous blood after administration of sodium chloride, sugar, salyrgan, and insulin. G. DELL'ACQUA (Z. ges. exp. Med., 1933, **88**, 385—390).—No correlation was observed between the variations in blood-sugar (I) and NaCl of the capillary and venous blood after administration of NaCl followed by salyrgan or insulin or after insulin followed 30 min. later by glucose. The rise of (I) in diabetic patients after salyrgan, observed by Bix and Wechsler, was not observed in several diabetics with hyperglycæmia, but, in some, administration of NaCl prior to the salyrgan prevented the rise. Osmotic changes cannot be an important factor in causing simultaneous changes in (I) and NaCl content of the blood. NUTR. ABS. (*b*)

Action of diuretics on the aglomerular kidney. R. N. BIETER (J. Pharm. Exp. Ther., 1933, **49**, 250—256).—Injection of equimol. quantities of the respective chlorides into the toad fish (*Opsanus tau*) produces diuretic effects, with the order Mg> Ca>Sr>Hg; Rb>K>Na, Li; the last two ions having practically no action. $Na_2S_2O_3$, NH_4Cl, and creatinine have also a diuretic action on the aglomerular kidney. W. O. K.

Action of arsenic on gastric digestion. R. FRANK (Arch. exp. Path. Pharm., 1933, **173**, 180—186).—Oral administration of Fowler's solution does not initiate a flow of gastric juice, but increases an already existing secretion. With subcutaneous injection the period of increased flow is prolonged. F. O. H.

Absorption of nitrite after oral ingestion of "bismuth subnitrate." R. H. WILSON (Proc. Soc. Exp. Biol. Med., 1932, **29**, 961—962).—In man daily ingestion of 1·5 g. $BiONO_3,H_2O$ caused an increase in urinary NO_3-N from 4·9 to 57·8 mg. per 24 hr. within 2 days. The excretion continued at 8 times the normal for the 30 days of ingestion. Bi and NO_3' were not found in the urine. CH. ABS.

Action of minute amounts of copper on the mammalian organism. III. Phenylhydrazine anæmia in dogs. H. HANDOVSKY and D. VON COTZHAUSEN (Arch. exp. Path. Pharm., 1933, **173**, 187—191).—Inclusion of Cu tyrosine (0·5 mg. of Cu per day) in the diet of dogs has a favourable influence on $NHPh{\cdot}NH_2$ anæmia. F. O. H.

Thallium. V. Behaviour in the organism. P. TESTONI (Arch. int. Pharm., 1933, **44**, 328—351).—After oral administration of Tl, elimination is mainly by way of the kidneys. The % fixed is greatest in brain and liver, least in muscles and testicles. NUTR. ABS.

Blood-sugar in poisoning by colloidal lead. E. MERLINI (Arch. Ist. biochim. Ital., 1933, **5**, 395—410).—Intravenous injection of colloidal Pb in rabbits generally causes hypoglycæmia, transitory in sub-lethal doses, or progressive in lethal doses. Hyperglycæmia occurred in one case. R. K. C.

Effect of dietary calcium and phosphorus on toxicity of lead in the rat. D. H. SHELLING (Proc. Soc. Exp. Biol. Med., 1932, **30**, 248—254).—Among groups of rats receiving $PbCO_3$ with or without addition of $CaCO_3$, $MgCO_3$, or Na_2HPO_4 and not receiving vitamin-*D* the wt. and longevity were in the order $MgCO_3<CaCO_3<PbCO_3$ alone; all rats given vitamin-*D*, except the Na_2HPO_4 group, died sooner than corresponding animals. Rats given Na_2HPO_4 gained wt. and appeared normal. CH. ABS.

Effect of rare earths on metabolism. A. BICKEL and M. KOJIMA (Biochem. Z., 1933, **266**, 18—24; cf. Dominguez, A., 1932, 1060).—$SmCl_3$, $PrCl_3$, $NdCl_3$, $ZrOCl_2,6H_2O$, and YCl_3, given internally, have little or no effect on oxidations (I) in the body (rabbits). $CeCl_3$ and $LaCl_3$ restrict, whilst $ThCl_4$ slightly increases, (I). W. McC.

Action of metallic salts on tissue cultures *in vitro*. J. VERNE and C. SANNIE (Bull. Soc. Chim. biol., 1933, **15**, 1022—1043).—Drops of a solution of the salt in Ringer's solution, of chicken plasma, and of embryonic fluid were mixed, the transplanted fibroplasts from embryo chicks' hearts added, and the whole was allowed to coagulate. The emigration and the number of mitoses of the cells were observed. The alkali metals and earths together with Mn are scarcely toxic, the most active being NH_4, Sr, and Ba. The heavy metals vary in toxicity from $CrCl_3$, which inhibits growth at $N/200$, to $HgCl_2$ at $N/30{,}000$. H. D.

Protoplasmic potentials in *Halicystis*. III. Effects of ammonia. L. R. BLINKS (J. Gen. Physiol., 1933, **17**, 109—128; cf. A., 1932, 1180).—A threshold concn. of NH_4Cl exists (0·0005—0·002*M*) at which a reversal of the p.d. across the protoplasm of impaled multinuclear cells of *Halicystis* occurs. The effect is reversible. Higher concns. of NH_4Cl cause a more rapid reversal. At p_H 5 no reversal occurs with 0·1*M*-NH_4Cl, whereas at p_H 10·3 the threshold concn. is 0·0001*M*, indicating that the reversal is due to undissociated NH_3. The actual $[NH_3]$ in the sap, however, is not significant. A linear relation exists between p_H of the sap and the log $[NH_3]$ in sea-H_2O; hence the sudden reversal of p.d. which occurs at p_H 6·0—6·5 is ascribed to some system in the cell dependent for its state on p_H. H. D.

Possible physiological effect of the heavy isotope of hydrogen in water. T. C. BARNES (J. Amer. Chem. Soc., 1933, **55**, 4332—4333).—Filaments of *Spirogyra* in "heavy" H_2O (*d* 1·000061) were characterised by lack of movement, absence of abscission or cell disjunction, and greater longevity. J. G. A. G.

Action of sulphur on carbohydrate metabolism. P. M. NICCOLINI (Arch. int. Pharm. Ther., 1933, **45**, 54—88).—Guinea-pigs received twice daily an injection of S in H_2O, EtOH, and glycerol solution in doses of 0·08—440 mg. per kg. After fasting for 24 hr. they were given oats for an hr. and killed at intervals up to 24 hr. afterwards. The S inhibited glycogen (I) formation in the liver, but had little effect on that in the muscles. In pigeons treated similarly, liver-(I) formation was delayed at first, but increased later, whilst muscle-(I) was increased. Very small doses (≯ 0·2 mg.) frequently increased the rate of (I) formation. In rabbits which had fasted for 18 hr., 0·2 mg. per kg. lowered the blood-sugar (II), and caused the hyperglycæmia (III) and subsequent hypoglycæmia after orally given glucose to begin earlier. In atropinised or vagotomised fasting rabbits 0·2 mg. caused (III) and lowered or retarded the (III) following glucose ingestion. The same dose had no effect on the (III) in totally depancreatised rabbits. The hypoglycæmic action of S is probably due to excitation of the islets of Langerhans by way of the vagus. The hypoglycæmic action was also found in rabbits the (II) of which had been raised by adrenaline or Et_2O. NUTR. ABS. (*b*)

Chronic fluorine intoxication. F. DE EDS (Medicine, 1933, **12**, 1—60).—A review. CH. ABS.

Relation of thyroid to the conversion of cyanides into thiocyanate. E. J. BAUMANN, D. B. SPRINSON, and N. METZGER (J. Biol. Chem., 1933, **102**, 773—782).—Thyroidectomy (I) reduces the conversion of CN in MeCN (II) into SCN from 27—35% to 3—5% in rabbits. With KCN and $CH_2Ph{\cdot}CN$ about 75% is converted, with only a temporary decrease after (I). 90% of inorg. SCN is recovered in urine after injection. Thyroid catalyses demethylation of (II), but does not affect SCN formation. H. G. R.

Sodium nitrite and thiosulphate as antidotes for potassium cyanide. A. BUZZO and R. E. CARRATALA (Semana Med., 1933, i, 1966—1969). CH. ABS.

Cytochrome and intracellular respiration enzymes. D. KEILIN (Ergebn. Enzymforsch., 1933, **2**, 239—271; Chem. Zentr., 1933, i, 3726).—A review. A. A. E.

Spectroscopic detection of cytochrome and of the oxygen-carrying enzyme. O. WARBURG, E. NEGELEIN, and E. HAAS (Biochem. Z., 1933, **266**, 1—8; cf. this vol., 862).—In addition to those of cytochrome, bands (I) at 599 mμ (593 in presence of CO) and 639 mμ due to the presence of the O_2-carrying enzyme are exhibited by *B. Pasteurianum*. The effects of O_2 and HCN on (I) show that they are probably due to two hæmin derivatives which differ in the stage of oxidation of the Fe which they contain and in other ways. W. McC.

Amines and oxidations of brain. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1933, **27**, 1609—1613).—$CH_2Ph{\cdot}CH_2{\cdot}NH_2$, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2$, tyramine, indole, *iso*amylamine, and mescaline strongly inhibit the oxidation of glucose and Na lactate, pyruvate, and glutamate by the brain-tissue of guinea-pigs. All except tyramine have little effect on the Na succinate oxidation, and in all cases the inhibitions are of the same order as those caused by

narcotics such as luminal, hyoscine, and chloral. It is suggested that a disturbance in the hepatic detoxicating mechanisms might be responsible for certain types of mental disorder. A. L.

Oxidation of lactic acid and of β-hydroxybutyric acid by heart-muscle. I. BANGA, K. LAKI, and A. SZENT-GYORGYI (Z. physiol. Chem., 1933, 220, 278).—Pure $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$ does not act as H-donator (cf. this vol., 748). J. H. B.

Transformation of pyruvic into lactic acid in liver. E. AUBEL, Y. KHOUVINE, and G. ARRAGON (Bull. Soc. Chim. biol., 1933, 15, 1070—1082).—Chicken liver, washed in Ringer's solution, is suspended in the latter at p_H 7·3; $AcCO_2Na$ (I) is added, and the vessel evacuated and incubated at 39° for 4 hr. The CO_2, (I), lactic acid (II), and total reducing power are determined. The ratio (II) : CO_2 increases with the quantity of liver used; for a given quantity of liver it increases with the (I) added. Of a no. of substances added only Na citrate (III) produces a similar increase of CO_2. Addition of (III), succinate, cysteine, glutathione, MeCHO, or H_2 fails to produce an increase in (II) formation. H. D.

Intermediary processes in glycolysis in muscle. G. EMBDEN, H. J. DEUTICKE, and G. KRAFT (Klin. Woch., 1933, 12, 213—215; Chem. Zentr., 1933, i, 2970—2971).—Polysaccharides and hexosediphosphoric acid in minced muscle in presence of F′ give a mixture of difficultly hydrolysable P esters. Ba_2 phosphoglycerate (I) from this source is converted by minced muscle into H_3PO_4 and $AcCO_2H$. (I) and glycerophosphoric acid, added alone to minced muscle, produce only a small quantity of lactic acid (II); together they form much. A scheme for the formation of (II) is advanced; glyceric acid and AcCHO are not considered to be intermediate products. A. A. E.

Amylosynthease. V. S. NISHIMURA (J. Agric. Chem. Soc. Japan, 1933, 9, 436—442).—Most of the amylase (I) of yeast can be extracted with H_2O at the beginning of autolysis; amylosynthease (II) can be extracted from the residue and purified with kaolin. Separation of (II) from (I) with $Pb(OAc)_2$ was incomplete. (I) free from (II) has a weak amylolytic action. (II) loses its activity in presence of a small amount of malt-(I); amylopectase accelerates the action of barley-(I) on glycogen. CH. ABS.

Amylosynthease. X, XI. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 425—428, 428—430).—Amylosynthease (I) is unaffected by small quantities of trypsin, lecithase, and lipase, but can be purified by treatment with these enzymes. It is not a protein. Sol. starch from the glutinous varieties of true and foxtail millet is polymerised by (I); dextrin prepared from starch by the action of acid and heat is not polymerised. CH. ABS.

Starch-digesting and sugar-forming enzymes of wheat. M. CREIGHTON and N. M. TAYLOR (Iowa State Coll. J. Sci., 1933, 7, 253—260).—Solid amylolytic enzyme with low sugar-forming power and solid saccharogenic enzyme with low amylolytic power were prepared from wheat extract. Optimum [H·] for amylolytic activity is p_H 4·6—6·3, and for saccharogenic activity is p_H 4·9—5·3. CH. ABS.

Liquefaction and saccharification of starch by the action of amylases of different origin. G. ORESTANO (Arch. Farm. sperim., 1933, 56, 383—406).—When heated in the dry state the decreases in liquefying and saccharifying activities of amylases prepared from soya bean, canine pancreatic secretion, or malt extract are parallel, and both activities are lost at 140—150°. The results do not support the assumption that two different enzymes are responsible for these two activities. R. K. C.

Adsorption of α-amylase. O. HOLMBERG (Biochem. Z., 1933, 266, 203—215; cf. this vol., 425, 749).—At const. temp. the adsorption (I) of α-amylase (II) on starch increases with time (III). (I) is promoted by low temp. (to −10°) and (III) is reduced by maintaining low p_H (4·4). For purification of the adsorbed (II) it is washed with 50% EtOH containing 1% of maltose. β-Amylase and other materials are thus removed. The activity–p_H curve of (II) exhibits a max. at 4·7—5·2. Various kinds of starch, amylose, amylopectin, dextrin, and cellulose also adsorb (II) selectively. There is also selective adsorption by $Ca_3(PO_4)_2$ (optimum at p_H 7). It is not known if pancreatic amylase is a mixture. W. McC.

Amylases. V. Activation by ethylamine hydrochloride. F. CAUJOLLE and S. LAFFITE (Bull. Sci. pharmacol., 1933, 40, 167—169; Chem. Zentr., 1933, i, 3952).—Activation of amylase (pancreatin), heated for 20 min. at 65°, by NH_2Et,HCl, is the greater the smaller is the activity of the amylase itself. A. A. E.

Effect of radiant energy on diastase activity. A. H. HUTCHINSON and M. R. ASHTON (Canad. J. Res., 1933, 9, 49—64).—Irradiation by a Hg arc retards both the dextrinogenic (I) and the saccharogenic (II) phases of the activity of amylases from saliva and from malt in inverse proportion to the intensity. With salivary diastase green and far ultra-violet radiation retard, but red, yellow, and near ultra-violet rays stimulate, both (I) and (II). Monochromatic light in general inhibits (I) and stimulates (II) in malt diastase. The presence in the diastases of two enzymes, differently affected by light of the varied wave-lengths, is indicated. A. G. P.

Comparative hydrolysis of polysaccharides by invertase. A. CHAUDUN (Bull. Soc. Chim. biol., 1933, 15, 1117—1120).—By addition of the enzyme solution (I) in increasing vols. to a sugar a point is reached at which the speed of inversion ceases to increase. By multiplying these crit. vols. of (I) for sucrose, raffinose, and stachyose by their respective mol. wts. a const. val. is obtained, indicating the existence of a single enzyme acting in the three hydrolyses. H. D.

Mechanism of deamination in skeletal muscle. T. MANN (Biochem. Z., 1933, 266, 162—168; cf. this vol., 742).—Deamination (I) of adenylic acid increases in muscle extracts on keeping. The inhibiting action (II) of Mg on (I) does not account for the accompanying activation of glycolysis. (II) depends on

the ratio Mg : enzyme, not on the ratio Mg : substrate. W. McC.

Mono-layers of proteolytic enzymes and proteins. J. H. SCHULMAN and E. K. RIDEAL (Biochem. J., 1933, **27**, 1581—1597).—The reaction kinetics of the digestion of mono-layers of protein are similar to those of the bulk phase reaction. Proteinase (I) of pancreas digests 10% ovalbumin and 15% caseinogen, whilst carboxypolypeptidase (II) removes a further 25% and 16%, respectively. Purified (I) and (II) form protein-like films, which are hydrolysed by pancreatin without loss of surface activity. The tryptic enzymes can be freed from their protein-like carriers, but must be adsorbed on a protein (III) in order to be active for (III) solutions. The disappearance of a film of (III) on an enzyme-containing substrate is due to digestion only. H. G. R.

Gluten-dissolving enzyme of wheat and barley seeds. A. V. BLAGOVESCHENSKY and N. I. SOSSIEDOV (Biochem. J., 1933, **27**, 1575—1577).—The change in the state of the protein from grain damaged by the "tortoise bug" is of an enzymic nature and is unaccompanied by an increase of free $\cdot NH_2$. The enzyme, which acts in both acid and alkaline media, is formed in the damaged seeds and in the diastatic prep. from malt. H. G. R.

Proteolytic enzyme of pyloric cæcum of *Scriola quinqueradiata*. S. MACHIDA and K. MASUNAGA (J. Agric. Chem. Soc. Japan, 1933, **9**, 431—436).—Optimum proteolytic activity was observed at 7·7 and 50°. CH. ABS.

Range of action of proteinases and polypeptidases appearing during the autolysis of organs. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1933, **14**, 43—53).—Proteinases sp. for proteins derived from the same organ were found in the lung, heart, kidneys, and adrenals, but not in the spleen. Ereptic dipeptidase, but not carboxypolypeptidase or "ereptic" and "tryptic" acylase, were lacking in the kidney; the two last were absent from spleen and lung. Hydrolytic processes were accelerated in presence of *l*-adrenaline and *l*-3 : 4-dihydroxyphenylalanine. The cell-sp. proteinase of the lung is readily extracted by H_2O. J. H. B.

Determination of the action of various enzymes excreted in the urine of the human and animal organism. I. Determination of tryptic action. S. BUADZE (Fermentforsch., 1933, **14**, 56—75).—For determination of trypsin (I), the urine is treated with caseinogen and the latter is pptd. with AcOH. The initial reaction of the solution is restored with NaOH, and the process repeated. The ppts. carrying adsorbed (I) are dissolved in aq. NH_3–NH_4Cl and examined for tryptic action by Willstatter titration. Only active (I) is thus removed, but the inactive portion may be activated with kinase and then in turn determined. (I) is of general occurrence in normal urine. J. H. B.

Behaviour of polypeptides containing proline towards the erepsin and trypsin-kinase complex. E. ABDERHALDEN (Fermentforsch., 1933, **14**, 128—129; cf. A., 1930, 1475).—Glycyl-*l*-proline, now obtained cryst. (cf. Bergmann *et al.*, this vol., 94), is hydrolysed by erepsin. Glycine-*l*-prolineamide has m.p. about 190° (not 90°). J. H. B.

Behaviour of dipeptides containing ε-amino-*n*-heptoic acid towards trypsin and erepsin. E. ABDERHALDEN and F. BROICH (Fermentforsch., 1933, **14**, 115—117).—From *dl*-ε-amino-*n*-heptoic acid by the action of the requisite bromoacyl bromide and amination there were prepared: *bromoacetyl*-, m.p. 74°, and *glycyl*- (I), m.p. 245° (corr.), *α-bromoisohexoyl*- and dl-*leucyl*- (II), m.p. above 290°, -dl-ε-*amino*-n-*heptoic acids*. (I) and (II) are not hydrolysed by erepsin or trypsin. J. H. B.

Influence of heavy-metal salts on the hydrolysis of polypeptides of different composition and their derivatives and halogenoacylamino-acids by enzyme complexes contained in erepsin and trypsin solutions. E. ABDERHALDEN and G. EFFKEMANN (Fermentforsch., 1933, **14**, 27—42).—Amino- and carboxy-polypeptidase, acylase, and prolinase are inhibited to a different extent by different metallic salts under similar conditions. Prolinase is extremely sensitive to $Ag^{\cdot}$. The p_H optimum for hydrolysis of polypeptides is altered in presence of metallic salts. The effect of the metal on the hydrolysis of a given substrate is influenced by compounds of similar structure which are not attacked by the enzyme complex. This indicates a combination of metal ion or salt with the substrate. J. H. B.

Production of ereptic action in "erepsin-free" trypsin solutions prepared according to Waldschmidt-Leitz and Harteneck. IV, V. E. ABDERHALDEN and E. VON EHRENWALL (Fermentforsch., 1933, **14**, 1—12, 118—127).—IV. The following were prepared: dl-*α-bromopropionyl*-l-*cystine*, m.p. 195° (decomp. from 180°), giving dl-*alanyl*-, decomp. 260°, and dl-*α-bromoisohexoyl*-l-*cystine*, m.p. 199° (decomp.). Different erepsin-free trypsin solutions need minute but varying amounts of *l*-3 : 4-dihydroxyphenylalanine (I) to hydrolyse *dl*-leucylglycine. Amounts of (I) inadequate alone suffice in presence of glycine. *l*-Ephedrine and *l*- and particularly *d*-adrenaline act similarly to (I). Hordenine and tyrosol, inactive alone, are activated by glycine. Ereptic action was further tested on di-*l*-alanyl-, di-*dl*-alanyl-, and di-*dl*-leucyl-cystine.

V. Erepsin (I), inactivated by heating, contains a dialysable substance, which, when added to trypsin (II), renders it capable of hydrolysing *dl*-leucylglycine. H_2S destroys this activating power of (I), but does not affect (II). J. H. B.

Interferometric method [applied to Abderhalden's reaction]. Controls and interpretation. A. DURUPT and A. SCHLESINGER (Fermentforsch., 1933, **14**, 13—26).—The increase in serum concn., measured by the interferometric method, is due to two factors: swelling by H_2O absorption and degradation of the insol. coagulated proteins due to the defence enzymes in pathological sera. When the physical action is allowed for, no Abderhalden reaction is obtained in normal cases. J. H. B.

Specificity of defence enzymes. (*a*) Differentiation of proteins from blood-plasma or -serum of different blood-groups of healthy and diseased

individuals, also of species-specific tissue-proteins. (*a*) E. ABDERHALDEN and S. BUADZE. (*b*) E. ABDERHALDEN and G. EFFKEMANN (Fermentforsch., 1933, **14**, 76—103, 104—114; cf. this vol., 636).—(*a*) Examples of the high specificity of the defence enzymes are provided. Thus injection of serum-globulin of healthy individuals of blood-group *A* into rabbits produces enzymes sp. for globulin *A*. They do not hydrolyse albumin *A* of healthy or globulin *A* or *AB* of diseased, *e.g.*, carcinomatous, subjects. Species-specificity is also observed; *e.g.*, injection of rabbit's liver-protein gives rise to enzymes sp. for liver-protein of the rabbit, but not of other animals.

(*b*) Further examples of organ- and species-specificity are given. J. H. B.

Behaviour of cerebron towards enzymes. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1933, **14**, 54—55).—Cerebron is hydrolysed by trypsin free from erepsin. J. H. B.

Urease activity as influenced by oxidation and reduction. L. HELLERMAN, M. E. PERKINS, and W. M. CLARKE (Proc. Nat. Acad. Sci., 1933, **19**, 855—860).—The phenomena of activators are ascribed to oxidation and regeneration of the SH groups of the enzyme. H. G. R.

Tooth-phosphatase. A. S. E. MACKENZIE (Brit. Dent. J., 1933, **54**, 153—159).—Phosphatase is present in teeth (rat). The enzyme content per g. of tooth decreases rapidly with age. The distribution and activity of the enzyme are directly related to the rate of deposition of mineral matter in the tissue. The phosphatase of teeth resembles that of bone with regard to (*a*) relation between p_H and activity in the hydrolysis of β-glycerophosphate; (*b*) activation by Mg; (*c*) power to synthesise phosphoric esters. NUTR. ABS.

Vital properties of yeast-plasma. V. JONAS (Chim. et Ind., 1933, **29**, Spec. No., 1164—1167).—Yeast-plasma may retain primitive vital powers after the cells are dead. In yeast killed by treatment with 3% aq. CH_2O for 1 hr. and then transferred to wort, extrusion of part of the plasma through the cell wall was observed after 1 or 2 weeks, and the extruded portion grew into arborescent clusters of ill-defined granules and in some cases formed small yeast-like cells, $1{\cdot}8 \times 1$ μ, of very feeble reproductive power and incapable of fermentation (cf. A., 1931, 1333). J. H. L.

Hydrolysis of amides by *Torula utilis*. Dependence of development of enzymes in plants on nitrogen assimilation. G. GORR and J. WAGNER (Biochem. Z., 1933, **266**, 96—101; cf. A., 1932, 1289).—The extent to which *Torula* (I) hydrolyses amides greatly depends on the kind of N source (II) in the nutrient medium in which (I) is cultivated. When (II) is inorg. $[(NH_4)_2SO_4]$ the hydrolytic power (III) is nil or very small unless the growing (I) is first treated with glucose. With other (II) (NH_2-acids, urea, malt extract) there are wide variations. Extracts of autolysed (I) behave like (I) itself. The (III) of (I) is reduced by treatment with $COMe_2$. W. McC.

Determination of metabolism of moulds. A. J. KLUYVER and L. H. C. PERQUIN (Biochem. Z., 1933, **266**, 68—81).—Satisfactory material cannot be obtained except by the "shaking method," since it is necessary to have a large amount of homogeneous culture and to restrict the duration of growth as much as possible. W. McC.

[Optimum] conditions for production of kojic acid by *Aspergillus flavus*, Link. A. J. KLUYVER and L. H. C. PERQUIN (Biochem. Z., 1933, **266**, 82—95).—The most favourable conditions (giving 67% yield) for the production by *A. flavus* (I) of kojic acid (II) from glucose (III) are: use of the "shaking method," cultivation of (I) in a medium (IV) containing sugar and mineral matter (optimum composition given), lack of assimilable N compounds, high acidity (p_H 2·2) of (IV), plentiful supply of O_2. When (III) is substrate (V), (II) is probably a direct product of transformation, but with other (V) (fructose, galactose, xylose, arabinose, mannitol, erythritol, glycerol) there is probably intermediate production of C_6 carbohydrates. W. McC.

Degradation and consumption of protein by moulds. T. CHRZĄSZCZ and F. PISULA (Biochem. Z., 1933, **266**, 29—45).—The ability of *Penicillium* to grow in milk (I) varies greatly according to the species used (77 moulds tested). There is also great variation in the extent and rapidity of decomp. (II) of the proteins of (I). The type of (II) which proceeds to NH_3 production (III) is not related to the N consumption or to the change in acid content (IV) of the (I). During the growth (IV) usually decreases in consequence of (III) or because acids are consumed by the moulds. W. McC.

Action of various fungi on aldoses and related substances. A. ANGELETTI (Atti R. Accad. Sci. Torino, Cl. Sci. Fis. Mat. Nat., 1932, **67**, 272—276; Chem. Zentr., 1933, i, 3461).—*Penicillium luteum-purpurogenum* forms from *d*-fructose and sucrose small quantities of citric acid; *P. crustaceum* forms this only from fructose, whilst from sucrose it forms considerable quantities of *d*-gluconic acid. A. A. E.

Biochemistry of micro-organisms. XXXIX. Mechanism of production of phenolic acids from glucose by *Penicillium brevi-compactum*, Dierckx. A. E. OXFORD and H. RAISTRICK (Biochem. J., 1933, **27**, 1473—1478; cf. this vol., 949).—A Raulin-Thom medium was incubated with *P. brevi-compactum* and the contents were analysed after periods of 8, 11, 15, 22, and 56 days. Destruction of glucose and tartaric acid occurs concurrently. The end-products of metabolism are mycophenolic acid (I), hydrated 3 : 5-dihydroxy-2-carboxybenzoyl Me ketone (II), and 3 : 5-dihydroxyphthalic acid (III). Acetyl-3 : 5-dihydroxy-2-carboxyphenylcarbinol (IV) is an intermediate product. The yield of (I) increases continuously throughout the period. About 40% of (II) formed appears towards the end of the incubation period. The yield of (IV) rises rapidly to a max. in 15 days; after 56 days all has disappeared. (III) is never present in large amounts. (II) is present in small amounts in the early stages, but disappears after 22 days. H. D.

Fermentation products of *Mucor*. III. Production of glycerol and effect of addition of $NaHSO_3$ and Na_2CO_3. T. TAKAHASHI and T. ASAI (J. Agric. Chem. Soc. Japan, 1933, **9**, 443—448).—The production of glycerol by twenty-three varieties of *Mucor* (3·8—9·0% of the sugar assimilated) was approx. parallel to the production of EtOH, and was increased by addition of $NaHSO_3$ (optimum, 6·0%, yield 21·5%) or Na_2CO_3 (4·0%, 23·5%). CH. ABS.

Thermophilic fermentation of cellulose and cellulosic materials. W. H. PETERSON and S. ŚNIESZKO (Zentr. Bakt. Par., 1933, II, **88**, 410—417).—An organism isolated from horse manure is examined. A. G. P.

Mannitic fermentation of fructose: possible mechanism. V. BOLCATO (Annali Chim. Appl., 1933, **23**, 405—410).—The fermentation of fructose by a mannito-acetic organism yields lactic acid, mannitol, AcOH, and CO_2. The amount of lactic acid formed is independent of the amounts of the other products, but the latter accord with the equation $3C_6H_{12}O_6=2C_6H_{14}O_6+2AcOH+2CO_2$. A probable mechanism of the fermentation is suggested. T. H. P.

Cheese ripening. Caseinogen-splitting abilities of lactic acid bacteria. B. A. EAGLES and W. SADLER (Canad. J. Res., 1933, **9**, 44—48).—The activities of a no. of cultures isolated from cheese are recorded. Differences occur in the proteolytic processes brought about by the various organisms. A synthesis of protein is indicated in certain cases. The process of autoclaving skim milk with or without $CaCO_3$ causes changes in the N compounds of the milk. A. G. P.

Bacterial phosphatases. I. Decomposition of phosphoric acid esters by *Clostridium acetobutylicum*, Weizmann. II. Phosphatases of *Cl. acetobutylicum*, Weizmann, and *Propionibacterium Jensenii*, Van Niel. L. B. PETT and A. M. WYNNE (Biochem. J., 1933, **27**, 1655—1659, 1660—1671).—I. Na hexose diphosphate (I) (1·2%) is not fermented by living *Cl. acetobutylicum* (II), but in glucose–peptone cultures both (I) and Na β-glycerophosphate (III) are hydrolysed, apparently by a true phosphatase present in the cultures. In 0·75% concn. both (I) and (III) completely inhibit the fermentation of glucose.

II. The max. activities of the phosphatase (IV) system of *P. Jensenii* (V) are at p_H 7·0 for α- or β-(III), 6·0 for (II), and 7·0 for Na pyrophosphate; whilst for (II) the corresponding vals. are 5·1, 6·0, and 7·2, respectively. The pyrophosphatase (VI) of (V) is much weaker than the other two phosphatases (VII), whereas in (II) it is much more active. All (VII) are activated in various degrees by $Mg^{\cdot\cdot}$, but the latter is probably not a true co-enzyme. Of other ions tested $Zn^{\cdot\cdot}$ has an activating effect on the (VI) system of both organisms, but not on the other (VII). Free phosphate has an inhibitory effect, as in the case of mammalian (IV). Other properties of the enzymes are described. W. O. K.

Hydrogenase and hydrogenlyase. II. Bacterial formation of methane by reduction of one-carbon compounds by molecular hydrogen. III. Formation of formic hydrogenlyase by *B. coli*. M. STEPHENSON and L. H. STICKLAND (Biochem. J., 1933, **27**, 1517—1527, 1528—1532).—II. An organism has been isolated which can live anaerobically on an inorg. medium with a 1-C compound as sole source of C. AcOH and many other higher fatty acids are not attacked by the organism. With HCO_2H the reaction occurs in two stages, the CO_2 first produced being subsequently reduced to CH_4.

III. No formation of fermic hydrogenlyase takes place with young cultures of *B. coli* in presence of formate alone. The enzyme synthesis takes place in tryptic broth probably by interaction of the cells and the medium, and is a linear reaction. P. G. M.

Mechanism of respiration of pneumococci. M. G. SEVAG (Annalen, 1933, **507**, 92—110; cf. this vol., 867).—The O_2 consumed by solutions of glucose (I) and lactic acid (II) containing virulent pneumococcus type I (III) during 10—20 min. is converted almost quantitatively into H_2O_2; during 60—120 min. the vals. are 61·5—77·1%. With non-virulent type I (IV), the corresponding vals. are all smaller. The O_2 consumptions of (I) and (II) with other virulent and non-virulent types, and the amounts of O_2 transformed into H_2O_2 during 180 min. are determined. The end-products are AcOH and CO_2; AcCHO, (II), $AcCO_2H$, or MeCHO from (I) or $AcCO_2H$ or MeCHO from (II), could not be detected. (II) may be oxidised thus: $OH{\cdot}CHMe{\cdot}CO_2H+O_2\longrightarrow[OH{\cdot}O{\cdot}CMe(OH){\cdot}CO_2H]\longrightarrow AcOH+CO_2+H_2O$. The ratio CO_2 evolved : O_2 consumed during oxidation of (II) is, however, 0·52—0·77 for all the pneumococci used. With (III) or (IV) the val. is 0·73 for both (I) and (II); this is decreased to about 0·45 by addition of catalase and increased to about 1·3 by addition of $AcCO_2Na$. The O_2 consumptions of (I) and (II) with all the types are increased by varying amounts (27—1772%) by addition of $AcCO_2Na$ or catalase; the amounts of CO_2 evolved increase also. The above oxidations are accelerated by 0·004—0·02*N*-KCN, especially when young cultures are used; the acceleration is > with the virulent types. Addition of KCN to (I) or (II) $+AcCO_2Na$ also increases the activity. EtOH and PrOH are not attacked using the virulent types; reaction is slow with the non-virulent types. H. B.

Bacteriological oxidation of sulphur in an Australian soil. P. M. ROUNTREE (Austral. J. Exp. Biol., 1933, **11**, 210—218).—The rate of S oxidation in the Renmark clay loam is optimum with a H_2O content between 60 and 90% saturation, and at 16—35°. A member (I) of the *Thiobacillus* group isolated from the soil is described and its relations to *T. thio-oxidans* and *T. trautweinii* are discussed. By the action of (I) the p_H of the soil is changed from 8·4 to 4·5 in 12 days, the accumulation of acid then preventing further growth. A. L.

Nitrogen and vitamin requirements of *B. typhosus*. P. FILDES, G. P. GLADSTONE, and B. C. J. G. KNIGHT (Brit. J. Exp. Path., 1933, **14**, 189—196).—Four strains of *B. typhosus* grew readily in a synthetic medium containing a mixture of NH_2-

acids. Tryptophan (I) appeared to be essential for growth, and the absence of leucine, lysine, or cystine delayed, but did not completely inhibit, growth. Full growth was obtained with 0·0004% of (I), and traces when this was diluted 125 times. Some strains were educated to grow without (I) by a process of serial sub-cultures in increasing dilutions of (I) in a medium containing NH_4Cl. The "*sporogenes*" vitamin improved growth of the bacteria both with and without (I) in the medium. NUTR. ABS. (*b*)

Variation in the character of tubercle bacilli derived from filterable elements of the virus. J. VALTIS and F. VAN DEINSE (Ann. Inst. Pasteur, 1933, **51**, 419—427).—Injection of a $COMe_2$ extract of the tubercle bacillus facilitates the development of acid-fast bacilli in animals previously injected with the filterable virus. Starting from the bovine virus it is possible to obtain, according to the species of animal employed, a predominance of the variant *R* (mammalian type) or of the variant *S* (avian type). The existence of only one virus, common to all species, is suggested. P. G. M.

Production and properties of β-tuberculin. P. KALLÓS and G. HOFFMANN (Biochem. Z., 1933, **266**, 132—136).—When the ultrafiltrate from culture media in which tubercle bacilli have been grown is treated with EtOH–Et_2O mixture (1 : 1) a stable, hygroscopic, highly active solid, β-tuberculin (I) (C 44·5, H 7·5, N 9·85, P 1·44, O 36·72%) is pptd. (I), which is sol. in dil. alkali yielding solutions not inactivated by boiling, and contains no protein, is also obtained from the skin, urine, and blood-serum of tubercular patients. It is probably a polypeptide and can be colorimetrically determined by means of the Adamkiewicz reaction. W. McC.

Physiology of luminous bacteria. A. MUDRAK (Zentr. Bakt. Par., 1933, II, **88**, 353—366).—Organisms grow and are luminous in media containing $NaClO_3$ (up to 9%), $KClO_3$, or $Na_2S_2O_3$. Development is inhibited by $NaClO_4$, $NaBrO_3$, $NaIO_3$, and KIO_3. The presence of Na is essential to the growth of all species examined. As sources of N the organisms can utilise asparagine, aspartic acid, or glycine, but urea, tyrosine, K or NH_4 nitrate are unsuitable. Only the NH_2-N of aspartic acid is utilised. Normal development occurs in the absence of dissolved N, and the possible fixation of atm. N_2 is discussed. The presence of free O_2 is essential for luminescence, although respiratory O may be derived from NO_3' or ClO_3' in the nutrient. Oxidation of peptone by NaOCl is accompanied by luminescence. The latter is not apparent when aq. Br or H_2O_2 is used. A. G. P.

Microbiology of common salt. E. K. PETROWA (Arch. Mikrobiol., 1933, **4**, 326—347).—Micro-organisms surviving in salt solutions are found to resemble those found on the sea bottom. A. G. P.

Production of mucus during the decomposition of plant materials. I. Effect of environmental conditions. II. Effect of changes in the flora. J. G. SHRIKHANDE (Biochem. J., 1933, 27, 1551—1562, 1653—1574).—I. A physical test for the evaluation of stickiness (I) is described. An alkaline reaction, final p_H 9·5—10, and an abundance of microbial tissue tend to give high vals. for (I) during decomp. by mixed flora. $Na^{\cdot}$ and $K^{\cdot}$ produce more (I) than $Ca^{\cdot\cdot}$ or $Mg^{\cdot\cdot}$.

II. Fungi (II) and bacteria working independently, (II) followed by *M. agreste*, and simultaneous inoculation of (II) and *S. cytophaga* (III) produce little (I), whereas (I) is produced by (II) followed by (III), even if the action of (II) is brief. During decomp. the loss of carbohydrate and N is approx. in proportion to the loss of dry matter. H. G. R.

Coagulation of bacterial suspensions. G. YAMAHA (Arch. Phys. biol., 1933, **10**, 134—143; Chem. Zentr., 1933, i, 3955).—Isoelectric points are recorded. A. A. E.

Methods of mitigating filterable viruses by precipitation for the purpose of preventive immunisation. I. Precipitation of vaccine virus by aluminium or ferric hydroxide and the antigenic value of the precipitated virus. T. KODAMA (Kitasato Arch. Exp. Med., 1933, **10**, 243—258).—Vaccine virus becomes inactivated on adsorption by $Al(OH)_3$, $Fe(OH)_3$, or $Zn_3(PO_4)_2$ gels. The virus can be reactivated by elution with Na_2HPO_4 or by dissolution in Na citrate or tartrate. $Al(OH)_3$ ppts. contain smaller amounts of adsorbed protein than do other ppts. CH. ABS.

Oligodynamic action of copper. II. W. SCHWARTZ and H. STEINHARD (Arch. Mikrobiol., 1933, **4**, 301—326; cf. A., 1931, 1334).—Stimulatory effects of Cu on the growth of *Aspergillus niger* (I) occur in nutrients containing 0·00001—0·000001% of Cu. An increase in p_H of the medium during growth favours the intake of Cu and a falling p_H leads to a partial return of absorbed Cu to the medium. Of the Cu taken up by the mycelium a portion is readily leached out by H_2O; the remainder is probably chemically combined. The pigment of the conidia contains no Cu. The N balance of (I) is influenced by Cu only in the second growth stage. The filtrate from Cu-containing cultures contains more NH_3 and less NH_2-N than corresponding controls. Reduction of NO_3' in all cultures was rapid. Reduction products appear to react with sugar in the medium and accumulate temporarily in this form. Cu is essential to the normal development of (I). A. G. P.

Sterilising action of acids. II. Saturated monobasic fatty acids. I. S. TETSUMOTO (J. Agric. Chem. Soc. Japan, 1933, **9**, 388—397).—At the same mol. concn., the sterilising action for *Eb. typhi* and *V. cholerœ* of HCO_2H is > that of any acids from C_2 to C_5. Octoic, nonoic, and decoic acids have a strong action owing to their undissociated mols. The effect of fatty acids < C_5 depends on p_H and concn. of the undissociated mols.; *n*- are more effective than *iso*-compounds. The effects of mineral acids are > those of saturated monobasic acids at the same mol. concn., but the effects are reversed at the same p_H. CH. ABS.

Bactericidal efficiency of menthol and camphor. L. GERSHENFELD and R. E. MILLER (Amer. J. Pharm., 1933, **105**, 490—502).—1% solutions of menthol (I) and camphor (II) in petroleum have no

bactericidal action on *S. aureus* or *B. typhosus*. Saturated aq. solutions of (I) but not of (II) were effective, and both solutions were bacteriostatic against *B. coli*. PhOH-coeffs. are given for solutions of (I) and (II) in a solvent containing EtOH 31, glycerol 31, and soap 6·6%. S. C.

Influence of hormones on absorption. Internal secretions and permeability. II. E. GELLHORN and D. NORTHUP (Amer. J. Physiol., 1933, **103**, 382—391).—In frogs the small intestine was perfused with 3·15% glucose and the mesenteric vessels with Ringer's solution with and without hormones. Adrenaline (1 in 5×10^5 to 5×10^6), thyroxine (1 in 5×10^4 to 2×10^5) and insulin (0·02—0·01 unit per c.c.) increased absorption of sugar; adrenaline (1 in 10^6 to $2{\cdot}5\times10^6$) and insulin (0·005 unit per c.c.) decreased it. NUTR. ABS.

Spleen hormone. Y. TOKUMITSU (Trans. Japan. Path. Soc., 1932, **22**, 345—351).—There are possibly two splenic hormones, (*a*) sol. in H_2O, controlling thrombocytosis after ultra-violet irradiation, and (*b*) insol. in H_2O but sol. in Et_2O, regulating Ca metabolism. CH. ABS.

Action of the diuretic liver hormone. J. MOSONYI and L. VOITH (Arch. exp. Path. Pharm., 1933, **173**, 72—77).—With a frog's kidney prep., the passage of a perfusion fluid through the liver and heart to the kidney [*i.e.*, glomeruli (I) and tubuli] produces increased diuresis, which also occurs when (I) are omitted from the perfusion, the content of NaCl in the urine being then considerably diminished. F. O. H.

Intestinal wall as site of formation of choline and its importance for intestinal movement. G. KAHLSON (Klin. Woch., 1933, **12**, 1015—1017).—The intestinal wall is able to liberate large amounts of choline (I) from lecithin; the entire small intestine of the guinea-pig produces in about 12 hr. as much (I) as is in the entire animal. Muscles may, under powerful tetany, set free considerable amounts of (I); the small gut contains 2—3 times as much (I) as the stomach or muscles; blood carries very much smaller amounts. The uterus is rich in (I). During peristalsis (I) is liberated from the lecithin of the gut, but the immediate peristaltic stimulus is distension of the gut by ingesta. Acetylcholine is of importance as a chemical adjunct to the distension effect. NUTR. ABS. (*b*)

Concentration and purification of a growth inhibitor extracted from kidney. F. A. MCJUNKIN and C. D. HARTMAN (Proc. Nat. Acad. Sci., 1933, **19**, 823—824).—The prep. from ox kidneys of a substance that inhibits the mitotic activity of the renal epithelium of young rats is described. H. G. R.

Presence of melanophore hormone in human organs. A. JORES and W. VELDE (Arch. exp. Path. Pharm., 1933, **173**, 26—30).—The hormone (cf. this vol., 1086) occurs only in the eye and mid-brain; the thyroid, liver, and kidney give a positive but non-sp. response to the test used. F. O. H.

Presence of melanophore hormone in human body-fluids. A. JORES (Arch. exp. Path. Pharm., 1933, **173**, 31—35).—Normal blood contains an average of 1·27 units of the hormone (I) per litre. The level is not related to the hair pigmentation. A substance occurs in the urine which causes melanophore formation but does not show the chemical properties of (I). The occipital and lumbar fluids of man are free from (I), whilst the occipital fluid and, after exposure to darkness, the aq. humour of the rabbit contain (I). F. O. H.

Biological assay of callicrein. H. WEESE (Arch. exp. Path. Pharm., 1933, **173**, 36—41).—Callicrein (A., 1932, 972) can be detected in urine by its action on the carotid blood-pressure of dogs (but not of cats or rabbits), using its heat-lability to differentiate it from the other depressor substances which are relatively heat-stable. F. O. H.

Effect of callicrein in decreasing blood-sugar. G. STRAUBE (Deut. Arch. klin. Med., 1933, **175**, 221—225).—Intramuscular injection of callicrein decreases to a small extent the blood-sugar of diabetics, and, usually, of normal individuals. It is uncertain whether this action is characteristic or due to traces of other hormones, *e.g.*, insulin, in the prep. NUTR. ABS. (*b*)

Salivary glands. III. Y. HIKI, K. AKAZAKI, T. BANN, Y. MIZAZAKI, and N. TAKIZAWA (Trans. Japan. Path. Soc., 1932, **22**, 273—281).—Hyperglycæmia followed injection of extract of salivary gland. CH. ABS.

Salivary glands and carbohydrate metabolism. G. ROSENFELD (Klin. Woch., 1933, **12**, 711).—Injection of a solution of diastase resulted in a fall of the blood-sugar (I) level in normal rabbits and a decrease in the urinary sugar and (I) in diabetic dogs. The fall in (I) which follows ligation of the ducts of the salivary glands is due to absorption of pytalin or amylase, rather than to the internal secretion of an insulin-like substance by these glands. NUTR. ABS. (*b*)

Mechanism of the regulation of the blood-sugar with differentiated anastomoses of the vessels between liver and abdominal organs. I. F. MEYTHALER and T. NAEGELI (Arch. exp. Path. Pharm., 1933, **172**, 630—644).—A sub-normal supply of arterial blood to the liver produces liver damage which can be diminished by arterio-portal anastomosis (I). Normal glycæmic reactions are obtained from animals with (I), whilst changes in carbohydrate metabolism (II) occur when the liver is not supplied directly with insulin-containing blood from the portal vein. Thus insulin acts as a functional stimulant of the liver cells in their regulation of (II). F. O. H.

Influence of insulin on the conversion of carbohydrate into fat. J. W. SOPP and H. SELBACH (Pfluger's Arch., 1933, **231**, 543—562; Chem. Zentr., 1933, i, 3210).—High fat and low sugar vals. synchronised. Hyperlipæmia is a function of hyperlactacidæmia. A. A. E.

Insulin and diabetes. A. GIGON (Klin. Woch., 1933, **12**, 294—296; Chem. Zentr., 1933, i, 3588).—Injury to liver parenchyma results in subnormal sensitivity towards insulin; in nephritis there is increased sensitivity. Insulin is concerned with processes leading to the production of glycogen from

assimilated carbohydrate; other metabolic processes are affected by the thyroid hormone. A. A. E.

Differential inactivation of insulin. B. DAVIS, jun., J. M. LUCK, and A. G. MILLER (Biochem. J., 1933, **27**, 1643—1647).—Treatment at 0° with 0·75*N*-HCl in 75% aq. EtOH and irradiation with soft *X*-rays both cause differential inactivation of the physiological activities of insulin, the PO_4''' -lowering activity (I) being the most resistant. Loss of hypoglycæmic activity by *X*-irradiation was accompanied by 50% loss in (I). Insulin therefore owes its multiple activity to active centres of varying stability. A. L.

Action of thiol compounds on insulin. O. WINTERSTEINER (J. Biol. Chem., 1933, **102**, 473—488).—The NH_3 liberated by the interaction of insulin (I) with cysteine in absence of O_2 at p_H 7·2 is due to impurities in the (I) prep. The reduction and inactivation of (I) are plotted against time. The reduction approaches a limiting val. No proportionality exists between the max. reduction attained with any given (I) prep. and the physiological activity; hence the reacting groups are not sp. for (I). With cryst. (I) the equilibrium reduction val. represents a reduction of 1/3 of the S·S linkings, and corresponds with a complete loss of activity. The reduction is uninfluenced by CN'. Between p_H 6 and 8 the rate of inactivation increases with p_H. Thioglycollic and α-thiolactic acids inactivate (I) at the same rate between these p_H. H. D.

Effects of insulin and adrenaline on the amino-acid content of blood. J. M. LUCK and S. W. MORSE (Biochem. J., 1933, **27**, 1648—1654).—Cryst. and amorphous insulin (I) are equally effective in reducing the NH_2-N content (II) of the blood of normal rabbits. Adrenaline (III), like (I), causes a reduction in (II) of the blood, liver, and muscle, and although balanced injections of (I) and (III) prevent hypoglycæmia (IV), the reduction in (II) still continues. Pitocin injected with (I) lessens (IV), but increases slightly the (II)-lowering activity. The action of pitressin is similar except for an initial hyperamino-acidæmia. A. L.

Oxidation-reduction. XX. Adrenaline and related compounds. E. G. BALL and T. T. CHEN. —See this vol., 1248.

Photometric determination of small quantities of adrenaline. G. N. THOMIS (Praktika, 1932, **7**, 17—21; Chem. Zentr., 1933, i, 3990).—Seidell's method is untrustworthy and fails in the presence of HCl. Beer's law holds only for concns. of 0·002—0·006%. PbO_2 is used instead of MnO_2. A. A. E.

Action of adrenaline on respiratory exchange. M. LABBÉ and M. RUBINSTEIN (Compt. rend. Soc. Biol., 1933, **112**, 637—639). NUTR. ABS.

Physiology of the autonomous nervous system. III. Comparison of sympathin and adrenaline. Z. M. BACQ (Arch. int. Physiol., 1933, **36**, 167—246; Chem. Zentr., 1933, i, 3208—3209).—Phenomena attributed to the presence of "sympathin" (I) arising from excitation of the sympatheticus are described. In cats (I) raises the blood-sugar. After excitation of the sympathetic optic nerves Vial's reaction for polyphenols in the aq. humour is intensified. The effect of sympathectomy is described. (I) is closely related to adrenaline, and is an NH_2-derivative of pyrocatechol or a mixture of such derivatives. Excitation of the sympathetico-adrenal system produces a small quantity of highly active polyphenols which are brought into circulation by the adrenals. A. A. E.

Significance of the adrenal cortex in the metabolism of carbohydrates. G. VIALE (Klin. Woch., 1932, **12**, 467—469; Chem. Zentr., 1933, i, 2965).—In animals which died of adrenal insufficiency, the liver is free from glycogen; the muscle contains a relatively large amount, but is practically free from lactacidogen. On autolysis the muscle-glycogen diminishes much more slowly than does that of normal animals. Also in the blood of adrenalectomised animals glycolysis is abnormally slow. These phenomena are attributed to the absence of adrenal cortex. A. A. E.

Adrenal cortex hormone and cholesterol in blood and tissues. M. SARDA (Rev. sudamer. endocrinol., 1932, **16**, 619—620).—The hypercholesterolæmia following injection of the hormone represents transportation of the cholesterol from the reticulo-endothelial system to the brain and adrenals. CH. ABS.

Biological assay of the parathyroid hormone. M. T. RÉGNIER and H. SIMONNET (J. Pharm. Chim., 1933, [viii], **17**, 560—576).—In thyroid-parathyroidectomised dogs the administration of parathyroid hormone always causes an increase in the blood-Ca (I). Administration of Ca salts alone has no effect on (I), but the effect of the hormone is increased if $CaCl_2$ or Ca gluconate is simultaneously administered intravenously. Tests on normal dogs are much less pronounced and not so consistent. The tests are carried out when incipient tetany appears and may be repeated at intervals on the same animal. S. C.

Serum-calcium in guinea-pigs after small doses of parathormone. B. N. E. COHN and R. STOHR (Klin. Woch., 1933, **12**, 1021—1022).—Daily administration of 1—5 units of parathormone to young guinea-pigs over a period of 7—28 days caused no alteration in the serum-Ca or in the Ca of the bones. Administration of 40—100 units in a single dose leads to removal of Ca from the bones. NUTR. ABS. (*b*)

Action of parathormone on blood-calcium, -phosphorus, and -protein. M. TAUBENHAUS (Klin. Woch., 1933, **12**, 626—629; Chem. Zentr., 1933, i, 3209).—Parathormone, administered in post-operative tetany, caused a fall in blood-P, whilst -Ca was little changed; the high -albumin was diminished, whilst the -globulin rose. A. A. E.

Monosodium thyroxine, desiccated thyroid, and an impure sodium salt of thyroxine. Comparison of their effects when administered orally with the effect of thyroxine injected intravenously in an alkaline solution. W. O. THOMPSON, P. K. THOMPSON, and L. F. N. DICKIE (Arch. Int. Med., 1933, **52**, 576—592).—In myxœdematous patients, the effect on the basal metabolism of the Na_1 salt of thyroxine (I) given by mouth was only about 0·2 of that of (I) administered intra-

venously. When administered by mouth the efficiency is in the following order: $Na_2 > Na_1$ salt > (I). For equal I content, desiccated thyroid administered by mouth is as active as (I) given intravenously. Solubility is an important factor in determining the effects of (I) compounds. W. O. K.

Comparative effects on metabolism of intravenously injected tyrosine, di-iodotyrosine, di-iodothyronine, and thyroxine. A. CANZANELLI and D. RAPPORT (Amer. J. Physiol., 1933, **103**, 279—287).—The max. rise due to 1·0 g. of tyrosine (I) was 10% of the total metabolism. Di-iodotyrosine (II) produced 7·5 times as much effect as (I), di-iodothyronine (III) 15 times that of (II), and thyroxine about 17 times that of (III). NUTR. ABS.

Detoxication of thyroid hormone. II. E. HESSE, H. VONDERLINN, and L. ZEPPMEISEL (Arch. exp. Path. Pharm., 1933, **173**, 192—204; cf. this vol., 539).—The toxic effects due to administration of thyroxine or thyroid gland prep. to dogs are alleviated by treatment with Cu, Fe, As, Ni, Pr, and with mineral H_2O containing small amounts of Cu, Fe, and As; Y, Zr, Nd, Ce, Th, Be, and Ti are inactive. F. O. H.

Blood-cholesterol in experimental hypo- and hyper-thyroidism (rabbit). J. J. WESTRA and M. M. KUNDE (Amer. J. Physiol., 1933, **103**, 1—4).—The fall of blood-cholesterol induced by thyroid feeding was not related to changes in hæmoglobin or red-cell content of the blood. NUTR. ABS.

Influence of the thyroid gland on the relation of temperature to plumage pigmentation. W. LANDAUER (Endokrinol., 1933, **12**, 260—273; Chem. Zentr., 1933, i, 3588).—Changes in plumage pigmentation of fowls due to changes in temp. are attributed to variation in the secretory activity of the thyroid gland. A. A. E.

Anterior pituitary and thyroid glands. Influence of thyreotropic substances on liver-glycogen and blood-ketones. H. EITEL, G. LOHR, and A. LOESER (Arch. exp. Path. Pharm., 1933, **173**, 205—220).—Intraperitoneal injection of a thyreotropic extract of anterior pituitary lobe into rats is followed within 2 hr. by decreases in the liver-glycogen and blood-ketones, the levels returning to normal after 24 hr. (cf. A., 1932, 1172). That these effects are due to a change in thyroid activity is indicated by their non-appearance after thyroidectomy. F. O. H.

Thyreotropic action of anterior pituitary gland on basal metabolism. W. SCHOEDEL (Arch. exp. Path. Pharm., 1933, **173**, 314—332).—A method for the determination of the basal metabolism (I) of guinea-pigs, using volumetric determinations of the O_2 consumption and CO_2 output, is described. The increase in (I) due to the thyreotropic action of anterior pituitary preps. (II) is small compared with that due to thyroid preps., is characterised by its rapid rise and fall, and is proportional to the dose. A "guinea-pig unit" is defined as 5% of the amount of (II) required to raise (I) 20% by three doses; it is approx.=23 mg. of fresh ox gland. Such an evaluation, which is applicable only to doses of 0—50 units, agrees with the extent of the morphological changes in the thyroid gland due to (II). F. O. H.

Mechanism of the action of posterior pituitary hormone on carbohydrate metabolism. S. THADDEA and A. WALY (Arch. exp. Path. Pharm., 1933, **172**, 535—550).—Of two posterior pituitary preps. tested, one (I) produced a hyperglycæmia (II) in rabbits, whilst the other was without influence on the blood-sugar (III). (II), which is due to a mobilisation of liver- and not of muscle-glycogen, is considerably weakened by previous administration of thyroxine. When the liver is damaged by P, the (II) due to (I) and the normally occurring antagonism between (I) and insulin in their action on (III) are not evident. F. O. H.

Effects of posterior-lobe pituitary extract on the serum and urine of normal dogs. A. R. McINTYRE and R. F. SIEVERS (J. Pharm. Exp. Ther., 1933, **49**, 229—236).—Injection into normal dogs of 0·75—2·0 units of posterior-lobe pituitary extract per kg. does not significantly alter the K/Na ratio or the Ca content of the serum (I), but raises the Na, K, and Ca content of the urine (II) and increases the K/Na and Ca/Na ratios. The $CuSO_4$ reducing power (Benedict modification of the Folin–Wu method) of (I) is increased, whilst that of (II) is decreased. W. O. K.

Mineral economy after administration of posterior pituitary gland preparations. R. ENGEL, I. McQUARRIE, and M. ZIEGLER (Arch. exp. Path. Pharm., 1933, **173**, 248—259).—Administration of a posterior pituitary prep. to normal and epileptic persons produced an increased excretion of K, Na, and Cl which, during the inhibition of diuresis, caused a negative balance in the mineral economy. The excretion of Ca, Mg, P, S, and N was not affected. F. O. H.

Site of the antidiuretic action of pituitary extract. W. W. BURGESS, A. M. HARVEY, and E. K. MARSHALL, jun. (J. Pharm. Exp. Ther., 1933, **49**, 237—249).—The antidiuretic action of pitressin (I) in the mammal is due to increased re-absorption of H_2O by the tubules; in the bird it increases re-absorption by the tubules and decreases glomerular filtration, whilst in the reptile its effect is due solely to decreased glomerular filtration. In the amphibian and fish, (I) has no antidiuretic action. W. O. K.

Anterior pituitary hormone. N. MOROZUMI (Trans. Japan. Path. Soc., 1932, **22**, 238—240).—The hormone was determined by observing the maturity of follicles after intramuscular implantation of the anterior pituitary lobe in infantile female mice. CH. ABS.

Determination of sexual hormones (anterior pituitary and follicular) in health and in mental and nervous disease. I. W. OESTERREICHER (Klin. Woch., 1933, **12**, 538—540; Chem. Zentr., 1933, i, 3588).—Zondek's method for detection of prolan in urine has been slightly modified. A. A. E.

Effect of anterior pituitary sexual hormone and thyreotropic active substance on respiratory metabolism. O. L. DIEFENBACH (Endokrinol., 1933, **12**, 250—260; Chem. Zentr., 1933, i, 3588).—

The anterior pituitary hormone does not affect gas metabolism; the thyreotropic hormone increases that of adult rats and guinea-pigs. A. A. E.

Sex behaviour of hypophysectomised male rats. B. P. WIESNER and N. M. SHEARD (Nature, 1933, 132, 641).—Hypophysectomy (I) in male rats is followed by the complete and persistent disappearance of sex behaviour (II). Partial (I) fails to affect behaviour in some cases, whilst in others various degrees of impairment in (II) are produced. The observations recorded can be interpreted by assuming the existence of a pituitary secretion conditioning the persistence of sexual potency. Certain gonadotropic extracts restore mating behaviour in some cases. L. S. T.

Sexual hormone and adrenals. H. POLL (Deut. med. Woch., 1933, 59, 567—570; Chem. Zentr., 1933, i, 3960).—The effects, in mice, of the injection of "proviron" and "progynon" are described. A. A. E.

Effect of testicular hormone on normal sexually mature rats. Method of biological assay. V. KORENCHEVSKY, M. DENNISON, and A. KOHN-SPEYER (Biochem. J., 1933, 27, 1506—1512).—The technique of assay previously described (this vol., 643) is applicable to mature rats, the effects being generally much smaller. The prep. of testicular hormone used has no stimulating effect on the prostate or seminal vesicles; it decreases the wt. of the thymus and increases that of the kidney. H. D.

Simultaneous administration of testicular hormone with antuitrin and prolan or with thyroid. V. KORENCHEVSKY, M. DENNISON, and A. KOHN-SPEYER (Biochem. J., 1933, 27, 1513—1516).—The hormones do not influence each other in regard to their typical effects. H. D.

Hypertrophy of seminal vesicles in rats. J. FREUD (Biochem. J., 1933, 27, 1438—1450).—Low doses of male hormone (I) are inert; with higher doses with seminal vesicles (II) above 14 mg. in wt. the frequency of positive epithelial response increases rapidly. There are doses of (I) insufficient to produce epithelial changes but just sufficient to help œstrin (III) to produce muscular hypertrophy. Both increased body-wt. and increasing growth increase the response to (I). Preps. of (I) from the urine or testis, whilst giving const. responses in capons, had variable effects on rats. A small amount of (I) insufficient to affect the epithelium may reinforce the effect of (III) on the smooth muscle of (II) if (I) and (II) are administered simultaneously. H. D.

Separation of male sexual hormone from female sexual hormone (follicular hormone). F. WADEHN (Endokrinol., 1933, 12, 241—243; Chem. Zentr., 1933, i, 3587—3588).—The male sexual hormone (I) is extracted with 75% H_2SO_4 from Et_2O or C_6H_6 solution, a loose compound being formed and subsequently hydrolysed by addition of H_2O. (I) is readily extracted from 20% H_2SO_4 with Et_2O or C_6H_6. A. A. E.

Thermostability of prolan. F. A. ASKEW and A. S. PARKES (Biochem. J., 1933, 27, 1495—1497).—The findings of Zondek and Ascheim (A., 1930, 255) are confirmed. A crude dry prep. heated at 100° for 1 hr. in O_2, N_2, or in a vac. retained its activity. H. D.

Hormone of the placenta. Y. OTSUKA (Trans. Japan. Path. Soc., 1932, 22, 227—228).—Effects of injection are described. CH. ABS.

Hormone content of the corpus luteum and action of luteinic extracts. M. MAINO (Arch. Ist. biochim. Ital., 1933, 5, 211—224).—Following the method of Hisaw (cf. A., 1932, 308) for the extraction of "corporin" from corpus luteum, two fractions are obtained, one containing œstrin, whilst the other is free from œstrin but provokes proliferation characteristic of the ante-pregnancy luteinic phase in the uterine mucosa. R. K. C.

Œstrin content of sow ovaries. F. E. D'AMOUR, M. C. D'AMOUR, and R. G. GUSTAVSON (J. Pharm. Exp. Ther., 1933, 49, 141—145).—Follicular fluid contained approx. 950 rat units of œstrin per litre and corpora lutea 65 rat units per kg. W. O. K.

Systemisation and correlation of vitamins. W. KOLLATH (Z. Vitaminforsch., 1933, 2, 266—272).—A systematic classification of the vitamins from the viewpoint of the associated metabolic disturbances is given. F. O. H.

Vitamins in ox-serum. I. J. FINE (Biochem. J., 1933, 27, 1498—1500).—When ox-serum (I) is added to a diet deficient in vitamin-*A* (II), the growth of rats proceeds normally; the (II)-potency of (I) is about 45% of that of a cod-liver oil sample. Vitamin-*B* is absent from (I). H. D.

Lipochrome pigments and vitamin-*A* in nutrition of young fish. R. J. MACWALTER and J. C. DRUMMOND (Biochem. J., 1933, 27, 1415—1420).—Fertilised eggs of trout were allowed to develop in tap-H_2O and after 30 days groups of fish were fed on rat-liver (I), cod-muscle (II), and (II) with algæ (III). Those fed on (I) increased more rapidly in wt. than those fed on (II) and (II)+(III); transference from the (I) to the (II) diet, however, caused a rapid decline in wt. The ultra-violet absorption of $CHCl_3$ extracts of the fish at 328 mμ ran parallel with the wt., the increases being accompanied by a corresponding decrease in absorption at 480 mμ. Vals. for absorption due to vitamin-*A* are obtained on the assumption that the absorption of the eggs at 328 mμ is wholly due to carotene and related pigments. H. D.

Absorption spectra and constituents of fish oils. J. R. EDISBURY, R. A. MORTON, and J. A. LOVERN (Biochem. J., 1933, 27, 1451—1460).—The absorption max. (I) of the total acids from the saponification of fish oils are summarised; vitamin-*A* is responsible for approx. all the ultra-violet absorption of the unsaponifiable matter. From considerations of the intensity and frequency differences of (I) the bands are separated into discrete groups, explaining the fact of the 259 mμ band not always being observed, the long inflexion at about 290 mμ and 360 mμ, and the existence of a band near 427 mμ; thus at least five absorbing entities are postulated. Straight-chain di- and tri-ethylenic acids cannot be responsible for the selective absorption at 270 mμ. The possibility of

the absorbing acids being derived from the clupanodonic acid by isomerisation or cyclisation is adopted. A summary of the absorption of simpler unsaturated compounds with conjugated double linkings (II) shows that an increase in (II) shifts the (I) towards the visible and increases the absorption intensity. H. D.

Variations in vitamin-*A* content of fish-liver oils and seasonal fluctuations in potency of halibut-liver oil. J. A. Lovern, J. R. Edisbury, and R. A. Morton (Biochem. J., 1933, **27**, 1461—1469).—The vitamin-*A* (I) potency of the liver oils of haddock, whiting, and immature fish is inferior, that of the oils of pollack, saithe, hake, and ling similar, and that of the oils of salmon, sturgeon, and halibut is superior, to that of an average cod-liver oil. No parallelism between (I) and vitamin-*D* potencies exists. The potency of (I) increases with the size and age of the fish; at the spawning season it varies inversely as the oil content of the liver. A parallelism between the seasonal abundance of plankton organisms and the % (I) in halibut-liver oils is shown. H. D.

Diet of halibut and intensity of feeding in relation to vitamin-*A* potency of liver oil. J. A. Lovern and J. G. Sharp (Biochem. J., 1933, **27**, 1470—1472).—There is no relation between the vitamin-*A* potency of the liver oil of halibut and the glycogen content of its liver. H. D.

Avitaminosis and keratinisation. V. Klemola and W. Hohlweg (Z. Vitaminforsch., 1933, **2**, 249—253).—Female rats fed on diets deficient in vitamin-B_2 do not develop colpokeratosis (I), which is therefore typical of *A*-avitaminosis (cf. this vol., 432). Epidermal changes (*e.g.*, scaling and scanty hair growth) and subnormal body growth are common to both *A*- and B_2-avitaminosis. Differences between (I) and œstrus are discussed. F. O. H.

Alcohol-extractable substances of rice and vitaminotic conditions. C. Scaglioni (Arch. Ist. biochim. Ital., 1933, **5**, 303—320).—Pigeons fed on polished rice show prodromal symptoms of polyneuritis (I) more rapidly when an EtOH extract of polished rice is administered, whilst extracted rice or extract of whole rice delays the onset of (I). A diet of potato with extract of polished rice did not cause (I). Similar results were obtained with rats on Hofmeister's diet. It is concluded that polished rice contains a substance enhancing polyneuritic symptoms, whilst the husk contains a curative agent. R. K. C.

Vitamin-*B* and intestinal resorption. H. G. K. Westenbrink and G. A. Overbeek (Arch. neerl. Physiol., 1933, **18**, 416—428).—Addition of 0·3% of activated "acid clay" to a vitamin-*B*-free diet suffices to maintain normal resorption of glucose. Lack of either the thermolabile (B_1 and B_4) factors or the thermostable factors produces a lowering of glucose resorption equally with a completely *B*-avitaminotic diet. P. G. M.

Vitamin-*B* and liver-glycogen. H. G. K. Westenbrink (Arch. neerl. Physiol., 1933, **18**, 429—445).—There is no difference in the ability of the liver to synthesise glycogen in normal rats and in those fed on a vitamin-*B*-free diet. P. G. M.

Influence of *B*-vitamins on the glycogen and glutathione content of rabbit's liver. M. Labbe, F. Nepveux, and J.-D. Gringoire (Compt. rend. Soc. Biol., 1933, **113**, 152—155).—Of sixteen rabbits receiving a basal diet of green vegetables, bran, and bread, ten received additional vitamin-*B* complex as a vegetable extract. Both groups showed wide variations in the amount of glycogen and glutathione in the liver, but the average content of both substances in the control group was $<$ in the group receiving the supplement. Nutr. Abs. (*b*)

***B*-Vitamins and carbohydrate metabolism.** H. Bierry and F. Rathery (Compt. rend. Soc. Biol., 1933, **113**, 545—546).—Mainly a review. A substance which lowered the blood-sugar of diabetic patients was obtained from top yeast extract by fractional pptn. with EtOH at varying p_H. Nutr. Abs. (*b*)

Determination of vitamin-B_1. K. H. Coward, J. H. Burn, H. W. Ling, and B. G. E. Morgan (Biochem. J., 1933, 27, 1719—1743).—New methods are described for the determination of vitamin-B_1 (I), involving (*a*) the curing of head-retraction in pigeons, and (*b*) growth-promotion in rats previously fed on a deficient diet. These two methods give the same estimation of potency of a soft extract of yeast in comparison with the International Standard, indicating equal ability on the part of the rat and pigeon to deal with (I) of the standard. From tests on two different samples of dried yeast (II), however, it appears that the rat is less able to respond to (I) of (II) than is the pigeon. Examined statistically, the results indicate the following probable errors for the tests (nine animals in a test): pigeon (duration of cure) +31 or −26%; pigeon (% cured), +29 or −23%; rat (mean increase in wt. in 3 weeks), +6·1 or −5·5%. The standard deviation of the results with pigeons in tests with solids is $\frac{1}{2}$ for liquids. The pigeon test, although giving a much greater probable error than the rat test, is preferable because it is more sp. and may also give truer results with certain substances, *e.g.*, (II). A. W.

Incidence of dermatitis among rats deprived of vitamin-B_2. M. H. Roscoe (Biochem. J., 1933, 27, 1533—1536).—Inflammatory dermatitis (analogous to human pellagra) was noted in about 55% of rats fed on a vitamin-B_2-deficient diet. The condition takes about 10 weeks to develop; its incidence is irregular. P. G. M.

Vitamin-B_2 content of various materials compared by their power to promote growth and cure dermatitis. M. H. Roscoe (Biochem. J., 1933, 27, 1537—1539).—The growth-promoting and dermatitis-curing factors associated with the vitamin-B_2 of yeast extract, egg-white filtrate, and meat have a similar stability to heat in both acid and alkaline media. There is no evidence of the separate identity of the two factors. P. G. M.

Heat-stability of vitamin-B_2. III. Rate of destruction of vitamin-B_2 in different materials at various reactions. M. H. Roscoe (Biochem. J., 1933, 27, 1540—1544).—The vitamin of aq. yeast and liver extracts and marmite solutions shows similar

stability to heat. At p_H 1·4 little decomp. takes place at 120° in 5 hr.; at p_H 3·0—3·3 there is 50% destruction in 4 hr., at p_H 7·2—8·7 50% in 1 hr., and at p_H 8·7—9·2 83% in 1 hr. P. G. M.

Vitamins. VII. Vitamin-*C* content of some unusual foodstuffs. F. V. VON HAHN (Z. Unters. Lebensm., 1933, **66**, 261—270).—100 c.c. of an infusion of pine needles, containing 1·04% of solids, contained 8 guinea-pig units (G.P.U.) of vitamin-*C*, rowan berries (*Sorbus aucuparia*) 200 G.P.U.%, wild apples 25 G.P.U.%, apples of the Reinette variety and the fruit of *Malus floribunda* approx. 20 G.P.U.%, and wild-rose fruits, both fresh and after 2 years' storage in the dry state, 100 G.P.U.%. *Cydonia japonica* fruits had a content > that of the fruits of allied cultivated genera. E. C. S.

Influence of vitamin-*C* on intracellular enzyme action. A. PURR (Biochem. J., 1933, **27**, 1703—1705).—Ascorbic acid (I) activates the catheptic enzyme system (hydrolysis of gelatin at p_H 4·0), and (I)+Fe activates arginase. It is suggested that other intracellular enzymes may require the participation of SH compounds and (I), and a hypothesis is presented to explain respiration and metabolism of tissues. A. W.

Action of vitamin-*C* on oxidation of tissues *in vitro*. D. C. HARRISON (Biochem. J., 1933, 1501—1505).—The increase in O_2 consumption of scorbutic tissue on addition of ascorbic acid (I) is > that of non-scorbutic tissue. No correlation exists between the increased O_2 uptake due to the addition of (I) and the degree of scurvy of the animal. H. D.

Vitamin-*D*. G. WEIDLICH (Z. Vitaminforsch., 1933, **2**, 253—266).—A review. F. O. H.

Difference between synthetic and naturally occurring vitamin-*D*. F. ENDER (Z. Vitaminforsch., 1933, **2**, 241—249).—Purification of the unsaponifiable fraction of fish-liver oil (from *Thunnus thynnus*) by cooling the MeOH solution to −60° yields a prep. (I) 10 times as rich in vitamin-*D* as the original oil. (I) has a characteristic absorption band (II) at 328 mμ, whilst the typical band of calciferol (III) at 265 mμ is not apparent. (I), further purified by fractionation of the phthalic esters (A., 1926, 980), yields a prep. (IV) 10^4 times as active as (I) (daily rat dose = $0{\cdot}05—0{\cdot}06\times10^{-6}$ g.). (IV) has no (II) in the region 260—270 mμ, but has a regular absorption over 250—285 mμ. The (II) of (III) is apparent in mixtures of (III) and (IV). A further distinction between (III) and (IV) is that whilst (IV) readily reacts with o-$C_6H_4(CO)_2O$ at room temp., (III) does so extremely slowly. F. O. H.

Destruction of activity of vitamin-*D* by lung tissue. P. A. COPPENS and G. A. METZ (Biochem. Z., 1933, **266**, 169—174, and Arch. néerl. Physiol., 1933, **18**, 407—415).—The lungs and blood (but not the liver) of mammals inactivate and perhaps degrade irradiated ergosterol *in vitro* probably because they contain an enzyme which attacks the vitamin (I). Possibly, *in vivo*, the blood supplies (I) to the lungs until the body contains no more. An explanation is thus provided for the difference between the (I) content of mammals and that of fish. W. McC.

Effects of irradiated ergosterol on metabolism of normal dogs. C. I. REED, E. A. THACKER, L. M. DILLMAN, and J. W. WELCH (J. Nutrition, 1933, **6**, 355—370).—Large doses of irradiated ergosterol increased the metabolic rate of dogs to an extent unrelated to any other factor observed. With small doses there was normally a positive Ca balance, but with increased Ca elimination in urine. Similar but smaller changes occurred in the P metabolism. The N metabolism was not influenced. Heavy dosages are associated with increased consumption of body-fat. A. G. P.

Distribution of irradiated ergosterol in the animal body after oral administration. P. A. COPPENS and G. A. METZ (Arch. néerl. Physiol., 1933, **18**, 407—415).—0·1 mg. of irradiated ergosterol per kg. body-wt. was administered *per os* to dogs; 10 hr. afterwards the animals were anæsthetised with morphine hydrochloride and bled. Vitamin-*D* was found in the phosphatide-free extracts of the blood and all organs except the heart, brain, skin, and pancreas. P. G. M.

Calcification of tissues by excessive doses of irradiated ergosterol. C. I. REED, L. M. DILLMANN, E. A. THACKER, and R. I. KLEIN (J. Nutrition, 1933, **6**, 371—381).—The increased Ca content of the tissues of dogs produced by intravenous injection of toxic doses of irradiated ergosterol was not related to the dosage. The P content of the tissues was affected, if at all, in a more irregular manner. A. G. P.

Changes suffered by white rats on poisoning with irradiated ergosterol. B. KELLNER (Arch. path. Anat. Physiol., 1933, **288**, 491—526; Chem. Zentr., 1933, i, 3212).—Pathological changes are described. Ergosterol has $\frac{1}{8}$ and viosterol of the toxic action of devitol or organtol. A. A. E.

Atmospheric oxygen, a factor in wood formation. C. G. SCHWALBE and K. E. NEUMANN (Cellulosechem., 1933, **14**, 133—134).—If access of O_2 to a growing stem is prevented by a suitable bandage the OMe, and therefore the lignin, content of the wood of beech and birch is reduced, whilst that of pine is increased. Pine contains sol. tannins in the bark, and these probably prevent access of atm. O_2 to the wood. A. G.

Comparative germination of varieties of pea. C. BOURDOUIL (Bull. Soc. Chim. biol., 1933, **15**, 1121—1123).—The relative swelling of wrinkled and smooth peas is directly correlated with their glucoside contents. During germination a progressive loss of starch and stachyose occurs; sucrose is replaced as quickly as consumed. H. D.

Chemistry of some beetroot hybrids. E. BOUGY (Diss., Paris, 1933, 76 pp.).—The sugar content varies even in pure strains of the sugar-beet (I); the character appears to be relatively dominant in hybrids, and, as a rule, runs parallel to the no. of vascular rings in the root. The org. N of hybrids is always < the mean val. for the parent (I), whilst the insol. N is nearly = that of (I); NH_2-N is = the mean of the vals. for the parents. The ash of all hybrids examined, in common with that of (I), has a

high content of insol. bases, but the sol. alkali content is < that of the Vauriac (low sugar) beet. Approx. the same interdependence of the various constituents is found in the F_2, F_n, and F_n generations. P. G. M.

Conversion of fat into carbohydrate in the germinating castor bean. I. Respiratory metabolism. J. R. MURLIN. **II. Combustion respiratory quotient.** R. G. DAGGS and H. S. HALCRO-WARDLAW. **III. Chemical analysis and correlation with respiratory exchange.** H. B. PIERCE, D. E. SHELDON, and J. R. MURLIN (J. Gen. Physiol., 1933, **17**, 283—302, 303—309, 311—325).—I. R.Q. (I) of germinating beans has a val. 0·30—0·58, indicating conversion of the oil into carbohydrate; (I) is lowest when the hypocotyl measures 20—35 mm. (I) of the young plant (II) separated from the endosperm (III) is 0·78—1·00, indicating considerable combustion of sugar, whilst the val. for (III) is lower. (II) produces relatively 2·6 times as much CO_2 as (III), but absorbs 1·3 times as much O_2.

II. After germination (IV) was well started (I) increased with (IV), indicating a change from O-poor to O-rich substance, taking place probably in (III).

III. During (IV) there is a continual decrease in fat (V) with an increase in sugar (VI) up to about 40% (dry wt.), after which (VI) decreases as fibre is formed. The balance between (V) and (VI) can be accounted for only by the presence of an undetermined residue, possibly an oxidation product of a pentose. The protein (VII) in the ungerminated bean is about 26% and rises to 35% during (IV). The ash is in the same ratio to (VII) throughout. (I) can be accounted for by assuming that, out of 6 mols. of ricinoleic acid, 2 are converted into sucrose, 1 into cellulose, and 3 are oxidised. H. G. R.

Physiology of anaerobic respiration of higher plants. K. WETZEL (Ber. Deut. bot. Ges., 1933, **51**, 46—51).—Changes in the ratio EtOH : CO_2 production during anaerobiosis in potatoes are associated with the activity of a plant dehydrase. A. G. P.

Transfer of fixed nitrogen from bacterium to host in soya bean. G. BOND (Nature, 1933, **132**, 748—749).—Throughout practically the whole life cycle of the host (I), the rate of transfer of N is 80—90% of the rate of fixation, and there is little tendency for the products of fixation to be retained by the bacteria (II) before becoming available to (I). This supports the view that transfer of N arises from excretion by (II) into the (I) cytoplasm in preference to digestion of (II) by (I) enzymes. L. S. T.

Natural regulation of protein metabolism in plants. K. MOTHES (Ber. Deut. bot. Ges., 1933, **51**, 31—46).—The influence of H_2O and carbohydrates on protein metabolism is discussed. The importance is indicated of the oxidation potential of the protoplasm in controlling the SH S·S equilibrium and therefore the activity of proteases in the tissue. A. G. P.

Role of organic acids in plant metabolism. III. T. A. BENNET-CLARK (New Phytol., 1933, **32**, 197—230).—The literature is discussed; a general scheme explanatory of metabolic changes in plant acids is advanced. A. G. P.

Influence of time of cutting on the growth, yield, and composition of tropical fodder grasses. I. Elephant grass (*Pennisetum purpureum*). D. D. PATERSON (J. Agric. Sci., 1933, **23**, 615—641).—With increasing intervals between cutting (up to 12 weeks) there was a progressive increase in the total dry matter yield, total yield of protein per acre, and in the % of crude fibre in the material, but a decline in % of protein and mineral constituents. The % of crude protein, ash, and dry matter of the grass decreased and that of crude fibre increased with rainfall. The mineral contents of the grass (with the exception of Ca) were adequate for cattle. With advancing maturity there was a decline in the % of Ca, P, and SiO_2. Max. feeding val. was obtained by a three-monthly rotational system. A. G. P.

Germination of *Apocynum* seeds in variously salinised soils. A. F. PUPUIKIN (Trud. Inst. Nov. Lubyan. Suir., 1933, **4**, 31—37).—Injury was caused by $CO_3'' > Cl' > HCO_3' > SO_3''$; limits for injury are, respectively, < 0·002, ≯ 0·05, ≯ 0·05, ≯ 0·2—0·4%. CH. ABS.

Ultra-violet light and photosynthesis. W. ARNOLD (J. Gen. Physiol., 1933, **17**, 135—143).—Ultra-violet light renders inactive an unidentified unit in the mechanism of the photosynthesis of *Chlorella pyrenoidosa*, but does not affect the normal respiration. The chlorophyll is unchanged.

Order of the Blackman reaction in photosynthesis. W. ARNOLD (J. Gen. Physiol., 1933, **17**, 145—149).—The reaction is of the first order, assuming that photosynthesis is a cyclic process and that the reaction coeffs. are not changed by irradiation. H. G. R.

Changes in composition of the pear during ripening. I, II. H. KOJIMA (J. Agric. Chem. Soc. Japan, 1933, **9**, 498—504, 504—510).—Reducing sugars reached a max. at the middle of August (max. increase in size) and then decreased rapidly. Increase in sucrose was marked at the latter stage. Starch was present only in the former stage. Pectin gradually became solubilised. CH. ABS.

Zymasis. IV. Accumulation of zymasic products in apples during senescence. V. Seasonal fluctuations in zymasis and carbon dioxide/alcohol number ratios in apples in the absence of oxygen. J. C. FIDLER. **VI. Zymasis by apples in relation to oxygen concentration.** M. THOMAS and J. C. FIDLER (Biochem. J., 1933, **27**, 1614—1621, 1622—1628, 1629—1642).—IV. Little zymasis (I) as determined by the sum of the concn. of EtOH and MeCHO in g. per 100 g. of fresh tissue [alcohol no. (II)] occurs in Newton Wonder and Bramley's Seedling apples, when these are stored at 1—4°, until the colour change from green to yellowish-green commences. Senescence and rise of storage temp. cause a marked increase in (I).

V. (I) in N_2 follows the same seasonal curve as that of the CO_2 output in air. In any one season the ratio CO_2 output to (II) varies within wide limits about a mean val. (III) which does not change with age, but varies from season to season and with the

variety of apple. For the two above varieties during three seasons (III) was 100/80—85.

VI. The rates of CO_2 production and C loss [CO_2+(II)] in the above varieties decrease from max. vals. in N_2 to min. vals. in 3—5% O_2 in the early storage season, but in 8—10% O_2 for older apples. The rates gradually increase with increasing O_2 concn. due to stimulation of respiration. The O_2 concn. at which no EtOH is produced (N_2 respiration extinction-point) varies for different varieties of apples in the same season and for any one variety in different seasons. A. L.

Effect of yeast extract on the growth of plants. V. Subrahmanyan and G. S. Siddappa (Nature, 1933, **132**, 713).—The results of Virtanen and Hausen (this vol., 1093) confirm the authors' earlier observations with sunflowers. L. S. T.

Formation of citric acid in the lemon. A. Ricevuto (Annali Chim. Appl., 1933, **23**, 411—413).—Citric acid is formed in the lemon at the expense of the reducing sugars and pentosans during the warmer months and at that of the pentosans alone later. It is suggested that this acid results from the action of an enzyme produced by *Aspergillus* occurring in the soil. T. H. P.

Nitrate supply and transpiration ratio in plants. L. A. T. Ballard (Austral. J. Exp. Biol., 1933, **11**, 161—176).—Experiments on the growth and loss of H_2O in Sudan grass and barley indicate that the reducing effect of NO_3' on the transpiration ratio (I) (H_2O transpired to dry wt. produced) is due to growth and not to any continued effect on the process of transpiration. The ratio of dry matter produced increases with the NO_3' supply, and the transpiration rate falls with age. The reduction in (I) caused by these is, however, not compensated for by the increased transpiration resulting from increase in leaf wt. ratio. A. L.

Nitrogen fixation by the endophyte of *Lolium*. R. Brown (J. Agric. Sci., 1933, **23**, 527—540).—Evidence is presented indicating that part of the N supply of *Lolium* may be obtained from atm. N_2 fixed by the endophyte. A. G. P.

Variations in the composition of plants. N. N. Ivanov (Social. Plant Ind., 1932, No. 4, 147—155).—Data concerning the influence of geographical locality and annual variations in protein contents of wheat and barley, on variations in the sugar content of melons, on essential oils in *Lavandala vera*, on lupin alkaloids, and on linseed oil, are recorded. Ch. Abs.

Cell-wall constituents of *Cetraria islandica* ("Iceland moss"). H. W. Buston and V. H. Chambers (Biochem. J., 1933, **27**, 1691—1702).—The cell-wall of *C. islandica* consists mainly of hemicelluloses (I) and cellulose, in addition to lichenin and *iso*lichenin. Pectins, pentosans, and lignin are absent. Of the carbohydrates present, the last three contain glucose only as the parent sugar, whilst the three types of (I) isolated all give on hydrolysis mannose (II), galactose (III), and about 10% of galacturonic acid (IV), but no glucose. It is suggested that in two of the (I), the mol. consists of a resistant acid nucleus, containing (II), (III), and (IV) units, and a more loosely combined portion containing no (II). A. W.

Grape pectin. A. Mehlitz (Allg. deut. Konserven-Ztg., 1933, **20**, 113—115, 136—138, 156—158, 189—191; Chem. Zentr., 1933, i, 3640—3641).—As ripening proceeds the pectin (I) content of the juice diminishes, particularly in over-ripe fruit. The pectins (EtOH pptn.) have steadily increasingly ash content, but, except for a small initial rise, falling Ca pectate vals.; jellying vals. and the unexpectedly small OMe contents are parallel. The usual formula for calculation to Ca pectate is inapplicable. Other components of the (I) complex besides the OMe content determine the jellying val. Extraction juice of dried grape marc contains practically only hydrolysed (I); the (I) pptd. with EtOH has a low ash and high OMe val. Marc (I) is unsuitable as a jellying agent. A. A. E.

Oxalic acid content of vegetable foods. E. M. P. Widmark and G. Ahldin (Biochem. Z., 1933, **265**, 241—244).—A table summarises the $H_2C_2O_4$ contents of a large no. of vegetables. P. W. C.

Carrot-leaf carotene. G. Mackinney and H. W. Milner (J. Amer. Chem. Soc., 1933, **55**, 4728—4729).—Extraction of the leaf powder (6 kg.) by Smith's method (A., 1932, 619) gives 0·37 g. of carotene, m.p. 176·8° (corr.) (Berl block), $[\alpha]_{6573}^{22}$ +37·3° in C_6H_6 (when crystallised from *n*-heptane), containing about 10% of α- and (probably) some γ-carotene. H. B.

Occurrence of a higher homologue of ceryl alcohol in mountain-ash berries. A. Jermstad (Pharm. Acta Helv., 1933, **8**, 69—70; Chem. Zentr., 1933, ii, 77).—Hydrolysis of a waxy substance from the fruit of *Sorbus aucuparia*, L., affords *sorbol*, $C_{34}H_{70}O$ (*Ac* derivative, m.p. 66—67°), which is considered to be a higher homologue of ceryl alcohol. A. A. E.

Isolation of a sodium galactan sulphate from *Irideæ laminarioides* (*Rhodophyceæ*). W. Z. Hassid (J. Amer. Chem. Soc., 1933, **55**, 4163—4167).—The plants are extracted with MeOH and EtOH until free from chlorophyll and then with H_2O, the aq. extract is evaporated and then added to 90% EtOH; further evaporation of the remaining solution in a vac. and addition to 95% EtOH gives *Na galactan sulphate* (I), $[\alpha]_D$ +69·2°. (I) contains the ·O·SO_3Na group, gives galactose on hydrolysis (2% H_2SO_4 at 105—110°) (in the ratio of one unit per one ·O·SO_3Na group), and when dialysed affords the free acid. A structure is suggested. H. B.

Soluble sugars in *Mercurialis perennis*, L. M. Bouillenne and R. Bouillenne (Bull. Acad. roy. Belg., 1933, [v], **19**, 849—866).—A survey of existing methods of separating the sugars in vegetable tissues. J. L. D.

Feulgen's reaction as a critical stain for wheat cytology. H. C. Gurney (Austral. J. Exp. Biol., 1933, **11**, 157—159).—The material is treated with *N*-HCl for 10 min. at 60° and stained for 2 hr. Cell walls, nuclear membrane, cytoplasm, spindle fibres, and nucleoli remain unstained. A. L.

Distribution of sugar and nitrogenous substances in wheat grain. W. KRETOVITCH (Biochem. J., 1933, **27**, 1687—1690).—In wheat, the endosperm contains more sucrose than the germ, and the concn. in the outer layers of the former is about 4·8 times that in the inner layers. No sugar was found in the aleurone layer (I). (I) contains no gliadin and only an insignificant amount of globulin, the principal proteins being glutenin and albumin. W. O. K.

Sitosteryl palmitate in ether extract of wheat-meal. A. DANGOUMAU (Bull. Soc. Chim. biol., 1933, **15**, 1083—1093).—The Et_2O extract of wheat contains a substance which, when fractionally recrystallised from $EtHSO_4$, has m.p. 95·5° and the same crystal form as phytosterol, but gives colour reactions similar to those of coprosterol. After hydrolysis with EtOH–KOH sitosterol is separated with light petroleum. Addition of dil. HCl to the hydrolytic products ppts. palmitic acid. H. D.

Amylases in resting and germinating seeds. II. Rye. E. OHLSSON and C. E. UDDENBERG. **III. Oats.** E. OHLSSON and O. EDFELDT (Z. physiol. Chem., 1933, **221**, 165—173, 174—179; cf. A., 1932, 303).—Germinating rye and oats each contain an α- or dextrinogen- and a β- or saccharogen-amylase which show very similar behaviour and relationships to those already obtained from germinating barley. J. H. B.

Real and apparent amount of diastase in various cereals before and during germination. T. CHRZASZCZ and J. JANICKI (Biochem. Z., 1933, **265**, 260—281).—Every amylase extract has an apparent (direct determination), a real (determination after addition of peptone as elution agent), and a sisto-amylase content (difference of apparent and real). Sistoamylase (I) is present in cereals before germination and increases at first slowly, then quickly during germination. Oats contain least and buckwheat most (I). The variation of the ratios of starch-liquefying, dextrin-forming, and saccharifying powers for different cereals and the different behaviour during germination are investigated in presence and absence of peptone. P. W. C.

Isolation and identification of organic nitrogenous and non-nitrogenous compounds occurring in the Alaska pea. I. Presence of citric acid. S. L. JODIDI (J. Amer. Chem. Soc., 1933, **55**, 4663—4664).—The peas (I) are dried at 60—65° and extracted with H_2O at 55°; extraction of the H_2O-sol. material with EtOH gives citric acid [0·36% of dry (I)], isolable as the Cu salt. H. B.

Hexone bases in rice embryo. T. MIKI (Arb. med. Univ. Okayama, 1933, **3**, 499—500).—Protein from rice embryo yields arginine and traces of histidine but no lysine on hydrolysis. NUTR. ABS. (*m*)

Proteins of Indian foodstuffs. V. Alcohol-soluble protein of fenugreek (*Trigonella fœnum græcum*). Y. V. S. RAO, B. N. SASTRI, and N. NARAYANA (J. Indian Inst. Sci., 1933, **16A**, 85—87).—Extraction of the flour from fenugreek seeds with 70% EtOH yields a prolamine characterised by low basic N and high cystine and tryptophan contents (cf. this vol., 329). F. O. H.

Mucilage of fenugreek (*Trigonella fœnum græcum*). C. R. H. IYER and B. N. SASTRI (J. Indian Inst. Sci., 1933, **16A**, 88—90).—Electrodialysis does not purify the crude polysaccharide (A., 1932, 660), but saturation of its aq. solution with $MgSO_4$ or treatment with boiling EtOH yields a P- and N-free prep. which on hydrolysis yields equiv. amounts of mannose and galactose and appears to be a mannogalactan. F. O. H.

Phytosterol from *Phyllanthus acidus*, Skeels. A. J. ULTÉE (Pharm. Weekblad, 1933, **70**, 1173—1175).—The *phytosterol*, m.p. 228—229°, $[\alpha]_D^{20}$ +41° (*acetate*, m.p. 266°), is not identical with lupeol. S. C.

Rotenone in species of *Derris* and *Lonchocarpus*. H. A. JONES (J. Washington Acad. Sci., 1933, **23**, 493—496).—The stems and leaves of *D. elliptica*, *L. nicou*, and other species contain little rotenone. Appreciable amounts occur in the peripheral portions of the fine roots. P. G. M.

Saponin from *Orthosiphon*. P. CASPARIS and C. FÉVRIER (Pharm. Acta Helv., 1933, **8**, 72—79; Chem. Zentr., 1933, ii, 76).—Vals. for H_2O, ash, ash constituents, essential oil, and extracts of leaves of *O. stamineus*, Benth., are recorded. Van Itallie's glucoside, "orthosiphonin," was not found. A saponin, *sapophonin*, which affords on hydrolysis a sapogenin, arabinose, and glucose or fructose, is present. A. A. E.

Carotenoids of the fruits of *Citrus poonensis*, Hort. R. YAMAMOTO and S. TIN (J. Agric. Chem. Soc. Japan, 1933, **9**, 642—645).—β-Carotene (I), lutein (II), viola- (III), and carica-xanthin (IV), m.p. 166° (separated from carotene by adsorption on Al_2O_3), are present. Analysis by Kuhn's method indicates: (I) 33·1, (IV) 170·3, free (II) 3·2, (II) ester 22·0, (III) ester 48·2 mg. in the dry matter (9·49%) of 1 kg. of the fresh fruit. CH. ABS.

Oil from seeds of *Abutilon avicennæ*, G. G. R. STEPANOV (Trud. Inst. Nov. Lubyan. Suir., 1933, **4**, 123—126).—The oil (18·97%) had *d* 0·9186, sp. viscosity at 24° 8·4, Abbé refractometer index 1·47, f.p. 17°, sap. val. 190·5, neutralisation val. of fatty acids 199·81, average mol. wt. of fatty acids 280·7, I val. 123, I val. of fatty acids 125, glycerides 10·17%. The oil is of the semi-drying type. CH. ABS.

Coccids produced in Japan. II. Wax of *Ceroplastes ceriferus*, And. III. *C. floridensis*, Comst. M. KONO (J. Agric. Chem. Soc. Japan, 1933, **9**, 458—466, 467—474).—II. Wax extracted with C_6H_6 from *C. ceriferus* had d^{15} 0·9975, m.p. 58—58·5°, acid val. 47·23, sap. val. 139·44, ester val. 92·21, I val. 85·27, Ac val. 57·65, neutral fat 19·39%, unsaponifiable matter 26·87%. Melissic and "psyllostearilic" acids, ceryl alcohol, a cyclic alcohol, $C_8H_{14}O$, b.p. 95°/10 mm., ceryl melissate, m.p. 85—86°, and melissate of $C_8H_{14}O$ were isolated; a liquid resin acid, $C_{12}H_{22}O_2$, b.p. 72—74°/3 mm., $[\alpha]^{25}$ −34·77°, and three solid acids, $C_{38}H_{59}O_7$, m.p. 57° (inactive), $C_{28}H_{49}O$, m.p. 43—44° (inactive), and $C_{57}H_{87}O_{10}$, m.p. 33—38°, $[\alpha]^{30}$ +74·62°, together with resinol, $C_{16}H_{26}O$, were separated.

III. Wax extracted with C_6H_6 from *C. floridensis*

had d^{15} 1·012, m.p. 49—50°, acid val. 40·86, sap. val. 97·54, ester val. 56·65, I val. 61·61, Ac val. 80·23, neutral fat 27·68%, and unsaponifiable matter 22·45%. Melissic and psyllostearic acids, ceryl alcohol, a cyclic alcohol $C_{18}H_{14}O$, three resin acids and a cyclic alcohol, $C_{30}H_{52}O_4$ (inactive), $C_{33}H_{52}O_5$, m.p. 51 52°, $[\alpha]_D^{13}$ +81·56°, $C_{20}H_{30}O_3$, m.p. 177° (approx.), $[\alpha]_D^{13}$ +16·55°, and $C_{12}H_{22}O$, b.p. 140°/3—4 mm., $[\alpha]_D^{19}$ +46·44°, are present. CH. ABS.

***Platycodon grandiflorum*, D.C. I—III.** M. TSUJIMOTO (Bull. Kagoshima Imp. Coll. Agric., 1932, **10**, 83—85, 87—96, 97—106).—The air-dried root contains dry substance (I) 90·10%. (I) contains ash 2·194, Et_2O-sol. substance 0·924%; 87·56% is saponifiable matter containing stearic and oleic acids. The unsaponifiable matter contains phytosterol and storesinol, $C_{16}H_{25}O_2$. EtOH (95%) affords $C_{27}H_{46}O,H_2O$, m.p. 147—148°; anhyd. Et_2O affords $C_{27}H_{41}O$, m.p. 157°. CH. ABS.

Citrinin in *Crotalaria crispata*, F. v. M. A. J. EWART (Ann. Bot., 1933, **47**, 913—915).—The dried leaves yield 1·06—1·21% of a yellow pigment, m.p. 168° (decomp.), probably identical with citrinin (A., 1931, 1092). F. O. H.

Localisation and determination of chlorophyll in parts of plants. S. HILPERT and H. HOFMEIER [with K. HEIDRICH] (Ber., 1933, **66**, [*B*], 1443—1445). The parts of the plant are heated for 1—2 hr. in a sealed tube or brass autoclave with about 5% SO_2 containing a little $Cu(OAc)_2$ at 100°. An intense green colour, probably due to Cu phæophytin, shows the location of chlorophyll or of some of the products of its degradation. For the determination of chlorophyll, 0·1—0·3 g. of the finely-divided material is treated as described above, filtered, washed with H_2O, dried at 50°, and triturated with sand. The residue is extracted with 40% $COMe_2$ to remove remaining yellow pigments, after which the Cu compound is dissolved in 100% $COMe_2$ and determined colorimetrically after addition of EtOH. H. W.

Extraction of asperuloside from *Coprosma Baueriana*, Hook. H. HERISSEY (J. Pharm. Chim., 1933, [viii], **17**, 553—556).—The plant is extracted with EtOH, the extract taken up in H_2O, and finally crystallised from EtOAc. S. C.

Formation of betaine and alkaloids in plants. III. Formation of nicotine. G. KLEIN and H. LINSER (Planta [Z. wiss. Biol.], 1933, **20**, 470—475; cf. this vol., 758).—Addition to culture solutions of proline, ornithine, or glutamic acid increased the nicotine content of tobacco plants. A. G. P.

Drying and fermentation of tobacco. III. Do ammonia, methylamine, and pyridine arise from nicotine during fermentation? J. BODNAR and L. BARTA (Biochem. Z., 1933, **265**, 386—389).—During fermentation of Hungarian tobacco, the nicotine (I) content decreases due to enzymic oxidation but does not give rise to the above bases. An inverse relationship holds between the [H'] of the tobacco and the decrease of (I). P. W. C.

Organic iodine in *Laminaria ochotensis*, Miyabe: protein-iodine, and search for di-iodotyrosine. Y. TORYU (Sci. Rep. Tohoku [Biol.], 1933, **8**, 107—110).—About 6% of the total I in *L. ochotensis* is EtOH-insol., 5% being protein I and 1% non-protein. Di-iodotyrosine was not detected. NUTR. ABS. (*b*)

Localisation of tannins in the lignified tissue of chestnut wood. M. QUENDIAC (Compt. rend., 1933, **197**, 937—938).—In young branches tannin (I) is localised entirely in the medullary rays (II). Accumulation of (I) in the wood elements is first apparent in branches 18—20 years old in which lignified tissue is clearly differentiated into sap- and heart-wood. In sap-wood (I) is still confined to (II), whereas in all heart-wood elements cell-walls are impregnated with (I). In the area bordering the two regions (I) occurs in the small and medium but not in the large vessels. A. G. P.

Specific permeability of the cell wall. L. MICHAELIS (Deut. med. Woch., 1932, **58**, 1926—1927; Chem. Zentr., 1933, i, 3088).—The p.d. between KCl solutions separated by a collodion membrane, which is a measure of the resistance to the passage of anions, may in an extreme case reach 57 mv.; it is the smaller the more porous is the membrane. Such membranes are models of the surface membranes of many plant structures or of those of erythrocytes. A. A. E.

Precipitin reaction in plants. I. Specificity of the normal precipitin reaction. II. Nature of the normal precipitin reaction. K. S. CHESTER. III. Biochemical analysis. K. S. CHESTER and T. W. WHITAKER (J. Arnold Arboretum, 1932, **12**, 53—74).—I. When aq. extracts of leaves of unrelated species of woody or herbaceous plants are superimposed, a ppt. is often formed at the interface. The reactions increase with increasing difference in plant type, reach a max., and disappear with greater divergence.

III. The reactions are not comparable with those obtained in animal serology. The reactive substances are non-protein and non-lipin; in 50% of the cases the ppt. was CaC_2O_4. Three types of reaction between unknown factors are differentiated. CH. ABS.

Apparatus for gas microanalysis for the study of respiratory exchange. L. PLANTEFOL (Compt. rend. Soc. Biol., 1933, **113**, 33—36).—Pressure changes at const. vol. are measured; 2-c.c. samples may be analysed. NUTR. ABS. (*b*)

Decomposition of organic material in the detection and determination of mineral substances in liver and kidneys. D. FISZERMAN-GARBER, and M. J. H. FISZERMAN (Bull. Sci. pharmacol., 1933, **40**, 157—166; Chem. Zentr., 1933, i, 3749).—(1) The powdered organ is macerated for 5 min. with a mixture of fuming HNO_3 (*d* 1·49, 100 c.c.), $HClO_4$ (*d* 1·615, 50 c.c.), and H_2O (50 c.c.) and the mixture is heated until colourless. (2) The material (10 g.) is heated with 50 c.c. of a mixture of H_2SO_4 (*d* 1·84, 350 c.c.) and $HClO_4$ (*d* 1·815, 650 c.c.). Results for pig's liver and kidneys are recorded.

Sensitive test for boric acid suitable for biochemical investigations.—See this vol., 1261.

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